

**ULTRA-FAST SPECTROSCOPY OF
VIBRATIONAL EXCITATIONS AND SURFACE PLASMONS**

ACADEMISCH PROEFSCHRIFT

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aan mijn ouders
en aan Mirjam

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CHAPTER 1 : Nonlinear optical theory and stimulated Raman scattering

1.1 Introduction to nonlinear optics

The description of the interaction of light and matter is based on two cornerstones. Maxwell's equations describe the propagation of any electromagnetic (EM) field when the EM properties of the materials present in space, which interact with the field, are known. Maxwell's equations have to be supplemented with equations that describe the material's response to the driving EM force. Few materials show a strong magnetic response at optical frequencies and the magnetic forces can be neglected without too much loss of generality. The electric response is usually described with a phenomenological model specifying the electrical polarization of the materials as a function of the electric field strength.

In earlier days linear optics, assuming a proportionality between the induced polarization and the driving electric field, was practically always sufficient to explain the experimental results. With the introduction of the laser in the sixties larger light intensities became available and interesting deviations from the linear theory could be studied. In general the polarization of any material is a complicated function of the electric field, which can be expanded into powers of the field,¹

$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots \quad (1.1.1)$$

This equation is only schematic as the time (frequency) and space (wave-vector) dependencies are not shown. This hardly ever gives rise to confusion and all time and space dependencies will be omitted and reintroduced in this thesis when deemed appropriate. $\chi^{(1)}$ is the linear susceptibility, which manifests itself for instance in the linear absorption of radiation and the index of refraction. $\chi^{(2)}$ is the second-order susceptibility and gives rise to many fascinating effects. I only mention here the generation of EM radiation at twice the frequency of the incoming light (second-harmonic generation) and the static change of shape of some materials under the influence of an electric field (piezo-electric properties).

For materials that have inversion symmetry, like gases, liquids and centrosymmetric crystals, one can easily show that the polarization is an

odd function of the electric field and all even-order terms in expansion (1.1.1) vanish. For these materials the third-order nonlinear susceptibility tensor $\chi^{(3)}$ contains the prime deviations from linear theory. I will mainly concentrate on effects resulting from $\chi^{(3)}$.

When the electric field is far weaker than the internal atomic fields binding the electrons, the electronic wavefunctions are only slightly perturbed and expansion (1.1.1) converges quickly. Working with continuous wave (cw) mode-locked lasers one never attains field strengths large enough to match those inside the atoms (E order of 10^{11} V/m, Intensity I typically 10^{19} W/m²). Using tightly-focused low-repetition rate lasers it is possible to create enormously strong fields. The larger the intensity of the laser the more terms become important ($\chi^{(5)}$, $\chi^{(7)}$...), until finally convergence of the expansion is no longer guaranteed. Beyond this limit the driving fields are strong enough to rip the electrons from the nuclei. Via multi-photon absorption molecules get ionized and the material under study is destroyed. The laser intensities we use are high enough to see interesting third-order nonlinear effects, but they are far below ionization thresholds (typically 10^{17} W/m²).

1.2 Interaction of radiation and matter

The heart of any theory describing the interaction of matter and radiation is formed by the Hamiltonian

$$H = H_0 + H_{\text{rad}} + H_{\text{int}} , \quad (1.2.1)$$

where H_0 is the Hamiltonian of the molecular system in the absence of radiation, H_{rad} is the energy operator of the radiation field and H_{int} represents the coupling between the molecular system and the radiation field.

H_0 is the full Hamiltonian in the absence of radiation and thus contains all the intra and inter-molecular interactions. The degrees of freedom we are mainly interested in are the vibrational and rotational excitations of molecules in condensed phases (liquid, solid). It is often a good approximation to separate the degrees of freedom of the system into a few slow and interesting degrees of freedom, for which simple single-molecule variables are taken, and the faster degrees of freedom contained in

the so-called bath. The latter are often multi-particle variables and due to their complicated nature they are usually strongly coupled to each other.

It is recommendatory to separate the Hamiltonian H_0 in $H_0 = (H_S + H_C + H_{\text{bath}})$, where the system Hamiltonian H_S depends on the interesting slow variables only, H_{bath} represents the part that is completely unrelated to these variables, and H_C represents the coupling between the slow variables and the degrees of freedom of the bath. In section (1.3) the separation between slow variables and bath variables is discussed in more detail.

H_{rad} is the energy operator of the radiation field. Making use of second quantization and creation and annihilation operators, it is possible to treat the radiation field purely quantum mechanically, but this is rarely done.² Under typical experimental conditions the number of photons per quantized mode of the radiation field is high enough to validate a more classical description in terms of an electric (E) and a magnetic (H) field. The energy of the radiation field in these variables is

$$H_{\text{rad}} = \int d^3\vec{r} \left\{ (1/2)\epsilon_0 E^2 + (1/2)\mu_0 H^2 \right\}. \quad (1.2.2)$$

H_{int} is the interaction Hamiltonian between the molecular system and the radiation field. When one neglects weak diamagnetic currents this interaction Hamiltonian can be expressed in a $(\vec{r} \cdot \vec{E})$ - or a $(\vec{p} \cdot \vec{A})$ -form, $\vec{A}$ being the vector potential. Becker has proven for once and for all the equivalence of both representations.³ In the $(\vec{r} \cdot \vec{E})$ -representation the interaction Hamiltonian between a group of charges within a (neutral) molecule and the radiation field is

$$H_{\text{int}} = V(t) = \sum_{\alpha} -(e_{\alpha} \vec{r}_{\alpha} \cdot \vec{E}(\vec{r}_{\alpha}, t)) \approx -\vec{\mu} \cdot \vec{E}(t), \quad (1.2.3)$$

where the summation is over all charges present. As the size of a molecule is very small compared to the wavelength of visible light, the electric field will, in first approximation, be the same for all charges (at their various positions $\vec{r}_{\alpha}$) within the molecule. In the so-called dipole approximation the coupling of the radiation with the complicated distribution of charges is reduced to the coupling with only one variable, the dipole moment $\vec{\mu} = \sum_{\alpha} e_{\alpha} \vec{r}_{\alpha}$, as indicated in the second part of equation (1.2.3).

When the density of molecules is low the interaction of the radiation

field with the entire system is a summation of the interactions with all individual molecules. At high densities the interactions between the molecules should be accounted for and their EM response will change. An effect that can easily be included is the (induced) electric dipole-dipole interaction between the molecules. This interaction can be accounted by replacing the electric field appearing in equation (1.2.3) by an effective local electric field being the sum of the externally-applied field and the field created by the surrounding polarized molecules .

1.3 Relaxation processes

In the previous section we separated the degrees of freedom of the molecular system in a few slow and relevant variables and the "other" variables, grouped together in the so-called bath. In this section I want to take a closer look at the dynamics of the relevant (slow) degrees of freedom, being determined by their mutual coupling and their coupling to the bath. The most fundamental approach would be to take the full density matrix of the macroscopic ensemble of molecules, which is a monstrous colossus, and evaluate its time evolution. When the bath variables are integrated out a reduced density matrix results that excellently represents the excitation of the relevant degrees of freedom. This reduced density matrix is often an ensemble-average of single-molecule density matrices and contains information on the average population of the single-molecule levels as well as the coherence between the excited molecules.

Usually the time-evolution of the reduced density matrix depends only weakly on the bath variables and a second, less fundamental but more practical, approach can be followed. This other approach starts with the single-molecule Hamiltonian. The interaction with the bath will be (phenomenologically) accounted for via the addition of extra terms, depending on the bath variables, to the single-molecule Hamiltonian. The inter-molecular interactions can be included in a similar way. This approach has been used in many articles⁴⁻¹⁰ and will be used in this thesis as well. This single-molecule approach clearly fails to describe the dynamics of lattice modes in solids, where eigenstates of the whole system, being specified by their respective wave-vectors, must be used.

Usually certain assumptions can be made regarding the coupling between the relevant variables and the bath. In the weak-coupling limit one assumes

that the bath has many degrees of freedom and the coupling of the relevant variables with the bath variables is weak, compared to the coupling between the bath variables, being specified by a typical correlation time (τ_c) of the bath. In this limit coherence between the degrees of freedom of the bath, which might be called the memory of the bath, is lost rapidly. The coupling of the relevant variables with the bath effectively is an irreversible relaxation process, resulting in an exponential decay in time of the "relevant excitation", which is completely specified by two relaxation rates per slow variable. The relaxation rate of the on-diagonal elements of the density matrix is denoted as $(1/T_1)$ and is related to the relaxation of the excited-state population. The relaxation rate of the off-diagonal elements is denoted by $(1/T_2)$ and is related to phase relaxation.

Two processes contribute to the relaxation of the off-diagonal elements of the reduced density matrix. First of all the off-diagonal elements are directly affected by the decrease of the population of the excited state, which per definition is a T_1 process. Secondly pure dephasing of the excited molecules leads to a decrease in the off-diagonal elements of the density matrix as well. There is a correspondence between the amplitude of the vibrator or rotator that appears in the classical picture and the off-diagonal elements of the reduced density matrix in the quantum-mechanical picture, which are sometimes converted in the so-called coherent (vibrational,...) amplitude. When the molecules loose their phase relation and start to vibrate or rotate out of phase the off-diagonal elements of the reduced density matrices decrease, because the reduced density matrix is an ensemble-average of single-molecule density matrices. The pure dephasing time, denoted as τ_{ph} is usually defined as⁴

$$(1/T_2) = (1/(2T_1)) + (1/\tau_{ph}) . \quad (1.3.1)$$

In equation (1.3.1) a factor $(2T_1)$ appears, instead of T_1 , because in this thesis phase relaxation is defined with respect to the (coherent) vibrational amplitude, whereas the excited-state population is approximately related to the (coherent) amplitude squared, as will be shown in chapter 3.

Practically all models⁴⁻¹⁰ try to describe the pure dephasing process in terms of a slight dependence of the energy spacing between the single-molecule levels on the coordinates of the bath. In a more classical picture the energy spacing between these two levels is related to the instantaneous

frequency of the associated (vibrational, rotational) degree of freedom. If we are only interested in the time evolution of one (slow) variable, a two-level model often suffices. The groundstate will be denoted by $|g\rangle$ and the first (vibrational-, rotational-) excited state will be denoted by $|b\rangle$. Denoting the frequency difference between $|b\rangle$ and $|g\rangle$ as $\omega_{bg} = (E_b - E_g)/\hbar$ the phase of the related (classical) oscillator is

$$\varphi(t) - \varphi(0) = \int_0^t d\tau \omega_{bg}(\tau), \quad (1.3.2)$$

where the instantaneous frequency $\omega_{bg}(\tau)$ depends on the degrees of freedom of the bath or, in other words, the environment of the molecule. In the weak-coupling limit pure dephasing is exponential in time and the pure dephasing time is related to $\varphi(t)$ via^{4,6}

$$e^{-|t|/\tau_{ph}} = |\langle\langle e^{-i\varphi(t)} \rangle\rangle|, \quad (1.3.3)$$

where $\langle\langle \rangle\rangle$ denotes that an average has to be taken over all (stochastic) degrees of freedom of the bath. A more detailed description of the dynamics of vibrational degrees of freedom, and some experimental techniques to probe this dynamics, is given in section (1.7).

The dynamics of any degree of freedom can be probed by applying a (harmonic) driving force and observing its response as a function of the frequency of the driving force. The most common term for this frequency-dependent response is the "lineshape of the excitation". Linear response theory states that the response of the driven system is related to spontaneous fluctuations in the unperturbed system.⁴

In the previous paragraphs all the molecules were assumed to be equivalent, although this was not stated explicitly. When this assumption is valid the line is said to be homogeneously broadened and there is no way to excite part of the line. Naturally the system's response will be monochromatic on excitation with a CW monochromatic driving force, but after removal of the driving force the spectral response of the so-called free induction decay will contain all frequencies of the homogeneously-broadened line.

In some cases the molecules are not at all equivalent. This is e.g. often the case in solids, when different molecules can have different environments. In this case the response of the system is clearly composed of many individual contributions. The line is said to be inhomogeneously

broadened, because it can be divided into a number of narrower lines, which can be separately excited and which are called its homogeneously-broadened constituents. Each of these lines can be associated with a single mode, with its specific eigenfrequency and relaxation times (T_1 and T_2). A continuous distribution of the eigenfrequencies will result in overlap of the homogeneous (lines/packets) in the frequency domain and makes them combine into an inhomogeneously-broadened line. The separation into homogeneously-broadened (lines/packets) is often not so strict, because spectral diffusion of an excitation from one packet to another often takes place due to their mutual coupling. Whether a line is homogeneously or inhomogeneously-broadened is often tentatively decided on its spectral shape, as the former usually has a Lorentzian shape and the latter is often Gaussian-shaped.

Spectral hole burning¹¹ is one of the techniques that makes use of the possibility to excite and detect the individual homogeneously-broadened lines and enables the experimentator to resolve the inhomogeneously-broadened line in its constituents. Spectral hole burning is based on the saturation of one or several excitations. A second technique that allows for the separation of an inhomogeneously-broadened line in its components is the echo.¹¹ After the coherent excitation of the system with a first laser pulse the various excited modes start to oscillate with their specific frequency and accumulate a phase difference with respect to each other. In some circumstances it is possible to reverse the phases of the modes with a second intense laser pulse. The subsequent rephasing of the excited modes results, after some time, in the emission of a third pulse, called the echo. Observation of the strength of this echo as a function of the time delay between the first and the second pulse allows one to determine the linewidth of the homogeneous components of an inhomogeneously-broadened line.

1.4 Time-dependent perturbation theory

In this section I will review the use of time-dependent perturbation theory in determining the response of a quantum-mechanical system to a driving radiation field. This technique has been demonstrated by many authors¹¹⁻¹⁵ and forms the theoretical basis of nonlinear optics. I believe a review is appropriate as it can clarify many controversies. When the time evolution of the density matrix of the system is known the macroscopic (electric) polarization density $\vec{P}(t)$ can in principle be

evaluated and the link to the macroscopic Maxwell equations can be made.

The time evolution of the density matrix $\rho(t)$ obeys the equation

$$i\hbar \partial\rho(t)/\partial t = [H_0 + V(t), \rho(t)]. \quad (1.4.1)$$

where $V(t)$ is the interaction potential. In the dipole approximation the interaction potential is $V(t) = -\mu E(t)$.

The integral form of equation (1.4.1) is

$$\begin{aligned} \rho(t) = & e^{-(i/\hbar)H_0(t-t_0)} \rho(t_0) e^{+(i/\hbar)H_0(t-t_0)} \\ & + \{1/(i\hbar)\} \int_{t_0}^t dt' \{e^{-(i/\hbar)H_0(t-t')} [V(t'), \rho(t')] e^{+(i/\hbar)H_0(t-t')}\}. \end{aligned} \quad (1.4.2)$$

When the interaction potential is only a slight perturbation to H_0 the integral equation can be expanded by successive iterations into increasing orders of V . For each successive order of perturbation the commutator $[V(t'), \rho(t')]$ yields two terms, one with $V(t')$ acting on the left of $\rho(t')$ and one term in which it acts on the right. The n^{th} -order correction to the density matrix therefore consists of 2^n terms.

Graphically a nice visualization of the time evolution of $\rho(t)$ is given by Shen.¹¹ In fig.(1.4.1) one of the eight possible contributions to $\rho^{(3)}(t)$ is pictured as an example. The two vertical lines represent the evolution of the ket and the bra of $\rho^{(3)}(t)$ as time evolves from bottom to top.

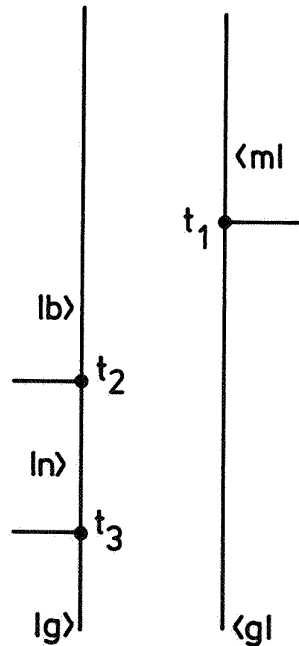


Fig.1.4.1:
One of the eight
diagrams representing
the evolution of
 $\rho^{(3)}(t)$.

$|n\rangle$, $|b\rangle$ and $|m\rangle$ are three different eigenstates of H_0 . The numbering might seem strange, but later on it will be shown that, although $|b\rangle$ can be any eigenstate, the strongest contribution to $\rho^{(3)}(t)$ corresponds to the situation that $|b\rangle$ is a specific (vibrational) eigenstate excited on resonance. Initially the system is in the groundstate and the density matrix of the molecular system is $\rho = |g\rangle\langle g|$. At $t'=t_3$ "operation" of $V(t')_{ng}$ on the left changes the density operator into $|n\rangle\langle g|$. At some later time in this example first $V(t_2)_{bn}$ works on the left and later $V(t_1)_{gm}$ operates on the right of the density operator. In between the time evolution of the density matrix is governed by the Green function or full propagator of the system in the absence of radiation, being $G(t) = (e^{-iLt})$, where $L = (1/\hbar)[H_0, \]$ is the Liouville superoperator. The integral form of the contribution to $\rho^{(3)}(t_0)$ that is pictured in fig.(1.4.1) is

$$-(1/(i\hbar))^3 \int_{-\infty}^{t_0} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \left(e^{-(i/\hbar)H_0(t_0-t_2)} V(t_2) e^{-(i/\hbar)H_0(t_2-t_3)} \right. \\ \left. \times V(t_3) \rho(t_3) e^{+(i/\hbar)H_0(t_1-t_3)} V(t_1) e^{+(i/\hbar)H_0(t_0-t_1)} \right). \quad (1.4.3)$$

In the more-practical interpretation, all operators and eigenstates mentioned in the previous text and used in eq.(1.4.1) and (1.4.2) are related to single molecules and the density matrix is an ensemble average over single-molecule density matrices. The enormous advantage of this interpretation is the drastic reduction of the number of eigenstates. A two-level model often suffices. In this interpretation the coupling between the molecules is introduced through the backdoor, via the inclusion of damping terms in the single-molecule Hamiltonian. In the weak-coupling limit the decay is exponential, and the action of the Green function, which is interpreted as the "single-molecule" propagator, is $G(t)|n\rangle\langle b| = e^{(-i\omega_{nb} - \Gamma_{nb})t} |n\rangle\langle b|$ ($t > 0$), where Γ_{nb} is the relaxation rate of the $|n\rangle\langle b|$ -part of the density matrix. This single-molecule Green function is the operator we are interested in, as it dictates the dynamical behavior of the system and contains all relaxation processes. More specifically we want to determine the relaxation rates Γ_{nb} .

The third-order polarization can be easily determined once $\rho^{(3)}$ is known via: $\vec{P}^{(3)}(t_0) = (N/V) \text{Tr}\{\vec{\mu}\rho^{(3)}(t_0)\}/\text{Tr}\{\rho(t_0)\}$, where (N/V) is the number of molecules per unit volume. The equation for $\rho^{(3)}(t)$ already contains three dipole operators, originating from the triple action of the

interaction potential $V(t) = -\mu E(t)$, which are now supplemented by a fourth. Through substitution one can show that the contribution of equation (1.4.3) to the (macroscopic) third-order polarization is

$$\sum_{n,b,m} \{1/(i\hbar)\}^3 (N/V) \times \tilde{\mu}_{mb}(t_0) \tilde{\mu}_{bn}(t_2) \tilde{\mu}_{ng}(t_3) \tilde{\mu}_{gm}(t_1) E(t_3) E(t_2) E(t_1), \quad (t_3 < t_2 < t_1 < t_0), \quad (1.4.4)$$

where the summation is taken over all single-molecule eigenstates, and we have introduced the interaction representation of the dipole operator, which we denote by a tilde

$$\tilde{\mu}_{mb}(t) = \langle m | e^{(i/\hbar)H_0 t} \mu e^{-(i/\hbar)H_0 t} | b \rangle. \quad (1.4.5)$$

Fig.(1.4.1) is just one of the eight possible graphs that contribute to the time evolution of $\rho^{(3)}(t)$. The other seven contributions can be cast in expressions similar to equation (1.4.4). When all contributions are added a multiple commutator of four dipole operators results (see equation (1.4.9)). With this example in mind it is possible to determine the magnitude of the induced polarization to any order in the incident fields.¹⁵

$$P_i^{(1)}(t) = \epsilon_0 \int_{-\infty}^t dt_1 \chi_{ij}^{(1)}(t, t_1) E_j(t_1), \quad (1.4.6)$$

$$P_i^{(2)}(t) = \epsilon_0 \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 \chi_{ijk}^{(2)}(t, t_1, t_2) E_j(t_1) E_k(t_2), \quad (1.4.7)$$

$$P_i^{(3)}(t) = \epsilon_0 \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 \int_{-\infty}^t dt_3 \chi_{ijkl}^{(3)}(t, t_1, t_2, t_3) E_j(t_1) E_k(t_2) E_l(t_3), \quad (1.4.8)$$

etc ...

$$\chi_{\alpha_0 \dots \alpha_n}^{(n)}(t_0, t_1, \dots, t_n) = (i/\hbar)^n (1/\epsilon_0) (N/V)$$

$$\times \langle [\dots [\tilde{\mu}_{\alpha_0}(t_0), \tilde{\mu}_{\alpha_1}(t_1)], \dots, \tilde{\mu}_{\alpha_n}(t_n)] \rangle \theta(t_0 - t_1) \dots \theta(t_{n-1} - t_n), \quad (1.4.9)$$

The vector character of the radiation is reintroduced through the index α_i . The Einstein convention is used for the indices i, j, k etc. This convention implies that a summation should be carried out over all identical cartesian indices $\{(1, 2, 3) \text{ or } (x, y, z)\}$.

The product of electric fields in the integral (1.4.8) is insensitive to the simultaneous permutation of one pair of indices (α_i, α_j) and its related pair of time variables (t_i, t_j) . This leads to an ambiguity in the choice of $\chi^{(n)}$. Any part of $\chi^{(n)}$ that is antisymmetric under this simultaneous permutation disappears in the implicit summation over the indices and the integration over the time variables. We found it useful to symmetrize $\chi^{(n)}$ with respect to these simultaneous permutations. Other choices of $\chi^{(n)}$, yielding identical physical results, are also possible. Our expression for $\chi_{\alpha_0 \dots \alpha_n}^{(n)}(t_0, \dots, t_n)$ thus becomes

$$\chi_{\alpha_0 \dots \alpha_n}^{(n)}(t_0, t_1, \dots, t_n) = (i/\hbar)^n (1/n!) (1/\epsilon_0) (N/V) \\ \times \Sigma_{\text{Perm}} <[\dots [\tilde{\mu}_{\alpha_0}(t_0), \tilde{\mu}_{\alpha_1}(t_1)], \dots, \tilde{\mu}_{\alpha_n}(t_n)] > \theta(t_0 - t_1) \dots \theta(t_{n-1} - t_n), \quad (1.4.10)$$

where Σ_{Perm} represents a summation over all permutations of the pairs $((\alpha_i, t_i), i \neq 0)$ and where the permutation of the time variables in the step functions is included.

The nonlinear response to a perturbing force, as specified by the nonlinear susceptibility response function $\chi^{(n)}(t_0, t_1, \dots, t_n)$ of the material under study, is directly related to the "spontaneous" fluctuations in the unperturbed system, specified by the $(n+1)^{\text{th}}$ -order dipole correlation function. The equations (1.4.9) and (1.4.10) are an extension of the well known fluctuation-dissipation theorem of linear-response theory into the realm of nonlinear interactions.

The response functions $\chi^{(n)}$ can be converted into the frequency domain via Fourier transformation. The invariance of the $(n+1)^{\text{th}}$ -order correlation function to translation in time, reduces the $(n+1)$ time variables to n time differences. The Fourier transform of $\chi^{(n)}$ is defined with respect to the latter n independent variables.

$$P_i^{(1)}(\omega) = \epsilon_0 \int_{-\infty}^{\infty} d\omega_1 \chi_{ij}^{(1)}(-\omega, \omega_1) E(\omega_1) \delta(-\omega + \omega_1) = \epsilon_0 \chi_{ij}^{(1)}(-\omega, \omega) E(\omega) \quad (1.4.11)$$

$$P_i^{(3)}(\omega) = (1/2\pi)^2 \epsilon_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 d\omega_3 \chi_{ijk}^{(3)}(-\omega, \omega_1, \omega_2, \omega_3) \\ \times E_j(\omega_1) E_k(\omega_2) E_l(\omega_3) \delta(-\omega + \omega_1 + \omega_2 + \omega_3) \quad (1.4.12)$$

etc ...

$$\chi_{ij}^{(1)}(-\omega_1, \omega_1) = \int_{-\infty}^{\infty} dt_1 \chi_{ij}^{(1)}(t, t-t_1) e^{i\omega_1 t_1} \quad (1.4.13)$$

$$\begin{aligned} \chi_{ijkl}^{(3)}(-\omega_1-\omega_2-\omega_3, \omega_1, \omega_2, \omega_3) = & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt_1 dt_2 dt_3 \\ & \times \chi_{ijkl}^{(3)}(t, t-t_1, t-t_2, t-t_3) e^{i(\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3)}. \end{aligned} \quad (1.4.14)$$

I use the Fourier convention

$$f(\omega) = \int_{-\infty}^{\infty} dt f(t) e^{i\omega t} \quad \text{and} \quad f(t) = (1/2\pi) \int_{-\infty}^{\infty} d\omega f(\omega) e^{-i\omega t}.$$

Let me next sum up some important symmetry relations of $\chi^{(n)}$:

- * The invariance of the $\chi^{(n)}$ to translation in time, reduces the (n+1) time variables to n independent time differences.
- * The symmetrized version of $\chi^{(n)}$ consists of $n!2^n$ terms.
- * The function $\chi^{(n)}(\omega_0, \omega_1, \dots, \omega_n)$ is only defined for $\omega_0 = -\sum_i \omega_i$.
- * The time domain response function $\chi^{(n)}$ is purely real for transparent nonmagnetic materials.¹⁵
- * $\chi^{(n)}(\omega, \omega_1, \dots, \omega_n) = \chi^{(n)*}(-\omega, -\omega_1, \dots, -\omega_n)$.
- * $\chi_{\alpha_0 \dots \alpha_n}^{(n)}(\omega_0, \omega_1, \dots, \omega_n)$ is invariant to simultaneous permutation of one pair (α_i, ω_i) and another pair (α_j, ω_j) , when $i \neq 0$ and $j \neq 0$.
- * Permutation of (α_0, ω_0) and (α_i, ω_i) renders the complex conjugate.
e.g. $\chi_{ijkl}^{(3)}(-\omega_1-\omega_2-\omega_3, \omega_1, \omega_2, \omega_3) = \chi_{jikl}^{(3)*}(\omega_1, -\omega_1-\omega_2-\omega_3, \omega_2, \omega_3)$
- * The demand of causality imposes a kind of Kramers-Kronig relation on $\chi^{(3)}$ for each frequency variable.² One of these relations is presented below. The symbol $\int_{-\infty}^{\infty}$ indicates that the principal value of the integral should be taken.

$$i\pi(\chi_{ijkl}^{(3)}(-\omega_1-\omega_2-\omega_3, \omega_1, \omega_2, \omega_3)) = \int_{-\infty}^{\infty} d\omega' \chi_{jikl}^{(3)*}(-\omega' - \omega_2 - \omega_3, \omega', \omega_2, \omega_3) / (\omega' \omega_1). \quad (1.4.15)$$

- * For most materials, various other symmetry relations hold, besides the general ones mentioned above. For the third-order susceptibility these relations can be found in the work of Hellwarth¹⁵. A few mistakes in his table are corrected in ref.16. In isotropic media, which have the highest symmetry, only 21 of the 81 elements of $\chi^{(3)}$ are nonzero and only three of them are independent. Written in a compact form their relation is

$$\begin{aligned}
xxxx &= yyyy = zzzz \\
xyyy &= xxzz = yyzz = yyxx = zzzx = zzyy \\
xyxy &= xzxz = yzyz = yxyx = zxxz = zyzy \\
xyyx &= xzzx = yzzy = yxxy = zxxz = zyyz \\
xxxx &= xxyy + xyxy + xyyx
\end{aligned} \tag{1.4.16}$$

For a crystal with cubic symmetry belonging to the classes $m\bar{3}m$, $\bar{4}3m$ or 432 the first four relations hold as well, only the last relation is invalid, and the number of independent elements of $\chi^{(3)}$ is four.

1.5 Third-order susceptibility tensor

Time-dependent perturbation theory allows one, in theory, to describe the interaction of radiation and matter to any order, at least if the expansion of the polarization in the electric field converges. From now on I will concentrate on the effects of the third-order susceptibility tensor $\chi^{(3)}$. Nonlinear optical experiments are often performed with one, or a few laser beams of limited spectral width. This drastically reduces the frequency integration in equation (1.4.12) to small ranges around the laser frequencies. Maker and Terhune¹⁷ have already demonstrated that the distinct sequences of the electric fields generate equivalent contributions, which can be grouped, the orders being accounted for by a permutation factor D . When the frequency width of each laser is narrow compared to the structure in the frequency dependence of $\chi^{(3)}$, close to the laser frequency, the integration can be replaced by a much easier summation over all possible combinations of $\pm \omega_i$. Treating this "quasi-monochromatic" light as "real" monochromatic light

$$E_j(t) = (1/2) \sum_i (E_{\omega_i, j} e^{-i\omega_i t} + E_{\omega_i, j}^* e^{i\omega_i t}), \tag{1.5.1}$$

$$E_j(\omega) = \pi \sum_i (E_{\omega_i, j} \delta(\omega - \omega_i) + E_{\omega_i, j}^* \delta(\omega + \omega_i)), \tag{1.5.2}$$

One finds

$$P_{\omega_1 + \omega_2 + \omega_3, i}^{(3)} = \epsilon_0 (D/4) \chi_{ijkl}^{(3)}(-\omega_1 - \omega_2 - \omega_3, \omega_1, \omega_2, \omega_3) E_{\omega_1, j} E_{\omega_2, k} E_{\omega_3, l}, \tag{1.5.3}$$

where the permutation factor D is

D=6 , when all three frequencies ω_i are different.

D=3 , when two frequencies are equal and the other one differs from them.

D=1 , when all three frequencies are identical.

Positive and negative frequencies are considered to be different, as they refer to different parts of the frequency axis.

Part of the reason I elaborated on the derivation of $\chi^{(n)}$ is the common confusion on the permutation factor, which can even be spotted in the work of Shen¹¹ on page 38-40. The misunderstanding is rooted in the ambiguity of the definition of $\chi^{(n)}$. We have constructed $\chi^{(n)}$ to be invariant under the simultaneous permutation of two indices and their two related frequency, or time, variables. With this choice $\chi^{(n)}$ varies continuously when two frequency variables approach each other and become equal. This is e.g. clearly observable from the quantum-mechanical expression of $\chi^{(3)}$ derived by Bloembergen¹⁸, of which the general structure is discussed in the next paragraph. When two frequencies of $\chi^{(3)}$ become equal the permutation factor D changes discontinuously, which seems to be strange on first sight. The electric fields involved do however add up to a larger field when they match in frequency!. This second discontinuity just compensates for the one in the permutation factor. A complication is the fact that both fields will interfere when their frequencies become equal and their phase relation will influence the total electric field strength and the amount of third order polarization strongly.

All 48 terms that contribute to the symmetrized version of $\chi_{ijkl}^{(3)}(-\omega_1-\omega_2-\omega_3, \omega_1, \omega_2, \omega_3)$ are written down in an article by Bloembergen, Lotem and Lynch¹⁸. It is of no use to reproduce their expression, as it would take several pages. The derivation is straightforward, though laborious. Starting with equation (1.4.3) I will show how one of the 48 term of $\chi^{(3)}$ can be found. When the radiation field, which forms the time-dependent part of $V(t)$, is expressed in its frequency components the time integrals can be evaluated, yielding equation (1.5.4). Five other terms can be produced through permutation of ω_1 , ω_2 and ω_3 (with their accompanying indices). Each of the seven other graphs yield 6 terms as well, bringing the total to 48.

Thus one of the 48 terms of $\chi_{ijkl}^{(3)}(-\omega_1-\omega_2-\omega_3, \omega_1, \omega_2, \omega_3)$ is

$$\frac{(N/V)}{(6\epsilon_0\hbar^3)} \sum_{n,b,m} \frac{(\mu_j)_{gm}(\mu_i)_{mb}(\mu_k)_{bn}(\mu_l)_{ng}}{(\omega_{bm}-\omega_1-\omega_2-\omega_3-i\Gamma_{bm})(\omega_{bg}-\omega_2-\omega_3-i\Gamma_{bg})(\omega_{ng}-\omega_3-i\Gamma_{ng})}, \quad (1.5.4)$$

where a threefold summation is taken over all eigenstates of the system.

A close look at the expression of Bloembergen can clarify a few issues. Firstly the third-order susceptibility is clearly a continuous function of each of its three frequency variables. Secondly the factor (1/6) in front of his expression arises from the procedure to symmetrize $\chi^{(3)}$ with respect to the often mentioned permutation operator. Thirdly the 48-term expression of $\chi^{(3)}$ is awfully complicated. Although some attempts have been made¹⁹ nobody has yet succeeded in calculating $\chi^{(3)}$ with the use of this expression.

The microscopic expressions for $\chi^{(n)}$ are strictly correct only for dilute media¹¹. In condensed media the interactions between the electric dipoles induced by the incident electric field become important. Polarized neighboring molecules will effectively induce an extra field that combined with the macroscopic field adds up to the so-called local field. In isotropic media, as well as in cubic media, the local field is just $[(\epsilon(\omega)+2)/3]$ times the macroscopic electric field. As the microscopic $\chi^{(3)}(\omega_0, \omega_1, \omega_2, \omega_3)$ is derived in terms of the EM field experienced locally by the molecules the macroscopic $\chi^{(3)}$ has to be corrected for the local field effect by a factor¹¹

$$\text{Local-field correction factor} = L = \frac{3}{\prod_{i=0}^3 [(\epsilon(\omega_i)+2)/3]}. \quad (1.5.5)$$

When the three-fold summation over the eigenstates, mentioned in equation (1.5.4), is carried out some terms will contribute far less to $\chi^{(3)}$ than others. Especially those combinations of $|n\rangle$, $|b\rangle$ and $|m\rangle$ that have a small denominator will contribute strongly. One speaks of a one, two or three-photon resonance when the factor $(\omega_{bm}-\omega_1-\omega_2-\omega_3-i\Gamma_{bm})$, $(\omega_{bg}-\omega_2-\omega_3-i\Gamma_{bg})$ or $(\omega_{ng}-\omega_3-i\Gamma_{ng})$ respectively is small. The other 47 terms of $\chi^{(3)}$ show similar resonances. In the next paragraph it will be shown that, in our situation, $\chi^{(3)}$ does not have one-photon resonances nor does it have three-photon resonances.

When the Born-Oppenheimer (BO) approximation is valid the eigenstates ($|n\rangle$, $|b\rangle$ and $|m\rangle$) can be partitioned in electronically-excited states and non-electronically-excited eigenstates, in which the electron configuration

is in its groundstate. Independent of the electron configuration, the molecule can of course be vibrationally and/or rotationally excited. The energy needed for electronic excitation is generally substantially larger than the energy necessary for vibrational or rotational excitation. For transparent media the energy of the "visible-light" quanta (of frequency ω_i) is too small to induce electronic transitions, for which ultra-violet radiation is necessary and too large to efficiently excite molecular rotations or vibrations. Although there probably are some higher-order rotation/vibration states, for which the energy difference with the groundstate almost matches the energy of the "visible-light" quanta, the transition matrix elements, situated in the numerator of equation (1.5.4), are (practically) zero when taken between a higher-order rotation/vibration state and the groundstate. In conclusion there will be no eigenstate $|n\rangle$, with a reasonably large transition matrix element $(\mu_\ell)_{gn}$, for which $(\omega_{ng}-\omega_3-i\Gamma_{ng})$ is small. For the same reason neither ω_{bm} will get close to $\omega_1+\omega_2+\omega_3$, at least when the optical frequencies are comparable in magnitude.

The only possibility for $\chi^{(3)}$ to have a small denominator lies in a two photon resonance, where $(\omega_i+\omega_j)$ matches the energy difference between a low-lying, non-electronically-excited, state and the groundstate $|g\rangle$. This is only possible when ω_i is positive and ω_j is negative, or vice versa, and $(\omega_i+\omega_j)$ represents the difference between two optical frequencies. I have chosen the symbol $|b\rangle$ for this state to indicate the resonance. When $|b\rangle$ differs from the groundstate the two-photon resonance can be attributed to the Raman effect $((\omega_i+\omega_j)\approx\omega_{bg})$. When $|b\rangle$ equals the groundstate another resonance arises, which can be attributed to the Kerr effect $((\omega_i+\omega_j)\approx 0)$. In both cases the resonant contributions to $\chi^{(3)}$ depend critically on the optical frequencies and have the well-known Lorentzian shape. There are six possibilities for a two-photon resonance in $\chi^{(3)}(\omega_0, \omega_1, \omega_2, \omega_3)$, namely whenever $(\omega_i+\omega_j = \pm\omega_{bg})$. Two typical resonances in $\chi^{(3)}$ look like

$$C_{12}/(\omega_{bg}+\omega_1+\omega_2+i\Gamma_{bg}) \quad \text{and} \quad C_{12}^*/(\omega_{bg}-\omega_1-\omega_2-i\Gamma_{bg}), \quad (1.5.6)$$

$$C_{12} = (N/V)L\epsilon_o/(6\hbar) \langle g|\alpha_{i\ell}(-\omega_0, -\omega_3)|b\rangle \langle g|\alpha_{jk}(\omega_1, \omega_2)|b\rangle^*, \quad (1.5.7)$$

$$\langle g|\alpha_{ij}(\omega_0, \omega_1)|b\rangle = 1/(\hbar\epsilon_o) \sum_n \left\{ \frac{\langle g|\mu_i|n\rangle\langle n|\mu_j|b\rangle}{(\omega_{ng}+\omega_0)} + \frac{\langle g|\mu_j|n\rangle\langle n|\mu_i|b\rangle}{(\omega_{ng}+\omega_1)} \right\}, \quad (1.5.8)$$

where the summation over n runs over all eigenstates, although the electronically-excited states contribute strongest to this summation, as will be shown later on. One might notice that α_{ij} can be interpreted as the polarizability operator. Indeed in the absence of damping $\langle g | \alpha_{ij}(-\omega, \omega) | g \rangle$ represents the polarizability at the (optical) frequency ω and is strongly related to the linear susceptibility $\chi^{(1)}(-\omega, \omega)$ defined earlier. The damping rate $i\Gamma_{ng}$ is omitted from equation (1.5.8), because it is negligible with respect to the "mistuning" from one-photon resonance given by $(\omega_{ng} - \omega_1)$. The four other (two-photon) resonances in $\chi^{(3)}$ are obtained via permutation of (1,2) into (1,3) or (2,3) and simultaneously permuting the indices.

The summation over $|b\rangle$ in equation (1.5.4) runs over all eigenstates. When $|b\rangle$ does not correspond to a two-photon resonance the associated contribution to $\chi^{(3)}$ will be rather insensitive to the optical frequencies. These other contributions can be lumped together in the so-called non-resonant contribution χ_{NR} . To decide which states are most important in the summation over $|n\rangle$ and $|m\rangle$ an order of magnitude estimate for the electric dipole-transition matrix elements, which by the way are related to the cross-section for absorption of radiation, will be given. Taken between vibrational states these elements are small, because the electron distribution hardly changes from one state to the other. When μ is sandwiched between rotational states the result can in principle be much larger, but for molecules with inversion symmetry it will be small as well. In condensed matter the rotation is strongly hindered and these elements are small anyway. By far the largest transition matrix elements are those taken between an excited electronic state and the groundstate. The largest non-resonant contribution in the summation over n, b and m in equation (1.5.4) therefore arises from the (high-lying) electronic levels. For this reason χ_{NR} , being the sum of all non-resonant contributions to χ , is a real, positive and slowly-increasing function of the optical frequencies. The increase in χ_{NR} will be the larger the higher the laser frequencies, and the closer they are to the UV absorptions of the material under study.

The following scheme can thus be used for the calculation of the third order susceptibility $\chi^{(3)}$. Look if any combination of two of the laser frequencies involved equals the energy difference between the groundstate and a low-lying (non-electronically-excited) level. If this happens to be the case determine the resonant term(s) as specified in (1.5.6)-(1.5.8). The total $\chi^{(3)}$ is equal to the sum of the resonant terms plus the non-resonant

contribution.

1.6. Born-Oppenheimer approximation

There is another method to introduce the Born-Oppenheimer approximation into the optical nonlinear-response formalism. This approach has been beautifully described by Hellwarth¹⁵, but I will review part of it here to derive a few useful equations. According to the BO approximation the electrons adiabatically follow the nuclear motion. In a transparent medium the energy difference between the electronically excited states and the groundstate is much larger than any optical frequency in the visible and the electrons will adiabatically respond to the external EM fields as well. They stay in their adiabatically-changing groundstate, the energy of which (E_{e1}) can most conveniently be expanded in ascending orders of the instantaneous electric fields as

$$E_{e1} = W(\{\vec{r}_\beta\}) - \mu_i(\{\vec{r}_\beta\})E_i - (1/2)\epsilon_o\alpha_{ij}(\{\vec{r}_\beta\})E_iE_j - \dots, \quad (1.6.1)$$

where each coefficient [$W(\{\vec{r}_\beta\})$, $\mu_i(\{\vec{r}_\beta\})$, $(1/2)\alpha_{ij}(\{\vec{r}_\beta\})$, etc.] depends parametrically on the nuclear configuration $\{\vec{r}_\beta\}$. $\mu_i(\{\vec{r}_\beta\})$ is the electronic dipole moment and $\alpha_{ij}(\{\vec{r}_\beta\})$ is the electronic polarizability of the system. E_{e1} acts as a potential that binds the nuclei and in the quantum-mechanical description each coefficient [$\mu_i(\{\vec{r}_\beta\})$, $(1/2)\alpha_{ij}(\{\vec{r}_\beta\})$, etc.] must be interpreted as an operator acting on the nuclear coordinates.

Both μ_i and α_{ij} are defined with respect to the microscopic EM fields. Up to now I have used microscopic and macroscopic electric fields, but in the rest of this thesis $E_i(\vec{r}, t)$ will, without exception, denote the macroscopic electric field. Instead of the microscopic polarizability (operator) $\alpha_{ij}(\{\vec{r}_\beta\})$, one might just as well use the macroscopic susceptibility operator $\chi_{ij}(\{\vec{r}_\beta\})$, which is defined with respect to the macroscopic fields. They are related via

$$\chi_{ij}(\{\vec{r}_\beta\}) = (N/V)L^{\frac{1}{2}}\alpha_{ij}(\{\vec{r}_\beta\}) ; L^{\frac{1}{2}} = (\epsilon(\omega)+2)^2/9. \quad (1.6.2)$$

The expectation value of the (electronic) susceptibility operator χ_{ij} used in equation (1.6.2) is the electronic contribution to the linear susceptibility $\chi_{ij}^{(1)}(-\omega, \omega)$, which is defined by equation (1.4.10). The molecular

contribution to the linear susceptibility is related to $\langle [\tilde{\mu}(t), \tilde{\mu}(0)] \rangle$ and is zero in the absence of direct (infrared) absorption of radiation.¹⁵

It is useful to divide the nuclear configuration into a number of eigenmodes (q_α). The use of group theory is often essential, though not sufficient, for an easy separation in normal coordinates q_α . When each of the coefficients ($\mu_i(\vec{r}_\beta)$, $(1/2)\alpha_{ij}(\vec{r}_\beta)$ etc.) is expanded in the nuclear normal coordinates q_α , the various coefficients in this expansion immediately reveal whether the electric field couples efficiently with this mode. A mode is "infrared-active" when the strength of the electronic dipole moment depends on the normal coordinate of this mode ($(\partial\mu_i/\partial q_\alpha)[q_\alpha=0] \neq 0$). A mode is Raman-active when the electronic polarizability depends on the normal coordinate of this mode ($(\partial\alpha_{ij}/\partial q_\alpha)[q_\alpha=0] \neq 0$).

The second and higher-order derivatives with respect to the normal coordinates are responsible for overtones and combination bands and are only observable when the coupling is very strong, for instance when they form a Fermi resonance with a single excitation process.²⁰

Hellwarth¹⁵ has demonstrated how time-dependent perturbation theory applied to the effective BO Hamiltonian for the nuclei yields the following expression for the third-order electric polarization

$$(1/\epsilon_0)P_i^{(3)}(t) = \sigma_{ijkl}E_j(t)E_k(t)E_l(t) + E_j(t) \int_{-\infty}^t ds \, d_{ijkl}(t-s)E_k(s)E_l(s). \quad (1.6.3)$$

σ_{ijkl} is called the electronic contribution to the third-order optical polarization. σ_{ijkl} results from the instantaneous displacement of the electrons for a fixed nuclear configuration, and corresponds roughly to χ_{NR} . d_{ijkl} describes the nuclear contribution to the third-order optical polarization. It represents the change in electron distribution due to the movement of the nuclei. In terms of the normal coordinates $\langle \tilde{q}_\alpha(t) \rangle = \text{Tr}(\rho(t)q_\alpha)$ the nuclear response function becomes

$$d_{ijkl}(\tau) = (1/2)(i/\hbar)\epsilon_0(V/N) \langle [\chi_{ij}(\tilde{q}_\alpha(\tau)), \chi_{kl}(\tilde{q}_\alpha(0))] \rangle \theta(\tau), \quad (1.6.4)$$

where the expectation value is taken over the "unperturbed" system, unperturbed meaning in the absence of radiation, and $\theta(\tau)$ is the unit step function. The expectation value involves per definition (BO approximation) only non-electronically-excited states

Once again we have a nice demonstration of the fluctuation-dissipation

theorem. The response of the nuclei to the driving EM field is completely determined by the magnitude of the "spontaneous" fluctuations of the nuclear positions in the unperturbed system. The comparison with linear response theory becomes very simple when the expression $E_i(t)E_j(t)$, appearing in the BO Hamiltonian in the interaction potential as $-(1/2)(V/N)\epsilon_o\chi_{ij}E_iE_j$, is interpreted as one field that drives the nuclear motion $\langle\tilde{q}_\alpha(t)\rangle$ and changes the expectation value of $\chi_{ij}(\tilde{q}_\alpha(t))$ in the driven system.

The various symmetry relations of σ_{ijkl} and d_{ijkl} to permutation of their indices leads in isotropic media to the relations

$$d_{ijkl}(\tau) = a(\tau) \delta_{ij}\delta_{kl} + (1/2) b(\tau) (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \quad (1.6.5)a$$

$$\sigma_{ijkl} = (1/6) \sigma (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \quad (1.6.5)b$$

$$\begin{aligned} (1/\epsilon_o)P_i^{(3)}(t) = & (1/2)\sigma E_i(t)|E(t)|^2 + E_i(t) \int_{-\infty}^{\infty} d\tau a(\tau) |E(t-\tau)|^2 \\ & + \sum_{j=1,2,3} E_j(t) \int_{-\infty}^{\infty} d\tau b(\tau) E_i(t-\tau)E_j(t-\tau), \end{aligned} \quad (1.6.6)$$

where $a(\tau)$ and $b(\tau)$ are called the isotropic and anisotropic part of the nuclear response function respectively. Causality demands the response functions to be zero for negative times: $a(\tau) = b(\tau) = 0$ when $\tau < 0$. For cubic media two extra terms must be added to equation (1.6.6), but these terms usually give only small contributions.¹⁵

The nonlinear response function $d_{ijkl}(\tau)$ and the related response functions $a(\tau)$ and $b(\tau)$ by definition contain all the information on the dynamics of the electronic susceptibility operator $[\chi_{ij}(\tilde{q}_\alpha(\tau))]$. Comparing expression (1.6.6) with the definition of $\chi^{(3)}$ from section (1.3), it is possible to express $\chi^{(3)}$ in terms of a, b and σ . The present form of equation (1.6.6) does not have full permutation symmetry in its indices and an unsymmetrized form of $\chi^{(3)}$ results. For comparison with equation (1.4.10) it is necessary to first symmetrize this $\chi^{(3)}$, which yields the following extremely important relationships²¹

$$\begin{aligned}
\chi_{ijkl}^{(3)}(t_0, t_1, t_2, t_3) = & \\
& (1/6) \sigma \delta(t_1 - t_0) \delta(t_2 - t_0) \delta(t_3 - t_0) (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + \\
& (1/3) a(t_0 - t_2) \delta(t_1 - t_0) \delta(t_2 - t_3) \delta_{ij} \delta_{kl} + \\
& (1/3) a(t_0 - t_3) \delta(t_2 - t_0) \delta(t_3 - t_1) \delta_{ik} \delta_{lj} + \\
& (1/3) a(t_0 - t_1) \delta(t_3 - t_0) \delta(t_1 - t_2) \delta_{il} \delta_{jk} + \\
& (1/6) b(t_0 - t_2) \delta(t_1 - t_0) \delta(t_2 - t_3) (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + \\
& (1/6) b(t_0 - t_3) \delta(t_2 - t_0) \delta(t_3 - t_1) (\delta_{il} \delta_{kj} + \delta_{ij} \delta_{kl}) + \\
& (1/6) b(t_0 - t_1) \delta(t_3 - t_0) \delta(t_1 - t_2) (\delta_{ij} \delta_{lk} + \delta_{ik} \delta_{lj}), \tag{1.6.7}
\end{aligned}$$

$$\begin{aligned}
\chi_{ijkl}^{(3)}(-\omega_1 - \omega_2 - \omega_3, \omega_1, \omega_2, \omega_3) = & \\
& (1/6) \sigma (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + \\
& (1/3) a(\omega_2 + \omega_3) \delta_{ij} \delta_{kl} + \\
& (1/3) a(\omega_1 + \omega_3) \delta_{ik} \delta_{lj} + \\
& (1/3) a(\omega_1 + \omega_2) \delta_{il} \delta_{jk} + \\
& (1/6) b(\omega_2 + \omega_3) (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + \\
& (1/6) b(\omega_1 + \omega_3) (\delta_{il} \delta_{kj} + \delta_{ij} \delta_{kl}) + \\
& (1/6) b(\omega_1 + \omega_2) (\delta_{ij} \delta_{lk} + \delta_{ik} \delta_{lj}). \tag{1.6.8}
\end{aligned}$$

Anticipating on theory on stimulated Raman scattering and the Kerr effect, effects which are introduced in the next section, one specific $\chi^{(3)}$ is evaluated below and presented as equation (1.6.9)

$$\begin{aligned}
\chi_{1111}^{(3)}(-\omega_s, \omega_l, -\omega_l, \omega_s) = & (1/2)\sigma + (1/3)\{a(0)+b(0)+a(\omega_s-\omega_l)+b(\omega_s-\omega_l)\} \tag{1.6.9} \\
& + (1/3)\{a(\omega_l+\omega_s)+b(\omega_l+\omega_s)\}
\end{aligned}$$

The determination of the third-order polarizability $P^{(3)}(t)$ is reduced, through the use of the Born-Oppenheimer approximation, to the specification of the electronic contribution σ and the isotropic and anisotropic nuclear response functions of the material, denoted by $a(r)$ and $b(r)$ respectively. The induced $P^{(3)}$ acts as a source term in the wave equation of the EM field and the amplitude of light emitted at a frequency in the neighborhood of ω_0 can be evaluated from

$$\Delta E_1(t) - \{\epsilon(\omega_0)/c^2\} \partial^2 E_1(t) / \partial^2 t = (1/\epsilon_0 c^2) \partial^2 P_1(t) / \partial^2 t. \tag{1.6.10}$$

1.7. Stimulated Raman scattering and the Kerr effect

In this section the nuclear response to the driving EM fields will be studied in greater detail. All media we have studied are transparent at "optical" frequencies. The absence of absorption at frequency ω_i is mathematically related to the absence of this frequency component in the electric-dipole correlation function $\langle[\tilde{\mu}(\tau), \tilde{\mu}(0)]\rangle$. For transparent media the coupling with the EM field is primarily determined by the polarizability of the material and can be specified by the nuclear response function $d_{ijkl}(\tau)$, being proportional to the susceptibility correlation function $\langle[\chi_{ij}(\tilde{q}_\alpha(\tau)), \chi_{kl}(\tilde{q}_\alpha(0))]\rangle$. Most of our measurements were performed in liquids, where the single molecule description is valid. In the following text this description will be used as well as the single-molecule polarizability (operator) α_{ij} . The susceptibility (operator) χ_{ij} is related to the average polarizability per unit volume (via equation (1.6.2)).

Under the influence of the incident radiation rotational and vibrational (nuclear) degrees of freedom of molecules can be excited. Rotational energies are generally much lower than vibrational energies and are also often much less than $k_B T$, where $k_B = 1.381 \times 10^{-23} \text{ JK}^{-1}$ is the Boltzmann constant. Most of our measurements are performed at temperatures where the rotations can be described classically, in which case it is possible to speak of the orientation of a molecule in space. In gases at low pressure the molecules rotate freely, in liquids the rotation is already strongly hindered and in practically all solids only librations around an average orientation are possible. A quantum-mechanical treatment of rotations can be found in ref.(22).

Rotations and vibrations are described completely differently, the former classically and the latter quantum-mechanically, which leads to two different contributions to the light scattering. In principle the polarizability tensor $\alpha_{ij}(\tilde{q}_\alpha(\tau))$ is an operator that depends on all nuclear coordinates. In the absence of rotation-vibration coupling²³, the dependence on the rotational coordinates can be split off and interpreted as a rotation of the molecular frame, where α_{ij} only depends on the vibrational coordinates, with respect to the laboratory frame. For simplicity only one vibrational excitation will be considered and its vibrational coordinate will be denoted by q_α . The polarizability tensor can be split in a part that is independent of the vibrational coordinate and a part that depends on this

coordinate. These two contributions to α_{ij} give rise to the (AC) Kerr effect and the Raman effect respectively. The Kerr effect will be treated first. There after the Raman effect is discussed in greater detail.

If the polarizability tensor of each individual molecule is anisotropic and thus depends on the molecular orientation, a polarized laser beam can exercise a torque on the molecules. The resulting alignment of the molecules leads to a (temporal) change in the index of refraction. On removal of the "exciting" laser the induced birefringence disappears as a result of "rotational decay/diffusion" of the molecules. This effect is called the Kerr effect. It gives rise to a non-oscillating decay term in $d_{ijkl}(\tau)$, and a peak in $d_{ijkl}(\omega)$ around zero frequency. The width of this peak shows how fast the molecules rotate away from the orientation they had at ($\tau=0$). In ref.15 it is shown that, for an isotropic liquid, $b(\omega=0) = -3a(\omega=0)$.

The Raman effect can be associated with the part of $\alpha_{ij}(\tilde{q}_\alpha(\tau))$ that depends on the vibrational coordinate. A vibration is Raman-active when $((\partial\alpha_{ij}/\partial q_\alpha)[q_\alpha=0] \neq 0)$. If molecules are vibrating, with an eigenfrequency Ω_α , and the vibrational coordinate $\tilde{q}_\alpha(t)$ as a consequence varies in time, this will also be reflected in a variation of the linear susceptibility. A time-dependent susceptibility will scatter part of the incident EM radiation, with a frequency ω_ℓ , to the frequencies $(\omega_\ell - \Omega_\alpha)$ and $(\omega_\ell + \Omega_\alpha)$. This process is called Raman scattering and the frequencies $(\omega_\ell - \Omega_\alpha)$ and $(\omega_\ell + \Omega_\alpha)$ are called the Stokes and the anti-Stokes frequency respectively. If the initial molecular vibrations result from spontaneous fluctuations the process is called spontaneous Raman scattering. If the molecular vibrations are driven out of equilibrium by a combination of two lasers, of which the frequency difference matches the frequency of the Raman-active mode $((\omega_\ell - \omega_s) = \Omega_\alpha)$ the process is called stimulated Raman scattering. This situation is described by equation (1.6.3). In the latter case the induced coherent vibrational amplitude inelastically scatters radiation and results e.g. in the absorption of photons at frequency ω_ℓ and the simultaneous emission of photons at frequency ω_s . The Raman excitation of vibrations leads to a time-dependent and sinusoidal-like variation in $d_{ijkl}(\tau)$, with an amplitude that decrease in time, usually according to an exponential. Each Raman-active vibrational mode of eigenfrequency Ω_α will show up as a peak in the Fourier-transformed response function $d_{ijkl}(\omega)$ at $\omega = \Omega_\alpha$. The width of this peak is proportional to the transverse relaxation rate ($\Gamma_{bg} = 1/T_2$) of the Raman-active mode.

The stimulated Raman effect is evidently linked with the dynamics of the vibrational mode and a closer study of this dynamics is appropriate. In many cases the anharmonicity of the nuclear vibration frustrates the transitions to higher-excited states and a two-level description suffices. Let us denote the groundstate as $|g\rangle$ and the (first) vibrationally-excited state as $|b\rangle$. The dynamics of this two-level system is completely specified by the time evolution of its normalized density matrix ($\rho_{gg} + \rho_{bb} = 1$). The EM field acts as a driving force on the density matrix. In the BO approximation the effective interaction Hamiltonian is $H_{\text{int}} = -(1/2)\epsilon_0 L^2 \alpha_{ij}(q_\alpha) E_i(t) E_j(t)$. The diagonal elements of the interaction Hamiltonian give rise to a shift in energy of the levels $|g\rangle$ and $|b\rangle$, the Stark shift, which will be omitted in further calculations, as it is negligible for the "low-power" lasers we use. The off-diagonal elements ($(H_{\text{int}})_{bg} = (H_{\text{int}})_{gb}^*$), which are non-zero only when $(\partial \alpha_{ij} / \partial q_\alpha)[q_\alpha=0] \neq 0$, drive the dynamic variable $\langle \tilde{q}_\alpha(t) \rangle$. In higher order they drive the excited state population as well.

The coupling of the Raman excitation to the other degrees of freedom, which determines the relaxation to equilibrium, is very complex. When the correlation time of the bath, which is typically 10^{-13} s, is small compared with the coupling time of the Raman excitation with the bath the weak-coupling limit is valid and all relaxations are exponential in time. The decay of the on-diagonal elements of the density matrix is specified by the longitudinal relaxation time T_1 . The decay of the off-diagonal elements of the density matrix is specified by the transverse relaxation time T_2 , which can be separated in a T_1 part and a pure dephasing part (τ_{ph}). Various models have been developed to evaluate T_1 and T_2 (see section (1.3)). Some models describe the pure dephasing process in terms of a randomly varying environment.^{8,9} For liquids the success of these models is quite good⁸, and typical dephasing times of 1-10 ps are obtained, being in reasonable agreement with the experimentally measured T_2 . For the relatively energetic excitations we study the population decay is many orders of magnitude slower and is less easily accessible, theoretically as well as experimentally.²⁴ The huge difference between T_1 and T_2 is explained by the fact that one quantum of Raman excitation (vibron) has to break up in several (typically 10) less-energetic quanta of the bath. Evidently this is a slow process.

With the inclusion of the just-introduced decay rates, the time evolution of the density matrix of an ensemble of molecules can be represented by the famous Bloch equations

$$d(\rho_{bb}-\rho_{gg})/dt = -2(i/\hbar)(H_{bg}\rho_{gb}-H_{gb}\rho_{bg}) - ((\rho_{bb}-\rho_{gg})-(\rho_{bb}-\rho_{gg})_{eq})/T_1, \quad (1.7.1)$$

$$d(\rho_{gb})/dt = i\Omega_\alpha\rho_{gb} - (i/\hbar)H_{gb}(\rho_{bb}-\rho_{gg}) - \rho_{gb}/T_2, \quad (1.7.2)$$

$$H_{bg} = -(1/2)\epsilon_0 L^{\frac{1}{2}} \langle b|\alpha_{ij}|g\rangle E_i(t)E_j(t), \quad (1.7.3)$$

where L is the local-field correction factor $\{\epsilon(\omega)+2\}/3\}^4$ and $H_{bg}=(H_{int})_{bg}$.

It is often more convenient to characterize the system by two other variables: the fraction of molecules in the excited state $(N_b/N)=\rho_{bb}$, and the coherent amplitude $\langle \tilde{q}_\alpha(t) \rangle$. The diagonal elements of the density matrix are related to the excited-state population. The off-diagonal elements of the density matrix measure the degree of coherence of the Raman excitation. These off-diagonal elements might be zero even when a considerable excited-state population exist. This is e.g. the case when all molecules in the system oscillate with different phases. More precisely the relation between the oscillator coordinate and the density matrix is

$$\langle \tilde{q}_\alpha(t) \rangle = \text{Tr}(\rho(t)q_\alpha) = (q_\alpha)_{bg}\rho_{gb}(t) + (q_\alpha)_{gb}\rho_{bg}(t), \quad (1.7.4)$$

where $(q_\alpha)_{bg} = \langle b|q_\alpha|g \rangle = (\hbar/(2M_\alpha\Omega_\alpha))^{\frac{1}{2}}$ defines the effective mass M_α of the vibrational normal coordinate.

At thermal equilibrium, denoted by the subscript eq, the excited-state population is determined by the Boltzmann distribution. In this situation the expectation value of the oscillator coordinate is zero, because no correlations exist ($\langle \tilde{q}_\alpha(t) \rangle_{eq}=0$).

The time evolution of the vibrational coordinate $\tilde{q}_\alpha(t)$ being given by the equations (1.7.1)-(1.7.4) we will now return to the evaluation of that part of the nuclear response function that is associated with the stimulated Raman effect. The description of the Raman process is complicated when the coupling of radiation to the Raman-active mode depends on the orientations of the molecules. This is the case when $\partial\alpha_{ij}(q_\alpha)/\partial q_\alpha$ is anisotropic. Mathematically the anisotropy is accounted for by the separation of the polarizability derivative into an isotropic component (a), which is independent of the molecular orientation, and an anisotropic component (γ). In liquids the macroscopic susceptibility, as a result, reflects the average orientation of the molecules. For molecules with cylindrical symmetry

(symmetric top molecules) the orientation of the individual molecules can be specified by $u_i(t)$, where $u_i(t)$ is the i^{th} component of the unit vector fixed to the symmetry axis of a molecule. The average dipole $p_i(t)$ induced in these molecules originating from a nonzero oscillator coordinate and the resulting susceptibility are given by²⁵

$$\langle p_i(t) \rangle = \epsilon_0 L^{\frac{1}{2}} \langle [a\delta_{ij} + \gamma(u_i(t)u_j(t) - (1/3)\delta_{ij})] \tilde{q}_\alpha(t) \rangle E_j(t), \quad (1.7.5)$$

$$\frac{\partial \chi_{ij}}{\partial q_\alpha} \tilde{q}_\alpha(t) = (N/V) L^{\frac{1}{2}} [a\delta_{ij} + \gamma(u_i(t)u_j(t) - (1/3)\delta_{ij})] \tilde{q}_\alpha(t). \quad (1.7.6)$$

I want to focus attention on the fact that a (and γ) are derivatives of the polarizability α_{ij} with respect to the oscillator coordinate q_α . When ($\gamma=0$) the further description is quite simple

$$\langle b | \alpha_{ij} | g \rangle = a \langle b | q_\alpha | g \rangle = a \{ \hbar / (2M_\alpha \Omega_\alpha) \}^{\frac{1}{2}}. \quad (1.7.7)$$

The Raman contribution to the nuclear response function $d_{ijkl}(t)$ can now be evaluated through substitution of equation (1.7.6) into equation (1.6.4). The nuclear response function is thus expressed as a function of the dynamic variables $\tilde{q}_\alpha(t)$ and $u_i(t)$. When the small rotation-vibration coupling is neglected and when one assumes that the light does not exercise too strong a torque on the molecules, the vibrational and orientational degrees of freedom can be separated and $d_{ijkl}(t)$ factorizes in a product of a vibration and a rotation correlation function. In an isotropic system, like a normal liquid, the molecules per definition are randomly orientated and rotate randomly. The rotational relaxation is then uniquely determined by the angle $\Delta(t)$ over which the symmetry axes of the molecules, if they have any, rotate in a time interval t . When the molecular orientation is integrated out one can show that the contribution of the Raman-active mode q_α to the nuclear response function is²⁵

$$\langle [x_{ij}(t), x_{kl}(0)] \rangle = (N/V)^2 L \langle [\tilde{q}_\alpha(t), \tilde{q}_\alpha(0)] \rangle$$

$$\times \langle [a\delta_{ij} + \gamma(u_i(t)u_j(t) - (1/3)\delta_{ij})] [a\delta_{kl} + \gamma(u_k(0)u_l(0) - (1/3)\delta_{kl})] \rangle = \quad (1.7.8)$$

$$(N/V)^2 L \{a^2 - (1/15)\gamma^2 \langle \cos^2 \Delta(t) - (1/3) \rangle\} \langle [\tilde{q}_\alpha(t), \tilde{q}_\alpha(0)] \rangle \delta_{ij} \delta_{kl}$$

$$+ (N/V)^2 L (3/15)\gamma^2 \langle \cos^2 \Delta(t) - (1/3) \rangle \langle [\tilde{q}_\alpha(t), \tilde{q}_\alpha(0)] \rangle (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}).$$

Comparing the result with equation (1.6.4) and (1.6.5) one finds

$$a(t) = \epsilon_0 (N/V) L (1/2\hbar) \{a^2 - (1/15)\gamma^2 \langle \cos^2 \Delta(t) - (1/3) \rangle\} \langle [\tilde{q}_\alpha(t), \tilde{q}_\alpha(0)] \rangle \theta(t), \quad (1.7.9)$$

$$b(t) = \epsilon_0 (N/V) L (1/2\hbar) (3/15)\gamma^2 \langle \cos^2 \Delta(t) - (1/3) \rangle \langle [\tilde{q}_\alpha(t), \tilde{q}_\alpha(0)] \rangle \theta(t). \quad (1.7.10)$$

Apparently the names isotropic and anisotropic response functions for $a(t)$ and $b(t)$ are a bit confusing. They are indeed the isotropic and anisotropic part of the 4th-order tensor d_{ijkl} , but part of $a(t)$ definitely results from the anisotropic part of the linear susceptibility.

The rotation correlation function can be easily evaluated in two limits. Firstly it has a simple form in the limit of "small-step rotational diffusion", which is often a good description in liquids.⁸ Secondly, when the rotation is hardly hindered, the rotation correlation function can be evaluated in the limit of almost-free classical rotors, with a Maxwell-Boltzmann distribution of rotational rates.⁸

The vibration correlation function $\langle [\tilde{q}_\alpha(t), \tilde{q}_\alpha(0)] \rangle$ can be evaluated with the use of equations (1.7.1)-(1.7.4). This function oscillates in time, with the vibrational eigenfrequency Ω_α , and its amplitude decays exponentially in time, with a characteristic time T_2 . The decay of the largest part of the isotropic response function $a(t)$ is determined by the transverse relaxation rate T_2 of the vibrational mode only. The decay of the anisotropic response function $b(t)$ is a combination of T_2 -decay and the reorientation rate of the molecules and is consequently faster. The correlation functions used in (1.7.9) and (1.7.10) are

$$\langle [\tilde{q}_\alpha(t), \tilde{q}_\alpha(0)] \rangle = \{\hbar / (2M_\alpha \Omega_\alpha)\} (2/i) \sin(\Omega_\alpha t) e^{-t/T_2}, \quad (1.7.11)$$

Small-step rotational diffusion: $\langle \cos^2 \Delta(t) - (1/3) \rangle = (2/3) e^{(-t/\tau_{\text{rot}})}$,
 (1.7.12)
 Almost-free rotors : $\langle \cos^2 \Delta(t) - (1/3) \rangle = (2/3) e^{(-t^2/\tau_{\text{rot}}'^2)}$,

where τ_{rot} and τ_{rot}' are parameters that determine the rate of "rotational decay".

The relaxation of the rotational and vibrational degrees of freedom being known, the complete time and frequency dependence of the nuclear response functions can be evaluated. In condensed media the rotation is often strongly hindered and the limit of small-step rotational diffusion, with a rotational correlation function that decays exponentially in time, is usually valid. One finds

electronic: $(3/2)\sigma \delta(t)$

Raman: $a(t) = \sum_{\alpha} 2A_{\alpha, \text{iso}} e^{-t/T_2} \sin(\Omega_{\alpha} t) \theta(t)$
 $+ 2A_{\alpha, \text{ani}} e^{-t(1/T_2 + 1/\tau_{\text{rot}})} \sin(\Omega_{\alpha} t) \theta(t),$
 (1.7.13)

$b(t) = \sum_{\alpha} -6A_{\alpha, \text{ani}} e^{-t(1/T_2 + 1/\tau_{\text{rot}})} \sin(\Omega_{\alpha} t) \theta(t),$

$A_{\alpha, \text{iso}} = \{\epsilon_0 (N/V) L a^2 / (4M_{\alpha} \Omega_{\alpha})\} = \{\epsilon_0 (N/V) L \langle b | \alpha_{ii} | g \rangle^2 / (2\hbar)\},$

$A_{\alpha, \text{ani}} = -(2/45) \{\epsilon_0 (N/V) L \gamma^2 / (4M_{\alpha} \Omega_{\alpha})\},$ ($A_{\alpha, \text{ani}} < 0$)

Kerr : $a(t) = A_{\text{Kerr}} e^{-t/\tau_{\text{rot}}} \theta(t),$
 ($A_{\text{Kerr}} < 0$)

$b(t) = -3a(t) = -3A_{\text{Kerr}} e^{-t/\tau_{\text{rot}}} \theta(t),$

Total: $a(\omega) = A_{\text{Kerr}} \tau_{\text{rot}} / (1 - i\omega \tau_{\text{rot}})$
 (R+K)
 $+ \sum_{\alpha} [A_{\alpha, \text{iso}} / (\Omega_{\alpha} - \omega - i/T_2) + A_{\alpha, \text{iso}} / (\Omega_{\alpha} + \omega + i/T_2)]$
 $+ \sum_{\alpha} [A_{\alpha, \text{ani}} / (\Omega_{\alpha} - \omega - i/T_2 - i/\tau_{\text{rot}}) + A_{\alpha, \text{ani}} / (\Omega_{\alpha} + \omega + i/T_2 + i/\tau_{\text{rot}})].$

The strength of the Kerr effect is : $b(\omega=0) = -3A_{\text{Kerr}} \tau_{\text{rot}}$

In the absence of anisotropic Raman ($\gamma=0$) : $|a(\Omega_{\alpha})| \approx A_{\alpha} T_2$

We choose the rotation correlation function needed for the evaluation of the Kerr effect to be identical to the one that describes the anisotropic Raman scattering. This approximation is only valid when vibrationally-excited molecules rotate just as easily as their non-excited counterparts. With the use of equations similar to (1.7.9) and (1.7.10), one can easily

show that for the Kerr contribution to the response functions the relation $\{b(t) = -3a(t)\}$ holds. We have used this relation in equation (1.7.13).

1.8 Stimulated Raman scattering treated as a pump-probe process

Although the nuclear response functions completely describe the nonlinear optical response of the material well below saturation of the Raman transition, I want to present another derivation of the nonlinear optical response, introduced by Laubereau and Kaiser²⁵. This model focuses on the mechanism that drives the coherent amplitude of one specific Raman-active mode $\langle \tilde{q}_\alpha(t) \rangle$ and gives a nice picture of what is happening with the system. Isotropic Raman scattering is usually more efficient than anisotropic scattering, being expressed by a low depolarization ratio ($R = 3\gamma^2/(45a^2+4\gamma^2)$). For simplicity I have therefore restricted my treatment to the isotropic component of the polarizability derivative (a) and to a linearly-polarized EM field.

The energy associated with the coupling of the vibrating molecules to the EM field (for a single molecule) is $-(1/2)\epsilon_0 L^{\frac{1}{2}} a \langle \tilde{q}_\alpha(t) \rangle E(t)E(t)$. In the "low-field" and "low-temperature" limit hardly any molecule is excited into the b-state. The time evolution of the coherent amplitude $\langle \tilde{q}_\alpha(t) \rangle$ represents the extent to which the density matrix is driven out of its equilibrium and can immediately be found from (1.7.2) and (1.7.4) to be²⁵

$$\partial^2 \langle \tilde{q}_\alpha(t) \rangle / \partial t^2 + (2/T_2) \partial \langle \tilde{q}_\alpha(t) \rangle / \partial t + \Omega_\alpha^2 \langle \tilde{q}_\alpha(t) \rangle = (1/2)\epsilon_0 L^{\frac{1}{2}} a / M_\alpha E^2(t). \quad (1.8.1)$$

The non-equilibrium coherent amplitude is reflected in an oscillating polarizability, which consequently induces a polarization $\{P^{(3)}(t)\}$.

$$P^{(3)}(t) = (N/V) \langle \mu(t) \rangle = (N/V) \epsilon_0 L^{\frac{1}{2}} a E(t) \langle \tilde{q}_\alpha(t) \rangle. \quad (1.8.2)$$

The amount of radiation emitted by $P^{(3)}(t)$ can be derived from the wave equation of the radiation field (see equation (1.6.10)).

In a stimulated Raman experiment two laser beams, of frequency ω_p and ω_s such that $(\omega_p - \omega_s)$ is close to Ω_α , are focused in a Raman-active material. As we work with laser pulses it is convenient to factorize the electric field of each incident light pulse in a harmonic oscillation and a (slowly-varying) envelope. The almost harmonic oscillation of the coherent amplitude

$\langle \tilde{q}_\alpha(t) \rangle$ can be written in a similar fashion. We reintroduce the spatial profile of the Raman excitation as well as the spatial profile of the field

$$E(\vec{r}, t) = (1/2)E_\ell(\vec{r}, t)e^{-i(\omega_\ell t - \vec{k}_\ell \cdot \vec{r})} + (1/2)E_s(\vec{r}, t)e^{-i(\omega_s t - \vec{k}_s \cdot \vec{r})} + \text{c.c.}, \quad (1.8.3)$$

$$\langle \tilde{q}_\alpha(\vec{r}, t) \rangle = (i/2)Q_\alpha(\vec{r}, t)e^{-i(\Omega_\alpha t - \vec{k}_\alpha \cdot \vec{r})} + \text{c.c.}, \quad (1.8.4)$$

where $Q_\alpha(\vec{r}, t)$ is defined as the envelope function of the coherent Raman amplitude.

Both the equation of motion of the coherent amplitude and the EM-wave equation can be turned into solvable first-order differential equations when one assumes that the envelopes E_s , E_ℓ and Q_α vary slowly with respect to the oscillations in $E(t)$ and $q_\alpha(t)$. This assumption is called the slowly-varying-envelope approximation. The rotating wave approximation states that when $(\omega_\ell - \omega_s)$ is close to Ω_α , positive frequency terms will only couple with other positive frequency terms.

In our experiment the lasers propagate in the z-direction and are almost parallel. When the group-velocity dispersion between the ω_ℓ and the ω_s -wave is small, it is convenient to define a new time variable that measures the local time relative to the moment a certain feature in the traveling EM wave passed ($t' = t - z/v_g$; v_g is the group velocity of light). In these new variables the interaction can be written as²⁵

$$\begin{aligned} \partial Q_\alpha(\vec{r}, t') / \partial t' + (1/T_2)Q_\alpha(\vec{r}, t') &= [\epsilon_0 L^2 a / (4M_\alpha (\omega_\ell - \omega_s))] \\ &\times E_\ell(\vec{r}, t') E_s^*(\vec{r}, t') e^{-i(\Delta\omega_\alpha t' - \Delta\vec{k}_\alpha \cdot \vec{r})}, \end{aligned} \quad (1.8.5)a$$

$$\begin{aligned} \partial (N_b/N) / \partial t' + ((N_b - N_{b,eq})/N) / T_1 &= \\ \epsilon_0 L^2 a / (8\hbar) \{ Q_\alpha^*(\vec{r}, t') E_s^*(\vec{r}, t') E_\ell(\vec{r}, t') &e^{-i(\Delta\omega_\alpha t' - \Delta\vec{k}_\alpha \cdot \vec{r})} + \text{c.c.} \} \end{aligned} \quad (1.8.5)b$$

$$\partial E_\ell(\vec{r}, t') / \partial z = -(N/V) L^2 \omega_\ell a / (4nc) E_s(\vec{r}, t') Q_\alpha(\vec{r}, t') e^{i(\Delta\omega_\alpha t' - \Delta\vec{k}_\alpha \cdot \vec{r})}, \quad (1.8.5)c$$

$$\partial E_s(\vec{r}, t') / \partial z = (N/V) L^2 \omega_s a / (4nc) E_\ell(\vec{r}, t') Q_\alpha^*(\vec{r}, t') e^{-i(\Delta\omega_\alpha t' - \Delta\vec{k}_\alpha \cdot \vec{r})}, \quad (1.8.5)d$$

where we have introduced the index of refraction n , the frequency mistuning $\Delta\omega_\alpha = (\omega_\ell - \omega_s - \Omega_\alpha)$ and the momentum mistuning $\Delta\vec{k}_\alpha = (\vec{k}_\ell - \vec{k}_s - \vec{k}_\alpha)$. (N_b/N) is the fraction of molecules in the excited state and is assumed to differ hardly from zero. $(N_{b,eq}/N)$ is the small fraction of excited molecules

present at equilibrium.

The set of equations (1.8.5) can be interpreted as follows. The combination $E_\ell E_S^*$ drives the amplitude of the oscillator coordinate Q_α and creates a space-dependent coherent Raman excitation, the coherent Raman wave. The coherent Raman wave in its turn makes the susceptibility vary in space and time. As a result the incident beams are scattered to different directions and different frequencies. The inelastic scattering results in a decrease in energy of the ω_ℓ -beam and an increase in energy of the ω_S -beam. The net energy loss of the total radiation field is converted into a build-up of population in the excited Raman state of the material. Far from saturation the amplitude of the coherent Raman excitation is proportional to $E_\ell E_S^*$, the increase in intensity of the ω_S -beam scales with the intensity of the ω_ℓ -beam and the built-up population in the excited state is proportional to the product of the intensities of both laser beams. This combined effect is called stimulated Raman scattering (SRS).

The group of Laubereau and Kaiser has unfortunately misinterpreted the effect of the spatial dependence of the coherent Raman excitation ($\vec{k}_\alpha$).^{25,26} In the limit of weak coupling between the molecules, the phase of each excited molecule is clearly solely determined by the EM field it experiences and ($\vec{k}_\alpha - \vec{k}_\ell - \vec{k}_S$). Laubereau and Kaiser originally believed that for strongly-coupled molecules $\vec{k}_\alpha$ would match ($\vec{k}_\ell - \vec{k}_S$) during the excitation of the mode, but would relax to the wave vector characteristic for the Raman excitation after the EM fields are gone. Laubereau and Kaiser originally thought that this process, which one might call "wave-vector relaxation", could enable them in a time-resolved Coherent Anti-Stokes Raman (CARS) experiment to observe the vibrational dephasing of a single subgroup out of an inhomogeneously-broadened line. They called this technique "selective phase matching". Unfortunately this technique does not work, there is no "wave-vector relaxation" as they found themselves.²⁸ Only modes, of which the wave vector matches the spatial dependence of the EM waves are excited in a SRS experiment and $\Delta \vec{k}_\alpha$ is zero at any time. Gale et al. used this criterion in a beautiful experiment²⁹ to selectively probe phonon polaritons of specific wave vectors (in NH_4Cl) and thus measure the relaxation time of these phonon polaritons as a function of their wave vector.

At this point I want to return to the solution of equation (1.8.5). When the band width of the lasers is smaller than the spectral width of the

Raman excitation (FWHM $\Delta\nu=1/(\pi T_2c)$ [cm^{-1}]) the quasi-steady-state situation can easily be evaluated.

$$\begin{aligned}
 & \text{(quasi-steady state)} \\
 Q_{\alpha}(\vec{r}, t') &= \{T_2/(1-i\Delta\omega_{\alpha}T_2)\} \epsilon_0 L^{\frac{1}{2}} a / \{4M_{\alpha}(\omega_{\ell}-\omega_s)\} E_{\ell}(\vec{r}, t') E_s^*(\vec{r}, t') e^{-i\Delta\omega_{\alpha}t'}, \\
 E_s(\vec{r}, t') &= E_s(0, t') e^{(g_{ss}/2)I_{\ell}z}, \quad I_{\ell} = (1/2)\epsilon_0 cn|E_{\ell}|^2, \\
 g_{ss} &= \{T_2/(1+i\Delta\omega_{\alpha}T_2)\} (N/V) La^2\omega_s / \{4n^2c^2M_{\alpha}(\omega_{\ell}-\omega_s)\}. \tag{1.8.6}
 \end{aligned}$$

The real part of the steady-state gain coefficient g_{ss} , which is usually specified in cm/MW, represents the actual increase in intensity of the ω_s -beam, whereas its imaginary part reflects an intensity-induced phase shift of the transmitted optical EM field.

The Raman gain coefficient can just as easily be expressed in terms of $\chi^{(3)}$. The nonlinear polarization induced at frequency ω_s is directly found from (1.5.3) to be

$$\begin{aligned}
 P_{\omega_s}^{(3)} &= (6/4)\epsilon_0 \chi^{(3)}(-\omega_s, \omega_{\ell}, -\omega_{\ell}, \omega_s) |E_{\ell}|^2 E_s \\
 &= \{3/(nc)\} \chi^{(3)}(-\omega_s, \omega_{\ell}, -\omega_{\ell}, \omega_s) I_{\ell} E_s. \tag{1.8.7}
 \end{aligned}$$

The propagation of a ω_s -beam is slightly changed in the presence of an intense beam at frequency ω_{ℓ} . Through substitution of the induced $P^{(3)}$ into the wave equation of light, the perturbed wave vector of the ω_s -beam and the gain coefficient g_{ss} can be found

$$\begin{aligned}
 k_s &= n\omega_s/c + 3\omega_s/(2n^2c^2\epsilon_0) \chi^{(3)}(-\omega_s, \omega_{\ell}, -\omega_{\ell}, \omega_s) I_{\ell}, \\
 g_{ss} &= 3\omega_s/(n^2c^2\epsilon_0) \{i\chi^{(3)}(-\omega_s, \omega_{\ell}, -\omega_{\ell}, \omega_s)\}. \tag{1.8.8}
 \end{aligned}$$

Comparison of the latter expression with (1.8.6), using only the Raman-resonant part of $\chi^{(3)}$ from (1.5.6)-(1.5.8) shows they are in perfect agreement.

1.9 Comparison between stimulated and spontaneous Raman scattering

In stimulated Raman scattering the incident EM field, consisting of a laser at frequency ω_l and a laser at frequency ω_s , excites a coherent amplitude and an associated (time-dependent) susceptibility, which inelastically scatter part of the incident radiation. This process is described by the response function $\langle [\chi_{ij}(\tilde{q}_\alpha(t)), \chi_{kl}(\tilde{q}_\alpha(0))] \rangle$ as was explained in the previous sections. Stimulated Raman scattering is thus treated as a classical "mixing" between induced variations in susceptibility and the incident radiation. The generated Stokes-shifted and anti-Stokes-shifted EM fields will be equally strong. Apart from inelastic scattering on the induced (non-equilibrium) coherent amplitude, the incident EM waves scatter also on the (spontaneous) fluctuations in the susceptibility, being described by $\langle \chi_{ij}(\tilde{q}_\alpha(t)) \chi_{kl}(\tilde{q}_\alpha(0)) \rangle$. This process is called spontaneous Raman scattering and needs only one light source, as there is no need to pump the vibrational excitation. It takes a quantum-mechanical treatment of the EM field to show that, when initially all molecules are in the groundstate ($T=0$), only Stokes radiation is emitted.

Spontaneous Raman scattering is usually specified by the Raman cross section of the material under study. The Raman cross section per molecule ($d\sigma/d\Omega$) is defined as the ratio of scattered power per radial angle over incident intensity, integrated over the frequency range of the Stokes radiation. The frequency derivative of the Raman cross section is closely related to the fluctuations of the oscillator coordinate via²⁹

$$\frac{d^2\sigma(\omega)}{d\omega d\Omega} \propto \int_{-\infty}^{\infty} dt \langle \tilde{q}_\alpha(t) \tilde{q}_\alpha(0) \rangle e^{i\omega t}. \quad (1.9.1)$$

Two different polarization geometries can be distinguished for spontaneous Raman scattering on isotropic materials and on crystals with cubic symmetry belonging to the classes $m\bar{3}m$, $\bar{4}3m$ and 432 . The polarization of the emitted (anti-) Stokes radiation can be either parallel to the polarization direction of the incident radiation or perpendicular. Let θ be the angle between the wave-vector of the emitted radiation and the polarization direction of a linearly-polarized incident laser beam of frequency ω_l . The cross section per molecule per radial angle integrated over the frequency range of the Stokes radiation, for the parallel and the perpendicular geometry, is given by^{2,29}

$$(d\sigma_{//}/d\Omega) = \omega_s^4 L / (16\pi^2 c^4) \{ \hbar / (2M_\alpha \Omega_\alpha) \} (a^2 + 4/45 \gamma^2) (\sin\theta)^2, \quad (1.9.2)$$

$$(d\sigma_{\perp}/d\Omega) = \omega_s^4 L / (16\pi^2 c^4) \{ \hbar / (2M_\alpha \Omega_\alpha) \} 3/45 \gamma^2. \quad (1.9.3)$$

The stimulated Raman gain on resonance experienced in a medium of density (N/V) , as derived in the previous section (equation (1.8.6)) is directly related to the spontaneous Raman cross section via

$$g_{ss, //} = 8\pi^2 c^2 (N/V) T_2 / (\hbar \omega_s^3 n^2) (d\sigma_{//}/d\Omega (\theta=\pi/2)). \quad (1.9.4)$$

Notice that the steady-state stimulated Raman gain is proportional to the Raman cross section times T_2 and is thus proportional to the peak height of the Raman line one measures in a spontaneous Raman experiment.

The analogy between ordinary Raman scattering and stimulated Raman scattering emerges more clearly from a quantum mechanical treatment of the radiation field.¹¹ The number of Stokes photons produced per unit time is proportional to $\bar{n}_\ell(\bar{n}_s+1)$, where $\bar{n}_\ell$ and $\bar{n}_s$ are the number of photons per mode of the EM field at the frequency ω_ℓ and ω_s respectively. The 1 in the formula represents spontaneous Raman scattering, whereas the $\bar{n}_s$ represents the stimulated Raman process. One might say that ordinary Raman scattering resembles stimulated Raman scattering and the vacuum fluctuations play the role of the second "Stokes" beam. Experimentally an important difference is the fact that light emitted in a spontaneous Raman process is diffuse, as the vacuum fluctuations have no preferential direction, whereas light emitted in a stimulated Raman process has a directionality.

1.10 Numerical results

There are various ways to specify the oscillator strength of a Raman-active mode. One might for instance use the Raman cross section, the imaginary part of $\chi^{(3)}$, the related $a(\Omega_\alpha)$, or the steady-state Raman gain coefficient g_{ss} . Comparing different literature values the conversion is just a nuisance, but the dependence of the measured physical quantities on the laser frequency is a real problem. An absolute measurement of the Raman cross section is very difficult in a spontaneous Raman scattering experiment, because many geometrical factors play a crucial role in the

obtainable strength of the Raman signal. Kato and Takuma^{30,31} have made an absolute calibration through comparison of the Stokes intensity with the known intensity of a source of blackbody radiation. They have thoroughly investigated the frequency dependence of the Raman cross section of several liquids and found that the ω_s^4 -dependence, appearing as the power emitted by a dipole oscillating at frequency ω_s , has to be corrected by the less important frequency dependences of two other factors. Firstly the local-field-correction factor depends on the index of refraction and thus (slightly) on the optical frequency. Secondly deviations from the (a,b, σ)-formalism used by Hellwarth are observable and the experimental results are better explained when one allows for a weak frequency dependence of the a,b and σ coefficient. This looks like a rather crude way to patch up the (a,b, σ)-formalism, but the corrections are small. The increase in magnitude of all three coefficients at higher optical frequencies emerges naturally from the formalism of Bloembergen as can be seen from equation (1.5.4).

Kato and Takuma have measured the total Raman cross section, integrated over a frequency range around the Raman-active mode, which included all weaker neighboring lines. For the (656 cm^{-1})-mode of CS_2 they found a Raman cross section of $(d\sigma/d\Omega)=1.4(1)\times 10^{-29} \text{ cm}^2\text{mol}^{-1}\text{sr}^{-1}$ at ($\lambda_p=590 \text{ nm}$) and $5.7(10)\times 10^{-30} \text{ cm}^2\text{mol}^{-1}\text{sr}^{-1}$ at the ruby frequency ($\lambda_p=694 \text{ nm}$). When the specified Raman cross section per molecule per angle is multiplied by the density of molecules ($(N/V)=1.0\times 10^{22} \text{ mol.cm}^{-3}$ for CS_2) this results in $(N/V)(d\sigma/d\Omega)=5.7(10)\times 10^{-8} \text{ cm}^{-1}\text{sr}^{-1}$. Shen¹¹ specifies the value $(N/V)(d\sigma/d\Omega)=7.5\times 10^{-8} \text{ cm}^{-1}\text{sr}^{-1}$ for this mode of CS_2 at the ruby frequency.

For the (992 cm^{-1})-mode of benzene Kato and Takuma measured $(d\sigma/d\Omega)=1.1\times 10^{-29} \text{ cm}^2\text{mol}^{-1}\text{sr}^{-1}$ at ($\lambda_p=590$) and $5.0(10)\times 10^{-30} \text{ cm}^2\text{mol}^{-1}\text{sr}^{-1}$ at ($\lambda=694 \text{ nm}$). At the ruby frequency Shen mention the value $(N/V)(d\sigma/d\Omega)=3.1\times 10^{-8} \text{ cm}^{-1}\text{sr}^{-1}$, whereas the data from Kato and Takuma on benzene ($(N/V)=6.9\times 10^{21} \text{ cm}^{-3}$) give $(N/V)(d\sigma/d\Omega)=3.5\times 10^{-8} \text{ cm}^{-1}\text{sr}^{-1}$, being in reasonable agreement.

The stimulated Raman technique provides a more accurate determination of the strength of the Raman mode, as the measured Raman gain coefficient is hardly sensitive to the geometry of the set-up. Below it will be shown how a Raman cross section can be converted, through calculation, into a steady-state Raman gain coefficient. As an example the (992 cm^{-1})-mode of benzene is used, for which the relevant numbers are

$$\begin{aligned}
(N/V)(d\sigma/d\Omega) &= 3.1 \times 10^{-8} \text{ cm}^{-1} \text{ sr}^{-1} = 3.1 \times 10^{-6} \text{ m}^{-1} \text{ sr}^{-1}, \\
T_2 &= 4.9 \text{ ps} = 4.9 \times 10^{-12} \text{ s}, \\
\lambda_L &= 694 \text{ nm}, \lambda_S = 746 \text{ nm}, \omega_S = 2.5 \times 10^{15} \text{ s}^{-1}, n = 1.49.
\end{aligned}
\tag{1.10.1}$$

Substitution of these numbers in eq.(1.9.4) yields $g_{SS} = 2.8 \times 10^{-11} \text{ J}^{-1} \text{ sm} = 2.8 \times 10^{-3} \text{ cm/MW}$ at ($\lambda_L=693 \text{ nm}$). A similar calculation can be performed for CS_2 . Both calculations give reasonable agreement with SRS measurements of the steady-state gain coefficient mentioned in ref.11 and 15. Apart from the just-mentioned materials our SRS experiments included a study of the (1332 cm^{-1}) Raman-active phonon in diamond. The symmetry of diamond introduces a fourth term in the (a,b, σ) formalism, but the corrections arising from this extra term are small (less than 15 %).¹⁵ The various properties of the Raman modes of the three materials we studied are presented in table (1.10.1). The values mentioned are averages taken over measurements of ourselves and data found in the literature.

For our experiments an accurate determination of the magnitude of the Kerr effect as well as the electronic contribution to $\chi^{(3)}$ is important. The strengths of these effects can be specified by the ratio of $b(0)$ and σ to $a(\Omega_\alpha)$ respectively. Experimentally an accurate determination of these ratios can be obtained from the "lineshape" measured in SRS, Raman-induced Kerr effect spectroscopy (RIKES) or CARS. In these experiments one observes the signal strength as a function of the frequency difference between both lasers, which is scanned through the Raman resonance. A fine combination of a RIKES and a CARS experiment has been performed by Song and Levenson.³² Their results, as well as results from ref.33 and 34, are used in table (1.10.1).

In the last paragraph of this section it will be demonstrated how I converted results from the work of Song and Levenson³¹ to the quoted numerical values. Comparison of their formulas with my own equations shows that, apart from the fact that they use cgs units, the $\chi^{(3)}$ they have defined is a factor 4 smaller than the $\chi^{(3)}$ defined in this thesis. This apparent discrepancy can be traced to a difference in the definition of the amplitude of the electric field: I use $E(t) = (1/2)E_s(t)e^{-i\omega_s t} + \text{c.c.}$, whereas they make use of the definition $E(t) = E_s(t)e^{-i\omega_s t} + \text{c.c.}$ Fortunately their a, b and σ coefficients are identical to the ones defined here. In ref.32 the strength of the Raman-active (992 cm^{-1}) mode of C_6H_6 is specified by

$$(N/V) \frac{L \langle b | \alpha | g \rangle^2}{12\hbar c \Gamma} = 3.2(2) \times 10^{-13} \text{ esu}, \quad (1.10.2)$$

where $\Gamma = (2\pi c T_2)^{-1}$ is the half width half maximum of the Raman line and the pump and the probe wavelengths are about 550 nm and 580 nm respectively. The esu's meant here are $\text{cm}^3 \text{erg}^{-1}$. The resonant part of $\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$ is just double the value given in equation (1.10.2) for the resonant part of $\chi^{(3)}(-2\omega_\ell + \omega_s, \omega_\ell, \omega_\ell, -\omega_s)$. Converting $\text{Im}\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$ from cgs units into SI units, using the relation ($1 \text{ cm}^3 \text{erg}^{-1} = 1.396 \times 10^{-8} \text{ J}^{-2} \text{C}^2 \text{m}^2$), one finds

$$\text{Im}(\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)) = -8.9(6) \times 10^{-21} \text{ J}^{-2} \text{C}^2 \text{m}^2, \quad (1.10.3)$$

on resonance $\{(\omega_\ell - \omega_s) = \Omega_\alpha (992 \text{ cm}^{-1})\}$ for bulk benzene. As a check this value will be substituted in equation (1.8.8). The resulting steady-state gain coefficient $g_{ss} = 4.4 \times 10^{-11} \text{ mW}^{-1}$, is in perfect agreement with the values mentioned earlier. The other calculations necessary to complete table (1.10.1) were performed in a similar fashion.

	CS ₂	C ₆ H ₆	Diamond
$(2\pi)^{-1}\Omega_\alpha$ [cm ⁻¹]	656	992	1332
$(2\pi)^{-1}\delta\Omega_\alpha$ FWHM[cm ⁻¹]	0.50	2.15	2.6
T ₂ [ps]	19.5(4)	4.9(1)	4.0(1)
τ_{rot} ref.35,36 [ps]	1.5-2.1		
n ($\lambda_\ell=590$ nm, T=20°C)	1.63	1.50	2.41
** at ($\lambda_\ell=694$ nm)			
(N/V)(dσ/dΩ) [cm ⁻¹ sr ⁻¹]	6.6(13)x10 ⁻⁸	3.3(3)x10 ⁻⁸	-
g _{SS} [cm/MW]	1.9(4)x10 ⁻²	3.0(3)x10 ⁻³	7(2)x10 ⁻³
** at ($\lambda_\ell=590$ nm)			
g _{SS} [cm/MW]	2.8(6)x10 ⁻²	4.0(5)x10 ⁻³	-
** at ($\lambda_\ell\approx 550$ nm)			
σ/ a(Ω _α) ref.32		0.063(1)	
ref.33		0.055(5)	0.043(6)
(σ+b(0))/ a(Ω _α)			
ref.32	0.98(11)	0.53(2)	-
σ/(σ+b(0)) ref.32		12(1)%	
ref.34	13(1)%	20(1)%	100 %
s/A _α [ps]	12(2)	1.6(3)	0.28(4)

With $s=(3/2)\sigma+(2/3)b(0)$ and $|a(\Omega_\alpha)|=A_\alpha T_2$

Table (1.10.1) : Various properties of Raman scattering, the Kerr effect and the electronic contribution to $\chi^{(3)}$ in numbers. The information was gathered from our own measurements and from data found in the literature (ref.32-35).

It proved to be useful to have a list of the variables used in this thesis and their dimensions in SI units. When experimentally-obtained values from other articles are used, a careful check of the definitions employed in these articles is always necessary. Unfortunately many conventions are in use to define the various physical quantities. A constant problem is the 4π difference between the dimensionless $\chi^{(1)}$ in the cgs-system and $\chi^{(1)}$ in the International System of Units (SI). A similar factor 4π arises when one converts $\chi^{(3)}$ from cgs units (in cm^{-3}erg) to SI units.

$\epsilon_0 = 8.842 \cdot 10^{-12} \text{ J}^{-1}\text{C}^2\text{m}^{-1}$	dielectric constant	$\text{J}^{-1}\text{C}^2\text{m}^{-1}$
$\hbar = 1.051 \cdot 10^{-34} \text{ Js}$	Planck constant	Js
I	intensity	$\text{Js}^{-1}\text{m}^{-2}$
$E(t)$	electric field	$\text{JC}^{-1}\text{m}^{-1}$
$P(t)$	polarization	Cm^{-2}
L	local-field correction	-
$\chi^{(1)}(-\omega, \omega)$	linear susceptibility	- $\{n^2 = 1 + \chi^{(1)}\}$
χ_{ij}	susceptibility operator	-
$\chi_{ijk\ell}^{(3)}(t_0, t_1, t_2, t_3)$	third-order susceptibility	$\text{J}^{-2}\text{s}^{-3}\text{C}^2\text{m}^2$
$\chi_{ijk\ell}^{(3)}(-\omega_1 - \omega_2 - \omega_3, \omega_1, \omega_2, \omega_3)$	third-order susceptibility	$\text{J}^{-2}\text{C}^2\text{m}^2$
σ	electronic contribution	$\text{J}^{-2}\text{C}^2\text{m}^2$
$a(t), b(t)$	nuclear response functions	$\text{J}^{-2}\text{s}^{-1}\text{C}^2\text{m}^2$
$a(\omega), a(0) = a(\omega=0)$	nuclear response functions	$\text{J}^{-2}\text{C}^2\text{m}^2$
$b(\omega), b(0) = b(\omega=0)$	nuclear response functions	$\text{J}^{-2}\text{C}^2\text{m}^2$
$A_{\alpha, \text{iso}}, A_{\text{Kerr}}$	"oscillator strength"	$\text{J}^{-2}\text{s}^{-1}\text{C}^2\text{m}^2$
μ	dipole moment	Cm
(N/V)	density of molecules	m^{-3}
$\alpha_{ij}(\omega_1, \omega_2)$	polarizability operator	m^3
$\langle g \alpha_{ij}(-\omega, \omega) g \rangle$	polarizability	$\text{m}^3 \quad \{\mu = \epsilon_0 \alpha_{ij} E\}$
Ω_α	eigenfrequency	s^{-1}
$T_2 = (\Gamma_{bg})^{-1}$	transverse relaxation time	s
q_α	oscillator coordinate	m
a, γ	polarizability derivative	m^2
g_{ss}	Raman gain coefficient	J^{-1}sm
$(d\sigma/d\Omega)$	Raman cross section	m^2

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2.1 Introduction

It is well known that Raman scattering is a direct two-photon process. One photon at frequency ω_1 is absorbed, while another photon at ω_2 is simultaneously emitted and the material makes a transition from the initial state to the final state. Energy conservation requires that $\hbar(\omega_1 - \omega_2)$ equals the energy difference between the initial and the final state, within the uncertainty introduced by linewidths. The emitted radiation is called Stokes ($\omega_2 < \omega_1$) or anti-Stokes ($\omega_2 > \omega_1$) scattering respectively. If only one (weak) laser beam, of frequency ω_1 , is incident on the material the process just described is called spontaneous Raman scattering. When two laser beams are focused in the material the Raman process can be stimulated. If the frequency difference between these beams $(\omega_1 - \omega_2) > 0$ equals the frequency difference between two states of the material, and if the related mode is Raman-active, the intensity of the ω_2 -beam will increase after passage through the sample, while the intensity of the ω_1 -beam will decrease ($\omega_1 > \omega_2$). This process is called stimulated Raman scattering (SRS) and has been treated theoretically in section (1.7) and (1.8).

In the present chapter I will describe some stimulated Raman scattering (SRS) experiments we have performed on carbon-disulfide, benzene and diamond. Using two tunable mode-locked dye lasers of different frequency (ω_ℓ and ω_s), pumped in parallel by a mode-locked Argon-ion laser, two synchronized pairs of a ω_ℓ -pulse and a ω_s -pulse are formed. With these two pulse pairs we have performed time-resolved SRS (TSRS) experiments. When we wanted to carry out non-time-resolved SRS we used only one of the two pulse pairs.

In the TSRS experiments the first synchronized pair, called the pump pair, is used to excite a Raman-active vibration of the material under study via the stimulated Raman process. After a variable delay the second pair, called the probe pair, is focused onto the sample. The gain experienced by the two "probe" pulses is proportional to the decaying coherent vibrational amplitude, which was excited by the pump pair. Observation of this optical "crosstalk" between the pump and the probe pair as a function of their time delay, allows one to observe the relaxation of the excited vibrational amplitude directly in the time domain. Time-resolved stimulated Raman

scattering enables one to study any Raman-active degree of freedom. In this thesis our research on vibrational degrees of freedom in liquids (CS_2 and benzene) and the 1332 cm^{-1} phonon in diamond is treated in detail.

The optical characteristics of our lasers are described in section (2.2). In section (2.3) some results of a (non-time-resolved) two-beam stimulated Raman measurement are presented. Apart from the stimulated Raman effect an other form of optical "crosstalk" between both laser beams could sometimes be observed. The origin of this new effect, which we have called mutually-induced focusing, is explained in section (2.3) as well.

For our laser intensities the Raman gain is typically 10^{-4} - 10^{-5} . The power spectrum of the noise from a mode-locked laser shows a broad minimum between 3 and 30 MHz. It is therefore advantageous to measure the Raman gain in a phase-sensitive way at a high frequency. We have introduced a special high-frequency (8.4 MHz) double-modulation technique to accurately measure the Raman gain and almost reach the quantum-noise detection limit. In section (2.4) I will describe this technique and demonstrate how we have converted an AM radio receiver into the high-frequency lock-in amplifier needed for detection. In section (2.5) the Raman gain factors we have measured are quantitatively compared with those presented in the literature.

The theoretical basis of the time-resolved SRS (TSRS) technique is presented in section (2.6). This technique enables one, via a pump-probe experiment, to study the relaxation of molecular excitations directly in the time domain. A detailed description of our experimental setup is given in section (2.7). In section (2.8) a model is presented to simulate a TSRS experiment. The computer simulations proved to be indispensable for the interpretation of the experimental results.

Some of the experimental results obtained with our TSRS setup are presented in section (2.9). In a TSRS experiment the signal does not disappear completely, when the frequency difference between both lasers is mistuned from the frequency of the Raman-active mode. It turns out that apart from the Raman effect, two other contributions, which are called the Kerr effect and the electronic contribution, are observed in TSRS. These contributions are not observed in a two-beam SRS experiment. Various methods to determine the relative strengths of the Kerr effect and the electronic contribution to the Raman effect are discussed in the sections (2.10) and (2.11). Section (2.12) deals with a new and interesting interference effect that arose when the frequency difference between both lasers was mistuned by

a "critical value" from the frequency of the Raman-active mode. In section (2.13) I will discuss what phase information is obtainable from TSRS experiments.

2.2 Laser characteristics

The optical "work-horse" we use is an Argon-ion laser (Spectra Physic SP171), which converts, in an awfully inefficient way (efficiency far less than 0.1%), electric energy into light. A prism inside the cavity makes the laser operate single line (514.5 nm). In this prism a standing acoustic wave is generated by a piezo-electric element. The acoustic wave periodically refracts the laser light and acts as a kind of shutter. As a result a single light pulse travels up and down the laser cavity and a train of pulses comes out of the laser with a repetition rate (82 MHz) equal to the inverse of the round-trip time (the length of the laser cavity is 1.77 m). The laser is said to work in the first-harmonic mode-locked operation. An alternative interpretation is that the acoustic wave couples each cavity mode to its neighbors, in the frequency domain. This explains the origin of the term active mode-locking.

When the acoustic frequency is tripled, the repetition rate of the laser is also tripled and three pulses move up and down the cavity. In this so-called third-harmonic mode-locked operation the average power of the laser is about a factor of 1.5 higher than in first-harmonic operation. The peak power of the pulses is however almost a factor 2 lower, as the shape of the pulses hardly differs from their shape in first-harmonic operation. As high peak power is essential for most nonlinear optical experiments, the Ar^+ -laser was usually set to first-harmonic operation.

In first-harmonic operation the average power of the Ar^+ -laser is about 600 mW. The most stable pulses have a rather odd shape. A trailing edge, at about 25% of the peak intensity, extends to some 200 ps after the main pulse. The pulse width, as measured with an ultra-fast photo-diode (SP304B), is typically 120 ps full width half maximum (FWHM). This is close to the theoretical limit, which is set by the spectral width of the laser line of 5 GHz.

The Ar^+ -laser beam is split into two parts of equal intensity, which are both used to pump their own dye laser (a SP375 and a SP375B). When the lengths of the dye lasers cavities equal that of the Ar^+ -laser cavity, and

this really is critical to some tens of μm , they are forced into mode-locked operation by the periodic pumping.¹ The mode-locked pulses produced by a synchronously-pumped dye laser can in principle be very short, due to the large spectral width of the dye gain curve. In practice the spectral width of the dye-laser output is limited by a two-plate birefringent filter inside the laser cavity to about 8.0 cm^{-1} (240 GHz), as is demonstrated in fig.(2.2.1). The average output power per dye laser is typically 80 mW. The pumping threshold of the dye lasers can be as low as 50 mW for mode-locked operation. The conversion efficiency is almost 30 %. The center frequency of the dye-laser output can be varied through rotation of the birefringent filter around its axis. The tunability of the Rhodamine 6G (R6G) dye we use is roughly from 570 nm to 635 nm, and thus covers a range of about 1800 cm^{-1} as is shown in fig.(2.2.2). When a larger frequency difference between both lasers is necessary one of the dyes, or both, have to be changed.

The width of a laser pulse can be specified in various ways. Two experimental methods to measure the pulse width will be presented below. The first one makes use of the autocorrelator that is schematically drawn in fig.(2.2.3). The beam that enters the autocorrelator is split into two parts, which follow a different path before they are focused and combined in a second-harmonic-generating crystal (KDP in our case). A photo-multiplier, situated behind a UV filter, detects the amount of generated second-harmonic light. The angle between the two beams incident on the KDP crystal, in combination with the beam stops behind the crystal, is such that only UV photons generated through combination of one photon from each beam are detected. The intensity of the second-harmonic light thus depends strongly on the overlap in time between the pulses of the two beams. When observing this intensity as a function of a variable delay in one of the paths, one has a measure for the width of the laser pulse. To be precise one measures the auto-correlation function of the intensity profile of the pulse, as is shown below.

A laser pulse of center frequency ω_ℓ can be characterized by

$$E(t) = (1/2)E_\ell(t)e^{-i\omega_\ell t} + (1/2)E_\ell^*(t)e^{+i\omega_\ell t}; I_\ell(t) = (1/2)\epsilon_0 c |E_\ell(t)|^2, \quad (2.2.1)$$

where the spatial (and vector) dependence has been left out.

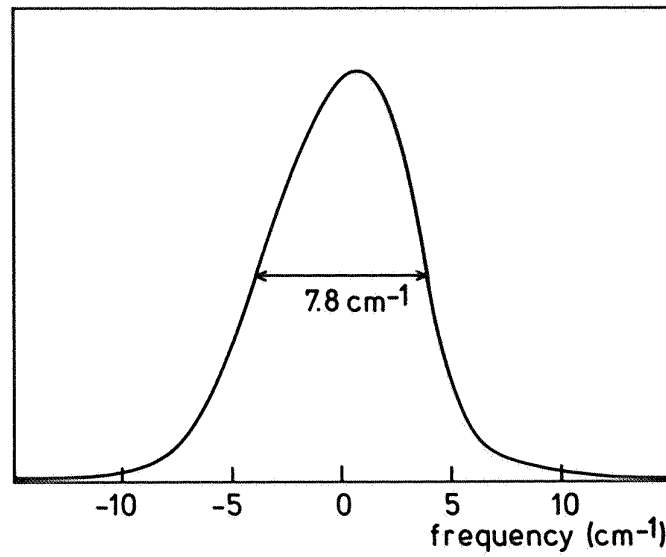


Fig.2.2.1: The spectrum of one of our mode-locked dye lasers, operating with a two-plate birefringent filter inside the cavity and R6G as active laser medium.

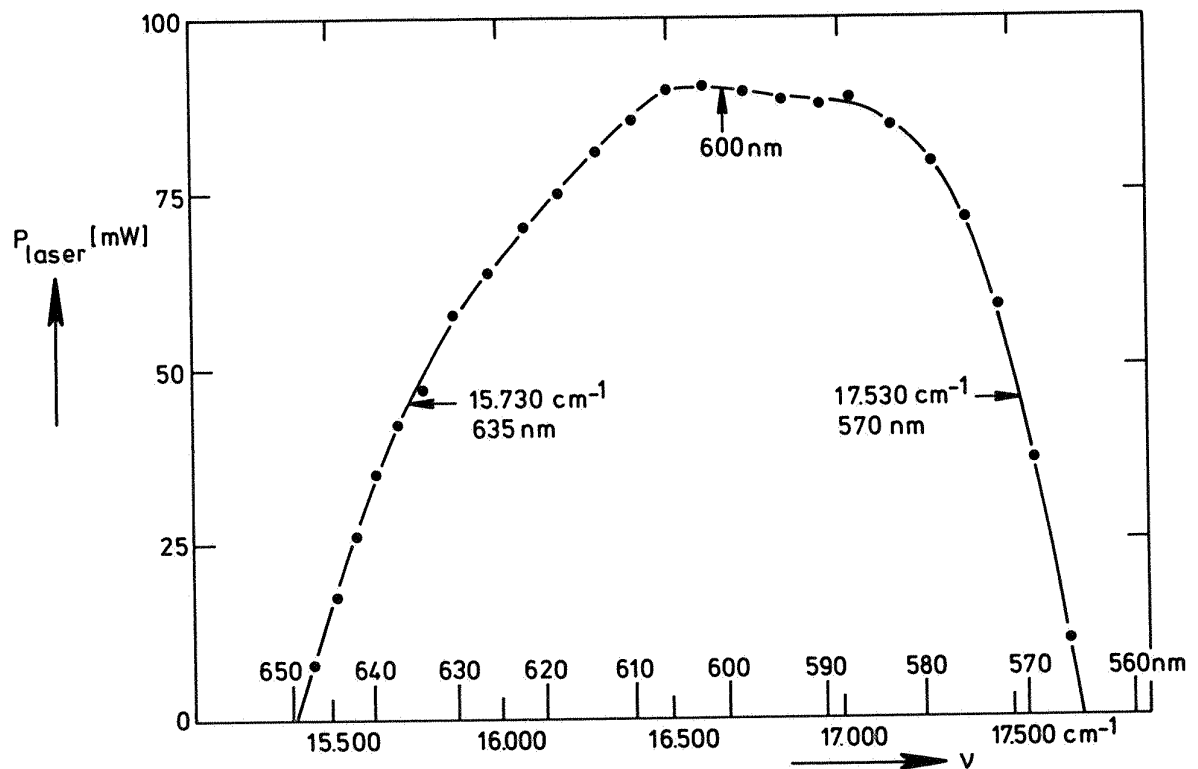


Fig.2.2.2: The tunability of a mode-locked dye laser, with R6G as active laser medium, pumped with 350 mW (514 nm) Ar^+ light.

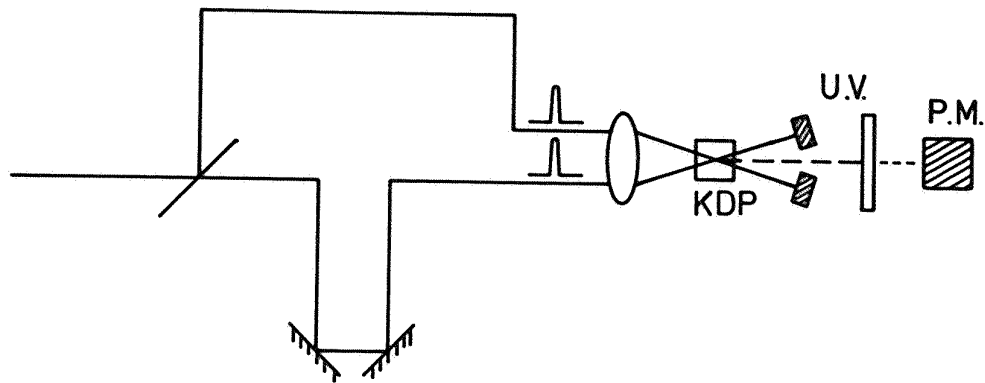


Fig.2.2.3: A schematic picture of the autocorrelator. A beam is split in two parts, which follow a different path before they are combined in a second-harmonic-generating crystal. The amount of generated UV light is measured as a function of the difference in length of the two paths.

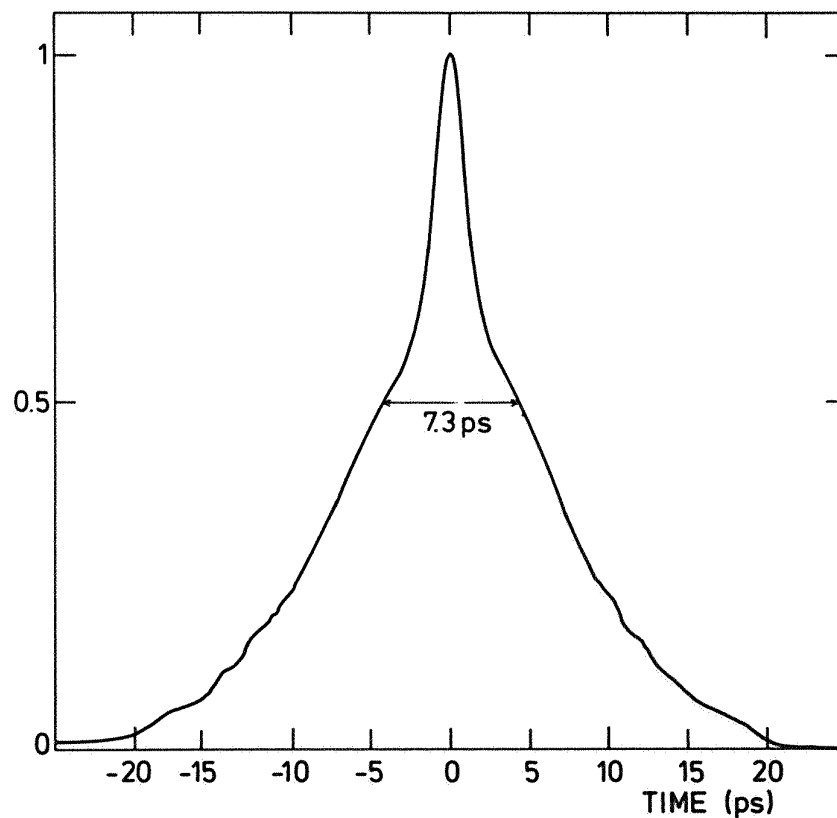


Fig.2.2.4: A typical auto-correlation function of the intensity profile of a mode-locked dye pulse, as recorded with the autocorrelator.

With an autocorrelator one measures $G(t)$ as a function of t

$$G(t) = \langle I_\ell(0)I_\ell(t) \rangle = \lim_{T \rightarrow \infty} \left(\frac{1}{2T} \right) \int_{-T}^T dt_1 I_\ell(t_1)I_\ell(t_1+t) . \quad (2.2.2)$$

It is handy, and often accurate, to assume the pulses have a Gaussian-shaped envelope. The complex exponent $(i\beta)$ of the envelope function $E_\ell(t)$ makes it possible to represent pulses with a linear frequency chirp. When $(\beta \neq 0)$ the "instantaneous frequency" varies inside the pulse.

$$\begin{aligned} E_\ell(t) &= E_{\max} e^{-(1+i\beta)t^2/\tau^2} ; \quad G(t) \propto e^{-t^2/\tau^2} , \\ E_\ell(\omega) &= E_{\max} (\pi/(1+i\beta))^{1/2} \tau e^{-\tau^2\omega^2(1-i\beta)/(4(1+\beta^2))} , \\ I(\omega) &= |E_{\max}|^2 (1/4)\epsilon_0 c \tau^2/(1+\beta^2)^{1/2} e^{-\tau^2(\omega-\omega_\ell)^2/(2(1+\beta^2))} . \end{aligned} \quad (2.2.3)$$

The FWHM of the auto-correlation function is: $2(\ln 2)^{1/2}\tau$. The FWHM of the frequency spectrum of the pulse, measured in real frequency units $(\nu = \omega/(2\pi))$, is: $((2\ln 2)^{1/2}/\pi\tau)(1+\beta^2)^{1/2}$.

$$\text{FWHM}(I(t)) \times \text{FWHM}(I(\nu)) = 0.44 (1+\beta^2)^{1/2} , \quad (2.2.4)a$$

$$\text{FWHM}(G(t)) \times \text{FWHM}(I(\nu)) = 0.62(1+\beta^2)^{1/2} = 20.8(1+\beta^2)^{1/2} \text{ pscm}^{-1} . \quad (2.2.4)b$$

Fourier has already shown that the product of the width of a function in the time domain and in the frequency domain is minimal for Gaussian pulses. If the dye laser would produce these transform-limited pulses, the FWHM of the auto-correlation function should be slightly less than 3 ps FWHM. Experimentally the best pulses our dye lasers produce have an autocorrelate of 7 ps FWHM ($\tau=4.2$ ps), as is shown in fig.(2.2.4). Consequently there must be a frequency chirp. Assuming the pulse is Gaussian-shaped and has a linear frequency chirp we can determine the chirp factor $\beta = \pm 2.5$. Unfortunately the auto-correlation function does not tell us whether the lower frequencies are in the front of the pulse, and the pulse has an up-chirp ($\beta > 0$), or whether they are in the back of the pulse, and the pulse has a down-chirp ($\beta < 0$). Time-resolved CARS measurements we have performed indicate that the pulses have a down-chirp, or anormal chirp.

The shape of the auto-correlation function is only roughly Gaussian. A

closer look shows the function peaks too strongly at its maximum, decreases too slowly in the wings, and is better fitted by a $\{\cosh(t/\tau)\}^{-2}$ -function. The peaked maximum, which is called the coherent spike, signifies that the pulse envelopes are not smooth and have an intricate structure, probably in the form of a frequency spread that is not (perfectly) linear in time.

Sending the pulses from the two dye lasers, with frequency ω_l and ω_s , simultaneously into the autocorrelator, and tuning the KDP crystal to their sum frequency, one can measure the cross-correlation function $\langle I_l(0)I_s(t) \rangle$ of both pulses. If both pulses would have a fixed time separation, the width of the cross-correlation function should be the root of the arithmetic mean of the squares of the widths of the respective autocorrelates. The experimentally-determined cross-correlation function is broader, indicating that the positions of the pulses vary in time. This so-called time jitter is hardly surprising as the Ar^+ -pulse that pumps both dye lasers, and takes care of their mutual synchronization, is very long compared to the dye-laser pulses. Although both dye lasers are of the same make, they will probably respond slightly differently to the pump pulses. Experimentally the time jitter of the dye-laser pulses depended strongly on the exact length of the Ar^+ laser, which makes it plausible that the time jitter indeed originates from noise in the Ar^+ -laser pulses.

The time jitter can be divided in long-term and short-term variations. The long-term jitter is reflected in a difference from one cross-correlation function, which takes a few ms recording, to another and is in the best cases about 2-3 ps (rms deviation from average). The width of each cross-correlation trace is typically 9.5 ps (FWHM) and thus considerable broader than the widths of the auto-correlation traces of the individual pulses. This difference is accounted for by an extra time jitter that is much faster than the one-ms recording time and has a rms amplitude of 2-3 ps as well.

A second method to determine the width of a laser pulse makes use of a Michelson interferometer. The beam is split in two and each part travels along an arm of the interferometer. On combination they will interfere when the path lengths of the interferometer practically match and the pulses overlap. Observing the modulation in average intensity of the combined beam as a function of the difference in path length, one gets another measure for the width of the pulse. The modulation depth reflects the auto-correlation function of the electric field.

$$(\Delta I_\ell / I_\ell)(t) \propto \text{Abs} \left\{ \lim_{T \rightarrow \infty} \int_{-T}^T dt_1 E_\ell^*(t_1) E_\ell(t_1+t) \right\} \propto e^{-(1+\beta^2)t^2/(2\tau^2)}, \quad (2.2.5)$$

where the integral is taken over one laser pulse and the latter expression is only valid for the linearly-chirped Gaussian-shaped example pulse.

The result of such an interferometric measurement is presented in fig.(2.2.5), where the modulation depth of the fringes is plotted as a function of time delay. The FWHM of 4.2(2) ps found with this technique is far smaller than that found with the autocorrelator. The interferometric technique is susceptible to the frequency build-up in the pulse, as different colors do not interfere, whereas the second-harmonic-generating technique, which records the auto-correlation function of the intensity $G(t)$, is insensitive to frequency build-up. Pulses with identical intensity envelopes, but different frequency contents, will yield identical intensity auto-correlation traces, whereas the interferometric technique would show a smaller profile for the pulse with the largest frequency spread. The huge difference in pulse shape we find between the interferometric technique and the second-harmonic-generating technique proofs once more that our dye-laser pulses are not transform-limited. It is clear that for many experiments both types of monitoring the pulse shapes are important, as they give complementary information.

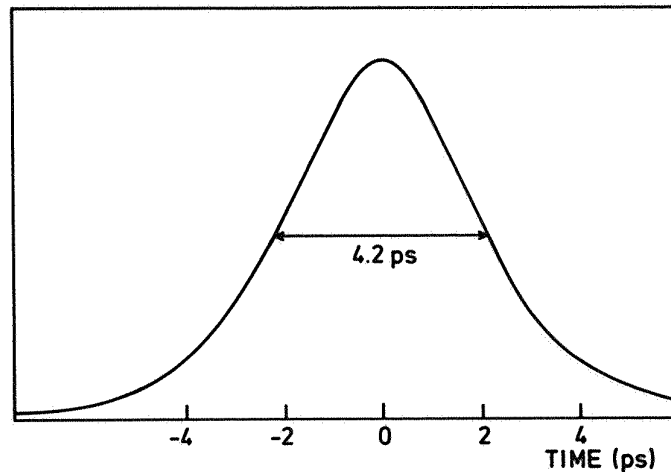


Fig.2.2.5: A typical auto-correlation function of the electric field of a mode-locked dye pulse, as recorded with an interferometric technique (see text).

2.3 Two-beam stimulated Raman spectroscopy (SRS)

Using two dye lasers we performed a two-beam stimulated Raman (SRS) experiment. The lasers are set to different frequencies, in the following denoted as yellow (ω_y) and red (ω_r), and a collinear pulse pair is formed through combination of one pulse from each dye laser, synchronized with a delay line. The mean frequency of each laser is determined with a wavemeter (Burleigh WA-10). When the combined beam is focused in a sample that has a Raman-active mode close to the frequency difference between the lasers the stimulated Raman effect results in optical "crosstalk" between the two beams. The intensity of the red beam will slightly increase and that of the yellow beam will slightly decrease on transition through the sample. After passage through the sample we separated the two collinear beams with a prism and singled out the red beam with a pinhole for detection with a fast photodiode (EG&G SGD100A).

Elastic scattering led to a leakage of some 10^{-4} of the yellow beam onto the photodiode (for $\Delta\nu=500\text{ cm}^{-1}$). We use colored-glass filters from Schott as extra wavelength-selective elements in front of the detector. When the frequency difference between both lasers is less than 400 cm^{-1} , the frequency-resolving power of our setup becomes the limiting factor for SRS. One could improve this resolution by using a spectrometer, but it has the disadvantage of a lower transmission coefficient.

The induced gain and loss in a SRS experiment can be most accurately measured when the intensity fluctuations at the detection frequency of the probe laser are as low as possible. Mode-locked cw dye lasers, have a noise characteristic with a broad minimum between 3 and 30 MHz.^{2,3} This minimum corresponds almost to the quantum-noise limit (Poisson noise due to fluctuations of the number of photons). At lower frequencies other noise is added mainly from mechanical origin, whereas at higher frequencies we are approaching the first harmonic of the mode-locking frequency (82 MHz). We have chosen a modulation frequency somewhere in the minimum of this noise band (8.4 MHz). The modulation is applied onto the yellow beam with an electro-optic (EO) modulator (Coherent 3010). The intensity of the transmitted red beam is monitored with a detection photodiode. The electrical signal from this photodiode can be analyzed either with a high-frequency lock-in amplifier (LIA) or with a radio-frequency receiver. For detection we make use of an AM radio, as will be discussed in section (2.4).

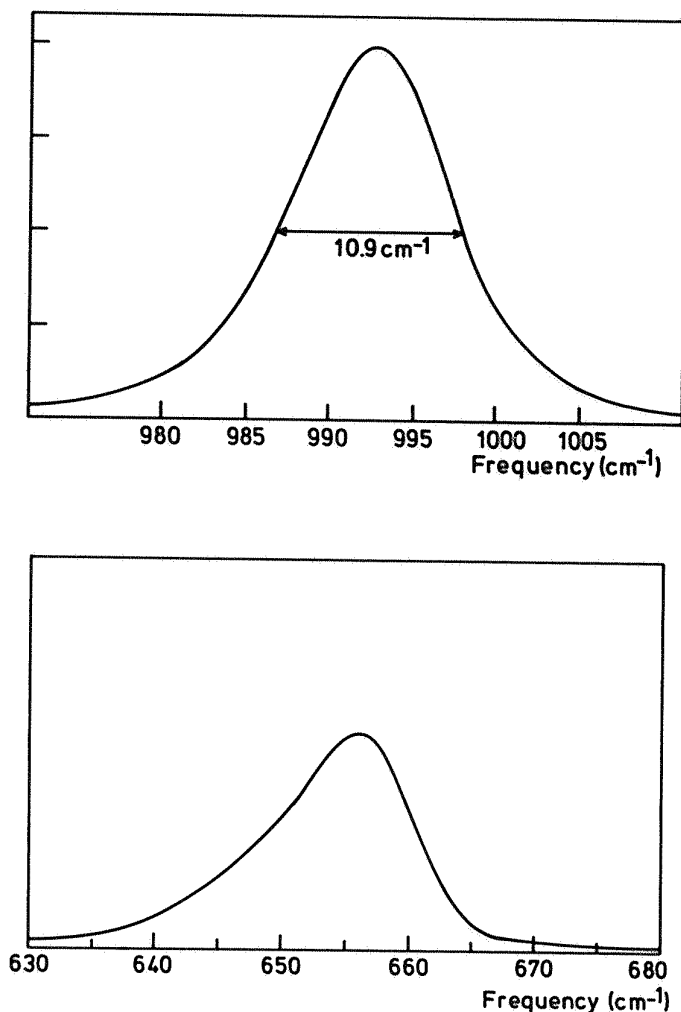
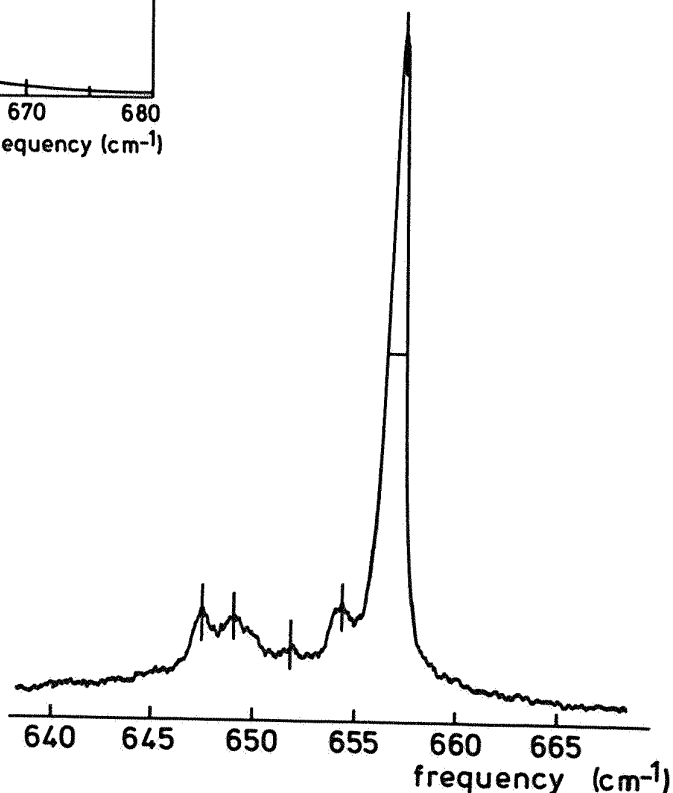


Fig.2.3.1:

The dependence of the stimulated-Raman signal on the frequency difference between both lasers ($\nu_L - \nu_S$). In the upper graph results are shown for the 992 cm^{-1} mode of benzene. In the lower graph results are shown for the 656 cm^{-1} mode of carbon-disulfide.

Fig.2.3.2:

An accurate spontaneous-Raman measurement of the Raman-active modes in CS_2 around 656 cm^{-1} . The spectral resolution for this run was 0.5 cm^{-1} .



Convincing experiments have been performed to demonstrate the large signal to noise ratio (S/N) obtainable with a mode-locked system like ours.^{2,4} Observing the optical crosstalk as a function of the frequency difference between both lasers, one measures the stimulated Raman spectrum of the sample. This frequency spectrum is proportional to $\text{Im}\{\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)\}$, convoluted over the frequency profiles of both lasers, and is identical to the "ordinary" spontaneous Raman spectrum. The spectral resolution of the SRS technique is limited only by the frequency width of the lasers which gives SRS an enormous advantage over spontaneous Raman scattering when one uses narrow-band CW lasers.⁵

We have performed SRS measurements on carbon-disulfide, benzene, diamond and carbon-tetrachloride. Some results are shown in fig.(2.3.1). The 992 cm^{-1} -mode of benzene is the symmetric "breathing" molecular excitation (ν_2^{CC}). The line width we measure (10.9 cm^{-1}) is far larger than the spontaneous line width (2.2 cm^{-1} FWHM) and solely reflects the spectral width of the dye laser pulses. In section (2.6) it will be shown that the measured spectral profile is the modulus squared of the Fourier transform of the function $E_\ell(t)E_s^*(t)$. Extra information on the shape of the dye-laser pulses can thus be obtained from SRS data.

Mistuning the overlap in time between the yellow and red pulse, the Raman gain decreases to half its value for a mistuning of about 6-7 ps (HWHM). This decrease is not as rapid as one would expect for "jitter-free" pulses, and is the second indication we have for the presence of time jitter between the pulses from both lasers. The measured sensitivity of the SRS signal to the pulse overlap between both lasers suggests a value for the total time jitter of 3-4 ps (rms deviation from average).

The asymmetry in the 656 cm^{-1} line of CS_2 is solely a result of the presence of neighboring spectral features. In fig.(2.3.2) a spontaneous Raman measurement on CS_2 at room temperature is displayed that gives better spectral resolution around 656 cm^{-1} . The strongest line is the symmetric stretch (ν_1) of C^{32}S_2 at $\nu=656.7\text{ cm}^{-1}$. The assignment of the other lines can e.g. be found in ref.6. The Raman excitation of molecules that have one ^{32}S substituted by an isotope, ^{33}S or ^{34}S , are visible at 651.7 cm^{-1} and 647.3 cm^{-1} respectively. A hot band is observable at 654.4 cm^{-1} from the transition of the singly-excited to the doubly-excited symmetric stretch. Another hot band at 648.9 cm^{-1} arises from the excitation of molecules that do already have one quantum of "bending mode" (ν_2^1). These measured Raman

frequencies are within 0.3 cm^{-1} of other values quoted in the literature, which were measured with spontaneous Raman scattering as well.⁶

The separation of the ω_l -beam and the ω_s -beam at the detection stage is partly done with a pinhole. Whenever the pinhole let only part of the ω_s -beam through, and we thus observed intensity variations in one specific area of the laser profile, extra optical crosstalk was observed. This optical crosstalk could be either a gain or a loss in intensity and its strength was comparable in magnitude with the SRS signal. A complicated geometrical distribution of the signal was found, when a small pinhole was scanned over the transverse spatial profile of ω_s -beam. We call this new phenomenon mutually-induced focusing.

Mutually-induced focusing is based on the fact that a non-zero real part of $\chi^{(3)}$ is reflected in an index of refraction that depends explicitly on the light intensity ($n(I) = n_0 + n_2 I$, where n_0 is the "linear" index of refraction at zero intensity and $n_2 \approx 3 \times 10^{-18}$ for CS_2 at ($\lambda = 600 \text{ nm}$)). The intensity dependence of the index of refraction leads the well-known effect of self-focusing of very intense laser beams. In our setup the yellow beam creates a spatial index of refraction profile, which refracts and deforms the red beam.⁸ The strength of this index of refraction profile is proportional to the real part of $\chi^{(3)}(-\omega_s, \omega_l, -\omega_l, \omega_s)$. The total intensity of the red beam is not disturbed by refraction, but redistributed in the transverse direction. This explains why mutually-induced focusing is only observable when part of the red beam is blocked at the detector. A related effect is the phenomenon of thermal lensing⁷, where the index of refraction is locally lowered through heating by absorption of radiation. Thermal lensing was not observable in our setup.

It is difficult to calculate mutually-induced focusing accurately, because it depends crucially on the exact alignment of both beams in the sample. In the small-signal regime the strongest effects are observable when the laser beams do not overlap in space. Through mutually-induced focusing the red beam is drawn towards the yellow beam. When the two beams are collinear the lens induced by the yellow light will increase the convergence of the incoming red beam before the focus, but after this focus it will try to refocus the emerging divergent beam. For collinear beams the action of mutually-induced focusing before and after the focus cancel to first order. We abandoned attempts to calculate the mutually-induced focusing and decided to prevent its appearance in our experiments. The pinhole is always kept

fully open and the total intensity of the red laser beam is thus measured.

In the previously-discussed two-beam SRS measurement both laser beams were linearly-polarized and the measured Raman gain was proportional to the imaginary part of $\chi^{(3)}(-\omega_s, \omega_l, -\omega_l, \omega_s)$. With a slightly different technique called Raman-induced Kerr effect spectroscopy⁹ (RIKES) the influence of a modulation in the direction of polarization of the yellow beam on the intensity of the transmitted red beam is studied. An advantage of RIKES over SRS is its slightly larger signal to noise ratio.¹⁰ Rosasco and Hurst^{11,12} interpreted the polarization-modulation of the yellow beam as a phase modulation between two collinear yellow beams, one with a horizontal direction of polarization and one with a vertical direction of polarization.

We have experimentally compared the RIKES technique with SRS. The described modulation of the direction of polarization is easily created with an ordinary EO modulator, removing the final polarizer, which in normal operation turns phase modulation into amplitude modulation. The DC offset voltage of the EO modulator affects the average phase difference between the horizontally and the vertically-polarized component. In a RIKES experiment this determines whether one measures the imaginary or the real part of $\chi^{(3)}$. We did some measurements that indeed show that one can selectively probe the real and the imaginary part of $\chi^{(3)}$. The RIKES method has two drawbacks. In the first place the interpretation of the data is slightly complicated as one does not probe a single specific tensor component of $\chi^{(3)}$, but always a linear combination of two components. Secondly the RIKES technique is very susceptible to birefringence in the EO modulator and to mixing of the two directions of polarization in other optical components. We got a demonstration of the latter effect when we found different results on moving the polarizer, situated right after the sample, to a position just in front of the detector.

2.4. Converting an AM radio into a high-frequency lock-in amplifier

In this section I want to discuss the double-modulation technique we use to get a good signal to noise ratio for detection of stimulated Raman gain. We are using a Drake R7 radio receiver (R.L. Drake Company 540 Richardstreet Miamisburg Ohio 45342 USA). Other physicist have made use of a radio for detection as well¹³⁻¹⁵, but the various detection schemes all differ from the one we use.¹⁶

One of the main purposes of this section is to demonstrate that the use of a radio to detect the 8.4 MHz modulation is often preferable over the use of a high-frequency lock-in amplifier (LIA) and in fact the radio can be transformed into a phase-sensitive detector by supplying it with an extra carrier. We show that by using this method the nonlinearity of an ordinary AM radio is removed.

The conversion of an optical signal into an electric signal on the antenna input of the radio is pictured in fig.(2.4.1). Although the noise introduced by a radio is very small ($2.4 \times 10^{-19} \text{ W/Hz}$) it is certainly not negligible and even dominates when the photodiode signal is directly coupled to the radio. This noise source is largely eliminated by using a low-noise preamplifier (Trontech W50ATC, 0.01-50 MHz, 50 dB, NF=1.5 dB). The photodiode we use is an EG&G SGD100A (50 KHz-50 MHz). This photodiode is fast enough to detect an 8.4 MHz modulation but too slow to resolve the individual mode-locked laser pulses.

In the following paragraphs it will be demonstrated that for our detection unit the quantum noise of the incident laser beam, of 0.3 mW average intensity (typical), is the dominant source of noise. When a laser of 0.3 mW of incoming light at 600 nm is detected with a quantum efficiency of 80 %, this results in $N=7 \times 10^{14}$ detected photons per second. When the photocurrent is directly routed through the preamplifier ($R=50 \Omega$ input impedance) the corresponding quantum noise at the input of the preamplifier is $2e^2RN \text{ W/Hz} = 1.9 \times 10^{-21} \text{ W/Hz}$. Because of the low input impedance of the preamplifier the thermal noise is mainly generated in this device and estimated to be $2-6 \times 10^{-21} \text{ W/Hz}$. We have obtained the quantum limit by increasing the effective input impedance of the preamplifier with a LC-

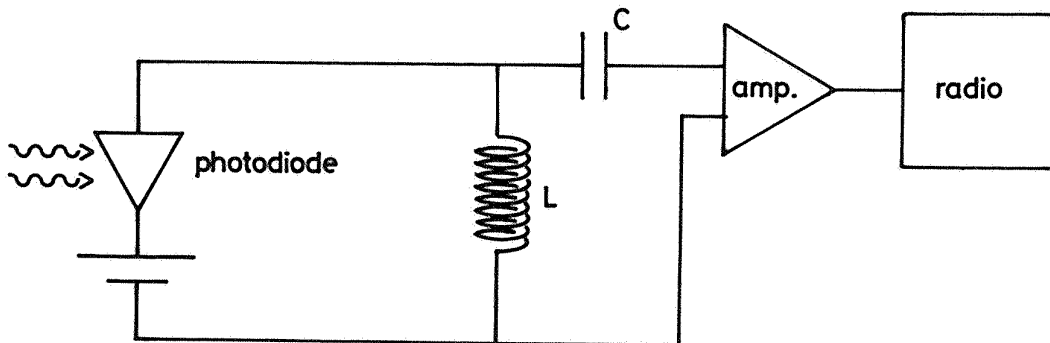


Fig.2.4.1: Conversion of an optical signal into a low-noise electric signal.

circuit ($L=3.7 \mu\text{H}$, $C=90 \text{ pF}$) resonant at 8.4 MHz having a Q of 4. The signal is passively preamplified by a factor 4, while the thermal noise generated in the preamplifier is unaffected. The quantum noise is intrinsic to the signal and is of course also amplified. The use of a higher-Q filter is inefficient, because this reduces the speed of the detection unit too much.

In the described configuration the laser noise is the dominant source of noise. This can experimentally be checked by directing an unmodulated laser beam of variable intensity onto the photodiode and measuring the noise as a function of the intensity of the beam. This measurement is presented in fig.(2.4.2). When the laser beam is blocked the noise in the electronic circuit is measured ($18 \mu\text{V rms}$, 125 ms on the low-frequency LIA). At 0.3 mW light intensity the noise amplitude is about 2x higher, which indicates a dominance, of about a factor 3, of the laser noise power. The fact that this laser noise power corresponds almost to the quantum-noise limit can be calculated using the (measured) responsivity of the total detection system, which is presented further on. For this measurement the linearity of the detection unit is essential. The "linearization option" described in the next few paragraphs was used during the recording of the data for fig.(2.4.2).

A modulation applied to one laser beam with the EO modulator is transferred, via the stimulated Raman process, onto the other beam and detected with the photodiode (signal S_g). At first we intended to use the

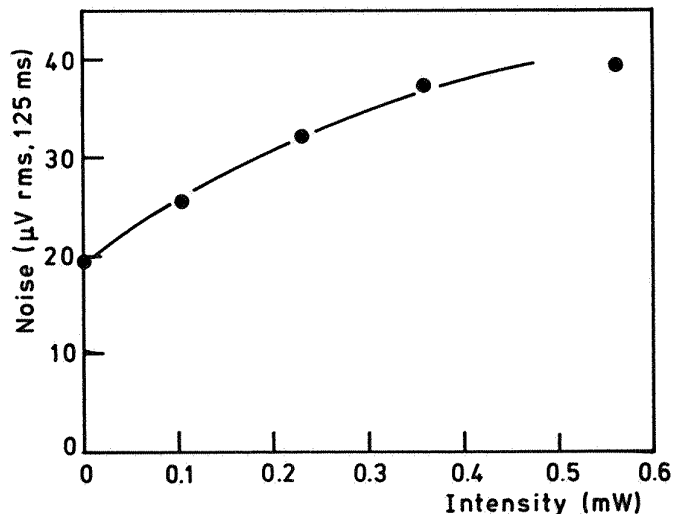


Fig.2.4.2: The noise, recorded with the low-frequency lock-in amplifier as a function of the power of an incident unmodulated beam.

radio in its single side band (SSB) mode to detect this signal S_s . In this case it is highly desirable to use the internal frequency generator of the radio to drive the EO modulator, because of the large drift in the frequency of the radio (50-150 Hz per hour). Even when the internal frequency generator of the radio is used problems arise: experimentally it is extremely difficult to circumvent the electric crosstalk between the amplifier for the EO modulator head (90 V_{pp}) and the detection unit (typical photodiode signal 10^{-7} V), resulting in a constant background signal for SSB detection.

The problem of the direct electric crosstalk can be circumvented by introducing an extra modulation on the pump or probe beam (preferable the probe beam to gain a factor in the rejection between the pump and probe at the detector). This extra modulation can be applied by a simple mechanical chopper (500 Hz in our case) as shown in fig.(2.4.3). Hence the signal to be detected becomes a 500 Hz amplitude modulated 8.4 MHz wave and can be excellently detected by a radio in its AM mode.

In the Drake radio the incoming signal is first transformed to an intermediate frequency, amplified and passed through a narrow band crystal

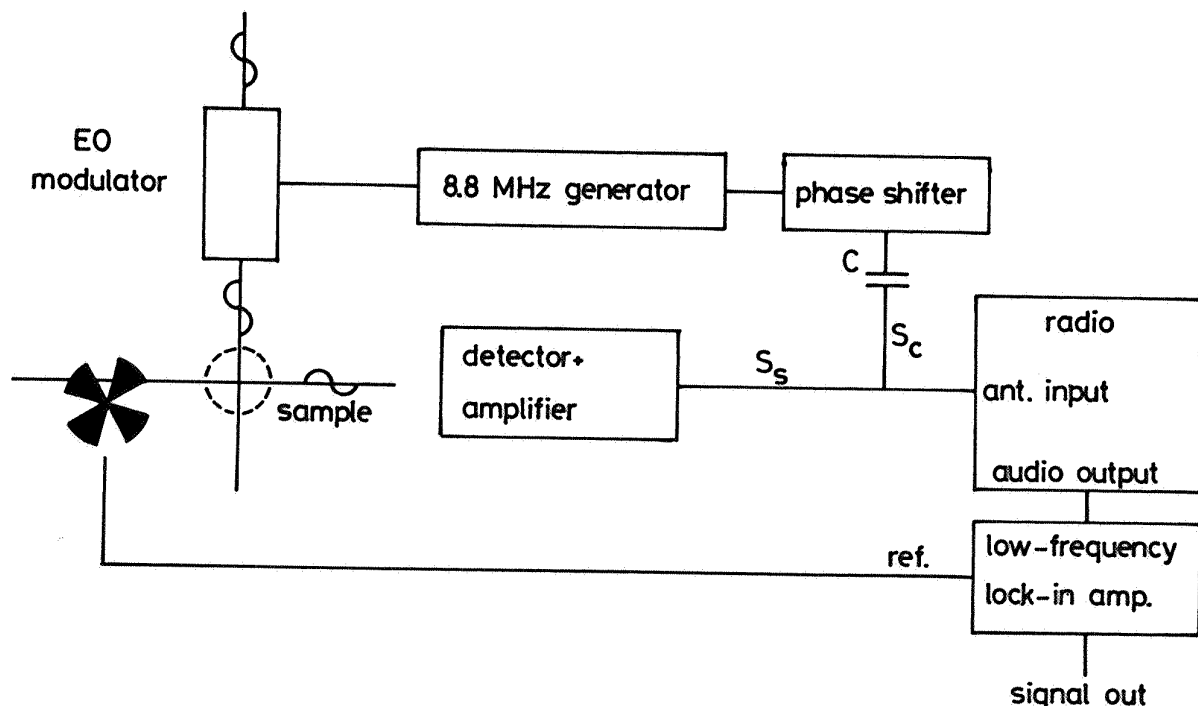


Fig.2.4.3: The complete detection scheme in a two-beam measurement using a double-modulation technique.

filter. After a few other operations the signal, now being at a frequency around 50 KHz, is separated in two parts. When operating properly the first one (S_1) is amplified until the amplifiers are saturated and, in the ideal situation of no noise, will be deformed into a square wave with an amplitude independent on the incoming signal strength. In a mixer this wave is multiplied with the non-amplified signal S_2 to produce, after a low-pass filter, the amplitude of the rf signal.

A measurement of the response of this AM detection system is presented in fig.(2.4.4). This figure shows that unfortunately the linearity of the detection unit is lost for weak signals. Measurements show that this is caused by the absence of saturation of the amplified signal S_1 . The amplification inside the demodulation chip for weak signals is apparently not enough to create a square wave of constant amplitude, but instead the amplitude becomes dependent on the magnitude of S_1 . This results at low signal levels in a loss of linearity between the incoming AM signal and the outgoing demodulated (500 Hz) audio signal, and more specifically this relation becomes quadratic. The signal level where the linearity is lost can be shifted to lower values by increasing the gain of signal S_1 . There is, however, another phenomenon that results in the loss of linearity of the detection unit. An AM radio derives the frequency of the carrier wave from the incoming signal via amplification of S_1 . When this incoming signal is very noisy the signal S_1 will not be a perfect square wave and the demodulation is performed at not exactly the right frequency. One can say the radio has trouble finding the carrier to demodulate with. This situation occurs when the signal strength is of the order of the rms noise (mainly quantum noise) in the total detection bandwidth (2.3 KHz) of the radio.

In this simple AM configuration the radio is only capable of detecting the magnitude of weak signals in a nonlinear way. Furthermore since there is no phase information on the signal it is impossible to decide whether a signal results from a gain or a loss of the probe beam.

To improve on this situation we have made the following change: the reference signal for the EO modulator is also fed into a 8.4 MHz homemade phase shifter. A small part of this phase-shifted 8.4 MHz signal S_c is capacitively coupled to the original signal S_s via a capacitor with a low capacitance (12 pF) (see fig.(2.4.3)). This small extra rf signal (17 mV peak-peak) has no disturbing influence on the preamplifier. The capacitance is chosen in such a way that the added carrier is much stronger than the

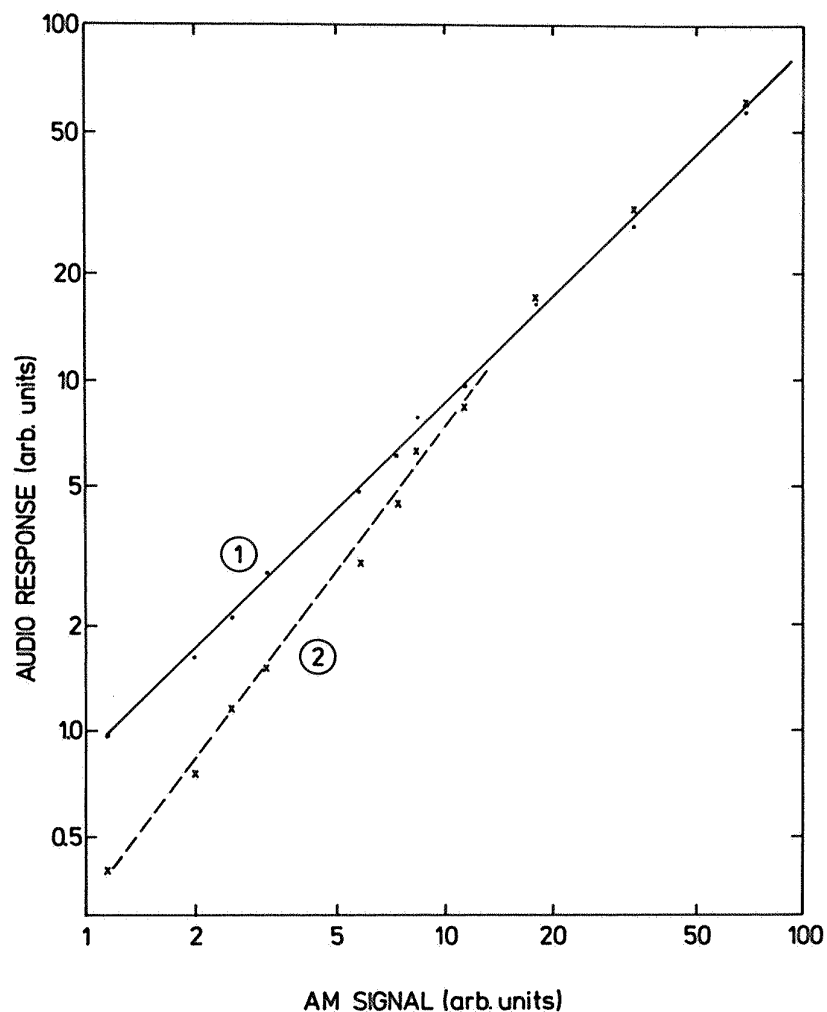


Fig.2.4.4: The response characteristic of our Drake radio. On the horizontal axis the amplitude of the double-modulated signal present at the antenna input is plotted. On the vertical axis the amplitude of the low-frequency signal on the audio output of the radio is plotted. Curve 1 is a measurement taken without the introduction of an extra carrier. When the radio was supplied with an extra phase-shifted carrier, curve 2 was the resulting response. Note the highly improved linearity in the latter case.

preamplifier signal and results in the desired saturation of the signal S_1 at the amplifier stage. The contribution of the artificially-introduced carrier will therefore dominate in the amplified signal S_1 and the demodulation is performed with this wave only (amplification until saturation). In that case the demodulation signal will be a pure undeformed square wave, independent of the signal S_s , and the detection unit regains its linearity (see fig.(2.4.4)). The amplitude modulations on the non-amplified wave S_2 are solely due to S_s (500 Hz AM). The demodulated audio signal hence becomes

$$S_{\text{audio}} = S_1 \times S_2 = \cos(\omega t + \varphi_{S_c}) \times \left\{ (1/2) + (2/\pi) \cos(\omega_{\text{am}} t + \varphi_{\text{am}}) \right\} \cos(\omega t + \varphi_{S_s}) \propto \cos(\varphi_{S_c} - \varphi_{S_s}) \times \cos(\omega_{\text{am}} t + \varphi_{\text{am}}) \quad (\text{only audio, no DC}), \quad (2.4.1)$$

where $\omega_{\text{am}} = 2\pi \times 500 \text{ Hz}$ and $\omega = 2\pi \times 8.4 \text{ MHz}$.

The phase of the 8.4 MHz signal is obtained by optimizing the audio signal with the 8.4 MHz phase shifter in exactly the same way as is done with a high-frequency LIA. To complete the detection unit the audio signal is fed into a low frequency LIA (500 Hz), getting its reference signal from the mechanical chopper (fig.(2.4.3)). In a two-beam SRS measurement neither the rf phase nor the AM phase change continuously. Once optimized one can keep these phases fixed. Only the sign of the detected signal changes, signifying a gain or a loss of the probe beam. Without the introduction of the extra carrier both situations would result in a positive signal and could not be distinguished.

We have calibrated the responsivity of our detection unit, through observation of the signal produced by a beam of known modulation. When a very weak beam is passed through the EO modulator, giving it a hundred

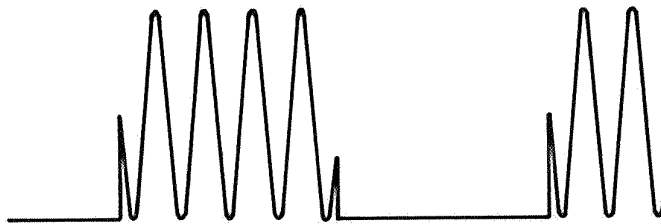


Fig.2.4.5: The double-modulated electrical signal produced by the SGD100A photodiode looks like this.

percent amplitude modulation, and afterwards modulated with a chopper at 500 Hz and detected with our photodiode the resulting electrical signal looks like fig.(2.4.5). A similar signal is produced by the photodiode in a SRS measurement. At an average (double-modulated) intensity of $0.88 \mu\text{W}$ the amplified electrical signal after the Trontech amplifier (at the usual impedance of 50Ω) has an average of about 8.3 mV. The responsivity of the photodiode-Trontech combination is thus about 10^4 V/W . This signal is demodulated at 8.4 MHz by the radio, which offers a sinusoidal 500 Hz at its audio output. The amplification inside the radio can be varied with a knob, the so-called gain control, that we keep fixed exactly in its upward position. It is important to keep the knob in this position for each measurement as it determines the responsivity of the total system, in combination with the automatic gain control (AGC) option of the radio, which we leave in the off-state. For the $0.88 \mu\text{W}$ beam mentioned above the lock-in amplifier recorded a signal of 88 mV. The response of the total system, defined as the LIA-output voltage divided by the average double-modulated input intensity of the laser beam, is thus 10^6 V/W .

The response being known I can compare the measured laser noise, as presented in fig.(2.4.2), with the quantum-noise limit. For pure quantum noise, or shot noise, the noise power, being defined as the rms deviation from the average number of photons detected in a frequency bandwidth B, is given by $\text{Noise} = 2NB [\text{photons}^2\text{s}^{-2}]$. When the Raman gain measured in a two-beam stimulated Raman experiment is denoted by G and the photodiode records N photons per second from the detection beam, the DC signal power (modulation off) in the detection beam is $\text{Signal} = G^2N^2 [\text{photons}^2\text{s}^{-2}]$. The unmodulated signal to noise ratio in terms of power is thus $(\text{Signal/Noise}) = G^2N/2B$. With the sinusoidal 8.4 MHz modulation we loose a factor (1/4) in power signal to noise ratio, whereas we loose a factor $(4/\pi^2)$ with the chopped 500 Hz modulation. Combining these numbers the theoretical power signal to noise ratio in the quantum-noise limit is

$$(\text{Signal/Noise}) = (1/2\pi^2)G^2N/B . \quad (2.4.2)$$

With $300 \mu\text{W}$ light on the detector the number of detectable photons per second is $N=7 \times 10^{14} \text{ s}^{-1}$ (quantum efficiency 75 %). When the low-frequency LIA is set to an integration time of 125 ms and a roll-off of 12 dB per octave the full bandwidth is 2 Hz. Substitution of these values in equation (2.4.2)

results in a minimum detectable gain of $G = 2.4 \times 10^{-7}$. Experimentally we measured a total noise of 35 μV rms at the LIA for 300 μW of incident light (integration time 125 ms). A gain G on this beam would result in an average double-modulated signal intensity of $75G \mu\text{W}$. Under the specified circumstances the experimentally-determined minimum-detectable gain is $G = 4.7 \times 10^{-7}$. As this value does not differ too much from the theoretical limit, especially when one corrects for the excess noise from the detection unit, I conclude that the laser noise, which limits the sensitivity of our detection unit, is almost quantum-noise limited.

To summarize, by using a simple high-frequency phase shifter and coupling the phase-shifted signal (S_c) as an extra carrier into an AM radio this radio can be converted into the equivalent of a high-frequency LIA. The technique involves an extra low-frequency modulation and an extra demodulation stage with a low-frequency LIA or a mixer. The costs are much less compared to the costs of a high-frequency LIA. Furthermore the rejection of unwanted frequencies is enormous (≈ 145 dB for frequencies not too close to the detection frequency). Commercial rf lock-in amplifiers do not have this high rejection rate and are often troubled by overload problems (one can usually solve these problems by installing a narrow-band filter at the input of the LIA). The double-modulation technique necessary for detection with an AM radio reduces the signal to noise ratio (chopped light has half the original intensity), but a technique of this sort is practically always needed to avoid the direct electric crosstalk between the EO modulator and the detection unit. In a more complicated four-beam time-resolved SRS experiment (section (2.6)) the optical phase becomes important and the low-frequency modulation can, with less loss in signal, be applied with a piezo-electric element.

The presented double-modulation technique and detection scheme is a very good alternative for a high-frequency lock-in amplifier, in any "optical crosstalk" experiment.

2.5 Measured Raman gain coefficients

In this section the Raman gain G we have measured is quantitatively compared with the steady-state Raman gain coefficient specified in the literature. In our SRS experiment two collinear laser beams of frequencies ω_l and ω_s are focused in a bulk sample. The transverse intensity profiles of

the beams, just before the focusing lens, are almost identical. They are Gaussian-shaped (TEM_{00}) with a FWHM of 0.83 mm. An achromatic lens is used to focus both beams and, as their frequency difference is relatively small, the shape of both focused beams is practically identical and is given by

$$I(z,r) = [P/(\pi w(z)^2)] e^{-r^2/w(z)^2}, \quad w(z) = (z_0/k)^{1/2} \{1+(z/z_0)^2\}^{1/2}, \quad (2.5.1)$$

where z is the space coordinate along the axis of the laser beam, r measures the distance from the axis, P is the power of the beam, $w(z)$ is the width of the beam at position z , $k=n(2\pi/\lambda_0)$ is the wave vector of the radiation and z_0 is a parameter that specifies the form of the focus. The beams are usually focused with a lens of 50 mm focus length. In vacuum this results in a minimum waist of 16 μm ($w(0)=9.5 \mu\text{m}$) and an extension of the focus region of about 3 mm ($z_0=0.95 \text{ mm}$). Focusing into a material with an index of refraction n the length of the focus region (proportional to z_0) is enlarged by a factor n , whereas the value of the minimum waist remains unaffected.

To determine the total gain experienced by the ω_s beam after passage through the focus, equation (2.5.1) has to be used. Via the steady-state gain coefficient g_{ss} one can calculate the local enhancement at each position (z,r) . To determine the increase in total power per unit length (along the axis) one should integrate along the transverse profile of the beam (r). Finally one should integrate over the whole focal region (z). The result of this three-step calculation is

$$G = (1/2)kPg_{ss} = (n\pi/\lambda_0)Pg_{ss}. \quad (2.5.2)$$

A similar equation for the Raman gain can be found in ref.17 by Owyong and Jones. Being in cgs units their equation only looks different. Both equations give identical results. Apparently the Raman gain observable in a two-beam SRS experiment is independent on the degree of focusing of the lasers, as long as they are collinear and the focal region lies completely inside the bulk sample. This gives the SRS technique a remarkable advantage over spontaneous Raman scattering in determining the absolute strength of a Raman-active mode.

For a bulk benzene sample ($\nu_\ell - \nu_s = 992 \text{ cm}^{-1}$) we have measured a gain $G=3.8(5) \times 10^{-4}$ for the red (ω_s) light, at an average intensity of 3.2 mW of double-modulated yellow (ω_ℓ) light. Due to the double-modulation technique

the increase in intensity of the red beam has a double-modulated intensity profile (see fig.(2.4.5)). G specifies the peak-peak value of this profile. The increase in average intensity of the red beam is thus only $(1/4)G$.

The pulse widths of our mode-locked lasers are comparable to the relaxation times of the modes under study and transient effects are important. This leads to corrections on the gain, which will be discussed in the next paragraph. In this paragraph the hypothetical steady-state gain will be determined that should be observable with two narrow-band lasers and with a pump-laser power identical to the peak power of our yellow pulses. The average intensity of the unmodulated yellow beam is 12.8 mW. Using the Gaussian pulse shape determined in section (2.2) ($\tau=4.2$ ps) and the mode-locking frequency (82 MHz) one finds a peak power of 30 W for the yellow laser. In the steady-state situation equation (2.5.2) predicts a gain of 7×10^{-3} for the (992 cm^{-1}) mode of benzene. This is a factor 18 more than the value we have measured.

The difference between the measured (transient) gain and the calculated steady-state gain is explainable when one takes the finite pulsewidth and the pulse jitter into account. The finite pulse width has a negative effect on the excitation strength, as it takes time for the Raman mode to respond to the short pulses. The decrease in signal strength due to this transient effect depends on the exact shapes of the laser pulses. For symmetric exponential laser pulses Levine and Bethea² have derived the ratio of transient gain to steady-state gain directly in the time domain. The use of their formula is disputable, because our pulses are roughly Gaussian-shaped and chirped (in frequency). The sign of the chirp on both laser pulses strongly affects the ratio G/G_{ss} . In combination with an effective pulsewidth derived from the auto-correlation function, one finds $G/G_{ss}=0.26$. This ratio comes out easier in the frequency domain and is related to the overlap of the Raman line with the combined spectrum of the laser pulses, the width of which is about 10.9 cm^{-1} (fig.(2.3.1)a). The term "combined spectrum" is used, because the combination $E_l(t)E_s^*(t)$ acts as the driving force in a SRS experiment (see section (2.6)). Assuming that the yellow and red pulse have a similar shape the transient gain measured in a two beam SRS experiment is proportional to

$$G = G_{ss} \pi^{-1/2} \int_{-\infty}^{\infty} d\nu \frac{e^{-(\nu/\Delta\nu)^2}}{\Delta\nu(1+(2\pi T_2)^2(\nu-\nu_a)^2)} , \quad (2.5.3)$$

where $2(\ln 2)^{1/2} \Delta \nu$ is the FWHM of the combined spectrum of the laser pulses and $(\pi T_2)^{-1}$ [ps⁻¹] is the FWHM of the Raman line. Equation (2.5.3) can be derived from the more general equation (2.6.6)b. Substituting the relevant numbers in equation (2.5.3), one finds a ratio of transient gain over steady-state gain of $G/G_{ss}=0.29$ for benzene.

The time jitter, present between the yellow and red pulses, will also deteriorate the Raman gain. For our situation the correction due to pulse jitter amounts to about a factor 0.5. Having accounted for the transient effect as well as for the pulse jitter the experimentally-observed gain is still almost a factor 3 short from the theoretical predictions. This might be partly due to the inaccuracy with which the effect of time jitter on the signal can be predicted. This effect depends strongly on the (complicated) frequency structure inside the laser pulses.

For bulk CS₂ we have measured a Raman gain of $6.5(10) \times 10^{-4}$, whereas the "theoretically-calculated" value is 4.9×10^{-2} . For CS₂ the correction for the transient effect is 0.075, far larger than for benzene as its relaxation time is much larger. The correction for the time jitter is identical (0.5). This leads to a calculated transient gain of 1.8×10^{-3} , which is once again about a factor 3 larger than the measured Raman gain. Clearly the use of mode-locked lasers is not advisable when an accurate determination of the absolute value of the Raman gain is needed. When a TSRS experiment is performed to determine the T_2 of a Raman-active mode and the relative strengths of the Kerr effect and the electronic contribution, the results are independent on signal strength. For this reason we settle for a relative determination of the Raman gain in one material to the gain in another.

2.6 Theory of time-resolved stimulated Raman spectroscopy (TSRS)

In this section the technique of time-resolved stimulated Raman spectroscopy (TSRS) is introduced, which was first used by Heritage¹⁸. This section is primarily based on an article that was published in Optics Communications¹⁹, one of the main differences being the fact that in ref.19 the cgs system was used whereas all formulas presented here are in SI units. In fig.(2.6.1) the experimental setup used in our TSRS experiment is pictured. Two pairs of laser pulses are formed, each one containing pulses of both frequencies (ω_l, ω_s), and each pair being identical to the single pair used in a two-beam SRS experiment. Both pairs of dye-laser beams are

focused into the sample, where their focal regions overlap. The first pair is used to excite a Raman-active mode of the system while the second pair, after a variable delay, is used to probe the coherent Raman excitation present at that moment. In this way it is possible to observe the relaxation of the coherently-excited system directly in the time domain.

One of the most startling characteristics of the TSRS signal is its critical dependence on the exact path length each beam traverses from the dye laser to the sample. When one of these four path lengths is slowly changed over a few wavelengths the measured gain on the red probe beam changes periodically from gain into loss and vice versa. The TSRS setup acts like a huge interferometer for four laser beams.

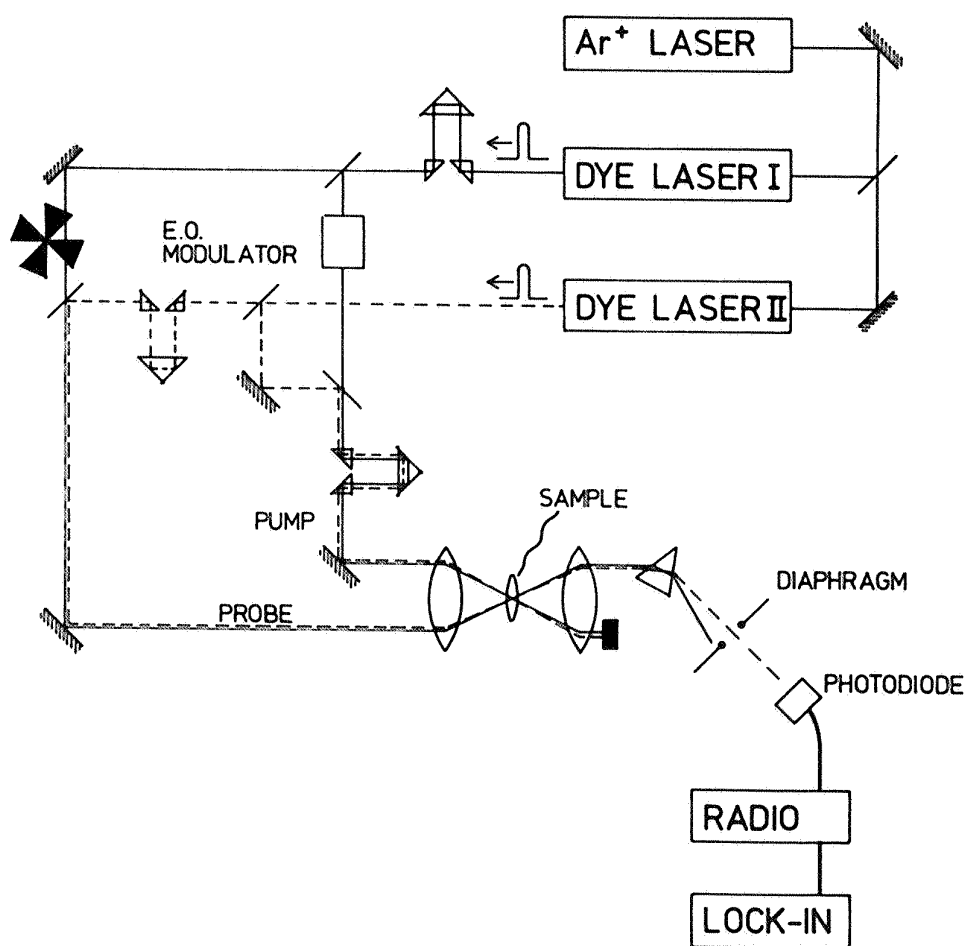


Fig.2.6.1: The experimental set-up for a four-beam time-resolved stimulated Raman scattering (TSRS) measurement.

During our time-resolved measurements we noticed that indeed the signal depended strongly on the frequency difference between the lasers, but surprisingly did not completely disappear when this frequency difference was totally mistuned from the Raman mode. In a two-beam experiment it was possible to pinpoint the various sources of non-resonant contributions to mutually-induced focusing of the laser beams and reflections and both could be eliminated (section (2.3)). In the time-resolved experiment we could not get rid of the background signal which forced us to concentrate on the theory. The literature was ambiguous about what is exactly measured in a time-resolved four-beam stimulated Raman experiment.^{18,20}

We have demonstrated, both experimentally and theoretically, that the results of a time-resolved measurement are fundamentally different compared with a two-beam experiment (apart from the obvious difference of time resolution). We will show that a time-resolved experiment produces information about the absolute value, and in principle also about the phase, of $\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$, convoluted with the pulse profiles, whereas the stimulated Raman gain measured in a two beam experiment is proportional to the imaginary part of $\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$. An important consequence is the appearance of an electronic contribution and a Kerr contribution to the TSRS signal whereas both are absent in a two-beam measurement.

The results of a TSRS experiment are most easily interpreted with the (a,b, σ)-formalism presented in section (1.6). Substitution of equation (1.6.6), which gives the third-order polarization induced by the incident radiation fields, into the wave equation for the propagation of the EM field (Maxwell's equation (1.6.10)) yields in principle all information on the changes in the radiation field arising from third-order optical processes. Via measurements of these changes we want to get a handle on the material properties of the sample as specified by $\chi^{(3)}$ and the nuclear response functions a(t) and b(t).

It is probably wise to summarize the approximations we introduce to solve the difficult differential equation and calculate the strength of the TSRS signal. These approximations are very plausible and do not conflict with the physics behind the experiment.

- (1) The final gain or loss experienced by the laser beams passing through the sample is very small ($<10^{-3}$), which enables us to substitute the original (unperturbed) electric fields in the equation for the third-order polarization.

- (2) We make use of the slowly-varying-envelope approximation, where the envelope functions are denoted by a subscript l or s .
- (3) We neglect dispersion effects between the red and the yellow pulse as well as inside each single pulse. The pulse overlap and the pulse shape remain stationary when the pulses move through the sample. It comes in handy to define a new time variable t' that measures time relative to the moment a certain feature in the traveling wave passed ($t' = t - z/v_g$). We will drop the index of the relative time variable and denote it simply by t .
- (4) We will treat our laser beams essentially as linearly-polarized plane waves. In our TSRS experiment the laser beams are focused to obtain a larger light intensity. When the laser foci overlap completely inside the bulk material a careful calculation shows the resulting gain or loss becomes independent of the strength of the focusing lens. This geometrical calculation is however an unnecessary complication and I will do without it.
- (5) For the isotropic media and materials with cubic symmetry that are described with the (a, b, σ) -formalism, one of the symmetry properties of $\chi^{(3)}$ is ($\chi_{1112} = 0$), which simplifies the calculation considerably. When all laser beams are linearly-polarized in the same direction, the induced polarization will consequently also be in that direction $P_2^{(3)}(z, t) = P_3^{(3)}(z, t) = 0$. As I will discuss this situation all cartesian indices will be dropped from now on.
- (6) The complexity of the equations is reduced by not considering the anisotropic response function $b(t)$ explicitly. The effect of the anisotropic response function can easily be determined afterwards (add extra terms in which $b(t)$ is substituted for $a(t)$), but the effect is small for the Raman process.

A straightforward substitution of the unperturbed electric field, with its two envelope functions and its two complex-conjugates, into the equation for the third-order polarization (equation (1.6.6)) yields 3×64 terms. When dealing with stimulated Raman scattering one is mainly interested in the non-linear polarization at the Stokes frequency and the only relevant terms are those with an explicit time dependence $e^{-i\omega_s t}$ (and $e^{i\omega_s t}$). As the envelopes E_l and E_s do not vary fast enough to mix any of the optical frequencies present, the so-called rotating-wave approximation, the

two terms in $P^{(3)}$ having a $e^{-i\omega_s t}$ time dependence can only result from $E_s E_s^* E_s$, known as the self action, and from $E_s E_\ell^* E_\ell$, represented below, part of which is a result of the Raman interaction.

$$\begin{aligned}
(1/\epsilon_0)P^{(3)}(t) &= \{1/(2\epsilon_0)\} \{P_s^{(3)}(t)e^{-i\omega_s t} + P_s^{(3)*}(t)e^{i\omega_s t}\} = \\
(6/16) \sigma E_s(t)E_\ell^*(t)E_\ell(t)e^{-i\omega_s t} &+ \text{c.c.} \\
(2/8) E_s(t)e^{-i\omega_s t} \int_{-\infty}^{\infty} d\tau |E_\ell(t-\tau)|^2 a(\tau) &+ \text{c.c.} \\
(2/8) E_\ell(t)e^{-i\omega_s t} \int_{-\infty}^{\infty} d\tau E_\ell^*(t-\tau)E_s(t-\tau)a(\tau)e^{-i(\omega_\ell-\omega_s)\tau} &+ \text{c.c.} \\
(2/8) E_\ell^*(t)e^{-i\omega_s t} \int_{-\infty}^{\infty} d\tau E_\ell(t-\tau)E_s(t-\tau)a(\tau)e^{i(\omega_\ell+\omega_s)\tau} &+ \text{c.c.} \quad (2.6.1)
\end{aligned}$$

For reasons of compactness I have, for the time being, omitted the explicit spatial dependence of the electric fields as well as of $P^{(3)}$. The three integrals on the right-hand side of equation (2.6.1) are associated with different physical processes. The Kerr effect produces the first integral, which probes $a(\omega)$ around $(\omega \approx 0)$. The Raman effect gives rise to the second integral, which probes $a(\omega)$ around $(\omega \approx \omega_s - \omega_\ell)$. The third integral corresponds to the "nuclear contribution" to two photon absorption. It probes $a(\omega)$ around $(\omega \approx \omega_\ell + \omega_s)$, where it is practically zero, and this term will be skipped from the calculations.

In the following pages the strength of the signal measured in a TSRS experiment will be derived step by step for the Raman term only. Afterwards the signals arising from the Kerr effect and the electronic contribution will just be presented as results.

At this stage the two envelope functions (E_ℓ and E_s) denote the total envelopes and are sums of the pump and the probe fields. From now on I will treat them separately. For that purpose I introduce the subscripts L, L', S, S' for the $\omega_{\ell, \text{pump}}^*$, the $\omega_{\ell, \text{probe}}$, the $\omega_{s, \text{pump}}$ and the $\omega_{s, \text{probe}}$ beam respectively. The symmetry between pump and probe is experimentally broken in two ways: via the spatial separation of the laser beams and by the use of a double-modulation technique. Both symmetry-breaking effects are discussed in the next paragraph.

At each position in the sample equation (2.6.1) describes the local $P^{(3)}(\vec{r}, t)$, induced by the laser fields at position $\vec{r}$. For each of the

three fields in equation (2.6.1) we can either take a pump field or a probe field. Depending on our choice the wave vector of the (plane-wave like) $P^{(3)}$ points into different directions. In fig.(2.6.2) we have graphically presented the effect of inclusion of the spatial dependence of $P^{(3)}$. The coherent Stokes light emitted at various position in the sample interferes constructively only in the direction the wave vector of $P^{(3)}(\vec{r},t)$ points to. The radiation emitted by $P^{(3)}(\vec{r},t)$ is directional. In practice the amount of "created" Stokes light is very small and is only observable through its interference with one of the laser beams. Experimentally we observe changes in the intensity of the red probe beam, thus selecting 3 of the 8 possible combinations of electric fields that set up the spatial-varying third-order polarization.

We modulate the ω_L -pump beam at 8.4 MHz to get a good signal to noise ratio. In addition the ω_L -probe is modulated with a frequency of 500 Hz. Our detection unit is only sensitive to a 500 Hz amplitude modulation on a 8.4 MHz (carrier) wave. With the double-modulation technique the measured signal thus is only related to those combinations of electric fields, in equation (2.6.1) that contains each of the ω_L -beams exactly once. This excludes the interaction of the ω_S -probe beam with the ω_L -pump or the ω_L -probe alone. The only detectable $P^{(3)}(\vec{r},t)$ is thus set up by the combination E_L, E_L^*, E_S .

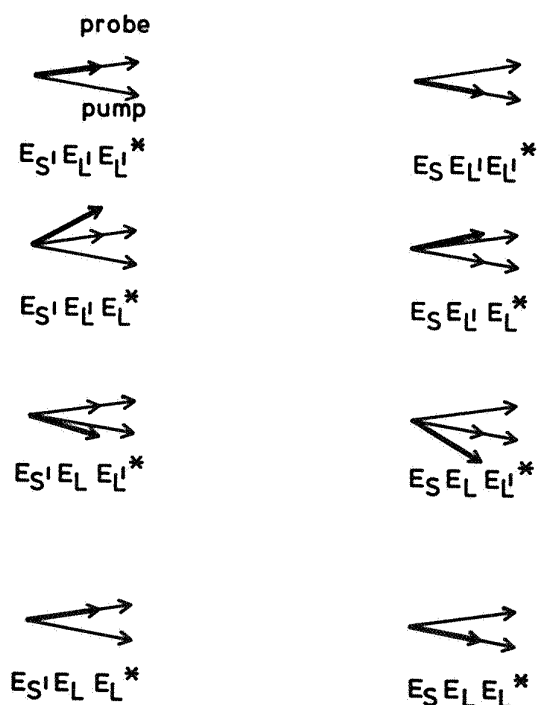


*Fig.2.6.2:
The eight possible combinations of EM fields that excite a third-order nonlinear polarization at frequency ω_S , the self-action $|E_S|^2 E_S$ being excluded. The thin arrows represent the wave vectors of the incident EM fields. The thick arrow represents the resulting wave vector of the induced $P^{(3)}(\vec{r},t)$.*

To determine the influence of the induced third-order polarization on the electric fields equation (2.6.1) has to be substituted into the wave equation. For reasons of compactness I will at first merely perform the calculation with the "Raman-sensitive" term. In the small-signal regime a linearization of the wave equation leads to a change of the red probe beam as it traverses the focal region of

$$\begin{aligned} \frac{\partial E_S(z,t)}{\partial z} &= \left\{ \frac{i\omega_s^2}{2\epsilon_0 k_s c^2} \right\} P_S^{(3)}(z,t) \\ &= \left\{ \frac{i\omega_s^2}{4k_s c^2} \right\} E_L(t,z) \int_{-\infty}^{\infty} d\tau a(\tau) E_L^*(t-\tau,z) E_S(t-\tau,z) e^{-i(\omega_L - \omega_s)\tau}. \end{aligned} \quad (2.6.2)$$

When the pulses have traversed a distance L through the sample the change in $E_S(t)$ can be calculated for any position within the laser pulse, denoted by the relative time variable t . The increase in intensity per pulse of the red probe beam, integrated over the pulse width and being denoted by W_S , $[Jm^{-2}]$, is obtained by integration over the pulse shape (variable t).

$$\begin{aligned} \Delta W_S &= W_{S,out} - W_{S,in} = \left(\frac{cn\epsilon_0}{2} \right) \int_{-\infty}^{\infty} dt |E_S(t)_{out}|^2 - |E_S(t)_{in}|^2 \\ &= \text{Re} \left[\left(\frac{i\omega_s L \epsilon_0}{4} \right) \int_{-\infty}^{\infty} dt E_L(t) E_S^*(t) \int_{-\infty}^{\infty} d\tau E_L^*(t-\tau) E_S(t-\tau) a(\tau) e^{-i(\omega_L - \omega_s)\tau} \right]. \end{aligned} \quad (2.6.3)$$

These formulas demonstrate once more that the *individual* laser beams cannot be treated as the linear driving fields of the Raman-active mode, but the combination of the two can. Hence we define a new function $f(t) = E_L(t) E_S^*(t)$. The Raman interaction is bilinear in the electric field, but linear in this newly defined "driving field" $f(t)$:

$$\Delta W_S = \text{Re} \left[\left(\frac{i\omega_s L \epsilon_0}{4} \right) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt d\tau f_{\text{probe}}(t) f_{\text{pump}}^*(t-\tau) a(\tau) e^{-i(\omega_L - \omega_s)\tau} \right]. \quad (2.6.4)$$

In a TSRS experiment the pump and the probe laser fields are strongly related as they originate from the same lasers. When we denote the time delay of the probe pair with respect to the pump pair by T (T is positive when the probe arrives later at the sample than the pump) the relations between the envelopes are simply given by equation (2.6.5). Using these relations equation (2.6.4) can be rewritten in terms of the pump fields only.

$$E_L(t) = E_L(t-T)e^{i\omega_L T}, \quad E_S(t) = E_S(t-T)e^{i\omega_S T},$$

$$f_{\text{probe}}(t) = f_{\text{pump}}(t-T)e^{i(\omega_L - \omega_S)T}, \quad f_{\text{probe}}(\omega) = f_{\text{pump}}(\omega)e^{i(\omega_L - \omega_S + \omega)T}, \quad (2.6.5)$$

$$\Delta W_S = \text{Re} \left[\left(\frac{i\omega_S L \epsilon_0}{4} \right) e^{i(\omega_L - \omega_S)T} \times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt \, d\tau \, f_{\text{pump}}(t-T) f_{\text{pump}}^*(t-\tau) a(\tau) e^{-i(\omega_L - \omega_S)\tau} \right], \quad (2.6.6a)$$

$$\Delta W_S = \text{Re} \left[\left(\frac{i\omega_S L \epsilon_0}{8\pi} \right) e^{i(\omega_L - \omega_S)T} \int_{-\infty}^{\infty} d\omega \, |f_{\text{pump}}(-\omega - \omega_L + \omega_S)|^2 a(\omega) e^{i(-\omega - \omega_L + \omega_S)T} \right]. \quad (2.6.6b)$$

At this point the two other important terms from equation (2.6.1) will be reintroduced, being the electronic contribution and the Kerr effect. Mathematically the response due to the Raman term and the electronic contribution can be described by an integral of a (short-pulse) response function and a simple four-field correlation function. The (short-pulse) Kerr response function is integrated over a correlation function that is slightly more complicated

$$\Delta W_S = \text{Re} \left[\left(\frac{i\omega_S L \epsilon_0}{4} \right) e^{i(\omega_L - \omega_S)T} \times \left\{ (3/2)\sigma \, C_R(T) + \int_{-\infty}^{\infty} d\tau \, C_R(T-\tau) [a(\tau) + b(\tau)] e^{-i(\omega_L - \omega_S)\tau} + \int_{-\infty}^{\infty} d\tau \, C_K(T, -\tau) [a(\tau) + b(\tau)] \right\} \right], \quad (2.6.7)$$

$$C_K(T, \tau_1) = \int_{-\infty}^{\infty} dt \, E_L(t-T-\tau_1) E_S^*(t-T) E_L^*(t-\tau_1) E_S(t); \quad C_R(T-\tau) = C_K(T-\tau, 0). \quad (2.6.8)$$

The results of a four-beam TSRS measurement are completely described by equation (2.6.7), where the first term represents the electronic contribution, the second term results from the Raman effect and the third term is associated with the Kerr effect. The $e^{i(\omega_L - \omega_S)T}$ -term explains the sensitivity of a TSRS experiment on the optical phases. When the path length between the pump and the probe pair is varied over one "Raman wavelength", T varies over $2\pi/(\omega_L - \omega_S)$ and a gain turns into a loss and into a gain again. The amplitude of the "Raman fringes" gradually decreases for large T , the envelope being a direct measure of the decay of the nuclear response functions $a(\tau)$ and $b(\tau)$. When the red and the yellow pulses have identical unchirped pulse shapes the amplitude of the Raman fringes around zero delay

is proportional to $\text{Abs}[\chi^{(3)}]$ integrated over the combined pulse shapes. When the probe-pair is delayed with respect to the pump-pair the three contributions to $\chi_{1111}^{(3)}(-\omega_s, \omega_l, -\omega_l, \omega_s)$ get different weights.

The results of a two-beam SRS measurement are also described by equation (2.6.7) by setting T identical to zero. For this situation the correlation functions are real-valued. Neither the electronic contribution nor the Kerr effect are observable in such an experiment, because $\text{Im}(\sigma)=0$ and the Kerr contribution to $a(\tau)$ and $b(\tau)$ are real-valued functions. With a two-beam SRS experiment one measures the imaginary part of $\chi^{(3)}$ convoluted over the profiles of the laser pulses and one is only sensitive to the stimulated Raman effect. These results were used to derive equation (2.5.3).

2.7. Some experimental details on TSRS

In this section I will try to mention all relevant experimental details of our TSRS setup. The pump and probe pair are formed through combination of a yellow and red beam with a beam splitter. When combined the red and yellow pump beam have to be collinear to within a few tenths of a milliradian. The red probe beam is not perfectly collinear with the yellow probe beam, but is aligned for optimum TSRS signal. The pump and probe pair are parallel, but not collinear, because we want to separate them spatially. They are focused with a 50 mm achromatic lens into the sample and cross each other at the smallest possible angle, about 2° , to insure maximum spatial overlap. The 8.4 MHz amplitude modulation of the yellow pump beam is applied with an EO modulator. The 500 Hz modulation of the probe beam is a phase modulation, which is applied with a piezo-electric element (PI P-170), being driven by a sinusoidal AC voltage. The delay between the pump pair and the probe pair is scanned continuously at typical scan rates of 2-20 $\mu\text{m/s}$. The position of the scanning delay line is accurately (within 1 μm) determined with a magnetic ruler of Sony Magnescale inc. (ruler SR-721SP, processor unit LY 101-12). Every 1 μm the processor unit attached to the magnetic ruler sends a pulse to our IBM PC and the IBM takes a sample. The data thus collected are afterwards send to the host computer (VAX-11/750) and run through a digital filter. This procedures yields the amplitude of the Raman fringes as well as the phase as a function of the delay between the pump pair and the probe pair.

Some experimental results of time-resolved experimental runs on liquid

CS₂ (T=293 K) are presented in fig.(2.7.1) and (2.7.2). In the inset of fig.(2.7.1) part of the unfiltered data are presented, being recorded with a continuously-scanning delay line. The rapid change between gain and loss of the ω_s -probe beam is clearly visible. The complete 40 picosecond run includes hundreds of oscillations and took us about 30 minutes to record. In the principal part of the figure only the envelope of the Raman fringes is plotted as a function of the delay between the pump-pair and the probe-pair. A better visualization of the data can be obtained from fig.(2.7.2), where this envelope is plotted on a log-scale. Notice the enormous dynamic range (three decades) obtainable with our setup. For large delays the decrease of the TSRS signal goes exponential ($T_2=19.5(4)$ ps) and can be attributed to the decay of the isotropic part $\{a(t)\}$ of the Raman excitation. The initial rapid decrease has been attributed to the fast decay of the Kerr contribution and the electronic contribution to the third-order susceptibility.^{18,21} From our data we can extract both the T_2 and the strength of the electronic and Kerr contribution. The relaxation time T_2 can in principle also be obtained from measurements of the spontaneous Raman line width. The electronic and Kerr contribution are not observable in spontaneous Raman scattering.

The strong dependence of the signal on the exact time-delay between the pump and probe pair imposes a strong requirement on the stability of the optical equipment as noted by Heritage.¹⁸ The stability should be as good as in holographic experiments, because a four-beam TSRS experiment is just as sensitive to the optical phase. Our experiment is performed on a large metal table which rest on air-filled tires and is thus disconnected from most vibrations of the floor. For stability reasons the height of the optical components is chosen as small as possible. A second source of disturbances are air currents. The stability improved when a curtain was erected around the setup. However, especially the fast fluctuations in the optical path lengths were suppressed in that case. As the optical stability was already better than $(\lambda/4)$ rms hardly anything is gained by suppressing the fast fluctuation. The slow fluctuations (drift) did not seem to improve when the curtains were closed, which made us decide to work without curtains.

To ease the alignment of the four beams we have built a stabilization loop that couples the strength of TSRS signal to a piezo-electric transducer, which can vary one of the optical paths over 7λ . The stabilization loop locks on null-signal for the second-harmonic of the

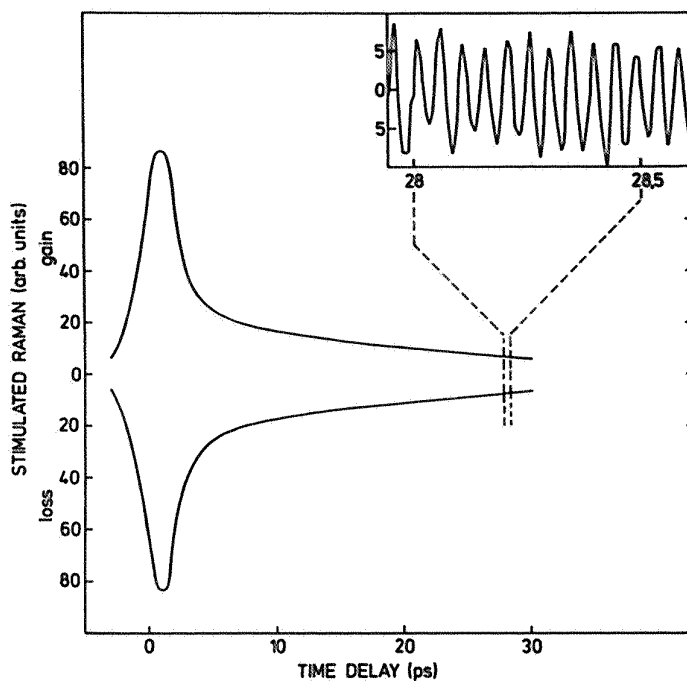


Fig.2.7.1: A TSRS measurement of the $656 \text{ cm}^{-1} \nu_1$ -mode of liquid CS_2 . In the inset we have pictured part of the experimental data. Notice the rapid oscillations which exactly correspond to the inverse Raman frequency of this mode.

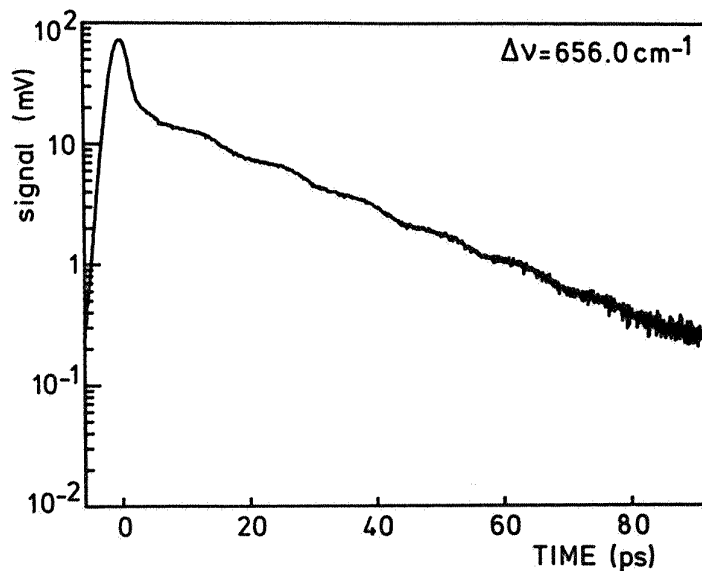


Fig.2.7.2 A TSRS measurement of the $656 \text{ cm}^{-1} \nu_1$ -mode of liquid CS_2 , similar to the one presented in fig.(2.7.1), plotted on a log-scale to give a better visualization of the exponential decay. From a set of these measurements we derived $T_2 = 19.5(4) \text{ ps}$.

500 Hz modulation. Via this method phase fluctuations can be suppressed by a factor 10-20, though only for alignment purposes. The stabilization is off when a time-resolved run is made.

The fact that the pump and probe beams are not collinear and cross each other in the sample under a certain angle has two consequences. The first consequence is a reduction of the spatial overlap between the beams. This reduces the strength of the TSRS signal and one should thus try to keep the angle between the pump pair and the probe pair as small as possible. The second consequence can be explained in terms of phase matching. The two pump beams "implant" a spatial coherence in the excited mode. In combination with the yellow probe beam this determines the spatial coherence of the third-order polarization and the preferable direction of emission of the Stokes light created in the third-order process (see fig.(2.6.2)). At large angles between the pump pair and the probe pair the wave vector of the emitted light, the amplitude being determined by its (Stokes) frequency, can not match the wave vector of $P^{(3)}$. This "wave-vector mismatch" results in a decrease of the TSRS signal. In a two-beam SRS measurement the problem of phase matching does not arise, whereas in a two-beam CARS experiment phase matching is import and the intensity of the emitted anti-Stokes radiation depends crucially on the angle between both beams. The difference in sensitivity to phase-matching gives two-beam SRS a huge advantage over CARS. The problem that arises in a four-beam TSRS experiment with the phase matching are also less severe than the problem one has to cope with in a time-resolved CARS experiment. In a TSRS experiment phase mismatch becomes a problem when $(k_l - k_s)L(1 - \cos\theta)$ is comparable to or larger than one, θ being the angle between the pump pair and the probe pair and L being the length of the focal region.

2.8 Simulations

When the response of the Kerr effect is faster than the width of the pulses it acts as if it is an instantaneous contribution and one can show that equation (2.6.7) simplifies to

$$\Delta W_S = \text{Re} \left[\left(\frac{i\omega_s L \epsilon_0}{4} \right) e^{i(\omega_l - \omega_s)T} \times \left[\left(\frac{3}{2} \right) \sigma - 2A_{\text{Kerr}} \tau_{\text{rot}} \right] C_R(T) + \int_{-\infty}^{\infty} d\tau C_R(T - \tau) [a(\tau) + b(\tau)] e^{-i(\omega_l - \omega_s)\tau} \right] \quad (2.8.1)$$

The Kerr effect and the electronic contribution are combined to a total instantaneous contribution, which I will denote by $s = [(3/2)\sigma - 2A_{\text{Kerr}}\tau_{\text{rot}}]$. The anisotropic Raman contribution is often very small and will be neglected in the following derivation ($b(t)=0$). The decay of the isotropic Raman mode is described by the following response function (see section (1.7))

$$a(t) = 2A_{\alpha}\sin(\Omega_{\alpha}t)e^{-t/T_2} \quad \theta(t) = -iA_{\alpha}e^{i(\Omega_{\alpha} - (1/T_2))t} \theta(t) + \text{c.c.} \quad (2.8.2)$$

Equation (2.8.1) has been used to fit all our measurements. To fit the experiments to a theory based on the excitation of a single Raman-active mode we have two parameters at our disposal, being the T_2 of the mode and the ratio of the instantaneous contribution to the Raman contribution, which is denoted by (s/A_{α}) . For most simulations we have used the Gaussian approximation of the four-field correlation function $C_R(t) = e^{-(t/\tau_C)^2}$, with the experimentally determined value $\tau_C = 1.7$ ps. When $C_R(t)$ is Gaussian shaped the Raman contribution to the TSRS signal, the integral in right-hand side of equation (2.8.1), can be reduced to a complex error function

$$\begin{aligned} \Delta W_{S'} = & \text{Re} \left\{ \left(\frac{i\omega_s L \epsilon_0}{4} \right) e^{i(\omega_{\ell} - \omega_s)T} \left[se^{-(T^2/\tau_C^2)} - iA_{\alpha}\tau_C(1/2)(\pi)^{1/2} \right. \right. \\ & \times e^{-(T/T_2)} e^{i(\Omega_{\alpha} - \omega_{\ell} + \omega_s)T} e^{\tau_C^2 [1/(4T_2^2) - (\Omega_{\alpha} - \omega_{\ell} + \omega_s)^2/4 - i(\Omega_{\alpha} - \omega_{\ell} + \omega_s)/(2T_2)]} \\ & \left. \left. \times (1 + \text{erf}((T/\tau_C) - (\tau_C/[2T_2]) + (1/2)i(\Omega_{\alpha} - \omega_{\ell} + \omega_s)\tau_C)) \right] \right\}, \end{aligned} \quad (2.8.3)$$

where $\text{erf}(z)$ is the well-known error function

$$\text{erf}(z) = 2/(\pi)^{1/2} \int_0^z dx e^{-x^2}, \quad \text{erf}(0)=0, \quad \text{erf}(-z)=-\text{erf}(z), \quad \text{erf}(\infty)=1.$$

Some physical insight in the behavior of the Raman term can be obtained through evaluation of the short-pulse limit of expression (2.8.3), where $\tau_C \ll T_2$ and $\tau_C(\Omega_{\alpha} - \omega_{\ell} - \omega_s) \ll 1$. In the short-pulse limit

$$(\Delta W_{S'})_{pp} \approx \text{Abs} \{ se^{-(T^2/\tau_C^2)} - iA_{\alpha}\tau_C(1/2)(\pi)^{1/2} e^{-(T/T_2)} e^{i(\Omega_{\alpha} - \omega_{\ell} + \omega_s)T} \theta(T) \}. \quad (2.8.4)$$

In the short-pulse limit the Raman contribution is suddenly switched on around $T=0$. For $T>0$ the decay of its amplitude is exponential, with a decay time T_2 . The ratio of the Raman contribution to the instantaneous

contribution decreases, when the width of $C_R(t)$ is decreased. The excitation of the coherent Raman mode is less effective for short pulses due to transient effects.

There is a nice correspondence between the theory of TSRS and the excitation of a damped harmonic oscillator (see section (1.8)). I will describe this equivalence in some detail to stress the much wider applicability of the results obtained from simulations of the TSRS signals. The correspondence becomes clear when the combination of the two laser pulses (ω_l, ω_s) is described as one quasi-harmonic driving force and the coherent amplitude of the Raman-active mode as the amplitude of the damped harmonic oscillator (see equation (1.8.1))

$$\partial^2 \langle q_\alpha(t) \rangle / \partial^2 t + (2/T_2) \partial \langle \tilde{q}_\alpha(t) \rangle / \partial t + \Omega_\alpha^2 \langle \tilde{q}_\alpha(t) \rangle = C f(t) e^{-i(\omega_l - \omega_s)t} + \text{c.c.},$$

where C is a constant proportional to the oscillator strength, or polarizability derivative, of the Raman-active mode. The driving force is applied only for a short time and $f(t) = E_l(t) E_s^*(t)$ is related to the shape of the laser pulses. Notice that $f(t)$ might be a complex function and one hereby includes pulses with a frequency chirp. Using the slowly-varying envelope approximation and the rotating-wave approximation, the previous equation can be solved

$$\langle \tilde{q}_\alpha(t) \rangle = (i/2) Q_\alpha(t) e^{-i\Omega_\alpha t} + \text{c.c.}, \quad (1.8.4)$$

$$Q_\alpha(t) = C \int_{-\infty}^t d\tau \frac{f(\tau)}{\Omega_\alpha} e^{(\tau-t)/T_2} e^{i(\Omega_\alpha - \omega_l + \omega_s)\tau}. \quad (2.8.5)$$

The exact eigenfrequency of the damped harmonic oscillator is of no importance. The mistuning of the driving force with respect to this eigenfrequency $(\Omega_\alpha - \omega_l + \omega_s)$ is the only important frequency scale.

It is interesting to observe what happens when the damped harmonic oscillator is excited with two pulses, denoted by pump and probe. After excitation by the pump pulse the harmonic oscillator starts oscillating. The amount of energy transferred by the second (probe) pulse to the harmonic oscillator will depend on the time delay between the probe pulse and the pump pulse. The functional form of this energy transfer is identical to the formula that describes the Raman contribution to the TSRS pump-probe

process. This energy transfer is proportional to $\text{Re}[f_{\text{probe}}^*(t)Q_{\alpha}(t) \times e^{-i(\Omega_{\alpha}-\omega_{\ell}+\omega_s)t}]$ and can be either positive or negative, depending on the phase of the driving "probe" force with respect to the phase of the oscillator. The peak-peak energy transfer is

$$\Delta W_{\text{pp}} \propto \text{Abs} \left[\int_0^{\infty} d\tau \int_{-\infty}^{\infty} dt f_{\text{probe}}(t) f_{\text{pump}}^*(t-\tau) e^{-\tau/T_2} e^{i(\Omega_{\alpha}-\omega_{\ell}+\omega_s)\tau} \right]. \quad (2.8.6)$$

When the quasi-harmonic driving force has a Gaussian envelope, the integrals in equation (2.8.5) and (2.8.6) both reduce to error functions. For this reason simulations of the energy transfer in a pump-probe experiment on a damped harmonic oscillator also yield information on the time evolution of the amplitude of a harmonic oscillator that is excited by one pulse only.

Simulation of the instantaneous contribution to the TSRS signal is easy. Its strength, relative to the strength of the Raman-active mode, is determined by the ratio (s/A_{α}) and its dependence on the time delay T is given by the function $C_R(t)$.

2.9 The transverse relaxation time T_2 and the appearance of quantum beats

One of the advantages of SRS over spontaneous Raman scattering is the ability one has to selectively excite one mode to a much higher degree of excitation than is possible in a spontaneous Raman experiment. It is possible to excite weaker modes, while the stronger modes are left untouched. Excitations of overtones does neither pose a problem and a nice example of this is given in ref.22.

The frequency difference between both lasers determines which Raman-active mode is probed. This extra variable, which is not available in a spontaneous Raman experiment, gives the technique a lot of its strength. In fig.(2.9.1) I have presented some TSRS measurements on bulk benzene (293 K, 1 bar) performed at various frequency differences between both lasers. The strongest Raman-active mode in benzene, in the frequency range we studied, has a frequency of about 992 cm^{-1} . Its transverse decay time (T_2) can be excellently measured with our TSRS setup and we have found the value $T_2=4.9(1) \text{ ps}$. When we mistuned the frequency difference between both lasers from the main Raman resonance some other effects became observable. At 997 cm^{-1} and at 1000 cm^{-1} interesting dips appears in the time-resolved runs shortly after $T=0 \text{ ps}$. This is the result of an interference effect

between the electronic and Kerr contribution on the one hand and the Raman contribution on the other hand. In section (2.12) I will extensively discuss the origin of this strange structure. At $(\nu_L - \nu_S) = 984, 986$ and 988 cm^{-1} an oscillation is visible on top of the (exponential) signal decay. An oscillation like this is often called a quantum beat²³ and results from the simultaneous coherent excitation of two adjacent modes. The measured beat period (3.9(2) ps) equals the inverse of the frequency spacing between the excited modes, which is thus determined to be $\Delta\nu = 0.26 \text{ ps}^{-1} = 8.5(4) \text{ cm}^{-1}$. The frequency of the weaker mode is less than 992 cm^{-1} as this specific quantum beat was only observable when $(\nu_L - \nu_S)$ was tuned below 992 cm^{-1} . Via the laser tuning we have preferentially excited the weaker mode thus making its coherent amplitude comparable to the amplitude of the stronger mode and producing quantum beats of large enough amplitude. A second, though less pronounced, beat was visible when $(\nu_L - \nu_S)$ was tuned to 1000 and 1002.5 cm^{-1} . The existence of this beat indicates the presence of a very weak Raman-active mode in this region. From the beating period (4.5(5) ps) we conclude its frequency must be $7.4(9) \text{ cm}^{-1}$ higher than the frequency of the (992 cm^{-1}) mode. The slow decay of the amplitude of the quantum beats, their observability at large delays between pump and probe, shows that each of the two weaker Raman-active modes must be fairly sharp defined in frequency, and must have a T_2 that is comparable to the T_2 of the main mode.

According to Herzberg (chapter 1, ref.23), where spontaneous Raman spectra on benzene are presented, the strongest Raman-active mode, the a_{1g} breathing mode, has an eigenfrequency of 991.6 cm^{-1} . There are indeed two weaker modes, one at 984 cm^{-1} , the breathing mode of an isotopic molecule (one ^{12}C atom replaced by a ^{13}C atom), and one at 999 cm^{-1} , a hot band with one ν_{18} (C-C bending, 605 cm^{-1}) quantum present before excitation. Our data indicate that the frequency of the "lower mode" is 983 cm^{-1} . For the frequency of the "higher mode" we do have excellent agreement with Herzberg.

In fig.(2.9.2) I have presented a TSRS measurement on CS_2 . In this measurement the frequency difference between both lasers was tuned to 647.5 cm^{-1} , to enhance the degree of excitation of the weaker modes below the strong (656 cm^{-1}) mode. The recorded oscillation is not a simple harmonic, but is composed of several quantum beats, being generated by the various Raman-active modes around 656 cm^{-1} . The dominant beating period is 3.59 ps, indicating a frequency spacing of 9.3 cm^{-1} . We have observed other beatings, with a longer period, when $(\nu_L - \nu_S)$ was tuned closer to the

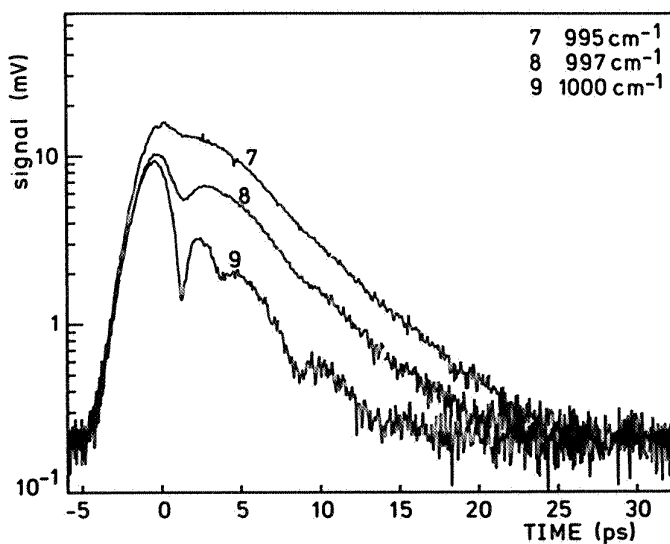
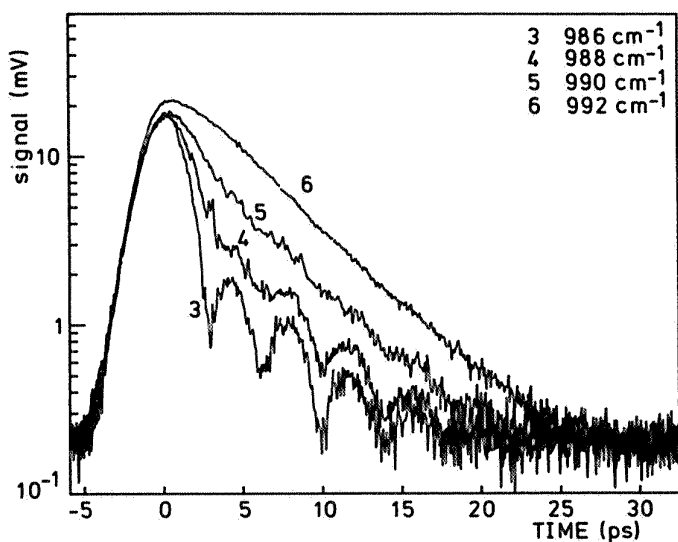
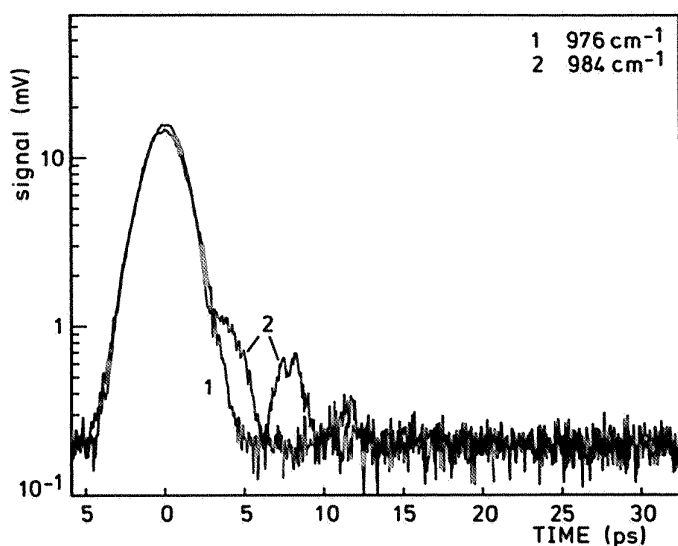


Fig.2.9.1 : TSRS measurements on liquid benzene taken for various differences between the frequencies of both lasers. The study concentrated on the Raman-active modes around 992 cm^{-1} and the frequency differences ($\nu_L - \nu_S$) ranged from 976 cm^{-1} to 1008 cm^{-1} .

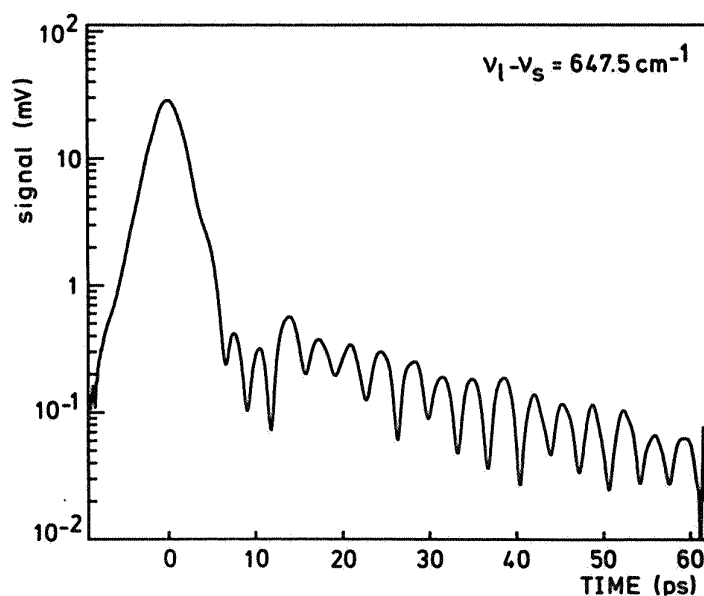
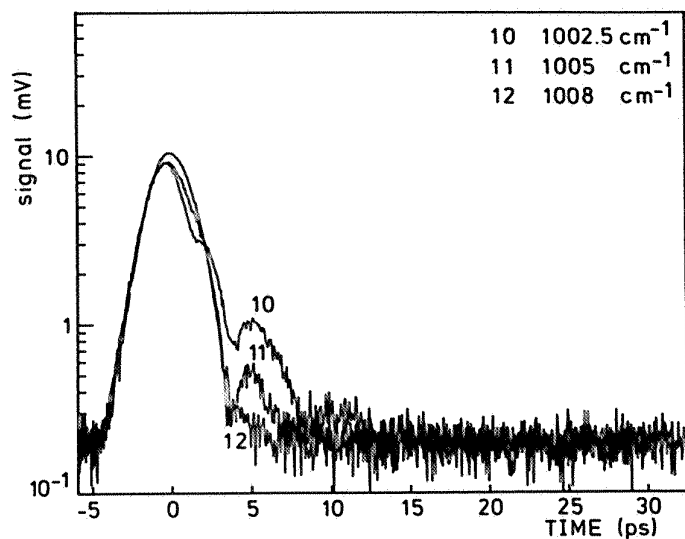


Fig.2.9.2 A TSRS measurement on liquid carbon-disulfide. The frequency difference between both lasers was tuned to 647.5 cm^{-1} to enhance the degree of excitation of the weaker modes below the strong (656 cm^{-1}) mode. The observed oscillations are complicated and more than one beating period can be derived from the data. Many Raman-active modes contribute to the TSRS signal.

656 cm^{-1} mode. An elegant method to obtain part of the Raman spectrum from a TSRS run is to Fourier transform the original measurement, including all the Raman fringes. For the Fourier transformation the phase information in the measurement is of vital importance (see section (2.13)). Unfortunately this phase information is slightly distorted by vibrations of the optical components and the Fourier-transformation technique, though being in theory an ideal tool to interpret the data, is only of limited use.

When $(\nu_L - \nu_S)$ is far from any Raman-active mode, large mistuning, the TSRS signal results from the electronic contribution and the Kerr effect only. The response of the electronic contribution is too fast to be resolved with our pulses. The orientation time of the molecules, which determines the response time of the Kerr effect, is typically 1 ps for liquids. One can mathematically show that when the Kerr response time is far shorter than the width of the laser pulses, the Kerr contribution acts as if it were instantaneous. The width of the response for large mistuning thus directly shows the time resolution $\{C_R(t)\}$ of our system in a TSRS measurement. In fig.(2.9.1) a few runs for large mistuning were shown. The response function has a Gaussian shape around zero delay. The wings of the response function decrease exponentially with a characteristic time of 0.8-1.0 ps. This poses a lower limit on the T_2 that can be measured with our setup. The response function is best fitted by a cosinus hyperbolic function to a certain power. One of our best fits is $C_R(t) = \{\cosh(t/1.6 \text{ ps})\}^{-1.8}$. A Gaussian fit around zero delay yields $C_R(t) = e^{-(t/1.7 \text{ ps})^2}$. When the Ar^+ laser operates on third-harmonic the response function is slightly wider.

The TSRS-response function is much narrower than for instance the two-pulse response function that one measures on delaying the red pulses with respect a yellow pulses. The reason for this is that TSRS is sensitive to the optical phase and the response is not merely determined by the envelopes of the laser pulses but also by the frequency distribution inside the individual pulses. One can show that the width of the four-field correlation-function $C_R(t)$ is not affected by any time-jitter between the red and the yellow pulses. Time-jitter only influences the amplitude of $C_R(t)$ and consequently the strength of the TSRS signal.

For one experiment we deliberately tripled the width of the red and yellow pulses in time, through mistuning of their cavity lengths. The temporal resolution did not deteriorate in this TSRS experiment. The magnitude of the signal did of course react, it decreased. The spectral

width of the individual pulses is apparently a better measure for the sharpness of the TSRS-response function than the temporal width of the pulses. A beautiful demonstration of the truth of this statement can be found in ref.24 and 25. With the use of very broadband ns pulses the authors obtained a temporal resolution (FWHM of the coherence spike) of 75-100 fs. The authors made use of the short correlation time of their pulses, which they denote as incoherent-light pulses, to measure T_2 relaxation in the picosecond and sub-picosecond range.

Much information on the processes that contribute to the transverse relaxation time T_2 can be obtained when one studies the behavior of T_2 as a function of one or several physical parameters. The temperature dependence of T_2 has been used by Gale et al. in a study of the Fermi doublet in CO_2 at 1276 cm^{-1} and 1383 cm^{-1} .²⁶ At low temperatures the dominant relaxation channel is the mixing of each of these modes with the two-phonon continuum, which is a population decay. As usual pure dephasing becomes important at higher temperatures and T_2 decreases as a function of temperature.

In our group pressure-dependent studies by Baggen et al.²⁷ have revealed the pressure dependence of T_2 of the (656 cm^{-1}) mode of CS_2 up to 1 GPa and the (992 cm^{-1}) mode of benzene up to 5 GPa. In general molecular crystals are very compressible and the density, and therefore the inter-molecular distance, can be varied over a large range. We were the first to perform a TSRS experiment on a sample inside a diamond anvil cell. The details on this experiment can be found in ref.27. When liquid benzene is pressurized its T_2 decrease steeply from 4.9 ps at zero pressure to about 3.5 ps at the liquid-solid interface. On solidification T_2 changes drastically to 7.6 ps. Although the intermolecular distance decreases, the limited translational and rotational freedom of the molecules apparently makes the relaxation rate decrease drastically. Pressurizing solid benzene T_2 is almost constant up to 1.5 GPa, when benzene is in phase I, and decreases above 1.5 GPa, when benzene is in phase II. Another point of interest is the sudden change of the ratio of the instantaneous contribution over the Raman contribution on solidification of benzene. For the solid the instantaneous contribution is about a factor 0.4 times the value it has in the liquid and this ratio seems to decrease slowly as a function of pressure. The decrease of the instantaneous contribution as a function of pressure must be attributed to a decrease of the Kerr contribution due to the limited rotational freedom of the molecules.

A third method to obtain information on the processes that contribute to the T_2 relaxation is to dilute the liquid under study in a second liquid and observe the concentration dependence of T_2 . Such an experiment was e.g. performed by Geirnaert and Gale²⁸ on the (525 cm^{-1}) mode of CH_3I diluted in CS_2 . They observed an increase of the relaxation time by almost a factor two on dilution and noted T_2 stabilized at concentrations of CH_3I lower than 5%. Using the isolated binary collision model the authors conclude that at very low concentration the pure dephasing is apparently dominated by the collisions each CH_3I molecules makes with the CS_2 solvent molecules.

2.10 The electronic contribution and the Kerr contribution

For CS_2 the electronic and Kerr contribution to the TSRS, which in combination are denoted by the instantaneous contribution, are clearly observable as a peak around $T=0$ ps. The height of this peak is a measure for the strength of the instantaneous contribution to the oscillator strength of the Raman mode.^{30,31} In our experiment the presence of the instantaneous contribution results in an increase by a factor 3.0-3.5 of the TSRS signal around $T=0$ ps. In fig.(2.10.1) I have presented an experimental run on CS_2 in combination with simulations we have performed to determine the ratio (s/A_α) for CS_2 . In the inset of the figure fits for various values for (s/A_α) are shown. The best fit was obtained for $(s/A_\alpha)=12$ ps. The ratio thus determined depends critically on the width of the correlation function $C_R(t)$. Experimentally this width varied some 10 % from one day to another, resulting in a similar variation of the relative height of the instantaneous peak.

The measured (s/A_α) can be compared with the values presented in table (1.10.1). From this table one obtains $(\sigma+b(0))/|a(\Omega_\alpha)|=0.98(11)$ and $\sigma/(\sigma+b(0))=0.13(1)$. These two ratios must be rewritten in the variables I use, with the help of the relations $b(0)=-3A_{\text{Kerr}}\tau_{\text{rot}}$ and $|a(\Omega_\alpha)|=A_\alpha T_2$ (see section (1.7)). A "literature" value of $(s/A_\alpha)=15$ ps is thus found for the 656 cm^{-1} mode of CS_2 . This is in reasonable agreement with our measurements.

For benzene as well as for diamond the relative instantaneous contribution is much smaller than for CS_2 and can not be accurately determined from the time-resolved measurements. For these materials a different technique, which is described in the next section, has been used to measure the ratio (s/A_α) .

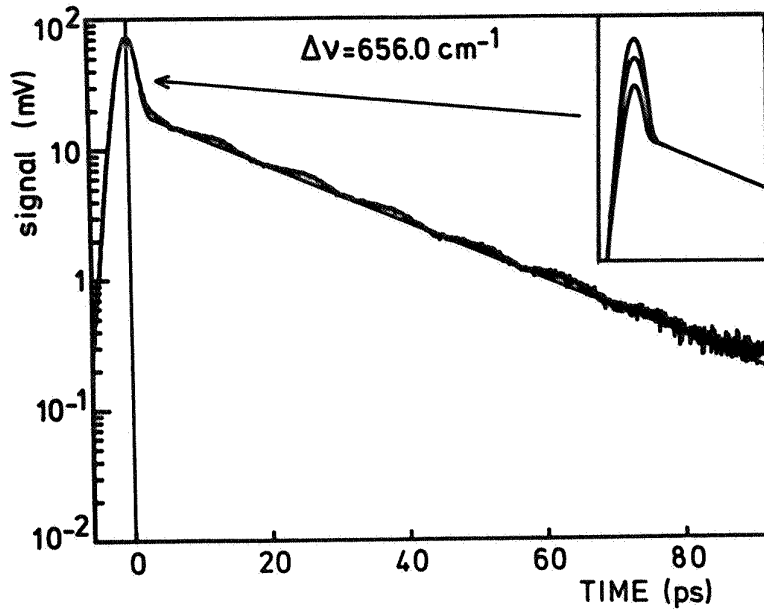


Fig.2.10.1 A comparison of a TSRS run on CS_2 with simulations. The long-time behavior is excellently fitted by an exponential decay with a characteristic time of $19.5(4)$ ps. The strength of the instantaneous contribution can be derived when one compares the peak measured around zero delay with the simulations. A detailed view of this comparison is pictured in the inset of the figure, where the simulations are obtained for $(s/a) = 17, 12$ and 7 ps from the upper curve to the lower curve.

Up to now all presented measurements were performed with laser beams polarized in the same (vertical) direction. With this geometry I have tried to study the behavior and the dynamics of the various contributions to $\chi_{1111}^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$. When the direction of polarization of one, or more than one, of the four beams is changed other elements of the $\chi^{(3)}$ tensor are observable. The various elements are strongly related. This allows one in principle to separately determine the electronic and the Kerr component of the instantaneous contribution from TSRS data obtained with beams with different directions of polarization.^{33,34}

For two different directions of polarization of the laser beams TSRS measurements have been performed on CS_2 . When all laser beams are polarized in the same (vertical) direction $\chi_{1111}^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$ is probed. From new

measurements with all beams vertically polarized we determined $(s/A_\alpha)=13.8$ ps, whereas older measurements, discussed on page 86, gave $(s/A_\alpha)=12$ ps. In the absence of anisotropic Raman scattering this should be equal to $(s/A_\alpha)=\{(3/2)\sigma+(2/3)b(0)\}/A_\alpha$. We subsequently set the direction of polarization of both probe beams orthogonal to the direction of polarization of the pump beams. In this setup $\chi_{1122}^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$ is probed and we found $(s/A_\alpha)=8.0$ ps. This should be compared to the theoretical value $(s/A_\alpha)=\{(1/2)\sigma+(1/2)b(0)\}/A_\alpha$. Combining these two results the electronic contribution (σ) and the Kerr contribution $\{b(0)\}$ can be separately determined: $(\sigma/A_\alpha)=3.8$ ps and $\{b(0)/A_\alpha\}=12.2$ ps. The accuracy in these values is dreadful, the relative errors are almost 50 %, as the separation of the electronic and the Kerr contribution is obtained by subtraction of two (s/A_α) ratios of comparable magnitude. From table (1.10.1) "literature" values of $(\sigma/A_\alpha)=2.5(3)$ ps and $\{b(0)/A_\alpha\}=17(2)$ ps can be derived. In CS_2 the Kerr effect clearly contributes stronger to our TSRS signal than the electronic contribution.

When the pump pair consists of two beams with crossed directions of polarization a third physically-interesting combination of directions of polarization arises. In this situation the isotropic component of the Raman mode can not be excited, but one can excite its anisotropic component. To probe the decay of the anisotropic Raman component, the probe pair must also consist of two beams with orthogonal directions of polarization. This can be derived from the relation $\{\chi_{1211}^{(3)}=0\}$. With these directions of polarization it is possible to determine the rotational relaxation time of the molecules. We have not yet performed this experiment with success.

One interpretation of the nature of the anisotropic coherent Raman excitation is that the vibrating rod-shaped CS_2 molecules aligned perpendicular to the direction of polarization of the yellow beam are 180° out of phase with the vibrating molecules aligned orthogonal to this direction. If a linearly-polarized yellow probe beam is inelastically scattered by this anisotropic coherent Raman excitation, only red light with a direction of polarization orthogonal to the direction of polarization of the yellow probe beam will emerge.

2.11 TSRS in the frequency domain

An alternative method for obtaining information out of the time-resolved SRS experiment is to measure, at a fixed time delay between the pump and the probe pair, the dependence of the signal on the frequency difference between both lasers. The signal of course depends strongly on the optical phases of the beams (gain-loss-gain for each 2π phase variation) and with the original technique the path lengths had to be (fine-)tuned to maximum gain for each frequency difference. A trick to circumvent this problem is to simultaneously perform a very slow scan of the time delay, when the frequency scan is made. The results of such a measurement are shown in fig.(2.11.1) for the (1332 cm^{-1}) mode of diamond.²⁹ The height of the peak with respect to the frequency independent background is a measure of

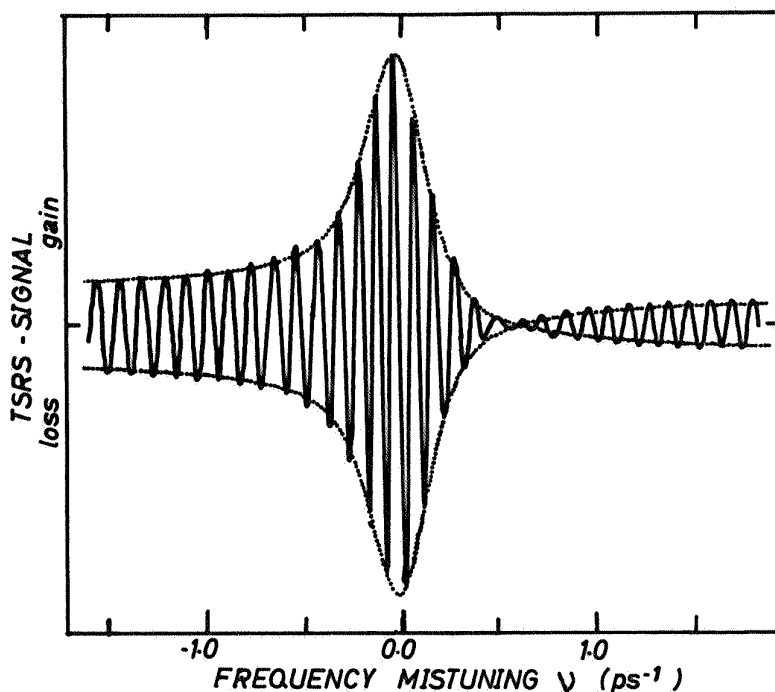


Fig.2.11.1 An experimental frequency scan on the 1332 cm^{-1} phonon in diamond, at zero time delay. The fringes in this plot are a result of a very useful trick employed to get rid of the dependence of the signal on the optical phases. Simultaneously with the frequency scan of the lasers, we performed a very slow scan of the time delay between the pump and probe pair. In this way one passes slowly through the maximum and minimum signal strength.

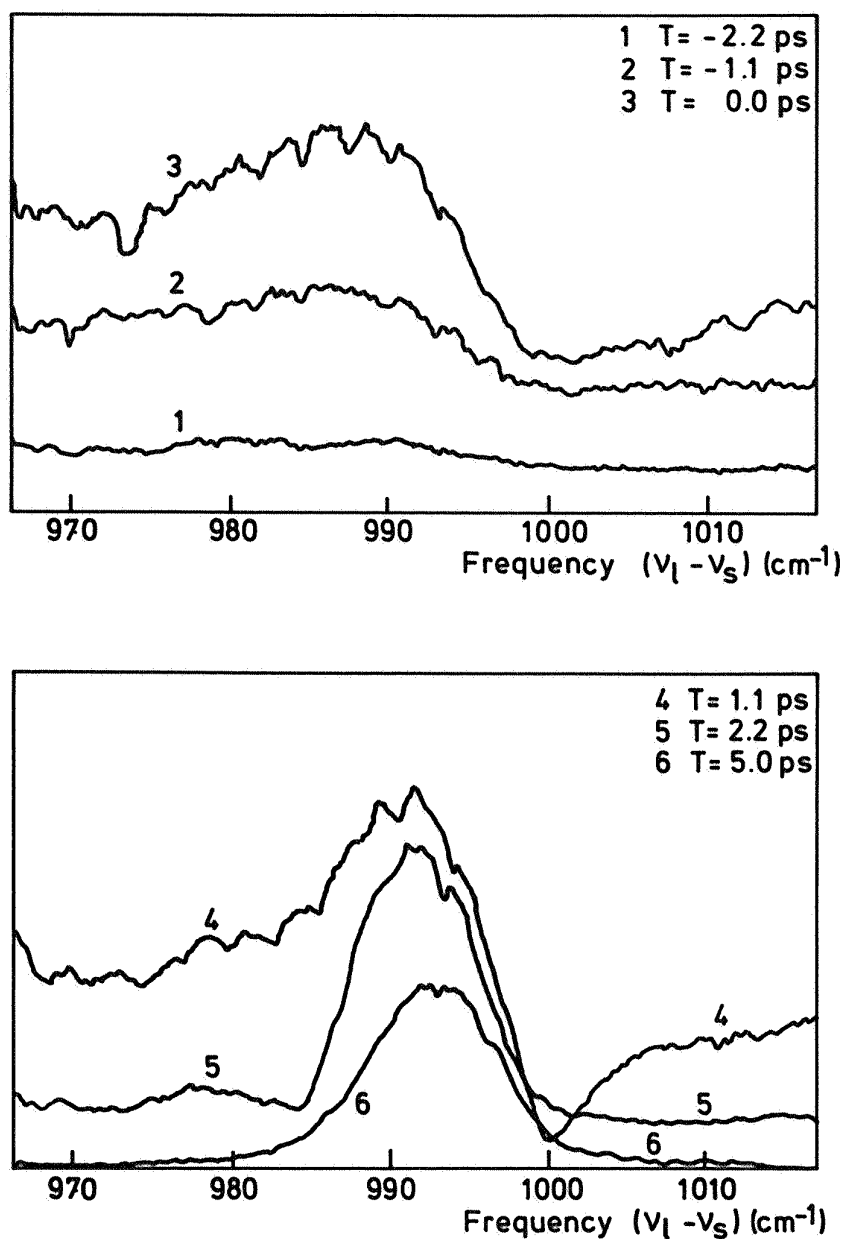


Fig.2.11.2 The TSRS signal on benzene around $(\nu_l - \nu_s) = 992$ cm⁻¹ at different, but fixed, time delays between the pump pair and the probe pair as a function of the frequency difference between both dye lasers. Notice that for negative time delays the instantaneous contribution is dominantly present, while the Raman contribution builds up as a function of delay. Around $T=0$ the real part of $\chi^{(3)}$ contributes most to the signal. Its imaginary part dominates at large delays and a line shape similar to the one observed in spontaneous Raman scattering is measured.

the strength of the Raman contribution with respect to the instantaneous contribution. Combining the measured ratio of peak to frequency-independent background (10.0) with the exact pulse shapes (C_R) one finds $(\sigma/A_\alpha) = 0.28$ ps. Taking the orientation of the diamond into account this is in good agreement with earlier CARS measurements (chapter 1, ref.33, $(\sigma/A_\alpha) = 0.26$ ps). A new modulation technique introduced by Martine de Mazière has eliminated the sensitivity to the optical phase and has simplified the measurements.

In fig.(2.11.2) I have presented some frequency runs on benzene taken at different, but fixed, time delays. Zero time delay is calibrated on maximum TSRS signal for large frequency mistunings. The measurements clearly demonstrate the difference in behavior of the instantaneous contribution (consisting of electronic and Kerr) and the Raman contribution to the TSRS signal. When the probe pair arrives 2.2 ps earlier than the pump pair the TSRS signal is practically independent on the frequency and originates almost completely from the instantaneous contribution. It takes time (T_2) to build up the coherent Raman excitation. Around $T=0$ ps the Raman effect starts to contribute considerably to the signal. As both contributions are added and the instantaneous contribution is real-valued only the real-valued part of the Raman contribution is visible and the maximum signal is observed when $(\omega_L - \omega_S)$ is just below the frequency of the Raman-active mode. The more the probe pair is delayed with respect to the pump pair the smaller the ratio of the instantaneous contribution to the Raman contribution becomes. Finally at large delays (5 ps) the instantaneous contribution is completely gone. The frequency dependence of the signal is then simply the product of the (complex) oscillator strength of the Raman-active mode with the spectral width of the response function and maximum signal is observed when $(\omega_L - \omega_S)$ matches the frequency of the Raman-active mode exactly. Notice that at $T=2.2$ ps an indication of the presence of the second Raman-active mode around 984 cm^{-1} is visible.

The important physical parameter we want to determine from these measurements is the ratio of the instantaneous contribution, denoted by $s=(3/2)\sigma+(2/3)b(0)$, to the Raman amplitude A_α . We do not split it up in its electronic and Kerr component. We already know the T_2 of the Raman-active mode from other experiments and the relative strength of the total instantaneous contribution is the only adjustable parameter in our fit. The results of simulation runs on benzene are presented in fig.(2.11.3). The

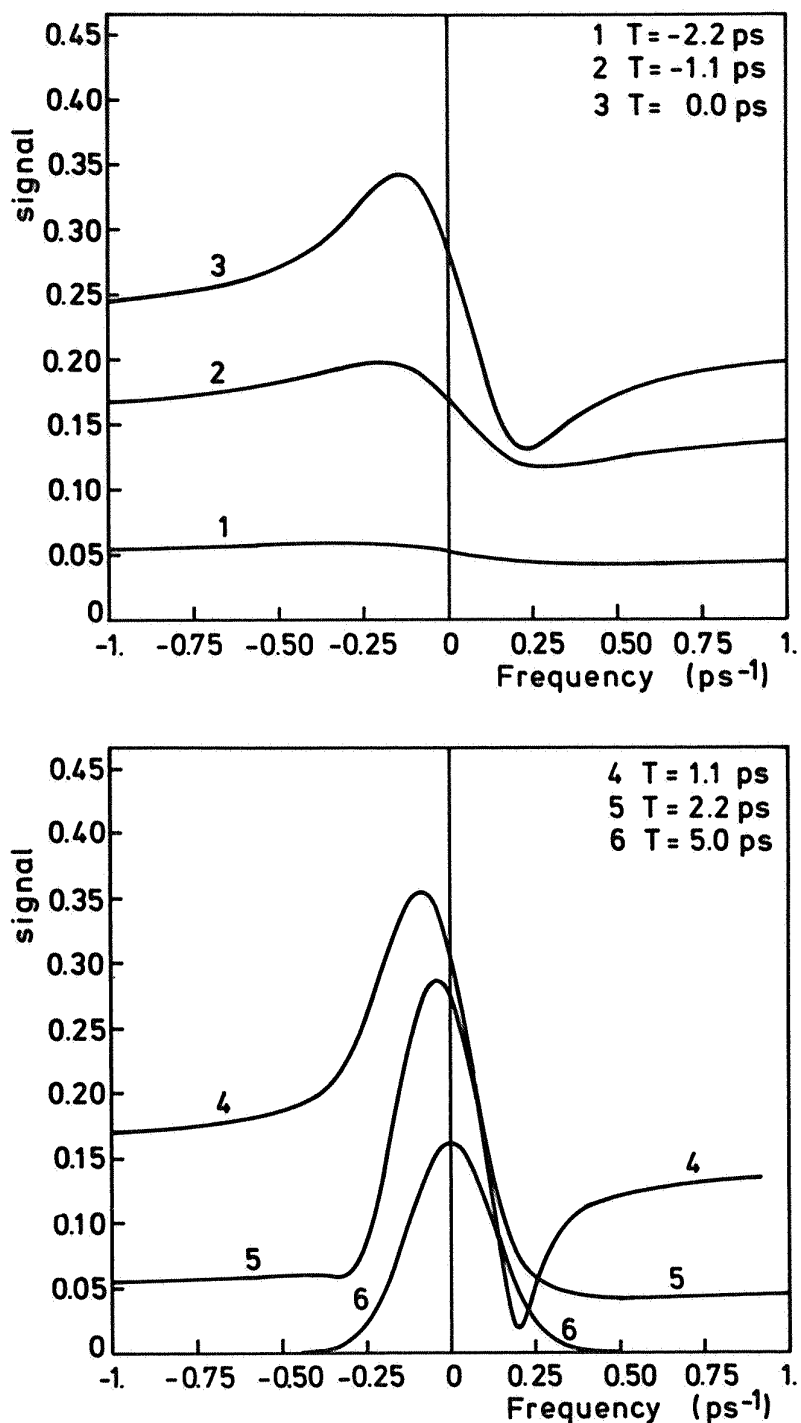


Fig.2.11.3 Simulations of the frequency scans on benzene that were presented in fig.(2.11.2). For conversion to cm⁻¹ one can use the relation 1 ps⁻¹=33.3 cm⁻¹. From these simulations I have derived the ratio of the instantaneous contribution to the Raman contribution. The best fit was obtained for (s/A)=1.6 ps.

best fit was obtained for an (s/A_Q) ratio of 1.6 ps. This must be compared with a value of 1.8 ps calculated from other experiments (chapter 1, ref.32).

2.12 Interference phenomena in TSRS

When the frequency difference of both laser is mistuned from the eigenfrequency of the Raman-active mode interesting phenomena occur, which I will explain in this section as being due to interference effects between the phase of the driving force and the phase of the excited mode. The phenomena were first observed in the simulations. Subsequent TSRS experiments agreed both qualitatively and quantitatively with the predictions.

We have simulated the increase in power of the low-frequency probe beam in a TSRS experiment as a function of the time delay between the pump pair and the probe pair. Both the amplitude and the phase of the complex function that describes this energy transfer are shown in figs.(2.12.1) and (2.12.2) for different fixed laser mistunings. Scanning the delay for a system driven exactly on resonance results in an initial sharp increase of the energy transfer as the pulse overlap is increased, followed by an exponential decrease resulting from the free induction decay (we do not yet consider the instantaneous contribution). When we compute the same response, but with the frequency difference slightly mistuned with respect to the eigenfrequency of the oscillator, a peak appears at zero delay and the signal strength again decreases monotonically into an exponential decay. Notice that this peak differs from the previously-mentioned peak arising from the instantaneous contribution, as we have not yet included this contribution in the simulations. At a still larger mistuning the decay is not monotonic. After a first spectacular very sharp decay the signal strength is temporarily increased before it starts its exponential decay: a dip appears in the time-resolved scans. Increasing the frequency mistuning further results again in a monotonic decay without a dip.

It is possible to define a "critical frequency mistuning" ν_c where a time-resolved scan shows a dip that in the simulations goes to zero signal strength. Fig.(2.12.2), which shows the phase of the TSRS signal, is especially interesting as it demonstrates clearly the change of the frequency of the harmonic oscillator from the frequency of the driving force

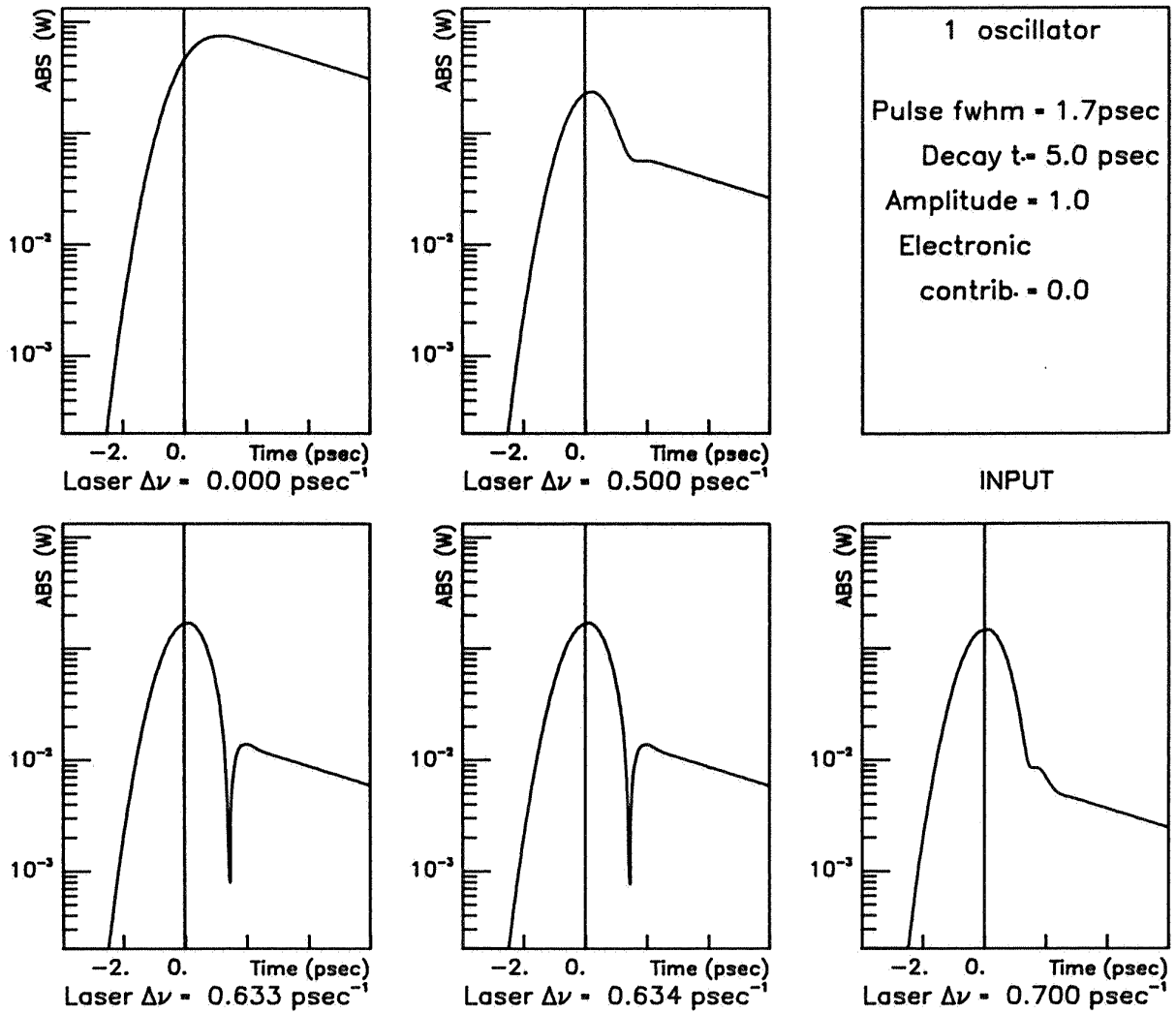


Fig.2.12.1 Simulations of the energy transfered in a TSRS experiment for different, but fixed, frequency mistunings. The mistuning $\Delta\nu$ used in this figure denotes the difference between $(\nu_l - \nu_s)$ and $(2\pi)^{-1}\Omega_\alpha$.

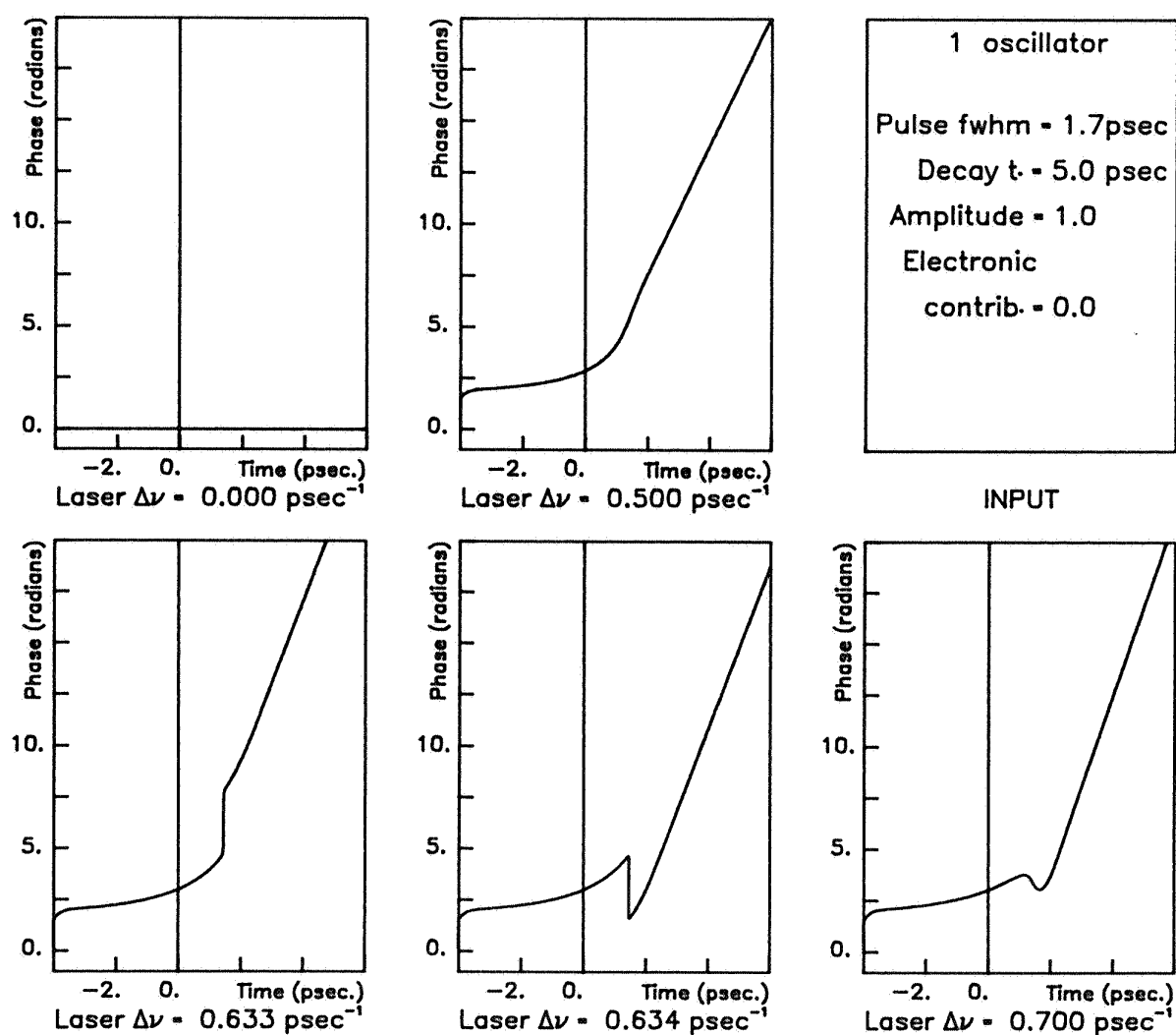


Fig.2.12.2 The "phase" of the energy transfer function in a TSRS experiment as a function of the delay time between the pump and probe pair. This figure is closely related to fig.(2.12.1).

to its eigenfrequency. Notice the apparent change of 2π as the mistuning passes a critical value. For the critical mistuning the "complex" function that describes the energy transfer as a function of the delay between pump and probe passes through the origin of the complex plane.

Due to the mathematical resemblance a similar dip should appear when one could directly observe the time evolution of the amplitude of the harmonic oscillator, being driven by the quasi-harmonic excitation pulse. The appearance of a dip in this system can be explained as an interference effect between the driving force and the free induction decay. When the intensity of the driving force diminishes the oscillator returns to its eigenfrequency. This results in a shift of the phase of the driving force still present with respect to the oscillator. The driving force might at one moment even damp the oscillator and make it almost stop. After the initially very fast decay the wing of the driving pulse will eventually excite the oscillator again.

The dip in the energy transfer, being more closely related to the time-resolved measurements, can also be explained as an interference effect. The time evolution of the phase of the driven oscillator is evidently reflected in the energy transfer and can at the critical mistuning for instance lead to an increase in intensity in the front of the " ω_s probe" pulse and a decrease in the back, resulting in a net gain zero. The critical mistuning for the energy transfer differs from the mistuning needed to stop the oscillator, the former being the larger. Mathematically both dips can be interpreted as roots of the complex error function.

Our simulations show the appearance of the dip and more specifically the value of the critical mistuning ν_c to be independent of the response time T_2 of the system. Its structure changes of course but the value of ν_c remains the same. This value is proportional to the frequency width of the pulse correlation function. For a system without electronic contribution excited and probed with Gaussian shaped pulses we have found the relation: $\tau_C \nu_c = 0.634$.

At some other frequencies, even further away from the resonance, it was possible to observe a dip structure in the simulations as well. The same critical dependence on the frequency mistuning was demonstrated for the higher order dips. For Gaussian-shaped pulses the second dip appears at: $\tau_C \nu_c = 0.85$ and the third dip appears at: $\tau_C \nu_c = 1.30$. In the experiments we were only able to find the first dip, which is to be expected as the

simulations show that the higher-order dips should appear at very small signal levels.

Inclusion of an instantaneous contribution in the simulations does not alter the presence of the dip in the time-resolved runs. It does alter the magnitude of the critical frequency. It also destroys the symmetry between positive and negative frequency mistunings and intensifies the dip structure.

Fig.(2.12.3) shows an experimental TSRS experiment performed on diamond (293 K, 1 Bar). We monitored the optical phonon at $(2\pi)^{-1}\Omega_{\alpha}=1332\text{ cm}^{-1}$. A very good reproducible dip was observed in the time runs when we tuned the frequency difference between both lasers to 1324 cm^{-1} . It was also possible to detect a dip at the same frequency mistuning on the other side $((\nu_{\ell}-\nu_s)=1340\text{ cm}^{-1})$. This symmetry indicates that the instantaneous contribution is small. Experimentally we have found a critical mistuning of 8 cm^{-1} . This should be in agreement with the experimentally-determined correlation function $C_R(t)$. The data presented in fig.(2.12.3) were recorded with the lasers in third-harmonic mode-locked operation. For this mode of

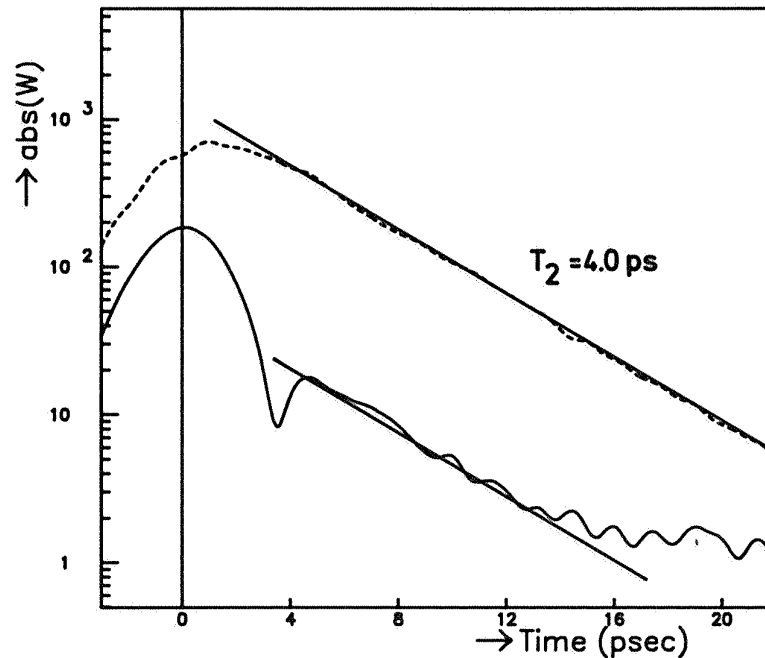


Fig.2.12.3 Experimental TSRS run on diamond (293 K) digitally filtered to eliminate the dependence on the optical phases. The upper curve is a run at a frequency difference of both lasers of $(\nu_{\ell}-\nu_s)=1332\text{ cm}^{-1}$. The lower curve was taken at 1324 cm^{-1} .

operation $G_R(t)$ is best fitted to a Gaussian function with $\tau_C = 2.0$ ps. Combining the two experimental results we find $\tau_C \nu_C = 0.48$. Quantitatively the agreement with theory is not perfect. This might be due to our choice to treat the Kerr effect as an instantaneous contribution. τ_{rot} is small, but not extremely small compared to τ_C .

In measurements on benzene and CS_2 dips similar to the one presented in fig.(2.12.3) were observed. The strong instantaneous contribution in these materials is manifested in three ways. Firstly in both materials the dip is only observable when $(\nu_L - \nu_S)$ is higher than the Raman frequency. Secondly the critical mistuning is less than 8 cm^{-1} . For CS_2 it is only $1-2 \text{ cm}^{-1}$, which might be due to interference with other weaker modes around 656 cm^{-1} . Thirdly the dip structure is more prominent than in diamond.

An interesting issue is whether the dip structure can also be observed in time-resolved CARS experiments. In a CARS experiment the intensity of the anti-Stokes light in a frequency band around $(2\omega_L - \omega_S)$ is measured. This intensity is proportional to the amplitude squared of the oscillator coordinate $Q(t)$, integrated over the probe-pulse profile (most simple case, no instantaneous contribution). Although the vibrational amplitude $Q(t)$ has a dip at some critical mistuning, the width of this dip structure is only a fraction of the width of the laser pulses. This leads us to the conclusion that, unless the probe pulses are very much shorter than the pump pulses, the dip structure is probably spread to an undetectable level in CARS. This is basically due to the insensitivity of CARS to the phase of the oscillator, which plays such a crucial role in the appearance of the dip structure in TSRS. In our group Martine de Mazière has performed simulation that show a minute interference structure in time-resolved CARS experiment. Only when the anti-Stokes intensity is observed in a narrow frequency band, the dip structure becomes deeper and more sensitive to the exact mistuning.

2.13 Phase information in TSRS

In a TSRS measurement the coherent excitation of a Raman-active mode, created by the pump pair, influences the propagation of the probe beams. Depending on the phase of the coherent Raman excitation with respect to the optical phases of both probe beams, energy flows from the radiation field to the Raman excitation (gain of red probe beam) or vice versa. When the delay is scanned the TSRS signal alternates almost harmonically between gain and

loss. Up to now my primary concern was the evolution in time of the amount of optical crosstalk or, in other words, the amplitude of the fringes. However, the oscillation period of the fringes is not constant during the scan of the delay. For some measurements the fringe period around $T=0$ ps differs clearly from the fringe period at large delay. In this section I will discuss the physical information contained in the phase of the fringes and the experimental accessibility of this phase.

One expects the Raman oscillator to start at the frequency of the driving force ($\omega_l - \omega_s$) and returns to its eigenfrequency (Ω_α) in the free induction regime ($T \gg \tau_C$). In a TSRS experiment this should results in a corresponding change in the rhythm of the gain and loss pattern present underneath the envelope of the measured energy transfer. Around $T=0$ ps the instantaneous signal contributes to the TSRS signal as well. The oscillation period that corresponds to this contribution evidently equals the frequency of the driving force at any time.

During the scan of the delay a sample is taken every μm . The observed fringe period almost corresponds to the Raman wavelength of the mode under study. For the (656 cm^{-1}) mode of CS_2 about 7-8 samples are taken per oscillation period, while for diamond (1332 cm^{-1}) about 4 samples are taken per oscillation period. Both sampling rates are high enough to allow for the retrieval of the phase of the fringes.

The phase $\varphi(T)$ can be defined with respect to the eigenfrequency (Ω_α) of the Raman mode or with respect to the frequency of the driving force ($\omega_l - \omega_s$). We have chosen for the latter definition and the pattern of the fringes is thus compared with the function $\cos\{(\omega_l - \omega_s)T - \varphi(T)\}$. This choice results in an almost constant value for the phase around $T=0$ ps, which we set to zero by definition. The data, consisting of a number of points taken at different delays T , is digitally processed on a VAX-11/750. The data points are first multiplied by $\cos\{(\omega_l - \omega_s)T\}$ and than filtered, with a low-pass filter, to reduce the noise and get rid of the second harmonic frequency generated by the multiplication stage. The same original set of data points is also multiplied by $\sin\{(\omega_l - \omega_s)T\}$ and filtered. Combination of the first-mentioned "in-phase" component and the "out-of-phase" component of the TSRS signal immediately yields the amplitude as well as the phase of the complex function that describes the transfer of energy in TSRS.

In fig.(2.13.1) the time evolution of the phase of the TSRS signal, obtained through filtering, of a typical run on diamond is shown. The smooth

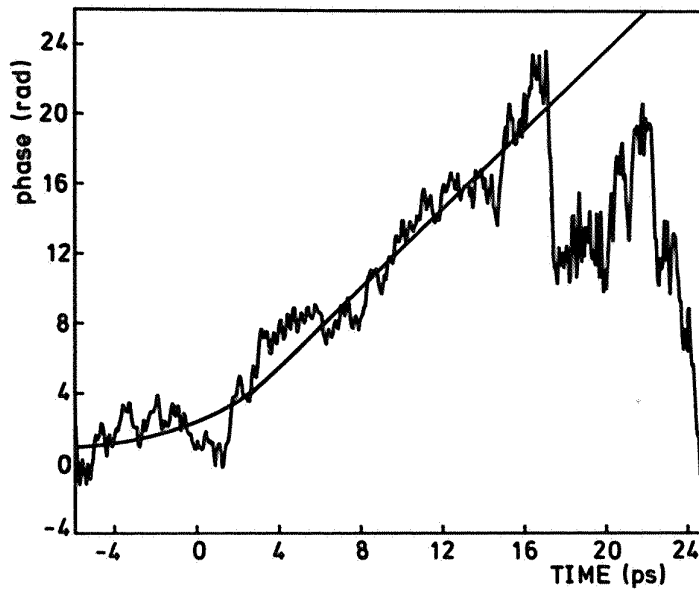


Fig.2.13.1 The time evolution of the phase of the TSRS signal of a typical run on diamond. The frequency difference between both lasers was 1338 cm^{-1} , while the optical phonon in diamond has a frequency of 1332 cm^{-1} . The mistuning was $6 \text{ cm}^{-1} = 0.18 \text{ ps}^{-1}$. The smooth curve is a simulation.

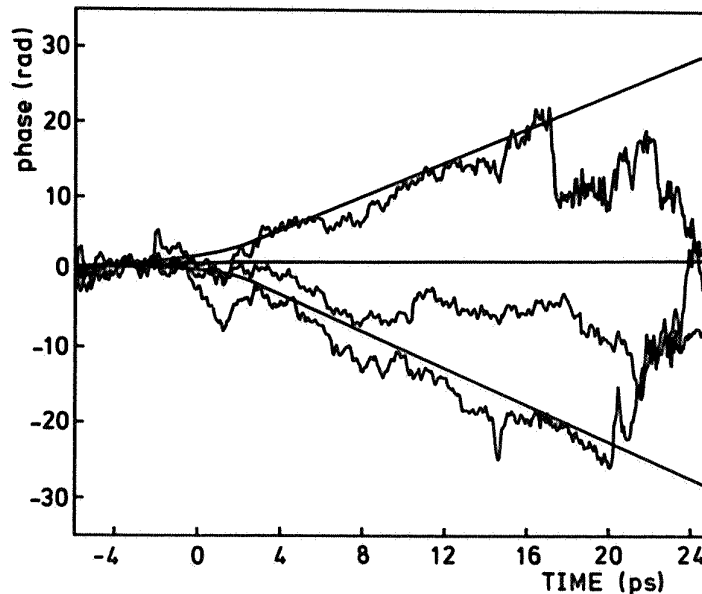


Fig.2.13.2 Measurements of the time evolution of the phase of the TSRS signal on the (1332 cm^{-1}) phonon in diamond for three different frequency differences between the lasers. The upper curve was taken for $((\nu_l - \nu_s) = 1338 \text{ cm}^{-1})$, the middle curve was taken for $((\nu_l - \nu_s) = 1332 \text{ cm}^{-1})$ and the lower curve was recorded for $((\nu_l - \nu_s) = 1325.5 \text{ cm}^{-1})$. The difference is evident.

curve is the outcome of a simulation of this experiment. All things considered the correspondence is extremely good. Lack of stability of the optical components (mirrors, beam splitters) can thoroughly destroy any phase measurement. The correspondence between theory and experiment leads us to an estimate of the drift in phase, due to moving optical components, of only about 2π during the 5 minutes this run took to record. Just before and around $T=0$ ps the phase is almost constant in time, while for large delays the linear increase in time of the phase is in perfect agreement with the frequency difference $(\omega_l - \omega_s - \Omega_\alpha)$. For very large delay the phase seems to vary rather wildly and rapidly as a function of time. This is caused by the smallness of the detectable TSRS signal. For very large delay time the fringes disappear in the noise, and the phase information is lost.

In fig.(2.13.2) we have combined three measurements of the time evolution of the phase of the TSRS signal for different values of $(\omega_l - \omega_s)$. When $(\omega_l - \omega_s)$ is larger than Ω_α , the phase of the TSRS signal $\varphi(T)$ increases as a function of the delay T , as the Raman oscillator returns to its eigenfrequency. When $(\omega_l - \omega_s)$ is smaller than Ω_α , $\varphi(t)$ decreases as a function of the delay time T .

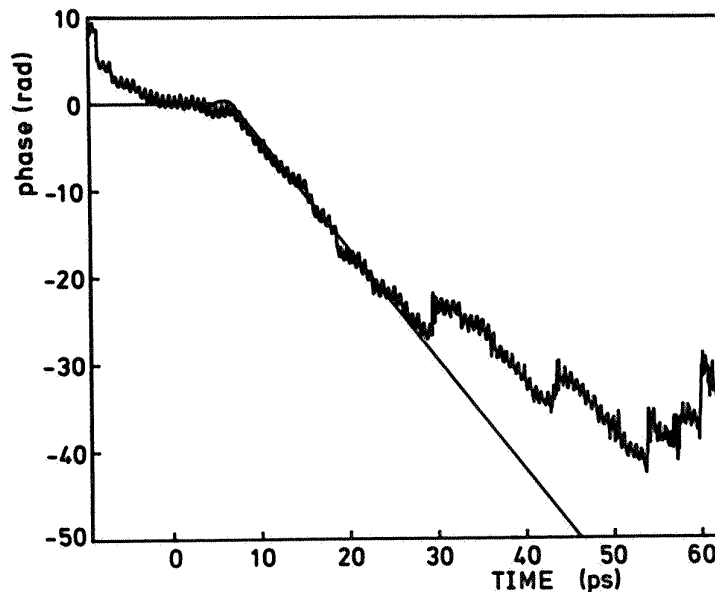


Fig.2.13.3 A typical measurement of the time evolution of the phase of the TSRS signal of the 656 cm^{-1} mode of CS_2 . As the T_2 of CS_2 is much larger than the T_2 of the 1332 cm^{-1} mode of diamond the evolution of the phase can be traced to larger delays.

The phase information we have derived from a TSRS measurement on CS₂ is shown in fig.(2.13.3). The frequency difference between both lasers was $(\nu_L - \nu_S) = 650 \text{ cm}^{-1}$ in this run. The Raman fringes are less closely spaced for CS₂ than for diamond, but due to the larger T₂ the fringes can be traced over a longer delay and the phase can consequently build up to higher values. The phase jumps around T=30 ps and T=43 ps are both approximately 2π high. They both result from a miscount of exactly one fringe, which was caused by the low signal level.

When one wants to Fourier transform the TSRS data to derive the shape of the Raman resonance in the frequency domain, the phase information of the TSRS signal is of vital importance. Knowledge of the time evolution of the amplitude is not sufficient, as this mainly reflects the decay times of the Raman-active modes and hardly contains information on their exact eigen frequencies. Lack of phase information can be compensated for by measuring the time evolution of the amplitude for various differences between the laser frequencies as we have done in section (2.9).

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3.1 The Bloch-vector model

When more than one Raman-active transition is permitted, the two-level description fails and the individual Raman-active modes must be labeled by an index α . When the modes are assumed to evolve independently in time, each mode can be assigned its own eigenfrequency (Ω_α) and its own relaxation times ($T_{1,\alpha}$ and $T_{2,\alpha}$). The equations that have been presented and are to be presented for the two-level system are equally valid for this system of non-interacting excited states. Each of the individual Raman-active modes will show up as a Lorentzian-shaped line in a frequency-resolved Raman experiment. The measured frequency dependence reflects the widths of the individual lines in combination with the distribution of eigenfrequencies of the various Raman-active modes, neither of which can be easily separated from the data. The combined line is said to be inhomogeneously broadened and the underlying lines, which results from the individual modes, are called the homogeneously-broadened components. Section (3.2) will treat the influence of inhomogeneous broadening in greater detail.

The excitation and relaxation of a two-level system, of which the transition is Raman-active, is described by the equations (1.7.1) and (1.7.2), which represent the time evolution of the (2x2) density matrix associated with this transition. In the previous chapters the degree of excitation was assumed to be low and the coherent amplitude could be derived in first order, keeping the groundstate population, $N\rho_{gg}$, fixed. This section goes beyond the first-order approach and the excited-state population is reintroduced as an important variable. As the trace of the density matrix, appearing in the equations (1.7.1) and (1.7.2) is one, the density matrix has only three independent variables, which are often combined to a real-valued vector^{1,2,3}, the so-called Bloch vector $\vec{R}$, in a fictitious variable space. The two diagonal elements of the density matrix are combined to the z-component of the Bloch-vector (R_z) which represents the fraction of excited molecules. The x- and y-component of the Bloch vector represent the coherent Raman excitation $\langle \tilde{q}_\alpha(t) \rangle$. The time evolution of the Raman-active mode can be rewritten in the following easy form

$$d\vec{R}/dt = \vec{\omega} \times \vec{R} - (R_x\vec{e}_x + R_y\vec{e}_y)/T_2 - (R_z - R_{z,eq})\vec{e}_z/T_1, \quad (3.1.1)$$

$$\begin{aligned} R_x &= (\rho_{bg} + \rho_{gb}) & \omega_x &= (H_{bg} + H_{gb})/\hbar \\ R_y &= i(\rho_{bg} - \rho_{gb}) & \omega_y &= i(H_{bg} - H_{gb})/\hbar \\ R_z &= (\rho_{bb} - \rho_{gg}) & \omega_z &= \Omega_\alpha \end{aligned} \quad (3.1.2)$$

where the $\times$ symbol has the usual vector-product meaning and $H_{bg} = (H_{int})_{bg}$, where H_{int} is the interaction Hamiltonian in Schrödinger representation and depends on time via the EM field. Notice that the x and y-components of $\vec{\omega}$ are time dependent in a similar way as H_{bg} is time dependent, because both can be expressed in the incident electric fields.

Equation (3.1.1) can be interpreted as a precession of $\vec{R}$ around $\vec{\omega}$. In the absence of radiation $\vec{R}$ precesses rapidly around the z-axis, with an angular frequency Ω_α . The second and third term in equation (3.1.1) represent the relaxation of the Bloch vector to equilibrium. In the weak-coupling limit this relaxation can be described by two relaxation constants. The z-component of $\vec{R}$, which is related to the fractional excited-state population, via $(N_b/N) = (R_z + 1)/2$ for the two-level system, decreases with the longitudinal relaxation time T_1 . The x and y-components decrease with the transverse relaxation time T_2 . The adjectives longitudinal and transverse are clearly related to the graphical representation of the relaxation of the Bloch vector. $R_{z,eq}$ denotes the equilibrium value of R_z and is -1 in the low-temperature limit. The equilibrium values of R_x and R_y are zero at any temperature, because no coherence can be present at thermal equilibrium.

In all practical situations Ω_α is by far larger than H_{bg} and the influence of H_{bg} , and the driving electric fields, on the rapid precession of $\vec{R}$ around the z-axis is averaged to zero unless the time-dependent function H_{bg} contains frequency components close to Ω_α . It is common practice to introduce the so-called Rabi frequency as a measure for the influence of H_{bg} on the time evolution of the Bloch vector.¹ The real-valued Rabi frequency ω_{Rabi} is usually defined as

$$H_{bg} = \hbar \omega_{Rabi} \cos((\omega_\ell - \omega_s)t + \varphi(t)). \quad (3.1.3)$$

It is possible to introduce a new x,y,z-coordinate frame that rotates with an angular frequency $(\omega_\ell - \omega_s)$ around the z-axis of the old frame. The transformation to this new rotating frame leaves equation (3.1.1), which

governs the time evolution of the Bloch vector, essentially unchanged, but changes the effective $\vec{\omega}$. In the rotating frame part of $\vec{\omega}$ is stationary and part of it rotates with $2(\omega_\ell - \omega_s)$ around the z-axis. In the rotating-wave approximation the influence of the latter part is neglected, as it will average to zero. For the proper choice of rotating coordinates, the stationary part of $\vec{\omega}$ is: $\omega_x = \omega_{\text{Rabi}}$, $\omega_y = 0$ and $\omega_z = (\Omega_\alpha - \omega_\ell + \omega_s)$.

For stimulated Raman scattering the coupling of the incident fields with the Raman-active mode is strongest when the frequency difference between both lasers ($\omega_\ell - \omega_s$) matches approximately the eigenfrequency Ω_α of the rotating Bloch-vector. The relevant part of the interaction Hamiltonian H_{bg} , being presented in equation (1.7.3), is

$$H_{bg} = -(1/4)\epsilon_0 L^2 a(\hbar/(2M_\alpha \Omega_\alpha))^{1/2} E_\ell(t) E_s^*(t) e^{-i(\omega_\ell - \omega_s)t} + \text{c.c.} \quad (3.1.4)$$

For a SRS experiment the Rabi frequency can be evaluated through combination of equation (3.1.3) and (3.1.4) with a few equations used in chapter one specifying the oscillator strength of the Raman mode in terms of its spontaneous Raman cross-section

$$\omega_{\text{Rabi}} = \frac{4\pi c}{\hbar n \omega_s^2} \left(\left\langle \frac{d\sigma}{d\Omega} \right\rangle I_\ell I_s \right)^{1/2}. \quad (3.1.5)$$

It is not at all trivial to solve equation (3.1.1) for complicated driving forces. Various approximation schemes have been proposed, depending on the shape of the excitation pulse, the Rabi frequency, the mistuning and the relaxation times T_1 and T_2 . The adiabatic-following approximation, which has been extensively treated by M.D. Crisp.³, is e.g. valid when the strength of the excitation pulse changes slowly with respect to the angular frequency of $\vec{R}$ in the rotating frame. A necessary condition to reach this limit is that the instantaneous frequency in the "wings of the excitation pulse", at low power, should be tuned off resonance. In the case of adiabatic following $\vec{R}$ will stay perpendicular to the $\vec{\omega}$.

The sudden regime of equation (3.1.1) is reached when the strength of the excitation pulse changes rapidly compared to both T_1 and T_2 . If a system is excited on resonance ($\omega_z=0$) and the pulse is short enough to validate the sudden approximation its time evolution becomes extremely simple. The interaction results in a rotation, during the duration of the excitation pulse, of the Bloch vector with the Rabi frequency around the x-axis of the

rotating frame. This explains why ω_{Rabi} is called a frequency.

The experimental situation corresponds reasonably well with the sudden approximation (e.g. for CS₂ pulsewidth=4.2 ps, T₂=20 ps). In our SRS experiment two laser beams of typically 13 mW average power, or 30 W peak power, are focused with a 50 mm lens into the sample. For our laser beams the smallest waist of the focus is about 16 μm ($w_0=9.5 \mu\text{m}$) and the length of the focal region is about 5 mm in CS₂. In the centre of the focal region the peak intensity is thus $1.0 \times 10^{11} \text{ W m}^{-2}$. Combining this with the Raman cross-section of CS₂ ($\frac{d\sigma}{d\Omega}=1.4 \times 10^{-33} \text{ m}^2$), $n=1.63$ and with $\omega_s=3.07 \times 10^{15} \text{ s}^{-1}$ ($\lambda_s=614 \text{ nm}$) one derives a Rabi frequency of $\omega_{\text{Rabi}}=9 \times 10^6 \text{ s}^{-1}$. After passage of the red and yellow laser pulse, which in combination form the driving force of the Raman-active mode, the direction of the Bloch vector makes an angle $\theta=(\pi/2)^{1/2} \tau \omega_{\text{Rabi}}$ with the vertical. For our experimental example the tipping angle after passage of one excitation pulse pair, with $\tau=4.2 \text{ ps}$, is $\theta = 4.6 \times 10^{-5} \text{ rad}$. For this two-level system the fraction of excited molecules, resulting from a single excitation pulse pair, can be directly determined from the graphical representation of the Bloch vector, and is directly related to the tipping angle via

$$N_b/N = (1/2)(1-\cos\theta) \approx (1/4)\theta^2. \quad (3.1.6)$$

For our experimental example I have calculated a fraction of excited molecules of 5×10^{-10} . Clearly the pulse intensities we use are relatively low and the system is never far from equilibrium.

There is a second method to determine the degree of excitation of the Raman-active mode, which is based on a direct count of the number of absorbed photons. In section (2.5) a steady-state gain $G=4.9 \times 10^{-2}$ was derived for CS₂ for our beam intensities on the basis of a $\chi^{(3)}$ extracted from the literature. Due to transient effects the theoretical "short-pulse" gain is only 3.7×10^{-3} . This number is just the fraction of the yellow photons being converted into red photons. When both the yellow and the red beam have an average intensity of 13 mW the number of photons per pulse is 4.9×10^8 (the mode-locking frequency is 82 MHz), of which 1.8×10^6 are converted from yellow to red. Most of the excited molecules lie within the focal volume, which we define as the cylinder whose radius and length are set by the points where the light intensity is half its maximum value. For CS₂ this focal volume is $6 \times 10^{-13} \text{ m}^3$ and contains approximately 6×10^{15}

molecules, some of them in regions of high intensity and others in regions of lower intensity. The average fraction of molecules excited per pulse pair within this volume is approximately $(N_b/N) = 3 \times 10^{-10}$. This is in good agreement with the degree of excitation calculated from the tipping angle.

The gain we have experimentally measured is, partly due to time jitter between the red and yellow laser pulse, almost a factor 6 lower than the transient gain cited above. The excited state population that is experimentally attainable is consequently also about a factor 6 lower. Experimentally $(N_b/N) = 1 \times 10^{-10}$ and a tipping angle of 2×10^{-5} rad are more likely quantities. A higher degree of excitation can be reached with the use of a lens with a very short focal length. Using a 13 mm lens instead of a 50 mm lens the intensity increases by about a factor 10 and the focal volume is reduced by a factor 100. With the present laser powers tipping angles of a few times 10^{-4} are thus obtainable in CS_2 .

When an inhomogeneously-broadened transition is excited with a short pulse all underlying transitions can in principle be excited. The excitation and decay of each of the underlying (independent) modes can be presented by the evolution of their Bloch vectors. As the eigenfrequencies of the various modes differ they will soon spread out, in " $\vec{R}$ space", and the coherent amplitude will decay with the so-called inhomogeneous T_2 , which is related to the inhomogeneous line width. In some cases it is possible to let these Bloch vectors rephase by the application of a second excitation pulse. As a result of the two-pulse excitation sequence the Bloch vectors combine after some time to create a macroscopic polarization, which can be detected in the form of an (optical) echo. The appearance of a photon echo was first observed by Kurnit, Abella and Hartmann⁴ on the 693.5 nm absorption in ruby. The first observation of a Raman echo in nitrogen gas was reported in ref.5. It would be fantastic if a Raman echo could be generated in condensed matter, as it would allow the experimentator to decide whether a given Raman transition is inhomogeneously broadened or not. To observe an echo tipping angles of the order 0.1-1.0 rad are necessary. Unfortunately the coupling of Raman-active modes with the radiation field is extremely low, the Raman cross-section of CS_2 is even larger than that most other materials, and we are a long way from the observation of Raman echoes with the present laser powers.

3.2 Can an inhomogeneously-broadened line be separated in its homogeneously-broadened components by TSRS ?

An inhomogeneously-broadened Raman line per definition consists of a number of underlying homogeneously-broadened lines, which overlap because the eigenfrequencies of the contributing Raman-active modes are spaced closer than their individual widths. With spontaneous Raman spectroscopy the individual lines can not be separately observed. In this section I will discuss whether or not the inhomogeneous broadening can be resolved in stimulated Raman spectroscopy.

The thorough evaluation in section (2.6) of what is exactly measured in a time-resolved stimulated Raman experiment, allows for an immediately extension of the results, and especially of equation (2.6.7), to the case of inhomogeneous broadening. Whatever the shape of the laser pulses, the maximum information one can derive from TSRS measurements on a set of Raman-active modes that are closely spaced in frequency is their combined response function $a(t) = \sum_{\alpha} a_{\alpha}(t)$, where the individual Raman-active modes are labeled by α . All Raman-active modes respond to the incident radiation. Though some might react stronger than others, because they are e.g. excited more on resonance, there is no extra criteria to distinguish one mode from the other, except the fact that they contribute differently to the combined response function. It is true that the Raman-active modes can be individually excited e.g. with two narrow-band laser, but unfortunately a scan of the frequency difference between both lasers will only yield the width of the inhomogeneous line.

A closer comparison with spontaneous Raman scattering is possible when the Fourier transform of the response function $a(t)$ is taken. As the order of the summation over the individual modes, $\sum_{\alpha}$, and the Fourier integration can be altered one finds

$$a(\omega) = \int_{-\infty}^{\infty} dt a(t) e^{i\omega t} = \int_{-\infty}^{\infty} dt \sum_{\alpha} a_{\alpha}(t) e^{i\omega t} = \sum_{\alpha} a_{\alpha}(\omega). \quad (3.2.1)$$

If the relaxation of the individual modes is exponential in time each homogeneously-broadened line $a_{\alpha}(\omega)$ has a Lorentzian shape, in the rotating-wave approximation ($\omega \approx \Omega_{\alpha}$, $\omega T_{2,\alpha} \gg 1$)

$$a_{\alpha}(\omega) = iA_{\alpha}T_{2,\alpha} / \{1 - i(\omega - \Omega_{\alpha})T_{2,\alpha}\}, \quad (3.2.2)$$

where A_α is the strength and $T_{2,\alpha}$ is the transverse relaxation time of the Raman-active mode that is labeled with α .

In many cases, e.g. when the inhomogeneous broadening results from differences in surroundings, the summation over the discrete modes α must be altered in an integration over a continuum of modes. As the integrations over α and t are interchangeable the above explanation remains valid for this situation and the maximum information one can derive from TSRS is, once more, the full behaviour of $a(\omega)$ in the complex plane.

The spectral shape one measures in spontaneous Raman scattering is proportional to the imaginary part of $a(\omega)$, which is equal to the (summation/integration) over the imaginary parts of the underlying Raman-active modes. From stimulated Raman scattering, the imaginary as well as the real part of $a(\omega)$ can in principle be derived, when the phase information is carefully analyzed. The imaginary and real part of each $a_\alpha(\omega)$ are connected via the Kramers-Kronig relations. As a consequence the imaginary and real part of the combined $a(\omega)$ should also be connected via the Kramers-Kronig relations. I conclude that "ordinary" TSRS does not allow for the separation of an inhomogeneously-broadened line in its homogeneously-broadened components.

My interpretation of the response-function formalism is based on the assumption that the degree of excitation is low and that the system remains close to equilibrium. If the driving force is too strong the occupation of the excited Raman state will become comparable to the occupation of the ground state and the Raman transition will saturate. In that situation it may become possible to look "inside" an inhomogeneously-broadened line, as is done in echo experiments. In absorption experiments the "saturation limit" has been reached many years before and indeed it has been possible to observe the homogeneous line width, with a technique that is called spectral hole burning.⁶ Data obtained from spectral hole-burning experiments should be interpreted with caution when the pump beam that burns the hole and the probe beam that probes the spectrum are simultaneously applied. In that situation a coherent artifact might appear (chapter 1, ref.11). In the future the technique of hole-burning might be extended to Raman transitions when it becomes possible to saturate them.

A second assumption used to derive of the TSRS signal strength for an inhomogeneously-broadened system is the absence of coupling between the individual Raman-active modes. If this assumption is valid every independent

Raman-active mode is separately excited and probed and the total TSRS signal is just a sum of the signals from the individual modes. In the weak-field limit this situation does not allow for the determination of the homogeneous line widths of the individual modes. The situation becomes different when the Raman-active modes interact (strongly) and part of the excitation of mode α_1 can be transferred into excitation of mode α_2 , through their mutual interaction. This process is called spectral diffusion and clearly destroys the independence of the modes. The various modes influence one another and the individual response functions are not properly defined. I conclude that in the case of spectral diffusion a comparison between spontaneous Raman scattering and TSRS data might yield extra information on the structure of an inhomogeneously-broadened line.

3.3 Time-resolved Coherent anti-Stokes Raman scattering (CARS)

In chapter two I explained how the coherent Raman excitation inelastically scatters a fraction of the light at frequency ω_ℓ into light at the Stokes-shifted frequency ω_s . In a two-beam SRS experiment this results in a Raman gain of the "red" laser beam. The driven coherent Raman excitation also scatters a comparable fraction of the ω_ℓ -light to the anti-Stokes frequency $(2\omega_\ell - \omega_s)$.⁷⁻⁹ As this coherent anti-Stokes light is directional, an extra beam of light is emitted by the sample. The described process is called coherent anti-Stokes Raman scattering (CARS). In this section I will present a few of our CARS experiments and compare the characteristics of CARS with SRS. A review of the theory and application of CARS can be e.g. found in ref.8.

Whereas two-beam SRS is self-phasematched the intensity of two-beam CARS depends strongly of the angle between the "red" and the "yellow" beam. The strong angular dependence of CARS is a combined result of the dispersion of the material under study and the fact that light is generated at a new frequency. The phase-matching property is the main weakness of CARS, compared to SRS.

We have studied CARS on bulk CS_2 .¹⁰ The experimental set-up for CARS is almost equivalent to the set-up for SRS. The generated $(2\omega_\ell - \omega_s)$ light is focused on the slit of a spectrometer and detected with a photomultiplier, working in photon-counting mode. No modulation technique was applied. At the usual beam intensities, which gave a Raman gain of $6-7 \times 10^{-4}$, the intensity

of the $(2\omega_\ell - \omega_s)$ beam was 5000 photons per second (5 Kcount/s) when the yellow and the red beam were collinear. The CARS signal intensified when the angle between both beams was increased and an optimum of 250 Kcount/s was reached for an angle of about 1.9° , being in reasonable agreement with the known dispersion in CS_2 (for $\nu_s = 16250 \text{ cm}^{-1}$ and $\nu_\ell = 16906 \text{ cm}^{-1}$).

The frequency spread of the $(2\omega_\ell - \omega_s)$ light is comparable to the frequency spread of the dye lasers. The detected intensity of course depends on the resolution of the spectrometer and scales linear with the widths of the slits of the spectrometer for small slits. The intensities just mentioned were measured with a spectral resolution of about 7 cm^{-1} . When the slits were opened any further, distortion of the anti-Stokes spectrum set in.

At first we tried to set up the CARS experiment with the same beams we used in the SRS experiments, but the CARS signal nearly drowned in the spontaneous fluorescence of the R6G dye, that was propagating on top of the laser beams. Using two prisms, situated directly after the dye lasers, we were able to reduce the spontaneous fluorescence to 100-200 count/s.

Any good comparison between CARS and SRS starts with a comparison of the induced third-order polarization at the frequency $(2\omega_\ell - \omega_s)$ and ω_s respectively. The $\chi^{(3)}$ that governs the CARS process can easily be found for a purely-isotropic Raman-active mode

$$\chi_{1111}^{(3)}(-2\omega_\ell + \omega_s, \omega_\ell, \omega_\ell, -\omega_s) = (1/2)\sigma + (2/3)a(\omega_\ell - \omega_s) . \quad (3.3.1)$$

This $\chi^{(3)}$ immediately shows that the Kerr effect has no influence on the CARS signal (absence of $a(0)$ and $b(0)$ term). When the induced third-order polarization at the Stokes and anti-Stokes frequency is calculated, one should notice that the permutation factor $D=6$ for the former and $D=3$ for the latter. When this calculation is performed, with the help of equation (1.6.9), one notices that the Raman contribution to $(P_{(2\omega_\ell - \omega_s)})$ and (P_{ω_s}) are exactly the same, whereas the electronic contribution in a CARS experiment is half as big as in a SRS experiment.

The increase in amplitude of the electric field at the frequencies $(2\omega_\ell - \omega_s)$ and ω_s can be derived from Maxwell's equation, with $P_{(2\omega_\ell - \omega_s)}$ and P_{ω_s} acting as sources. Although, for optimum phase matching, the increase in field amplitude at $(2\omega_\ell - \omega_s)$ is of the same order of magnitude as the increase at ω_s , the intensity of the beam generated at $(2\omega_\ell - \omega_s)$ will be far less than the change in intensity of the transmitted beam at ω_s . The

intensity of the beam generated at $(2\omega_\ell - \omega_s)$ is just proportional to the square of the electric field, whereas the beam generated at ω_s will interfere with the transmitted red probe beam. As a result the increase of the total intensity of the red beam can be much larger than the intensity of the added light at ω_s . Tentatively one might say that one added "coherent" photon (in a period τ) results in an increase of the intensity which is just detectable with a quantum-noise-limited detection circuit (and an integration time τ). The signal to noise (S/N) ratio obtainable in a CARS experiment, with a detection limit of one photon, is thus comparable to the (S/N) ratio obtainable in a SRS experiment with a quantum-noise limited detection circuit. The intensity at $(2\omega_\ell - \omega_s)$ is proportional to the square of the coherent amplitude $\{Q_\alpha^2(t)\}$, whereas the stimulated Raman gain is simply proportional to $Q_\alpha(t)$. When the stimulated Raman gain is e.g. a factor 10 above the detection threshold, a CARS signal of about 100 photons in a time interval τ is expected. These predictions are in reasonable agreement with our experiments.

For a time-resolved CARS experiment three beams are needed. A combination of a red and yellow pulse, which overlap in time and space, is used to coherently excite the Raman-active mode. Like in a TSRS experiment the frequency difference between both lasers must equal the eigenfrequency of the Raman-active mode to efficiently excite this mode. The coherent Raman amplitude can be probed with a single yellow beam. Observation of the emitted intensity at $(2\omega_\ell - \omega_s)$ as a function of the time delay T between the single probe pulse and the pump pair allows one to study the relaxation of the coherent Raman mode and determine its T_2 .

The phase-matching condition determines for which angles, between the three beams, the signal strength is maximum. In our geometry the yellow pump beam bisected the angle between the red pump and the yellow probe beam. After the sample a row of equidistant spots could be observed, originating from the red pump beam, the yellow pump beam and the yellow probe beam respectively. The "green" light from time-resolved CARS should be the fourth in the row. We used this knowledge to spatially separate the time-resolved CARS signal from the two-beam CARS signal, emitted approximately in the direction of the yellow probe beam.

Though most CARS experiments described in the literature are performed with low-repetition-rate high-intensity lasers, CARS experiments can be excellently performed with low-intensity mode-locked laser.⁹ The

disadvantage of a very weak coherent anti-Stokes beam (intensity less than 10^{-12} W) is partly compensated by the quasi-continuous-wave character of the emitted radiation, as we will demonstrate.

In fig.(3.3.1) two time-resolved CARS experiments are presented. When the frequency difference of the laser equalled the eigenfrequency of the Raman-active mode the upper curve could be observed. The laser frequencies were $\nu_s=16250$ cm^{-1} and $\nu_\ell=16907$ cm^{-1} and the spectrometer was set to $\nu_{AS}=17564$ cm^{-1} . While the delay between the probe pulse and the pump pair was scanned, the number of photons were counted during time intervals (integration times) of 0.1 s and the results were stored. For large delay times T the signal decreases exponentially in time with a characteristic time $(T_2/2)=9.8$ ps, being in excellent agreement with the transverse

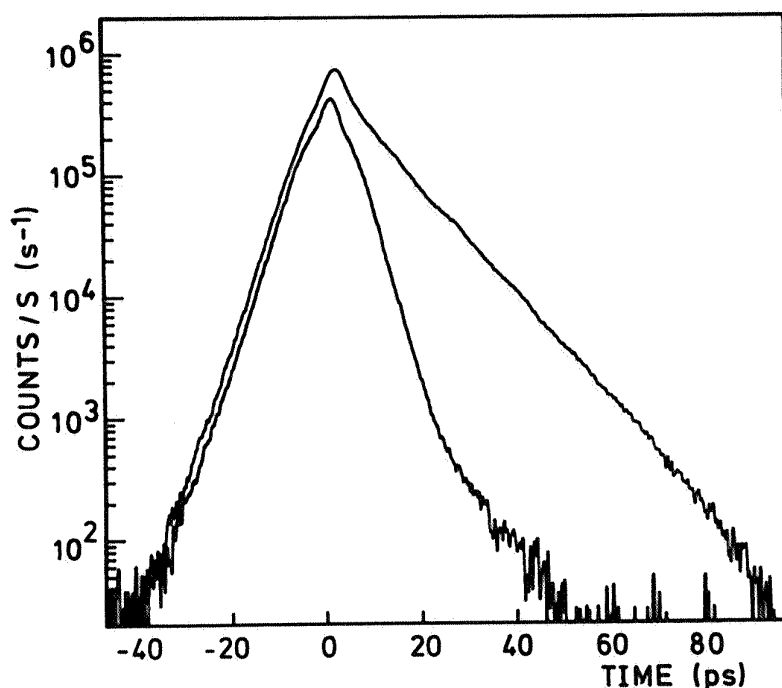


Fig.3.3.1 The results of a time-resolved CARS measurement on the symmetric stretch of CS_2 (656 cm^{-1}). When the Raman-active mode was excited almost on resonance ($(\nu_\ell - \nu_s) = 657$ cm^{-1}) curve 1 could be observed. The measured exponential decay time is directly related to the transverse relaxation time of the Raman-active mode via $(T_2/2) = 9.8$ ps. Curve 2 was measured for excitation off resonance and detection at $(2\nu_\ell - \nu_s)$. From this run the time resolution of a time-resolved experiment can be determined. We find a lower limit for the detectable T_2 of about 6 ps.

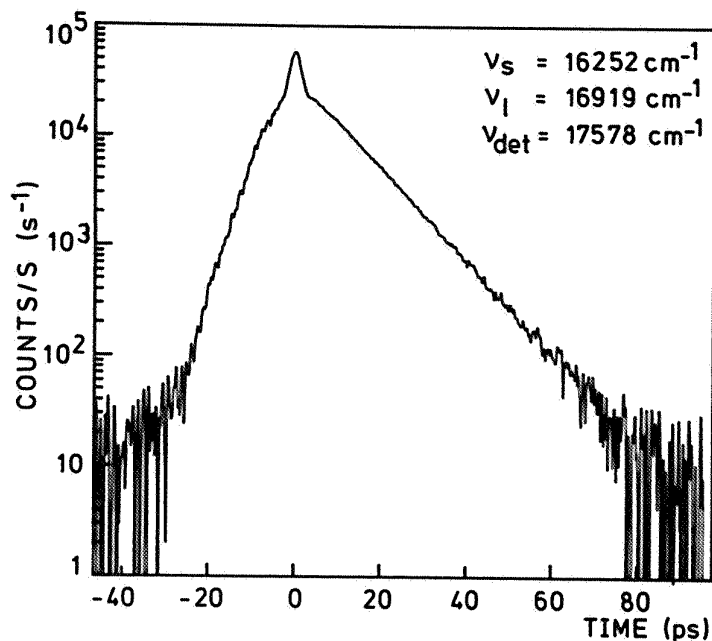


Fig.3.3.2 Another time-resolved CARS experiment on CS_2 . The signal strength of this run is less than the signal strength of the run presented as fig.(3.3.1). The detection threshold of about 10 count per second is reached after a background of typically 200-300 counts/s is subtracted from the data.

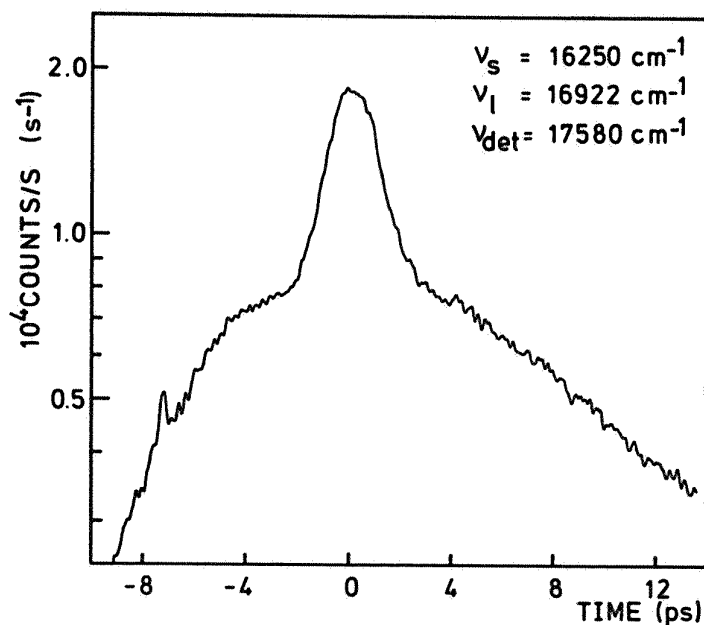


Fig.3.3.3 Most of the time-resolved CARS measurements showed a sharp structure around zero time delay, which is often called the coherent artifact.

relaxation time determined from TSRS experiments. The strongest signal was slightly more than 1000 Kcount/s and the time-resolved CARS signal could be traced over 5 decades. This should be compared with a dynamic range of 2.5 decade in a TSRS experiment, because the time-resolved CARS signal decays twice as fast as the TSRS signal.

When the laser frequencies were tuned off resonance, the lower curve in fig.(3.3.1) could be observed. The laser frequencies were $\nu_s=16250 \text{ cm}^{-1}$ and $\nu_l=16898 \text{ cm}^{-1}$ and the spectrometer was set to $\nu_{\text{det}}=17544 \text{ cm}^{-1}$. For excitation and detection off resonance the Raman contribution disappears and only the electronic contribution to the CARS signal remains. The shape of the measured response curve thus directly shows the temporal resolution of our time-resolved CARS experiment.

The smallest T_2 that can be measured with our time-resolved CARS set-up is set by the steepness of the wings of the lower curve in fig.(3.3.1) and is $T_2=6 \text{ ps}$. Evidently the time resolution obtainable in a time-resolved CARS experiment is considerably worse than the resolution obtainable in a time-resolved SRS experiment, where we observed a resolution of 0.8-1.0 ps with the same lasers. To explain this difference it should be noted that a time-resolved CARS experiment is not sensitive to the optical phases and its time resolution is determined by a convolution of intensity profiles of the laser pulses, whereas the time resolution in TSRS, which depends on the optical phases, is determined by a convolution of the (complex) electric field amplitudes of the laser pulses. For non-transform-limited pulses the former convolution can be much wider than the latter. Our experiments clearly demonstrate the difference in time resolution of CARS and SRS.

In fig.(3.3.2) the results of another time-resolved CARS experiment are presented. The lasers are tuned slightly off resonance with the Raman-active mode and the signal strength is consequently less than in fig.(3.3.1). In this figure the detection threshold of about 10 count/s is clearly visible. A background of typically 200-300 count/s had to be subtracted from the data points to reach this low a threshold.

All our time-resolved CARS measurements show a sharp peak around zero pulse delay. A nice close-up of this strange structure is given in fig.(3.3.3), where the Raman-active mode is excited slightly off resonance ($(\nu_l-\nu_s)=672 \text{ cm}^{-1}$) and probed "on resonance" ($(\nu_{\text{det}}-\nu_l)=658 \text{ cm}^{-1}$). A similar structure was observed when both the pumping and the probing were slightly off resonance. The sharp structure around $T=0 \text{ ps}$ is the so-called coherent

artifact and various articles have appeared on the subject.¹¹⁻¹⁴ One of the explanations of the coherent artifact is the following. Denote the pump beams with the labels L and S, for the beams with frequencies ω_L and ω_S respectively, and the probe beam with the label L'. For large time delay only the combination $E_L(t)E_S^*(t)$ excites the Raman mode, but for small time delays the combination $E_{L'}(t)E_S^*(t)$ can excite the Raman mode as well. This second contribution, where the L'-pulse acts as "pump" and the L-pulse acts as "probe", can be as large as the first contribution, as they have identical phase-matching conditions. The extra contribution disappears when the pulse overlap between the L-pulse and the L'-pulse diminishes. For this reason one expects the time-resolved CARS signal to display a maximum around zero delay. Unfortunately Bron et al.⁹ seem to have overlooked this extra contribution and failed to include it in their simulations.

The intensity of the $(2\omega_L - \omega_S)$ light around zero delay can be found by first adding the two contributions to the electric field at $(2\omega_L - \omega_S)$ and then squaring the result. The two cross products that result are complicated correlation functions of six electric fields, in which each L, L' and S field appears twice. These correlation functions depend on the optical phase, which explains why the coherent spike can be more narrow than the time-resolution of the CARS experiment would suggest. The width of the coherent spike is comparable to the temporal resolution obtained in TSRS. If the laser pulses would be transform-limited the coherent spike should still be observable, but would certainly not be as prominent as in our experiment.

In the CARS experiments presented up to now the spectrometer was usually set exactly to the frequency $(2\omega_L - \omega_S)$. When a Raman-active mode is excited on resonance the light generated through CARS is indeed solely emitted around this frequency. When a Raman active mode is excited off resonance the situation is different and a considerable amount of light is radiated around the frequency $(\omega_L + \Omega_\alpha)$.

For different, but fixed, delay times between the pump pair and the probe pulse, we have recorded the CARS signal as a function of the detection frequency of the spectrometer. In fig.(3.3.4) two of these runs are presented. The laser frequencies were $\nu_S = 16255 \text{ cm}^{-1}$ and $\nu_L = 16926 \text{ cm}^{-1}$ and the Raman-active mode at $(2\pi)^{-1}\Omega_\alpha = 656 \text{ cm}^{-1}$ was thus excited off resonance $\{(\nu_L - \nu_S) = 671 \text{ cm}^{-1}\}$. Curve 1 is a frequency run at $T = 1.5 \text{ ps}$ and curve 2 is a frequency run taken at a larger delay ($T = 8.0 \text{ ps}$). The spectrum clearly consist of two peaks, one around 17581 cm^{-1} ($\omega_L + \Omega_\alpha$) and another around

17597 cm^{-1} ($2\omega_{\ell}-\omega_s$). For large delay times (curve 2) the first peak around ($\omega_{\ell}+\Omega_{\alpha}$) is relatively stronger, compared to the peak at ($2\omega_{\ell}-\omega_s$), than for small delay times. Combining the frequency and time resolution it is possible to obtain additional information on the excitation process.¹⁵ One might say that the yellow probe pulse measures the "instantaneous frequency" of the coherent Raman excitation. The measurements presented in fig.(3.3.4) thus demonstrate that, around zero delay, the driven coherent Raman excitation responds primarily with the frequency of the driving force, and inelastically scatters radiation to the frequency ($2\omega_{\ell}-\omega_s$). For large delay times, when the driving force is gone, the coherent Raman excitation oscillates with its eigenfrequency, and inelastically scatters radiation to the frequency ($\omega_{\ell}+\Omega_{\alpha}$). An extra complication is the third-order polarization resulting from the electronic contribution to $\chi^{(3)}$. This contribution is

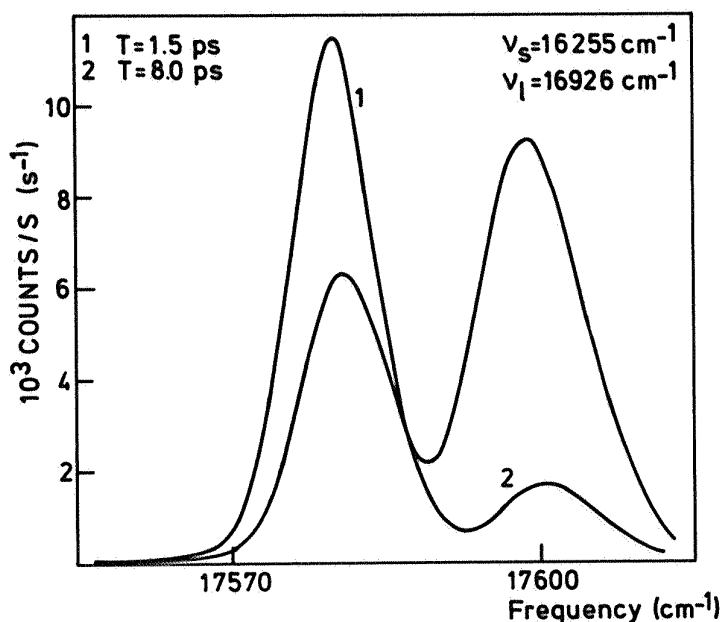


Fig.3.3.4 The frequency distribution of the emitted coherent anti-Stokes radiation, when the symmetric stretch of CS_2 is excited off resonance ($\nu_{\ell}=16926 \text{ cm}^{-1}$, $\nu_s=16255$, $(\nu_{\ell}-\nu_s)=671 \text{ cm}^{-1}$). The radiation emitted around 17582 ($\nu_{\ell}+\Omega_{\alpha}$) is related to the Raman-active mode, while the radiation emitted around 17597 ($2\nu_{\ell}-\nu_s$) originates from both the Raman-active mode and the instantaneous contribution. Curve 1 is taken at $T=1.5 \text{ ps}$ and curve 2 is taken at $T=8.0 \text{ ps}$. At $T=8.0 \text{ ps}$ the relative amount of radiation at ($\nu_{\ell}+\Omega_{\alpha}$) is far larger than at $T=1.5 \text{ ps}$.

only present around zero delay and the emitted radiation is solely concentrated around the frequency $(2\omega_p - \omega_s)$.

The laser mistuning used in fig.(3.3.4) was small enough to excite the Raman mode to a detectable degree. When the laser mistuning is drastically increased, the Raman contribution to the CARS signal is expected to vanish and only the electronic contribution to the CARS signal will remain. On the basis of the present interpretation I predict the disappearance of the coherent spike for very large laser mistunings. This prediction has not yet been checked.

Recently Felker and Hartland^{16,17} introduced an interesting variant of the CARS technique, which they referred to as Fourier transform coherent Raman spectroscopy (FTCRS). Instead of probing the excitation with a single yellow pulse they use a pair of a yellow pulse and a red pulse, similar to the pump pair. Using ns pulses they restricted their measurements to small time delays and kept large overlap between all four pulses. Felker and Hartland demonstrated the occurrence of a periodicity in the detected CARS signal when they delayed the "pump" pair with respect to the "probe" pair. This periodicity is the result of interference between the different contributions to the CARS signal: Any of the four possible combinations of a ω_p and a ω_s pulse can excite the Raman mode, while both ω_p pulses scatter light to the CARS frequency. The various contributions interfere to produce fast fringes, with a periodicity of typically half a wavelength of delay between both pairs, and slow fringes, related to the Raman wavelength.

The addition of a fourth, red probe, beam thus leads to the appearance of fringes, which are absent in a ordinary "three-beam" time-resolved CARS measurement. From the slow periodicity one can derive, via a Fourier transform, the shape and possible splitting of the excited Raman mode. FTCRS is strongly related to TSRS.¹⁸ Both techniques are sensitive to the optical phases and produce similar slow Raman fringes. The advantage of TSRS is the possibility to suppress the fast fringes, using a modulation technique in combination with the spatial dependence of the signal.

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CHAPTER 4 : Ultra-short surface-plasmon and phonon dynamics

4.1 Introduction to surface polaritons

The boundaries present in solids lead to surface states in the spectra of all (quasi)-particles. There are surface states of electrons, phonons, excitons, magnons etc. In many cases there is a strong coupling between the (electron/phonon/exciton..) excitation and the electromagnetic field and it is necessary to think in terms of a combination of a material excitation and an associated electro-magnetic (EM) field. These combined surface excitations are called "surface polaritons", in analogy with bulk polaritons. The EM-field character of the excitation even allows us to interpret surface polaritons as an EM wave that propagates at the surface of a medium, or along the interface between two media.

Surface polaritons emerge quite naturally as solutions of Maxwell's equations applied to an interface between two media. A necessary condition for their appearance is that the dielectric constant of the active medium, the medium that supports the (electron/phonon/exciton..) part of the polariton excitation, is smaller than -1. In the visible region this condition is fulfilled for most metallic media, where the propagation of EM waves is strongly influenced by the free electrons.^{1,2} Excitations of these free electrons to the widely-available higher energy levels makes up the "non-photon" part of the surface polariton. For this reason surface excitations at the interface of a metal and a dielectric are often called surface plasmon polaritons. They might just as well be denoted as surface plasmons³, a term used in this thesis.

Surface plasmons (SP) are accurate probes of the surface and through the observation of their decay much information on surface processes can be obtained. The pump-probe technique developed for stimulated Raman scattering seems to be ideally suited to study the dynamics of decay processes at a surface, because of its picosecond resolution and its capability to detect very small (10^{-7}) relative intensity changes. In the first part of this chapter some characteristics of SP, including an efficient way to produce them, will be discussed. In the second part a pump-probe experiment is described that allowed us to observe the decay of SP and the subsequent propagation and diffusion of phonons that were produced through the decay of SP.

Apart from the interesting physics related with their existence, there is a second motive to study surface plasmons. When they are generated by an incident laser beam in the so-called "attenuated total reflection" geometry, which will be thoroughly treated in section (4.4), the surface plasmon resonance can lead to an enhancement of the incident light intensity by almost two orders of magnitude. The large EM fields can lead to interesting nonlinear optical effects in both the dielectric and the metal. In chapter 5 some of these effects, and especially the stimulated Raman effect, will be discussed.

Surface plasmons emerge as solutions of Maxwell's equations when applied to the interface of a metal and a dielectric. The frequency-dependent conductivity of the metal can easily be incorporated in the dielectric constant of the macroscopic EM theory, which thereby becomes a complex quantity. A simple and often accurate model to describe the complex dielectric constant of metals ($\epsilon = \epsilon_r + i\epsilon_i$) is to separate the dynamics of the core electrons from the free electrons. As the core electrons are strongly bound their contribution to the dielectric constant (ϵ_{core}) is purely real at optical frequencies and only slightly frequency dependent. Only in the UV strong absorptions appear due to transitions of inner electrons. The influence of the valence electrons is usually accurately characterized with the Drude theory. According to this theory the valence electrons move as free particles between collisions, while the time each collision takes is neglected. In its simplest form the momenta before and after collision are assumed to be uncorrelated and the behavior of the free electrons is completely characterized by their damping time τ . It is convenient to introduce the plasma frequency $\omega_p = (ne^2/(\epsilon_0 m))^{1/2}$, where n is the density of valence electrons and m is their effective mass. At frequencies higher than ω_p a charge-density oscillation can be sustained by the metal, explaining why most metals are transparent in the UV. Actually the electron movement is coupled to an EM field and the energy quanta of this coupled excitation are called bulk plasmons. At lower frequencies EM waves can not propagate and are heavily damped in metals.

For our experiments we needed a metal with a very low (ϵ_i/ϵ_r)-ratio and silver was quite suited for this purpose. Actually pure sodium would have been better, but the reactivity of this metal poses too great a difficulty. In the literature one finds many values for the dielectric constant of silver and especially an accurate determination of its imaginary part,

related to the damping of the free electrons, is difficult. There is some consensus on the value mentioned in ref.(2,4,5,6), which is presented below

$$\begin{aligned}\epsilon_{\text{Ag}} &= -16.0(5) + 0.60(5) i, \quad (\lambda=600 \text{ nm}, \omega=3.14 \times 10^{15} \text{ s}^{-1}) \\ \epsilon_{\text{core}} &= 4.1, \\ \epsilon_{\text{free}} &= -20.1 + 0.60 i.\end{aligned}$$

The large dielectric constant of the core electrons is due to the presence of a nearby interband electronic transition in silver (at 4.0 eV). Unfortunately the frequency dependence of ϵ_{core} is not known very accurately. The frequency dependence of the free-electron part of the dielectric constant can be derived with the help of the Drude theory

$$\epsilon_{\text{free}} = - \frac{\omega_p^2}{(\omega^2 + i\omega\Gamma)}, \quad (4.1.1)$$

$$\begin{aligned}\omega_p &= 1.41 \times 10^{16} \text{ s}^{-1}, \\ \Gamma &= 9 \times 10^{13} \text{ s}^{-1}, \quad \tau = 11 \text{ fs} \quad (T=293 \text{ K}),\end{aligned}$$

where the parameters ω_p and Γ are derived from a comparison of equation (4.1.1) with the literature value of ϵ_{free} .

The derived plasmon frequency (ω_p) is in good agreement with the theoretical formula presented earlier. This implies that the effective mass of the single valence electron is close to its free value. The damping rate we have derived from the dielectric constant of silver is $\tau=11$ fs (300 K). This is almost ten times smaller than the damping rate one can derive from the DC electrical resistivity of silver ($\rho=1.6 \times 10^{-8} \Omega\text{m}$). This discrepancy can be understood in terms of a frequency-dependent damping time ($\tau(\omega)$).

The wave vector of an EM wave of frequency ω propagating in a metal is equal to the index of refraction $n=\sqrt{\epsilon}=(n_r+in_i)$ times (ω/c). In most metals, and in silver in particular, the index of refraction is mainly imaginary in nature and the EM wave is overdamped. The light intensity decreases exponentially in space and the length after which the intensity is at $(1/e)$ of its original value, which is called the penetration depth, is far less than the wavelength. As a direct result of the Drude theory this penetration depth (Λ) is almost independent of the wavelength at optical frequencies. For light at normal incidence the equation $\Lambda=(\lambda/(4\pi n_i))$ is valid, which yields $\Lambda=11.8(2)$ nm for silver (at $\lambda=600$ nm).

The formulas that describe the reflection and transmission of light do not change when one allows the index of refraction to be complex. Snell's law of refraction for instance originates from the demand of continuity of the EM field along the whole interface. As this demand holds for metals as well as for dielectrics the refraction of light going from a dielectric to a metal (or vice versa) is simply given by

$$n_2 \sin \theta_2 = n_3 \sin \theta_3 , \quad (4.1.2)$$

where n_2 and n_3 are the (complex) indices of refraction of the metal and the dielectric and θ_2 and θ_3 are the respective angles of incidence of the EM wave with respect to the normal of the interface.

Mathematically the complex nature of the angle θ_2 in the metal poses hardly any problem, but it has some interesting physical implications.¹ The amplitude of the EM wave decays exponentially inside the metal. It is a so-called inhomogeneous wave, as the planes of equal amplitude, which are parallel to the interface, do not coincide with the planes of equal phase. In the next sections it will be shown that with the complex nature of ϵ_2 alone the existence of SP can be predicted.

4.2 Reflectance and transmittance calculated with a transfer matrix

Snell's law of refraction combined with the demand for continuity of the components of H and E parallel to the interface enables one to compute the reflection and transmission at a boundary between two homogeneous media. For this purpose it is useful to define the optical impedance Z of an EM wave in a medium as ($\epsilon_0 c$) times the ratio of the tangential components of the electric and the magnetic field in a rightward-going wave (propagation to positive z).¹ For the leftward-going wave the negative of this value can be used. The optical impedance depends on the angle the EM wave makes with the boundary. For p-polarized light, where the magnetic field is perpendicular to the plane of incidence, the optical impedance in medium j is given by¹

$$Z_j = \epsilon_0 c (E_{\parallel} / H_{\parallel})_j = \cos \theta_j / n_j . \quad (4.2.1)$$

This definition of the optical impedance unfortunately contains the

angle of incidence in each medium. All these angles are related and can be reduced to one angle, for instance the angle of incidence in medium 1, with the use of Snell's law

$$k_j = (\omega/c) n_j \cos \theta_j = (\omega/c) \{ \epsilon_j - \epsilon_1 \sin^2 \theta_1 \}^{1/2} = \{ (\omega/c)^2 \epsilon_j - k_{1\parallel}^2 \}^{1/2}, \quad (4.2.2)$$

$$Z_j = (c/\omega) k_j / \epsilon_j, \quad (4.2.3)$$

A very nice and general method to evaluate the propagation of light through as many layers as one wants is the transfer-matrix approach¹, which originates from the theory of transmission lines. From the optical impedance of both media and the continuity of the parallel components of the electric and the magnetic field, the ratio of leftward propagating EM radiation (denoted by the subscript L) to right-ward propagating radiation (subscript R) in both media can be determined. When one defines the signs of E_{2R} and E_{2L} to be the same when they point towards the same direction on normal incidence, the electric fields at the boundary of medium 2 and 3 are related to each other via the transfer matrix given in equation (4.2.4). The corresponding magnetic fields can easily be evaluated using the impedance of the respective materials.

$$\begin{pmatrix} E_{2R} \\ E_{2L} \end{pmatrix} = (1/2) \begin{pmatrix} 1+(Z_2/Z_3) & 1-(Z_2/Z_3) \\ 1-(Z_2/Z_3) & 1+(Z_2/Z_3) \end{pmatrix} \begin{pmatrix} E_{3R} \\ E_{3L} \end{pmatrix} \quad (4.2.4)$$

The reflectance and transmittance of p-polarized light going from medium 2 to medium 3 can easily be extracted from equation (4.2.4) by setting the amplitude of the left-ward going wave in medium 3 to zero ($E_{3L}=0$). This results in

$$r_{23} = \frac{E_{2L}}{E_{2R}} = \frac{(Z_3-Z_2)}{(Z_3+Z_2)} = \frac{(\epsilon_2 k_3 - \epsilon_3 k_2)}{(\epsilon_2 k_3 + \epsilon_3 k_2)}, \quad (4.2.5)$$

$$t_{23} = \frac{E_{3R}}{E_{2R}} = \frac{2Z_3}{(Z_3+Z_2)} = \frac{2\epsilon_2 k_3}{(\epsilon_2 k_3 + \epsilon_3 k_2)}, \quad (4.2.6)$$

where k_j is the component of the wave vector in medium j perpendicular to the interface. We have chosen the easy notation " k_j " instead of the more accurate, but more cumbersome, notation " $k_{1,j}$ ". Notice that the equations (4.2.5) and (4.2.6) represent the reflectance and transmittance of the

amplitude of the electric field parallel to the interface. The intensity reflectance and transmittance can be easily calculated from these quantities.

The reflectance is small when the media have comparable impedances and increases with increasing impedance mismatch, when the media become so to say optically more and more dissimilar. For reflection on a denser medium r_{23} is negative at normal incidence, denoting a reversal of the reflected electric field vector with respect to the incident field.

4.3 Surface plasmons

The interface of a dielectric (medium 3) and a metal (medium 2) can support a very interesting wave, called a surface plasmon or surface plasmon polariton (SP). The wave is bound to the interface and consists of an oscillating surface-charge-density wave in the metal (plasmon character) and an associated EM field inside and outside the metal (photon character). The EM field as well as the charge-density wave are strongest at the boundary and decrease exponentially away from the interface. Surface plasmons (SP) can be classified as transverse magnetic (TM) waves as the associated magnetic field is perpendicular to their direction of propagation. Surface plasmon can consequently only be excited with p-polarized light. Mathematically the existence of surface plasmons is connected to a minimum in the quantity $(Z_2 + Z_3)$, which can e.g. be treated as a function of $k_{//}$. The electro-magnetic fields associated with the SP are⁷

$$\begin{aligned} \vec{E}_3 &= E_0(1, 0, ik_{sp}/q_3) e^{-q_3 z} e^{i(k_{sp}x - \omega t)} & \text{dielectric, } z > 0 \\ \vec{H}_3 &= i\omega\epsilon_0 E_0(0, -\epsilon_3/q_3, 0) e^{-q_3 z} e^{i(k_{sp}x - \omega t)} \end{aligned} \quad (4.3.1)$$

$$\begin{aligned} \vec{E}_2 &= E_0(1, 0, -ik_{sp}/q_2) e^{+q_2 z} e^{i(k_{sp}x - \omega t)} & \text{metal, } z < 0 \\ \vec{H}_2 &= i\omega\epsilon_0 E_0(0, \epsilon_2/q_2, 0) e^{+q_2 z} e^{i(k_{sp}x - \omega t)} \end{aligned}$$

$$k_{sp}^2 = (\omega/c)^2 \frac{\epsilon_2 \epsilon_3}{(\epsilon_2 + \epsilon_3)} \quad (4.3.2)$$

$$q_j = \{k_{sp}^2 - \epsilon_j(\omega/c)^2\}^{1/2} \quad (4.3.3)$$

The wave vector of the SP (k_{sp}), which is parallel to the interface, is complex. Its real part is always (slightly) larger than $n_3(\omega/c)$, being of

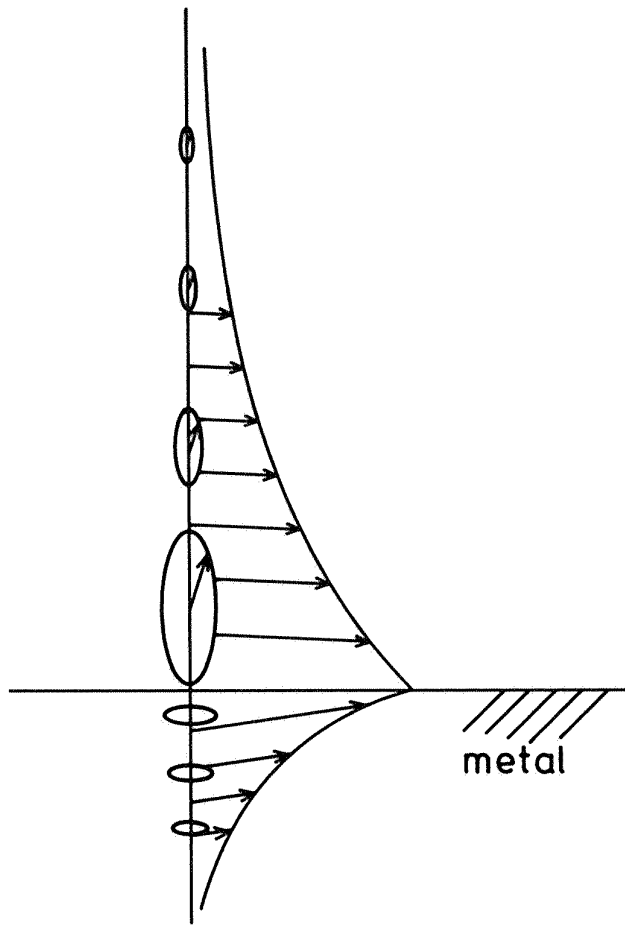


Fig.4.3.1

A graphical representation of surface plasmons at the interface of a metal and a dielectric. The ellipses represent the electric field associated with the SP. In the dielectric the electric field points dominantly perpendicular to the interface. The arrows represent the energy flow. The SP are trapped at the interface and propagate almost with the speed of light (to the right).

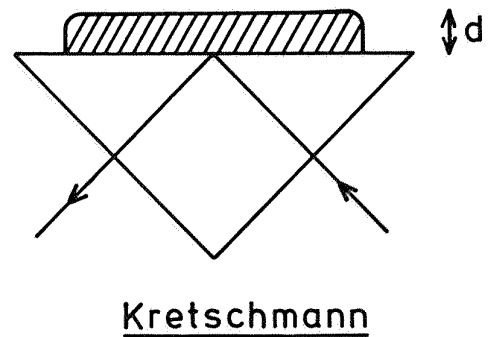
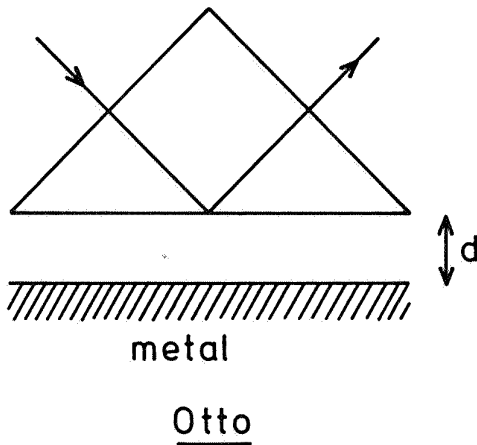


Fig.4.3.2 Two methods to excite surface plasmons. The two configurations are named after their inventors the Otto and the Kretschmann configuration.

course the reason SP do not decay radiatively into the dielectric and are bound to the interface. The imaginary part of k_{sp} reflects the decay of SP. This decay arises from scatter of the electrons that make up the "plasmon" part of the SP wave.

In fig.(4.3.1) I have sketched the electric field associated with SP. For a silver-air interface around $\lambda=600$ nm the light intensity penetrates $(1/2q_2) = 12$ nm into the silver and extends to slightly more than 250 nm into the air. These SP are thus very photon-like. When the frequency would be lower (more to the (infra)red), the field would extend further into the air, while the penetration depth into the silver would hardly change. "Low-frequency" SP are more photon-like, live longer and propagate over greater distances, than "high-frequency" SP.

The Poynting vector, which presents the direction of energy flow, is also depicted in fig.(4.3.1). Its parallel component represents the energy flow along the surface, and the propagation of SP. The group velocity of SP can be calculated from their dispersion relation and is slightly less than the speed of light. The Poynting vector is slightly tilted towards the interface in both the dielectric and the metal. The corresponding energy flow perpendicular to the surface results from damping and would be absent when $\text{Im } k_{sp}$ would be zero. It transfers the EM-field energy towards regions where (ohmic) dissipation, due to electron collisions, take place.

It is impossible to excite SP directly with light coming through the dielectric. There simply is not enough momentum available for excitation. Efficient excitation of SP is possible with the help of a grating³ or by making use of the physical effect of "the evanescent wave". Even though the transmittance at a boundary of two media might be zero, the intensity of light does not drop immediately to zero in the "forbidden" medium, but decays exponentially in space. This so-called evanescent field has more momentum associated with it, as $k_{//} = (\omega/c)n\sin\theta$, and can be used to excite SP, by bringing a third medium very close to the interface. The two methods generally used are named after their inventors the Otto and the Kretschmann geometry.^{8,9}

In the Otto configuration (fig.4.3.2) a dielectric prism is brought very close to a metal. As the angle of incidence of the depicted beam is slightly larger than the angle of total internal reflection the light is fully reflected at the inside of the prism when the prism is far from the metal. Bringing the prism close to the metal the reflectivity drops strongly

when part of the light is capable of exciting SP at the metal-air interface. For efficient excitation the distance between the prism and the metal has to be in the order of $d=0.5-1.0\ \mu\text{m}$, which is difficult to control experimentally. For this reason we, as many others, use the Kretschmann configuration (fig.4.3.2). In this configuration a beam is reflected at the interface of a substrate and a thin metal layer. Under certain conditions, which will be mentioned in the next section, the evanescent wave in the metal can excite SP at the other side of the metal film. The thickness of the metal film has to be optimized to get efficient production of SP (typically $d=30-60\ \text{nm}$). This thickness is easily controlled, but variation of thickness requires the production of a new film.

In both the Otto and the Kretschmann configuration choosing the optimum thickness is a necessary, though not sufficient, requirement for an efficient production of SP. The excitation of SP is strongly angle dependent, because only for one angle of incidence, called the plasmon angle, the law of conservation of parallel momentum is satisfied. A disadvantage of both coupling geometries is the fact that the SP can escape through radiative decay into the prism, similar to the way they were created. The character of the SP is therefore slightly changed and one calls them "leaky" SP.

4.4 Kretschmann configuration

We have extensively studied the dynamics of SP and the phonons into which they decay, using the Kretschmann setup depicted in fig.(4.4.1). A thin metal film lies on top of a transparent medium (1), which I will, without loss of generality, call a glass. The generation of SP at the metal-medium 3 interface manifests itself in a decrease in the reflectance observed from the glass side. In this section the reflectance of the three-media system will be derived for a plane wave coming through the glass, as a function of the angle of incidence. An approximation introduced by Kretschmann himself⁹, which facilitates the use of the derived formula, will be presented as well.

The reflectivity of the Kretschmann system can be derived through summation of all (multiple) reflections on the two interfaces. In the first representation of expression (4.4.1) the direct reflection at the glass-metal interface (r_{12}) is separated from all multiple reflections. The second

representation gives the combined reflectance as a function of angle of incidence, or parallel momentum $k_{//} = (\omega/c) n_1 \sin \theta_1$.

$$r_{123} = r_{12} + \frac{(1-r_{12}^2)r_{23}e^{i2k_2d}}{(1+r_{12}r_{23}e^{2ik_2d})} = \frac{(r_{12}+r_{23}e^{2ik_2d})}{(1+r_{12}r_{23}e^{2ik_2d})}, \quad (4.4.1)a$$

$$r_{123} = \frac{(\epsilon_1 k_2 - \epsilon_2 k_1)(\epsilon_2 k_3 + \epsilon_3 k_2) + (\epsilon_1 k_2 + \epsilon_2 k_1)(\epsilon_2 k_3 - \epsilon_3 k_2)e^{2ik_2d}}{(\epsilon_1 k_2 + \epsilon_2 k_1)(\epsilon_2 k_3 + \epsilon_3 k_2) + (\epsilon_1 k_2 - \epsilon_2 k_1)(\epsilon_2 k_3 - \epsilon_3 k_2)e^{2ik_2d}}, \quad (4.4.1)b$$

where $k_j = ((\omega/c)^2 \epsilon_j - k_{//}^2)^{1/2}$ is component of the wave vector of the EM field in medium j perpendicular to the interfaces. Notice that $k_2 = -iq_2$ and $k_3 = iq_3$.

Equation (4.4.1) is a function of the thickness of the metal layer and the angle of incidence, which is specified by $k_{//}$. The complex nature of the reflectivity from the glass-metal interface (r_{12}) and the metal-medium 3 interface (r_{23}) and the phase shift of the EM wave on propagation through the metal ($k_2 d$), combined with the dependence of these variables on the angle of incidence makes equation (4.4.1) hard to handle and difficult to interpret. In a practical situation the thickness of the metal layer is kept fixed (d fixed) and the reflectivity of the Kretschmann system is measured as a function of the angle of incidence ($k_{//}$ variable). It is convenient to extend the domain of the "reflectivity function", given by equation (4.4.1), to complex $k_{//}$. The angle dependence of the reflectivity is dominated by the resonance due to the surface-plasmon mode. The SP mode at the interface of the metal and medium 3 can be mathematically associated with a single pole

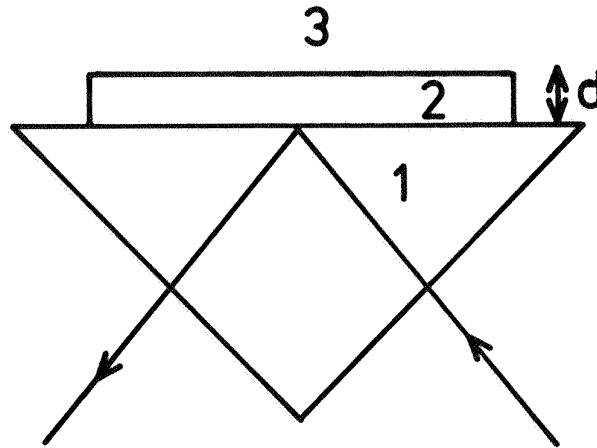


Fig.4.4.1 The Kretschmann configuration.

in equation (4.4.1), which I will denote by the "SP resonance condition" $((1/r_{23}) + r_{12}e^{2ik_2d} = 0)$. In the next paragraphs I will try to find the position of this complex pole.

SP at the interface of two semi-infinite media correspond with the resonance condition $(Z_2+Z_3=0)$. Probably one of the most intriguing things is the huge value $r_{23} = (Z_2-Z_3)/(Z_2+Z_3)$ can have close to resonance $((1/r_{23}) \approx 0)$. The "forbidden" wave, propagating heavily damped inside the metal, experiences a reflectivity far greater than one at the metal-medium 3 interface. This large reflectivity has practically no physical significance as it can not be measured. For a extremely thick metal layer the SP resonance is satisfied when

$$\hat{k}_{//}^2 = \frac{\epsilon_2 \epsilon_3}{(\epsilon_2 + \epsilon_3)} \frac{\omega^2}{c^2}, \quad (4.4.3)$$

where the real part of $\hat{k}_{//}$ determines the momentum of the SP, while its imaginary part is related to the damping.

When the metal film is not too thin, and has a transmission of a mere few percent (small e^{2ik_2d}), the properties of the SP are only slightly affected by the finite thickness of the metal film and this finite thickness can be treated as a small perturbation on the SP character. The pole of equation (4.4.1) $((1/r_{23}) + r_{12}e^{2ik_2d} = 0)$ can be found through expansion of $(1/r_{23}) = \alpha(k_{//} - \hat{k}_{//}) + \dots$ around $k_{//} = \hat{k}_{//}$, where $(\alpha > 0)$ is defined through this expansion. Due to the finite thickness of the film the SP mode is shifted over $\Delta \hat{k}_{//}$

$$\Delta \hat{k}_{//} = (-1/\alpha)r_{12}e^{2ik_2d} = \frac{2|\epsilon_2 \epsilon_3|^{(3/2)}(\omega/c)}{|\epsilon_2 + \epsilon_3|^{(3/2)}(\epsilon_2 - \epsilon_3)} r_{12}e^{2ik_2d}, \quad (4.4.4)$$

where the right-hand side has to be evaluated at $k_{//} = \hat{k}_{//}$.

In terms of the just defined $\hat{k}_{//}$ and $\Delta \hat{k}_{//}$ the reflectivity of the Kretschmann system (equation (4.4.1)) can be rewritten as

$$r_{123} = r_{12} \frac{(\alpha(k_{//} - \hat{k}_{//}) + (1/r_{12})e^{2ik_2d})}{(\alpha(k_{//} - \hat{k}_{//}) - \alpha \Delta \hat{k}_{//})}. \quad (4.4.5)$$

When the metal film is not too thin (e^{2ik_2d} small) and $(|\epsilon_1/\epsilon_r| \ll 1)$

equation (4.4.5) can be further reduced. It is easy to show that $(1/r_{12})e^{2ik_2d}$ can then be rewritten into $\alpha\Delta k_{//}^*$, because k_2 will be dominantly imaginary and $(1/r_{12}) \approx r_{12}^*$ ($|r_{12}| \approx 1$). With the two mentioned assumptions the equation for intensity reflectance ($|r_{123}|^2$) as a function of the angle of incidence ($k_{//}$) reduces to the equation derived by Kretschmann in ref.9

$$R_{123} = 1 - \frac{4 \hat{k}_{//}'' \Delta \hat{k}_{//}''}{(\hat{k}_{//}'' - \hat{k}_{//}' - \Delta \hat{k}_{//}'')^2 + (\hat{k}_{//}'' + \Delta \hat{k}_{//}'')^2}, \quad (4.4.6)$$

where real and imaginary parts are denoted with the symbols ' and '' respectively. In formulas (4.4.5) and (4.4.6) the physical properties of the surface plasmons are completely incorporated in the complex parameters $\hat{k}_{//}$, related to the unperturbed system, and $\Delta \hat{k}_{//}$, representing the deviations in the SP character due to the finite thickness of the film.

The dependence of the intensity reflectance on the angle of incidence is best presented in the form of the so-called Attenuated Total Reflection (ATR) curve. The ATR curve will have a minimum at the angle of incidence that fulfills the SP resonance condition. The position of the minimum of the ATR is only weakly dependent on the thickness of the metal film, but the width of this minimum depends strongly on the thickness. This width is proportional to the damping rate of the SP ($\hat{k}_{//}'' + \Delta \hat{k}_{//}''$). $\hat{k}_{//}''$ represents the non-radiative decay or the intrinsic damping of the SP. $\Delta \hat{k}_{//}''$ is related to the possibility for SP to escape through the film into the substrate, the same way as they were created, and represents the radiative damping.

The ratio of the imaginary parts of $\hat{k}_{//}$ and $\Delta \hat{k}_{//}$ is of special importance for the shape of the ATR curve. For very thin films the minimum in the ATR curve is wide, showing the strong radiative damping of the SP. Increasing the thickness of the film the ATR curve becomes narrower, reflecting the fact that the SP escape less easily into the glass and their confinement is more stringent. The minimum reflectance becomes lower as well and for optimum thickness d_{opt} and optimum angle of incidence, which is called the plasmon angle, the reflection vanishes. From formula (4.4.6) one observes that this optimum thickness is reached when the thickness-dependent radiative damping matches the thickness-independent non-radiative damping ($\Delta \hat{k}_{//}'' = \hat{k}_{//}''$). Films thicker than the optimum thickness show even narrower ATR curves, but the minimum reflectance becomes larger again. For thick

films the coupling between the SP and the radiation field is decreased, increasing the life time of the SP, but decreasing the probability of their creation. From equation (4.4.6) follows that the minimum of the ATR curve should be Lorentzian-shaped. In practice the Lorentzian shape is well reproduced for narrow ATR curves. For wider curves ($\text{FWHM} > 0.5^\circ$), corresponding to thin films or poor quality metal, deviations from formula (4.4.6) are observable and equation (4.4.1) should be used. Three theoretical ATR curves are presented in fig.(4.4.2).

It might seem strange that although radiative damping of SP is present no light emerges from the Kretschmann system for the optimum thickness and angle. This results from the fact that the phase of the SP is related to the phase of the incident radiation, the light from the radiatively-decaying SP is coherent, and the light interferes destructively with the direct reflection (r_{12}) at the glass-metal interface. The radiative decay of the SP

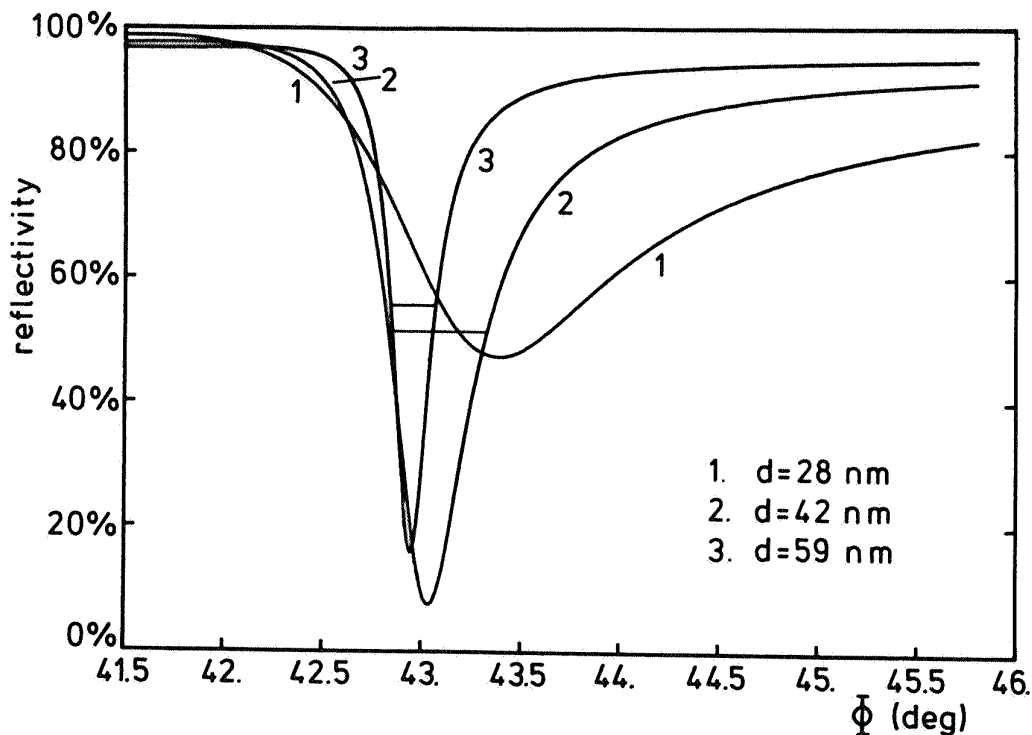


Fig.4.4.2 The theoretical dependence of the reflectivity of light propagating through BK7 glass on a (BK7-Ag-air) Kretschmann system as a function of the angle of incidence. The three curves are calculated for a silver film of thickness 28 nm, 42 nm and 59 nm respectively. Notice the decrease in width and the slight shift of the ATR curve on increase of the film thickness.

is comparable to leakage of light out of a cavity.

There is an equivalence between the (quantum-mechanical) picture of SP that propagate along the metal film and decay radiatively and the (classical) picture of multiple reflections inside the metal layer. The SP resonance condition corresponds to the situation that the amplitude of the EM wave reflecting inside the metal layer is hardly changed after one round trip ($r_{21}r_{23}e^{i2k_2d} \approx 1$). The propagating zig-zagging EM wave inside the metal layer is physically equivalent to a bunch of SP, seen from a different point of view. Due to the huge reflectivity r_{23} this EM wave is mainly concentrated at the interface of medium 2 and medium 3.

I will finish this section with a few useful equations that describe the creation and the decay of SP

$$\hat{k}_{//}(\frac{c}{\omega}) = \frac{(|\epsilon_r|\epsilon_3)^{1/2}}{(|\epsilon_r|-\epsilon_3)^{1/2}} + i \frac{\epsilon_1}{2|\epsilon_r|^2} \frac{(|\epsilon_r|\epsilon_3)^{(3/2)}}{(|\epsilon_r|-\epsilon_3)^{(3/2)}}, \quad (4.4.7)$$

$$\Delta \hat{k}_{//}(\frac{c}{\omega}) = -2r_{12} \frac{(|\epsilon_r|\epsilon_3)^{(3/2)}}{(|\epsilon_r|+\epsilon_3)(|\epsilon_r|-\epsilon_3)^{(3/2)}} \exp\{-\frac{4\pi|\epsilon_r|d}{\lambda(|\epsilon_r|-\epsilon_3)^{1/2}}\}, \quad (4.4.8)$$

$$\frac{d_{opt}}{\lambda} = \frac{(|\epsilon_r|-\epsilon_3)^{1/2}}{4\pi|\epsilon_r|} \ln\left(\frac{4|\epsilon_r|^2 \text{Im}(r_{12})}{\epsilon_1(|\epsilon_r|+\epsilon_3)}\right), \quad (4.4.9)$$

$$a^2 = |\epsilon_r|(\epsilon_1-1)-\epsilon_1; \text{Re}(r_{12}) = \frac{(\epsilon_1^2-a^2)}{(\epsilon_1^2+a^2)}; \text{Im}(r_{12}) = \frac{-2\epsilon_1 a}{(\epsilon_1^2+a^2)}. \quad (4.4.10)$$

To get a feeling of the order of magnitude, a few quantities are calculated below, for a Kretschmann configuration consisting of a silver film of optimum thickness on a BK7 glass substrate :

$$\epsilon_1 = 2.30; \epsilon_{Ag} = -16+0.6i; \lambda = 600 \text{ nm},$$

$$d_{opt} = 51 \text{ nm},$$

$$\hat{k}_{//} = 1.0328 + 0.0013i,$$

$$\Delta \hat{k}_{//} = 0.0009 + 0.0013i,$$

$$\text{Plasmon angle for this thickness : } \theta_{sp} = 43.0^\circ,$$

$$\text{FWHM ATR curve for this thickness : } \Delta\theta = 0.25^\circ.$$

4.5 Experimental determination of attenuated total reflection(ATR)

In this section I will present measurements of the angle-dependent reflectivity of thin silver films on glass substrates. The substrate was a 45° - 45° - 90° prism of BK7 glass of extreme good flatness ($\lambda/10$), of which the surfaces were carefully cleaned with acetone before use. Silver was evaporated onto the glass under a pressure of a few times 10^{-6} Torr, to insure the purity of the film. The thickness of the film was determined in situ with a quartz-oscillator, of which the resonance frequency changes as a result of its increase in mass under evaporation. The measured thickness is afterwards checked against the transmission of a silver film simultaneously evaporated on an extra chip of glass. Before the evaporation a glow discharge (sustained in the air at 0.1-1.0 Torr) bombards the surface to remove adsorbed gas molecules. Omitting the "glow stage" deteriorates the future attachment of the silver on the glass. When the "glow stage" was omitted we observed the formation of bladders and even some ruptures of the film, when it was locally heated with a laser beam. We have also experimented with a second experimental method to improve the attachment of the silver to the glass. First evaporating a few nm of NiCr onto the glass etches it a little and makes the silver stick better. We have used both methods, but finally decided to work without NiCr, as a thorough "glow stage" gave sufficiently good films and the NiCr layer did (slightly) influence the reflectance of the Kretschmann system.

Fig.(4.5.1) shows the measured dependence on the angle of incidence θ of the reflectance of a dye-laser beam ($\lambda=615$ nm) on our Kretschmann system, corrected for reflections at both glass-air surfaces. The prism was attached to a home-built rotating mount which allowed for a relative determination of angle θ to better than 0.02° . Calibration of the absolute angle was less accurate (0.05°) and was obtained via back reflection of the laser on the front surface of the prism.

The optimum film thickness was experimentally determined to be about 45 ± 2 nm, which is slightly less than the value given by theory. For this thickness we could get the reflectivity at the plasmon angle as low as 0.4-1.5 %. The position of the ATR minimum was only slightly dependent on the thickness of the film and was 42.8° for d_{opt} at 16250 cm^{-1} . Using light of another color (16907 cm^{-1}) the shape of the ATR-curve did not change, but the curve as a whole shifted about 0.20° towards larger angles. The

positions of these ATR minima is in reasonable agreement with theory.

The ATR-curves we have determined experimentally were always broader than could be explained by theory (with $\epsilon = -16 + 0.6i$). Our curves are best fitted with an effective $\epsilon_1 = 1.1$, instead of the literature value of $\epsilon_1 = 0.6$. The most likely explanation is that the SP experience extra damping due to roughness of, or impurities in, the silver film. This point of view is supported by the sample dependence of the measured ATR curves. The FWHM's of the ATR curves were spread between 0.35° and 0.55° for the various prepared films.

Various articles have appeared on the influence of roughness on the behavior of SP, but the theory is certainly not straightforward.^{3,10-12} Surface roughness leads to a decrease of the SP lifetime, an increase in the

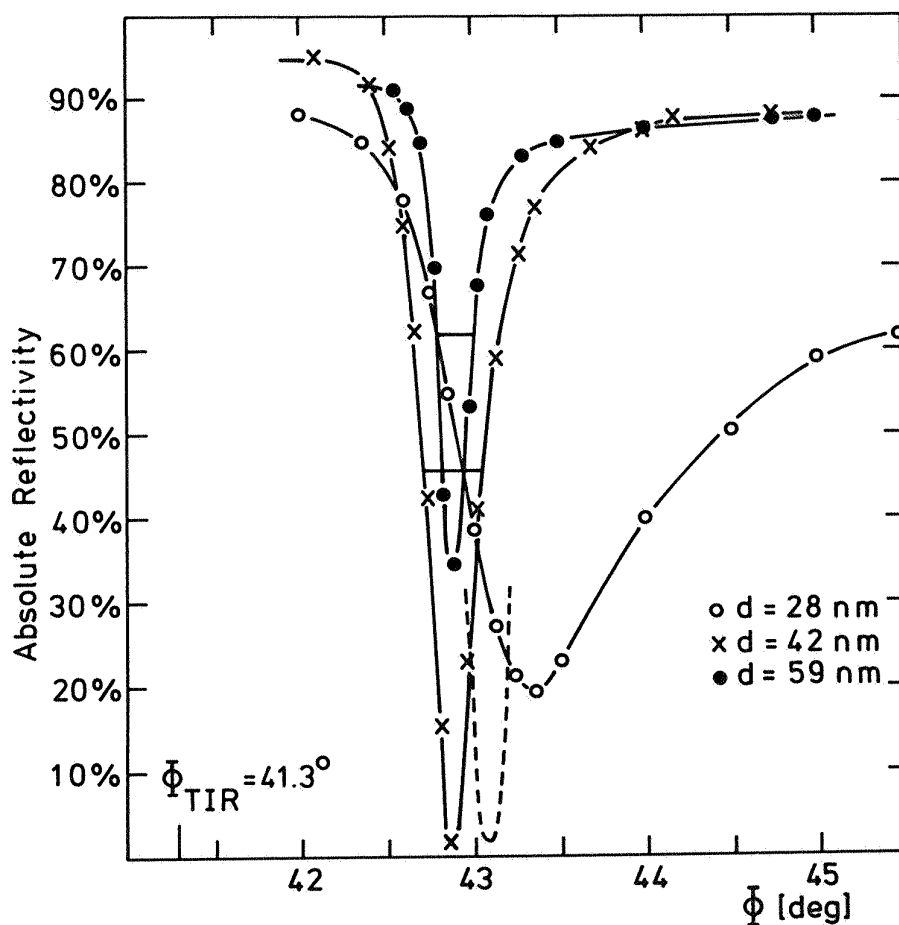


Fig.4.5.1 Experimentally-determined ATR curves of a BK7-Ag-air system for three different film thickness, measured with red light ($\lambda = 616$ nm). The dashed ATR curve was observed for yellow light ($\lambda = 592$ nm) and $d = 42$ nm.

width of the ATR curve and a shift of the minimum of the ATR curve to larger angles of incidence.¹¹ Furthermore surface roughness scatters SP and leads to the emission of light into medium 3.¹² The surface roughness can be either at the silver-air interface or at the silver-glass interface. In some articles the "natural roughness" of the glass substrate is enhanced through addition of an extra layer of CaF_2 .¹¹ Typical roughnesses have a height of 1-5 nm and a correlation length of 15-100 nm.

Separate measurements of the direct reflectance of silver in air were performed to get an independent estimate of the complex index of refraction of the evaporated silver. These measurements gave good agreement with the literature value for ϵ_r , but the measured ϵ_i differed from the literature value. Depending on the quality and age of the film the ϵ_i thus determined ranged from 1.1 to 1.7 .

An extra point of caution is the formation of a silver-disulfide layer on top of the silver film once exposed to air.^{13,14} The character of the SP is strongly influenced by this extra layer. Fortunately the formation of Ag_2S is a very slow process under ordinary SO_2 concentration in the air. In ref.9 the change in SP character resulting from an additional layer of thickness d_4 on top of a metal film is given as

$$\Delta k_{//}^{\text{deck}} = (\omega/c) \frac{(\epsilon_4 - \epsilon_3) \epsilon_r^2 (|\epsilon_r| + \epsilon_4) \epsilon_3^2 2\pi d_4}{\epsilon_4 (|\epsilon_r| - \epsilon_3)^2 (|\epsilon_r| + \epsilon_3) / |\epsilon_r| \lambda} , \quad (4.5.1)$$

where ϵ_4 is the dielectric constant of the extra layer. Using $\epsilon_4 = 8.7 + 2.2i$ for Ag_2S (ref.14) one can calculate that a 1 nm layer of Ag_2S results in a shift of the ATR curve of 0.22° and an increase of its FWHM of 0.05° .

Experimentally the deterioration of the film resulted mainly in a shift of the ATR curve. Under the conditions in our laboratory the growth of Ag_2S , as derived from the measured change in the ATR curve, was limited to 0.1-0.2 nm per day, allowing us to work a couple of days with each new film.

The silver can be protected against sulfidation with an extra layer (5-10 nm) of special evaporation glass on top of the silver. We have tried this with success and the films thus prepared showed no further deterioration. All measurements presented in this chapter are performed on unprotected silver films, because the protective glass layer changes the character of the SP, one measures (slightly) different ATR curves, and this complicates the physical problem.

A second technique to protect the silver film against sulfidation uses a vacuum pump to remove the air in contact with the silver. We did use a vacuum pump in some of the measurements and the deterioration of the silver film clearly slowed down, but the ease of alignment was also reduced and most of the measurements were done on a "hit and run" basis.

The angle-resolved ATR technique is very sensitive to disturbances of the surface and can be used to determine the presence and the character of upper layers as thin as a monolayer or even a sub-monolayer. The accuracy of the ATR probe has been demonstrated in many articles.¹⁵⁻¹⁷

4.6 Introduction to ultra short surface-plasmon and phonon dynamics

We have extended the angle-resolved ATR technique to a new time-resolved and position-resolved (pump-probe) ATR technique. We have studied a 45 nm film of silver evaporated on a prism of BK7 glass at room temperature. Two synchronously-pumped mode-locked dye lasers are tuned at slightly different frequencies and each one produces a synchronized train of pulses with a typical FWHM of 5 ps at a repetition rate of 82 MHz (12.2 ns). The two beams are almost collinear and they both reach the silver film from the glass side at approximately the plasmon angle ($\theta=43^\circ$ in our case). The experimental geometry is sketched in fig.(4.4.1), where the single line now represents both collinear beams. Each yellow pump pulse creates SP, propagating along the silver film at almost the speed of light. The energy dumped by the decaying "yellow" SP changes the dielectric constant of silver temporally. After a variable delay the red probe pulse measures the, slightly changed, reflectivity of the glass-silver-air system in the same ATR configuration. The results presented in the following sections are an extension of an article published in Physical Review Letters.¹⁸

Naturally the red probe beam also creates SP but, as the yellow pump beam is modulated and as the reflected intensity of the red probe beam is detected synchronously, heating due to the creation of "red" SP goes on undetected. Notice that we have three basic experimental variables : the angle of incidence of the (almost) collinear beams, the spatial overlap between their foci and the time delay between the pump and the probe pulses.

Under typical experimental conditions we focus two laser beams of 15 mW average power each on the film. One expects the temperature of the film to be independent of the direction normal to the interface after a few

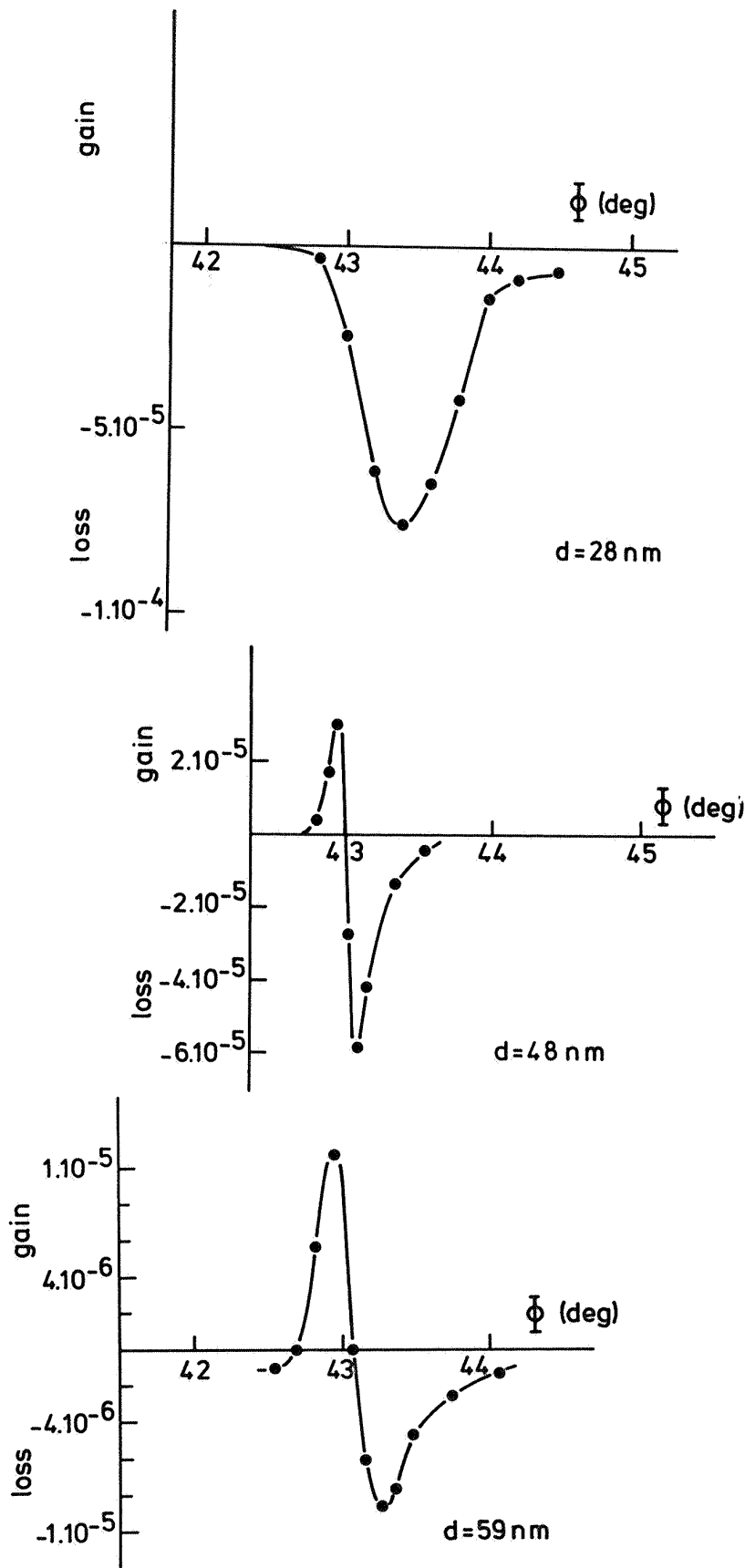


Fig.4.6.1 :

A yellow pump pulse heats a metal film. Some 100 ps later a red probe pulse experiences a slight change in reflectivity as a result of the rise in temperature of the metal. This pump-probe ATR signal is plotted for the BK7-Ag-air system as a function of the angle of incidence of both collinear beams for three films with different thickness. The film thicknesses were 28 nm, 48 nm and 59 nm for the upper, middle and lower figure respectively.

picoseconds. The calculated rise in temperature, corresponding to the energy dumped by one laser pulse, is about 1 K. The resulting gain/loss in the intensity of the reflected probe beam is typical 10^{-4} - 10^{-5} . The difference in color of the probe and the pump beam made the separation at the detection stage easy and our special double-modulation technique at 8.4 MHz allows us to reach almost the quantum-noise limit and detect changes in the reflectivity of 2×10^{-7} (RC-time=0.4 s).

The stronger we focus the beams onto the film the more signal we get until the opening angle of the focused beams becomes comparable with the width of the ATR curve. At this point the signal strength levels off and even decreases. The angular dependence of the ATR is smeared out for strong focusing. A 45 mm lens produced the strongest signal in our case. For a 127 mm lens a better angular resolution of the induced change in reflectivity could be obtained.

In fig.(4.6.1) the pump-probe ATR signal is presented as a function of the angle of incidence of the beams for three different film thicknesses. Before being fully able to understand these results I will first, in section (4.7) and (4.8), present the measurements obtained by scanning the other two degrees of freedom: the spatial overlap and the temporal overlap of the pump and the probe pulses.

Shifting the probe spot with respect to the pump spot we were able to monitor the surface-plasmon propagation. We have measured the dephasing of the surface plasmons via their mean-free path $\ell=13\mu\text{m}$ and a momentum life time of 48 fs was found. These measurements are presented in section (4.7).

We have also studied the change in reflectivity as a function of the time delay between the pump and the probe pulse. As we have a time resolution of 6 ps, including time jitter, there is no possibility to observe the decay of the SP directly in the time domain, but we can look at their decay products. After the very rapid plasmon decay the energy is transferred into a strain wave and an increase in temperature of the silver film. We have observed the acoustic phonons, associated with the strain, bouncing up and down the silver film as well as the heat diffusion on a picosecond time scale. The dynamics of both is presented in the time-resolved ATR experiments that make up section (4.8). In section (4.9) I will present a theory based on the temperature and pressure dependence of the dielectric constant of silver to describe both qualitative and quantitative the main results of the presented measurements.

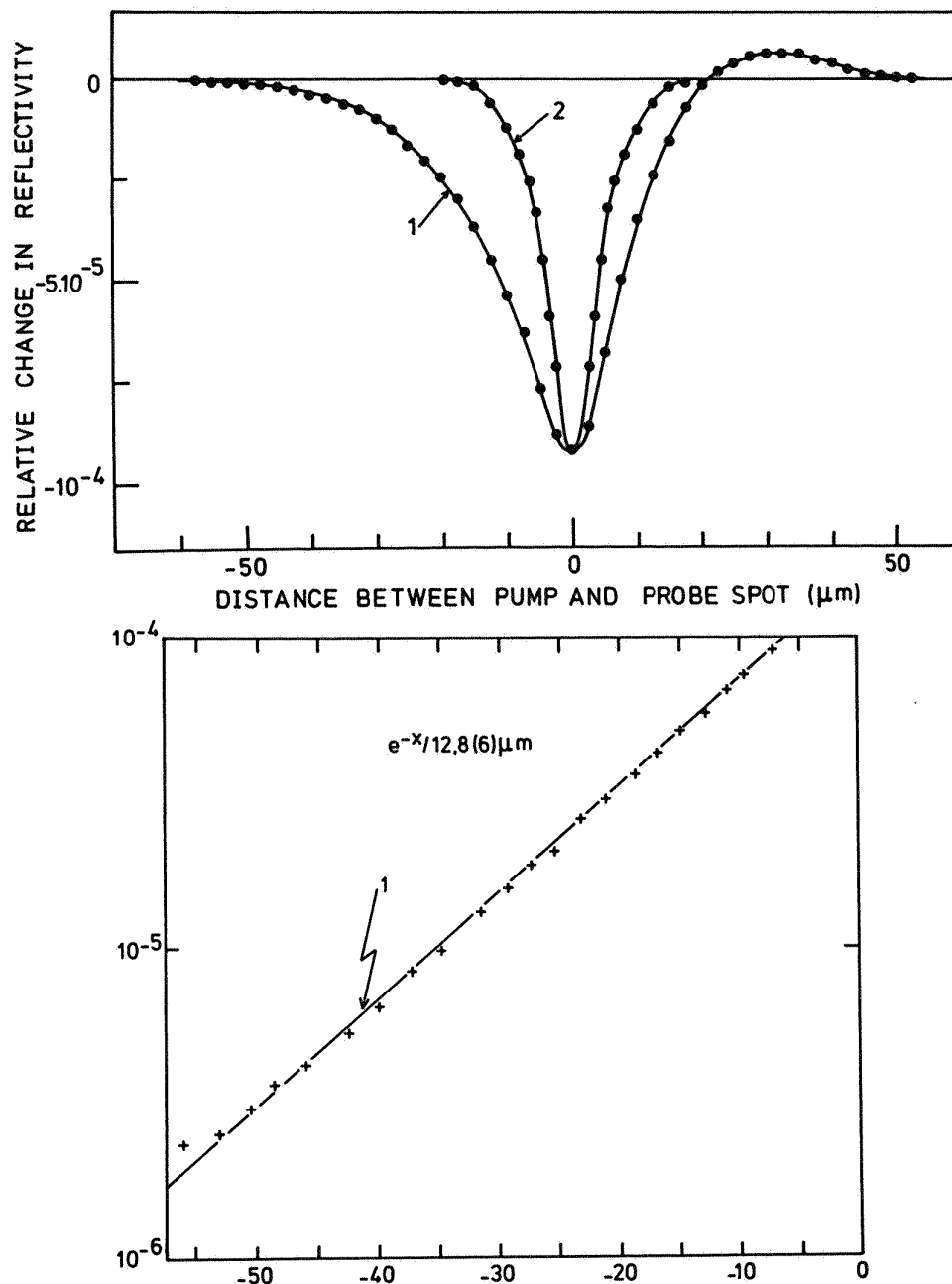


Fig.4.7.1 The change in reflectivity of a probe pulse, arriving a few tens of picoseconds after the pump pulse as a function of the spatial overlap between the focused pump and probe beam. In the upper graph a linear scale is used. Curve 1 displays the change in reflectivity for a displacement in the direction of propagation of the SP, whereas curve 2 shows the same effect for a perpendicular displacement. In the lower graph the left part of curve 1 is plotted on a logarithmic scale to demonstrate its exponential shape.

4.7 Surface-plasmon dynamics

Earlier studies on the propagation of SP were performed with only one laser beam¹⁹⁻²¹. In these experiments the profile of the reflected beam is compared with the incoming profile, making it possible to derive the mean free path of the SP, but only when it is relatively long. To comply with the restriction of a long lifetime these measurements had to be done on very photon-like SP, like infrared SP and long-range SP. The pump-probe technique we introduce does not have this restriction and enabled us to observe short-lived SP.

Propagation effects will lead to a plasmon density that is spatially different from the spot profile of the incoming laser beam. Conservation of momentum along the film (phase matching) restricts the propagation of the SP to one direction. One thus expects the heat distribution along the film, resulting from the decay of SP, to have an exponential tail. Experimentally we observe the spatial distribution of heat by moving the red probe spot with respect to the yellow pump spot over the film, meanwhile monitoring the signal strength. The time-delay between the pump and the probe pulse as well as the angle of incidence is kept fixed in this experiment.

We expect the mean free path l of optical SP to be small. Both laser beams thus had to be focused very tightly to see effects of the propagation of SP. Using a two-lens combination in the form of a telescope we had effectively a 14 mm lens, with a working distance of 80 mm. The spot profile of each focus was an ellipse with a short axis of about 6 μm and a 1.4 times larger long axis. Making use of the diminution of the telescope we could scan the probe spot with respect to the pump spot to better than 1 μm . Due to strong focusing the opening angle (numerical aperture) of the laser beams is larger than the angular width of the ATR curve. This smears out the ATR curve and the angle changes occurring simultaneously with the displacement can be neglected.

In fig.(4.7.1)a the change in reflectivity is pictured as a function of the spatial overlap between both lasers in the direction parallel as well as perpendicular to the wave vector, the latter as a check on the spot size. The measurements show a striking appearance of both negative signals (decrease in reflection) as well as positive signals, features which reproduced satisfactorily. A perfect exponential tail (more than two decades) is observed when the spot of the probe beam lies upstream with

respect to the spot of the pump beam, as is demonstrated in fig.(4.7.1)b. This is at the other side as we had expected it to be! When the spot of the pump beam was situated downstream of the probe spot no exponential spatial decay could be detected in the small positive signal. The decay length related to the exponential tail is $12.8(7) \mu\text{m}$.

To explain the appearance of an increase as well as a decrease in the reflectivity of the probe beam due to heating and induced strain one has to notice that the red probe beam creates SP as well. In ref.19-21 the reflection of a Gaussian-shaped laser beam from a glass-metal-air system, at an angle of incidence close to the plasmon angle, is calculated rigorously. Part of the light incident on the interface is directly reflected (mirror reflection). The rest excites SP at the silver-air boundary. When the angle of incidence of the laser differs from the plasmon angle the SP are excited off resonance and they accumulate a phase difference with respect to the phase of the laser when they move along the interface. As a result there will be a phase difference between light emitted by the radiatively decaying SP and the direct mirror reflection (see also section (5.4)). Reflectance thus is a non-local property and any change in the reflectivity of the red probe beam is a result of a change in the balance between SP generation at one place and radiative decay at another.

From the last paragraph it is clear how the reflectivity of the red probe beam can be influenced even when the probe spot lies upstream with respect to the pump. In this situation the "red" SP are created in a cool region and after a propagation of a few μm decay in a hotter region, being slightly different through a different ϵ_{Ag} (thermal gradients along the film of almost 10^6 K/m). This influences the radiative decay of the "red" SP and consequently the overall reflectivity. Although a detailed geometrical description is beyond the scope of this thesis the idea of a balance explains the induced increase as well as the decrease of the reflectivity. As I have only observed an exponential decay when the probe lies upstream of the pump I must conclude that the radiative decay is apparently much easier influenced by heating than the SP excitation process is.

The exponential "heat" tail of $12.8(7) \mu\text{m}$ signifies the decay of the light intensity associated with the SP. As the SP density is proportional to this intensity, the mean free path of the SP is just $\ell=12.8(7) \mu\text{m}$. From the theoretical dispersion relation of the SP we know their group velocity to be $0.89c$ so the measured mean free path reflects a momentum life time of

48(3) fs. We use the word momentum life time because elastic as well as inelastic processes can scatter SP to other directions (momentum states). One can associate these two contributions with pure dephasing and energy decay respectively. The dephasing time (T_2) is usually defined as the decay time of the amplitude of the excitation and is consequently twice the value determined from the intensity "decay" ($T_2=96$ fs).

The energy decay can be separated into a radiative process, SP emitted into the glass in the form of photons, and a non-radiative process, a multi-phonon decay process. It is very difficult to separate these two processes, but this has been done with the use of photo-acoustic techniques.^{22,23} For our film thickness both energy-decay processes are of equal importance. The measured mean free path corresponds approximately to an effective imaginary part of the dielectric constant of silver of $\epsilon_1=1.1$. Comparing this with the value $\epsilon_1=0.6$ given in the literature, we have reason to believe that elastic scattering, due to impurities and roughness, does also contribute in our experiment though not dominantly. This view is supported by the spread in quality of the various samples. Studies on the same film yet older and already slightly "eroded" resulted in a mean free path of $\ell=9.3(6)$ μm . This indicates an increase in the scattering of SP as the film grows old.

Concluding: It is rewarding to see that one can obtain this tremendous time resolution simply by observing the effect of a change in the relative position of the pump and probe spot on the pump-probe ATR signal.

4.8 Phonon dynamics

The previous spatially-resolved data were obtained for a probe pulse arriving about hundred picoseconds after the pump pulse. It is also very interesting to observe the change in reflectivity as a function of time for fixed angle and exact overlap between the laser foci. As we have a time resolution of 6 ps there is no possibility to observe the decay of the SP directly in the time domain, but we can look at their decay products. For these measurements we used a weaker lens (127 mm) as there is no need for high spatial resolution.

For various angles we have measured the change in reflectivity during the first few hundred picosecond. The angles marked in fig.(4.8.1) gave the most interesting results. I have reproduced these runs in fig.(4.8.2). For the smallest angle of incidence $\theta=42.6^\circ$ a tiny "instantaneous" increase of

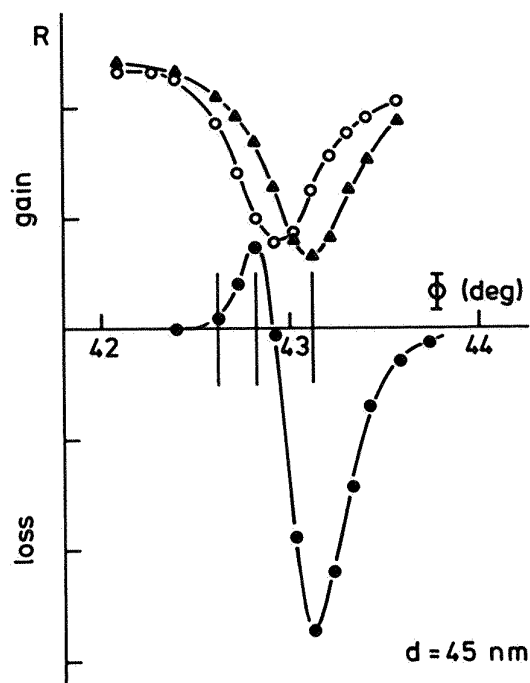
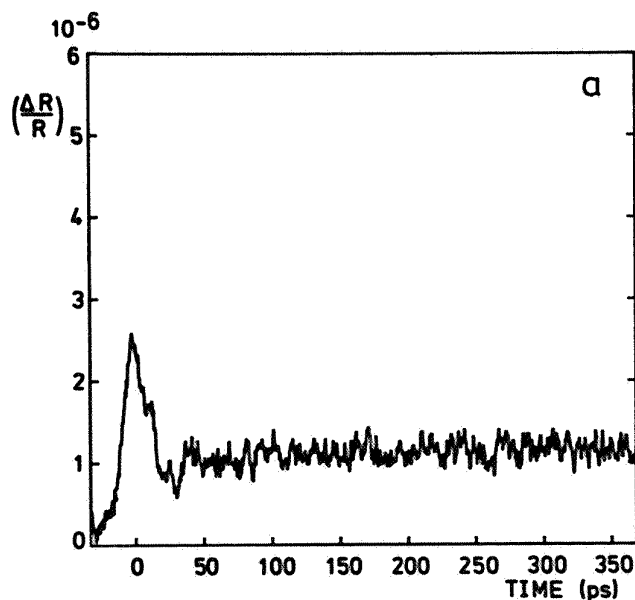


Fig.4.8.1 The change in reflectivity of a probe pulse, arriving a few tens of picoseconds after the pump as a function of the angle of incidence of the collinear beams. The angles marked gave the most interesting results, which are presented in fig.(4.8.2). The angle-dependence of the reflectivity (ATR-curve) of the red probe, left curve, and the yellow pump are also presented in this figure.



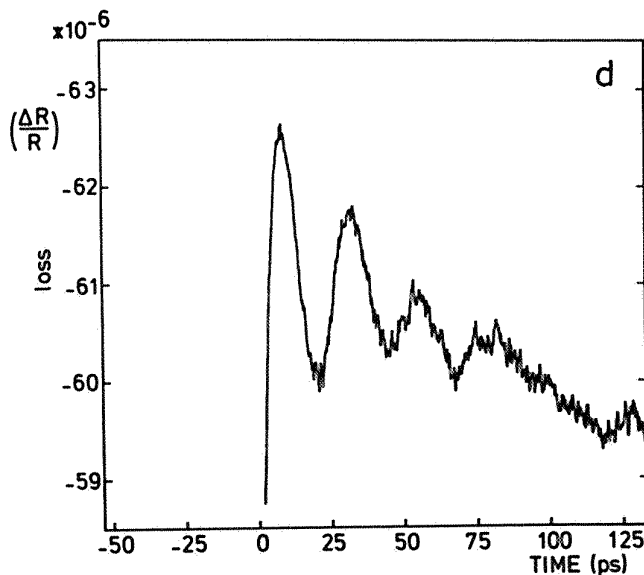
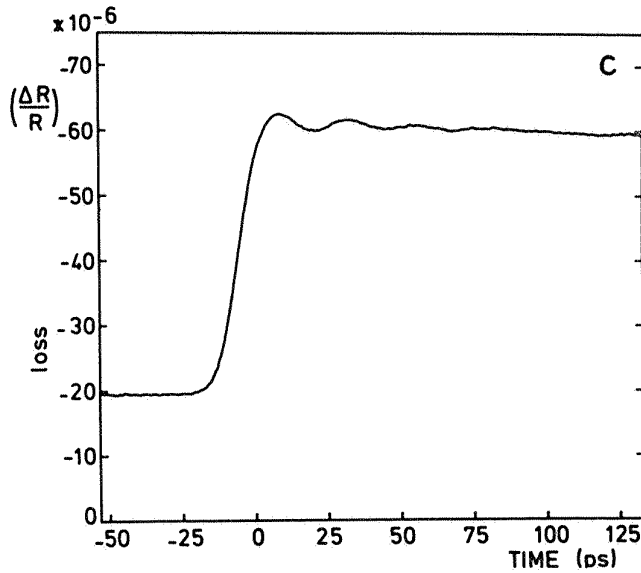
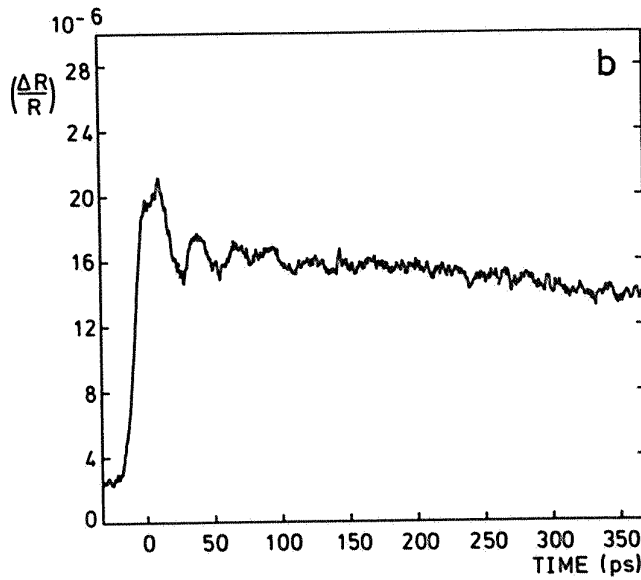


Fig.4.8.2 :

The change in reflectivity of the probe beam as a function of the time delay between the pump and the probe pulse, for three different angles of incidence. Run a is taken for $\theta=42.6^\circ$ and shows a strange peak around zero delay. The runs b and c are taken for $\theta=42.8^\circ$ and 43.1° respectively. Notice the oscillations present in both runs. Fig.(4.8.2)d is a blow-up of part of the run taken at $\theta=43.1^\circ$ (fig.(4.8.2)c). The noise in graph c is greatly reduced as it represents an average of 16 different runs.

the reflectivity appears at exact pulse overlap. At the moment we can only speculate about the physical processes that give rise to this tiny peak. It might be attributed to a non-equilibrium between the electron and the lattice temperature^{24,25}. For $\theta=42.8^\circ$ and $\theta=43.1^\circ$ an intriguing oscillation in the reflectivity appeared. The fact this oscillation was absent for $\theta=42.9$ seems to indicate it is related to the derivative of the reflectivity of the red probe beam as a function of the angle of incidence. The oscillations are better visible in another measurement plotted in fig.(4.8.3). These small and fast (24 ps) oscillations will be explained in terms of acoustic phonons bouncing up and down the film. Similar oscillations have been recently observed by Thomsen et al.^{26,27} in the absorption of a-As₂Te₃.

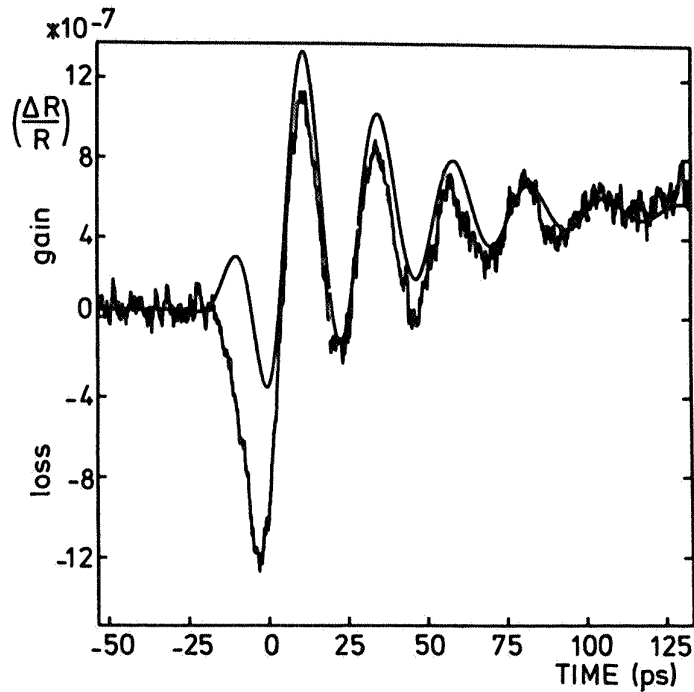


Fig.4.8.3 : A measurement showing in detail the short-time decay of the reflectivity (at -42.7°). This silver film differs from the one used for the runs in fig.(4.8.2) and more clearly shows the oscillations. The wiggles are due to acoustic phonons running up and down the silver film. They have an oscillation period of 23.8(3) ps. The decrease in amplitude is due to the 52 % acoustic reflection at the glass-silver interface.

When the relative weak oscillations due to the acoustic phonons have decayed we observe a further decay of the signal on a ns time scale. This long-time (ns) decay of the reflectivity results from the diffusion of heat along the silver film and, more importantly, the diffusion into the glass substrate. We will deal with it in the second part of this section.

The electric field associated with the surface plasmons has a penetration depth in the silver of only 12 nm, so most of the energy is released in a thin upper layer at the silver-air interface. The deposited energy first of all gives rise to an increase in the temperature but also creates an expansion of the lattice, part of it being stationary and part of it in the form of a "strain wave" travelling at the speed of sound perpendicular to the surface.²⁷ From a microscopic point of view acoustic phonons are generated by multi-phonon decay in the 12 nm thin upper layer and initially all directions of propagation are present. The phase relation between the "coherent" phonons (created at the same instant!) causes them to interfere destructively in all directions except perpendicular to the film. This gives rise to a strain wave in the macroscopic picture.

For an infinitely short laser pulse the wavelengths of the acoustic phonons will reflect the penetration depth of the light. For a laser pulse of finite duration the width of the phonon packet is spread out. The phonons generated by the front of the light pulse already move through the lattice while the back still generates new ones. As its width approaches the thickness of the silver film the phonon packet becomes more or less a broad modulation of the expansion of the lattice that bounces up and down the film, the most important wavelength present being twice the thickness of the film.

The experimental run of fig.(4.8.3) was fitted to an exponentially decaying sinusoidal curve, as our light pulses are relatively long. From the fit the oscillation period could be determined with one percent accuracy to be 23.8(3) ps. Using the 45 nm thickness of the film we calculate a longitudinal speed of sound of $v=3.78(5)$ km/s. The tiny difference with the sound velocity in bulk silver ($v=3.65$ km/s) should probably be attributed to the inaccuracy in the thickness measured with the quartz oscillator during the evaporation process.

The decay of the acoustic signal is almost completely due to transmission of phonons into the glass. At the silver-glass boundary the macroscopic acoustic reflection coefficient, as calculated from the acoustic

impedances of both materials²⁸, is 52 %. Our measurements agree with this reflection coefficient (measured 50 ± 5 %) and losses due to other scattering processes must therefore be weak. From our data we conclude that the lifetime of 42 GHz (24 ps) phonons in Ag is much more than 100 ps.

When the relatively weak oscillations due to the acoustic phonons have decayed we are left with the general rise in temperature of the film that decreases on a ns time scale as a result of the diffusion of the excess heat into the glass substrate and along the silver film (see fig.(4.8.4)).²⁹ Although the heat diffusion constant of silver is almost thousand times larger than that of BK7 glass the larger surface and larger thermal gradient perpendicular to the film make the heat diffusion into the glass dominant. This can also be concluded from the observed quasi-one-dimensional behavior of the heat diffusion; the ns decay is almost insensitive to the size of the focused laser spots.

We have measured the heat diffusion along the silver film and it is indeed very small. Scanning the position of the probe spot with respect to the pump spot, in the direction perpendicular to the propagation of SP, the enlargement of the heated spot from about 6 μm to about 7 μm in 12 ns could barely be resolved.

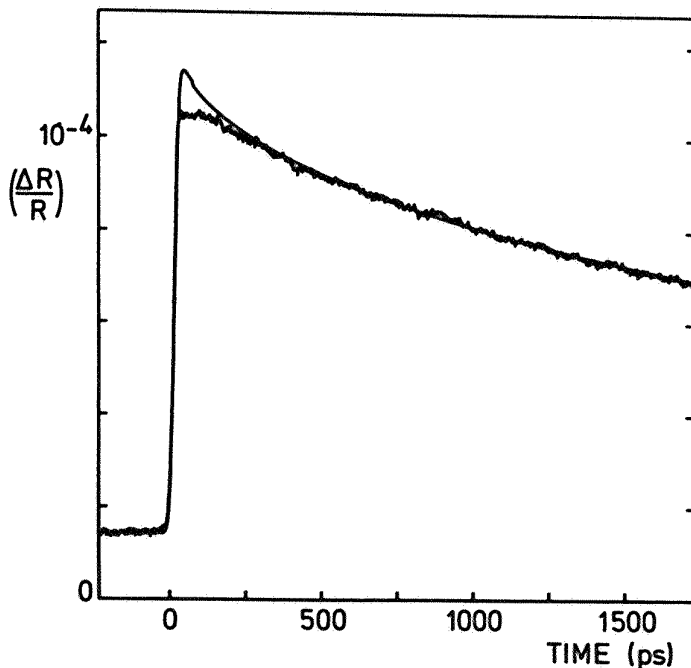


*Fig.4.8.4 :
The long-time change in reflectivity of the probe beam as a function of the time delay between the pump and the probe pulse. The nanosecond delay is a result of heat diffusion, primarily into the glass substrate.*

In fig.(4.8.4) an experimental run is presented in combination with a computer simulation of a simple one-dimensional heat-diffusion model. In this model the silver film is assumed to be at an uniform temperature at any time. This approximation is valid at times long after the pump pulse, but is certainly less good immediately after it heats the film, as we know the heat is preferentially dumped close to the silver-air interface and can not possibly diffuse fast enough. Assuming an uniform silver temperature the presence of the thin silver layer can be incorporated as a heat capacity in the boundary condition of the heat-diffusion equation of glass. In this model the one-dimensional heat diffusion is characterized by only one parameter τ_{heat} , which might be called the "heat-decay time". This characteristic time is equal to

$$\tau_{\text{heat}} = D(c_v d / \kappa)^2, \quad (4.8.1)$$

where D is the heat diffusion constant of the glass substrate [m^2s^{-1}], c_v is the specific heat of the silver [$\text{JK}^{-1}\text{m}^{-3}$], d is the thickness of the silver film and κ is the heat conductivity of the substrate [$\text{Js}^{-1}\text{K}^{-1}\text{m}^{-1}$]. The long-time changes in the reflectivity were practically independent of the angle of incidence θ , when this angle was close to the plasmon angle, and are excellently fitted with a heat diffusion constant $D=5.2(5)\times 10^{-7} \text{ m}^2\text{s}^{-1}$ for BK7 glass. This is in good agreement with the value given by the manufacturer.

A temperature rise of about one Kelvin per laser pulse has been calculated (section (4.9)). The average rise in temperature of the silver layer is far greater and diverges as $\sqrt{t}$ in a purely one-dimensional system. For diffusion lengths comparable with the size of the laser spot (a few μm) the three dimensional character of the problem fortunately removes the divergence. I estimate the average rise in temperature to be 50-100 Kelvin. This value is based on similar experiments (chapter 5) where, under certain circumstances, we observed boiling of the CS_2 or the CCl_4 , being in contact with the silver (as medium 3, instead of air). A three dimensional heat diffusion model, developed to calculate the steady state temperature distribution, produced comparable results.

When the angle of incidence differed much from the plasmon angle we measured a different (usually longer) long-time decay of the temperature. For certain angles however a faster decay (twice as fast) than the one we

normally measured could be observed. We attribute this fast diffusion to the existence of a peaked structure in the temperature profile of the silver film, enhancing the influence of heat diffusion along the film. When SP are excited off resonance the SP created upstream will interfere with the ones created downstream.¹⁹⁻²¹ In this way a complicated temperature distribution can be generated, in spite of the smooth intensity profile of the focused laser spots.

Observation of changes in the reflectivity of the glass-metal-air system from the glass side is just one way of observing the SP generation and subsequent decays. We have also observed changes in the reflectivity of a probe laser coming from the air side. Naturally the pump beam is still coming from the glass side, because this is the most efficient way to excite the SP. Although this method is about five times less sensitive than the one describe described before, we were able to see the long-time diffusion of heat as well as the 24 ps oscillation of the acoustic phonons even in this setup.

We have introduced a new sensitive method to probe ultra-fast surface dynamics. One can envisage many extensions and exciting applications of this contactless pump-probe technique. We only mention the feasibility to study electron-phonon dynamics. Recently Brorson et al.³⁰ have shown that, apart from a phonon packet, a bunch of hot electrons is generated. With fs light pulses they could observed the propagation of the electron packet, with approximately the Fermi velocity of the electrons, through the lattice. The ballistic nature of the heat transport made them conclude that the electron system was temporally out of equilibrium with the phonon system.

4.9 Induced changes in the ATR curve computed

In this section the previous experimental results will be analyzed in a more quantitative way. A model will be presented to describe the changes in the reflectivity of the glass-silver-air system resulting from heating and expansion.

The Kretschmann system contains three materials and the effect of heating on the optical properties of each must be analyzed. Starting with the air, calculations show that variations in its dielectric constant go unnoticed, as ϵ_{air} is close to one ($\epsilon_{\text{air}}=1.00055$, $T=293$ K, $P=1$ Bar) and hardly changes as a function of temperature. The inert nature of the air was

experimentally confirmed. Removing the air with a vacuum pump gave identical results.

The dielectric constant of the glass does change notably on heating. One of the two quantities that depends on ϵ_1 is the reflectance at the silver-glass interface (r_{12}) (see (4.4.9)). The heat-induced change in this quantity has only a minor effect on the overall reflectivity (r_{123}) and can be neglected. More drastic effects on r_{123} are expected from changes in the parallel momentum of the incident photons $k_{//} = n_1(\omega/c)\sin\theta_1$. This quantity seems to depend strongly on the dielectric constant of the glass. On further thought one notices that the incident laser, while entering the hotter region, is refracted on the gradient in dielectric constant in the glass. When this temperature gradient is perpendicular to the glass-metal interface the change in angle of incidence just compensates the change in dielectric constant and $k_{//}$ is unaffected. Snell's law of refraction by the way describes this invariance.

Apparently temperature changes in the air and the glass have hardly any effect on the overall reflectivity of the Kretschmann system (r_{123}). In the following paragraphs the effect of the temperature-induced changes in the silver film on the reflectivity will be evaluated. Even tiny changes in the dielectric constant of the silver have large influence on r_{123} , due to the resonant character of the SP generation. Unfortunately no value for the temperature dependence of the dielectric constant of silver around $\lambda=600$ nm has appeared in the literature yet. For the free electron contribution this dependence will therefore be estimated with the help of the Drude model:

$$\epsilon_{\text{free}} = - \frac{\omega_p^2}{(\omega^2 + i\omega\Gamma)} \approx - \frac{\omega_p^2}{\omega^2} + \frac{\omega_p^2\Gamma^2}{\omega^4} + i \frac{\omega_p^2\Gamma}{\omega^3}, \quad (4.1.1)$$

where the plasmon frequency ω_p and the collision rate of the electrons Γ both vary with the temperature. The contribution from the bound electrons to ϵ_{Ag} (around $\lambda=600$ nm) is expected to vary less dramatically with temperature than the free-electron contribution and is neglected.

Before evaluating the temperature dependence of ω_p and Γ , I want to divide the influence of heating in a pure temperature effect (at fixed volume) and an expansion effect. The expansion of the heated silver is frustrated in the transverse direction, because the hot spot is surrounded

by cold silver. The bulk Poisson ratio, being the ratio of relative transverse contraction to elongation of material under tensile stress (≈ 0.37 for silver), should be used to relate the "one-dimensional" expansion coefficient $\alpha = 1.9 \times 10^{-5} \text{ K}^{-1}$ to the volume expansion. For a limited temperature regime around ($T=293 \text{ K}$) one finds: $(1/n)(dn/dT) = -4.2 \times 10^{-5} \text{ K}^{-1}$.

The plasmon frequency ω_p is not affected by a pure temperature variation, but it does react on a change in the (electron) density. The plasmon frequency decreases when the lattice expands, according to $\omega_p = (ne^2/(\epsilon_0 m))^{1/2}$. With the use of the expansion just calculated, the temperature-induced changes of the plasmon frequency can be calculated: $(1/\omega_p)(d\omega_p/dT) = -2.1 \times 10^{-5} \text{ K}^{-1}$.

The damping rate Γ is primarily determined by electron-phonon interaction for silver at ($T=293 \text{ K}$). Electron-electron interaction plays a minor role. The damping rate Γ will thus be roughly proportional to the "phonon density", which is more easily altered by a pure temperature variation than by the slight change in density that usually accompanies this variation. As both the "optical" damping Γ and the DC electrical resistivity are related to electron-phonon interaction, in this temperature regime, we will assume that they react similar to changes in the temperature. The temperature dependence of Γ can then be found from the known behavior of the DC electrical resistivity. One gets: $(1/\Gamma)(d\Gamma/dT) = 2.6 \times 10^{-3} \text{ K}^{-1}$. This is in reasonable agreement with a calculation presented in ref.31.

On deriving the temperature dependence of ϵ_{Ag} , I was surprised by the almost complete separation of the effect of pure heating (at fixed volume) and the effect of expansion. The real part of ϵ_{Ag} is large and primarily sensitive to changes in ω_p , it is hardly influenced by pure heating and is mainly is affected by the thermally-induced expansion. On the other hand the imaginary part of ϵ_{Ag} reacts strongly on pure heating, via Γ , but is hardly affected by expansion. The result of my interpretation of the Drude model is:

$$(d\epsilon_r/dT) = 8.5 \times 10^{-4} \text{ K}^{-1} \quad (\text{essentially expansion, } \omega_p) \quad (4.9.1)$$

$$(d\epsilon_i/dT) = 1.5 \times 10^{-3} \text{ K}^{-1} \quad (\text{essentially pure heating, } \Gamma)$$

Although the silver film is preferentially heated in the top layer, the huge diffusion will distribute the heat uniformly in the direction perpendicular to the film in a few picoseconds. The temperature rise can then be easily estimated using the specific heat of silver ($2.5 \times 10^6 \text{ JK}^{-1} \text{m}^{-3}$), the energy per pulse of $1.3 \times 10^{-10} \text{ J}$ (10 mWatt) and the spot size ($w_0 = 20 \text{ } \mu\text{m}$, focusing with a 127 mm lens). At the plasmon angle all energy of the yellow beam is dumped into the silver film ($R \approx 0$) and a temperature jump at the heart of the focus of 0.9 K per pulse can be calculated.

The overall reflectivity r_{123} is the outcome of a detailed balance of SP generation at one position and radiative decay at another. Up to now no proper model has been found to include the exact temperature profile along the film. One is therefore forced to neglect the propagation of the SP, being somehow justified by the rather large spot size. The limited size of the hot spot will be disregarded and the whole silver film is assumed to rise uniformly in temperature, to the value derived for the centre of the hot spot. The numbers given below refer to the change in reflectivity of a plane wave incident on a silver film that is uniformly heated in temperature. The model is rather crude, and likely to grossly overestimate the effect, but very useful to get a feeling of what is happening in the pump-probe ATR experiment.

With the approximations mentioned above the reflectance r_{123} is solely determined by the parameters $\hat{k}_{//}$ and $\hat{\Delta k}_{//}$, and their dependences on ϵ_r and ϵ_i . $\hat{\Delta k}_{//}$ is also sensitive to the temperature-induced change in thickness d of the metal film, but this effect is small and can be neglected. The stationary change in thickness, resulting from the 0.9 K rise in temperature, is about 0.02 Angstroms. The dependence of $\hat{k}_{//}$ and $\hat{\Delta k}_{//}$ on ϵ_r and ϵ_i can be extracted from equation (4.4.7) and (4.4.8). Our calculations show that, for our film thickness, the temperature-induced change in $\hat{\Delta k}_{//}$ is always much smaller than the change in $\hat{k}_{//}$. The change in reflectivity measured in a pump-probe ATR experiment is thus mainly determined by the temperature dependence of $\hat{k}_{//}$. Substituting the derived dependences of ϵ_r and ϵ_i on temperature in equation (4.4.6), one finds :

$$(c/\omega)(d\hat{k}_{//}/dT) = 1.1 \times 10^{-6} \text{ K}^{-1} \text{ (dominated by changes in } \epsilon_r, \text{ expansion),}$$

$$(c/\omega)(d\hat{\Delta k}_{//}/dT) = 3.2 \times 10^{-6} \text{ K}^{-1} \text{ (dominated by changes in } \epsilon_i, \text{ pure heating).}$$

One might say a rise in temperature results in a change in shape of the ATR-curve. On heating the minimum of the curve shifts towards larger angles ($\hat{k}_{//}$ larger) and the curve as a whole broadens ($\hat{k}_{//}$ larger). This elegant view of shifting and broadening of the ATR curve immediately yields the change in reflectivity of a red probe pulse, due to heating by a yellow pump pulse, as a function of the angle of incidence. In fig.(4.9.1) the situation is pictured. At angles larger than the plasmon angle the presence of the pump beam will induce a loss on the probe beam. At smaller angles the shift of the ATR curve to the right, which induces a gain on the probe beam, is counteracted by the broadening of the ATR curve. The signal will thus certainly be smaller, than for larger angles, and will tend to be positive. The model predicts the sign and angle dependence of the observed changes in reflectivity very well. Especially the data presented in fig.(4.8.1) clearly show the agreement between experiment and theory.

In computing the change in reflectivity one is faced with the discrepancy between the measured width of the ATR curve and the smaller width calculated from $\epsilon_{Ag} = -16 + 0.6i$. By using the values given by the Drude model the sensitivity of the ATR curve to changes in $\hat{k}_{//}$ will probably be overestimated. The reflectivity is maximally influenced in the wings of the ATR curve. For the optimum thickness the calculated maximum temperature-induced loss on the probe beam due to broadening of the ATR curve is about 4×10^{-4} . The effective shift of the ATR curve results in a maximum variation in reflectivity of about 4×10^{-4} , being either positive or negative.

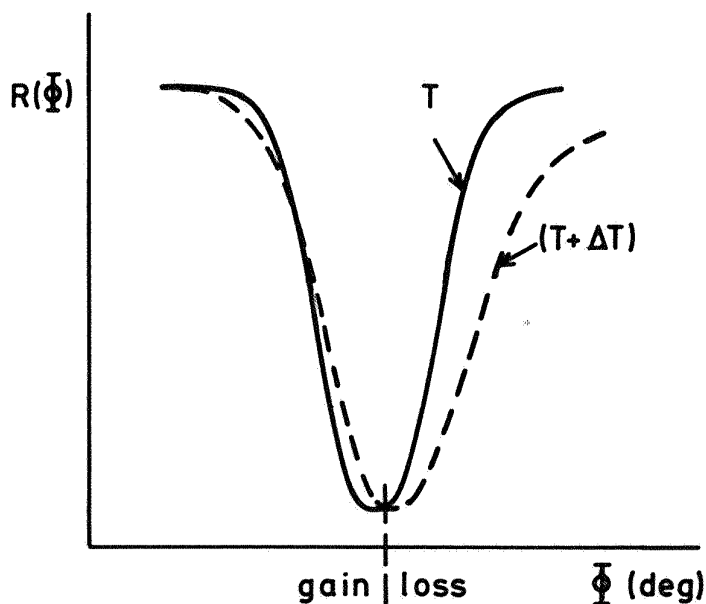


Fig.4.9.1 :
The effect of heating
on the shape of the
ATR curve as predicted
by the model developed
in this section.

The calculated signal strength is almost a factor ten larger than the value measured experimentally. We already predicted the theoretical value would end up too large for the following reasons: (1) We have assumed all the energy of the pump beam is dissipated. This is only correct when the angle of incidence of the yellow pump beam equals the plasmon angle (for this color). (2) The silver film is only locally heated, whereas the model assumes the temperature of the whole silver film increases to a temperature equivalent with the temperature at the hottest point in the experiment. (3) The measured ATR curve is almost twice as wide, and probably half as sensitive to temperature variations, than the ATR curve derived from the Drude model. Keeping these points in minds there is reasonable quantitative agreement between theory and experiment. For further studies an extension of the simple model presented here is certainly advisable. With this extended model one should also be able to predict the measured thickness dependence of the signal. Experimentally we have found that the time-resolved ATR signal was larger for a 28 nm film than for a 48 nm film and very small for a 59 nm film.

Having described the "stationary" or long-term change in reflectivity quantitatively, I will now pay attention to the transient effects. The observed oscillation in the reflectivity is related to a expansion-contraction wave propagating through the film or, from a microscopically point of view, phonons bouncing up and down the film. The effect of this wave on the reflectivity can only be calculated with a model that makes allowance for the index of refraction profile perpendicular to the silver film. Calculations of the reflectivity of a medium with a continuously varying index of refraction have appeared in the literature^{27,32}, yet not for the complicated case of SP resonance.

Not being able to predict the amplitude of the acoustic signal we can try to predict its phase. Experimentally the increase in signal strength around pulse overlap is well fitted by an error function. From this fit the position of pulse overlap can be derived. The amplitude of the acoustic signal reaches an optimum about 10-15 ps after the peak of the "yellow" excitation pulse. This time delay is expected for two reasons. First the produced phonons propagate downwards as well as upwards. It takes time for the phonons to leave the excitation region. Secondly the phase of the phonons at excitation is such that the lattice just starts expanding. It takes time for the lattice to reach its maximum expansion. When the angle of

incidence is larger than the plasmon angle a maximum-induced *loss* is reached 10-15 ps after the peak of the excitation pulse. When the angle of incidence is smaller than the plasmon angle the *gain* is maximum at that time. Both results correspond to an effective shift of the ATR curve to the right, as predicted by our model.

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CHAPTER 5 : Surface-enhanced stimulated Raman scattering

5.1 Surface plasmons and nonlinear optical effects

Many authors^{1,2} have mentioned the possibility to use surface plasmons (SP) as an efficient way to probe the physics of molecules close to a metal layer. Kretschmann was the first to demonstrate how SP could be efficiently generated at the interface of a metal and a dielectric in what is now called the Kretschmann configuration. This configuration is thoroughly described in section (4.4) and consists of a thin metal layer evaporated on a transparent (glass) substrate with a dielectric, denoted as medium 3, on top. A laser incident from the glass side can create SP at the metal-medium 3 interface, when its angle of incidence is close to the plasmon angle. In this chapter it will be shown that the EM field strength at the metal-medium 3 interface, which is associated with the SP, can be far larger than the field of the incident laser beam. In some cases the intensity enhancement can be almost a factor 100. The origin of this "surface enhancement" can be intuitively understood when the metal-medium 3 interface is interpreted as a cavity that confines EM radiation, in the form of SP. The EM field is confined, just like the radiation inside an etalon, and the intensity can therefore, in theory at least, be much larger than the EM field of the incident radiation, without violation of the law of conservation of energy. A quality factor Q can be associated with this cavity similar to the quality factor of an etalon, the difference being the absence of real transmitted light in the Kretschmann configuration. Simulations have shown that the field enhancement common to SP is also obtainable with related types of metal (and/or) dielectric cavities.³

The field enhancement resulting from the generation of SP has been used in various experiment to accurately probe properties of thin films. Even if the dielectric on top of the metal is not a thin film, but (semi-infinite) bulk material, the properties of molecules close to the metal-dielectric interface can be selectively probed, because the EM field associated with the SP extends only a few tens or a few hundreds of nm into the dielectric. The successful use of SP has been demonstrated in various optical techniques. There have been e.g. publications on "surface-enhanced" Raman scattering^{4,5}, "surface-enhanced" Brillouin scattering⁶ and "surface-enhanced" optical second-harmonic generation^{7,8}. In all these experiments

the SP were excited via the Kretschmann prism coupling configuration, and the signals were strongly enhanced when the angle of incidence of the exciting beam approached the plasmon angle. The emitted radiation was either observed at the "dielectric side" of the metal-dielectric interface⁵, or at the "substrate side"⁴. The Otto configuration is less popular for measurements on surface enhancement, because in this configuration a coupling prism is brought into, or against, the dielectric and the behavior of the dielectric will probably be influenced.

Nonlinear optical techniques seem to be very suitable to probe the properties of thin films and surfaces, as nonlinear effects are per definition more sensitive to the field enhancement than linear optical effects are. SP can be interpreted as a kind of (dressed) photons localized in the direction perpendicular to the interface. Ideas introduced in (three-dimensional) nonlinear optics are very well applicable to the nonlinear-optical theory of SP. A convincing example is "surface-enhanced" second-harmonic generation.^{9,10} This process can be considered as the simultaneous annihilation of two SP of frequency ω and the creation of one SP of frequency 2ω . For optimum second-harmonic generation the angle between the two incident SP should satisfy the phase-matching condition for SP.

An interesting question is whether the presence of a metal layer influences the dynamics of molecules close to this metal layer. To answer this question a distinction has to be made between the "intrinsic" properties of the molecules, which are related to their electronic structure and the positions and properties of their eigenstates, and their radiative properties. The "intrinsic" properties will hardly change by the presence of the metal. Merely the first few layers closest to the metal will be "intrinsically" changed by the van der Waals interaction or by more drastic processes like chemisorption. As the EM field associated with the SP penetrates typically over hundreds of layers, changes in the dynamics of the first few (surface) layers are probably not discernible.

In some specific situations a giant surface enhancement can increase the signal arising from just these surface layers to immense proportions (factors 10^4 - 10^6).¹¹⁻¹³ The giant surface enhancement is not yet completely understood and various models have been proposed for its explanation.¹¹ Experimentally giant-surface-enhanced Raman seems to be related to roughness of the surface and to chemical binding of molecules to the surface. The effect has been observed with metal films that break up in metal islands and

in colloidal suspensions of metal particles as well. For extremely flat films giant surface enhancement is not observable. Although our films are certainly not ideally flat, we found no experimental evidence for giant surface enhancement.

Whereas the presence of the metal will change the "intrinsic" properties of only the first few layers of molecules, the EM properties of far more molecules will be changed. One way to describe the change in EM properties is to let the emitted radiation reflect at the interface between medium 3 and the metal. The possibility of reabsorption of reflected radiation complicates the radiative behavior of the molecules. Another way to describe the change in EM properties is to let the emitted radiation create SP at the metal-dielectric interface. The coupling of the excited molecules to the SP can be very efficient and is often the dominant decay channel in fluorescence. This leads to a fluorescence decay time that is strongly dependent on the distance between the excited molecule and the metal.^{14,15}

In the previous paragraph the change in EM behavior of molecules close to a metal was depicted in general terms. Spontaneous fluctuations in the molecular dipole moment will be influenced in a similar manner, via coupling to the SP. One thus expects the dynamics of an infrared-active mode, being related to $\langle \tilde{\mu}(t) \tilde{\mu}(0) \rangle$, to be clearly affected by the presence of a metal. The dynamics of a Raman-active mode is related to fluctuations of the linear susceptibility in time ($\langle \tilde{\alpha}(t) \tilde{\alpha}(0) \rangle$) and one does not expect these to be dependent strongly on the environment. Hence, one hardly expects the metal to influence the dynamics of Raman-active modes. The difference in behavior of Raman-active modes and infrared-active modes stems from the fact that the excited Raman-active molecules don't radiate directly, and merely scatter incident radiation in an inelastic way, while infrared-active molecules do radiate. They "communicate" via electric dipole-dipole interaction and this long-range interaction is disturbed through coupling with SP.

Although the dynamics of a Raman-active mode is probably not influenced by the presence of the metal, and the time response is expected to resemble the bulk response, the magnitude of the response is of course strongly affected by the metal. We plan to make use of the SP resonance to enhance the signal strength and tried to use this surface enhancement to study stimulated Raman scattering (SRS) of molecules close to a metal. For this experiment two laser beams must be focused onto a metal layer to create SP

in the Kretschmann geometry. When the frequency difference between both lasers is equal to the frequency of a Raman-active mode of medium 3, surface-enhanced SRS should be observable in the form of a change in intensity of the reflected beams. For medium 3 we have chosen either CS₂ or CCl₄. In the sections (5.2)-(5.5) the theory of "surface-enhanced" SRS will be described quite extensively. The signal strength one expects in such an experiment will be calculated, using two different points of view.

In section (5.6) it will be shown that, just like in chapter 4, the measured ATR curves were wider than theory predicts. The discrepancy must be caused by the presence of additional scattering mechanisms for SP, which have a negative influence on the practically-attainable surface enhancement. A new effect was discovered when the laser beams were focused at the metal film. We observed large deformations of the ATR curve and hysteresis in the reflectivity. Both effects are discussed in section (5.7). The deformation is based on the fact that the local heating affects the index of refraction of medium 3, which in its turn is reflected in the SP characteristics. Analyzing the deformed ATR curves the average local temperature at the interface of medium 3 and the metal could be determined and the superheating that turned out to be present in medium 3 could be calculated. When we searched for surface-enhanced SRS, many other interesting new effects were observable. These effects are introduced in section (5.8). The time-dependent change in temperature of the metal layer, similar to the results presented in chapter 4, was one of the observed phenomena. Time-dependent diffusion of heat into medium 3 was another phenomenon that could be observed. These thermal effects were strong and probably drowned the surface-enhanced stimulated Raman scattering. Up to now we have been unable to detect surface-enhanced SRS.

5.2 Field enhancement due to surface plasmons

In this paragraph the enhancement of the local EM field, which is associated with the surface plasmon resonance, will be derived in a quantitative way. Replacing air, used in chapter 4, with a much more condensed medium 3 we intend to use this local intensity enhancement to accurately study molecules situated close to the silver film with the stimulated Raman effect.

Tracing all reflections in the glass-silver-medium 3 system the ratio

of the electric field parallel to the interface in medium 3 to this field in medium 1 (glass) is easily found to be^{1,2}

$$t_{123} = \frac{E_{//,3}}{E_{//,1}} = \frac{t_{12}t_{23} e^{ik_2d}}{(1 + r_{12}r_{23}e^{2ik_2d})}, \quad (5.2.1)$$

$$t_{123} = \frac{4k_2k_3\epsilon_1\epsilon_2 e^{ik_2d}}{((\epsilon_1k_2 + \epsilon_2k_1)(\epsilon_2k_3 + \epsilon_3k_2) + (\epsilon_1k_2 - \epsilon_2k_1)(\epsilon_2k_3 - \epsilon_3k_2)e^{2ik_2d})}, \quad (5.2.2)$$

where $k_i = (\epsilon_i(\omega/c)^2 - k_{//}^2)^{1/2}$ (see section (4.2)).

The equations given above accurately describe the "transmission" of incident light, but they are difficult to handle as all k_i 's depend on $k_{//}$, which is related to the angle of incidence. The ratio of the local intensity in medium 3 close to the silver film to the intensity of the original beam can be derived from t_{123} by first determining the total electric field (dividing by $\cos\theta$), squaring the result and finally multiplying it with the index of refraction. I have tried to clean up formula (5.2.2), making use of the parameters $\hat{k}_{//}$ and $\hat{\Delta k}_{//}$, which already proved their handiness in the previous chapter. This derivation, like many others presented in this chapter, depends critically on the assumption that the metal is a good conductor at optical frequencies ($|r_{12}|=1$). Expanding formula (5.2.2) around the SP resonance, the intensity enhancement of the incoming light, being denoted as K_{in} , is given by

$$K_{in} = \frac{\text{Intensity 3}}{\text{Intensity 1}} = \frac{|\epsilon_2|\epsilon_3}{|\epsilon_2^2 - \epsilon_3^2|} \frac{|\epsilon_2\epsilon_3 - \epsilon_1\epsilon_2 - \epsilon_1\epsilon_3|^{1/2}}{(\epsilon_1\epsilon_3)^{1/2}} \frac{4 \hat{k}_{//}' \hat{\Delta k}_{//}}{|k_{//} - \hat{k}_{//} - \hat{\Delta k}_{//}|^2}. \quad (5.2.3)$$

The factors containing the ϵ_i 's combine to a value that is usually in the range of 0.1-0.2. The angular dependence of the enhancement has approximately a Lorentzian-shaped maximum around the plasmon angle. Optimum enhancement of the local field is reached at the minimum in the attenuated total reflection curve. As both effects originate from the possibility to excite SP this was expected. The intensity enhancement at the optimum angle of incidence, is roughly proportional to $\{(4\hat{k}_{//}'\hat{\Delta k}_{//})/(\hat{k}_{//} + \hat{\Delta k}_{//})^2\}$. As noted before $(\hat{k}_{//} + \hat{\Delta k}_{//})$, which clearly plays a crucial role in the attainable enhancement factor, reflects the damping of the SP. To be more specific,

$2(\hat{k}_{//}'' + \Delta \hat{k}_{//}'')$ equals the inverse mean free path of the SP. This mean free path is the smaller the larger the index of refraction of medium 3 is. As a consequence "surface enhancement" is negatively influenced by a large index of refraction of the dielectric under study. Unfortunately large Raman activities per unit volume are only obtainable in optical dense media.

Let us now consider the, still hypothetical, case that the molecules making up medium 3, emit radiation towards the metal layer. This situation arises e.g. when (Stokes) radiation is emitted by Raman-active molecules, a situation treated in the sections (5.3)-(5.5). The emitted radiation can couple through the metal layer and emerge into the glass substrate. The efficiency to couple light out of the Kretschmann system is evidently related to the efficiency to couple light into the system and is, in a similar way, influenced by the SP resonance. The outcoupling efficiency can be far greater than one, meaning that the intensity of the output radiation is intensified when it is coupled out of the system! The intensity enhancement of the outgoing radiation, being denoted as K_{out} , is given by

$$\frac{K_{out}}{K_{in}} = \frac{\epsilon_1((c/\omega)^2 k_{//}^2 - \epsilon_3)}{\epsilon_3(\epsilon_1 - (c/\omega)^2 k_{//}^2)} = \frac{\epsilon_1 \epsilon_3}{(\epsilon_2 \epsilon_3 - \epsilon_1 \epsilon_2 - \epsilon_1 \epsilon_3)}, \quad (5.2.4)$$

$$(K_{in} K_{out})^{1/2} = |t_{123} t_{321}| = \frac{|\epsilon_2| \epsilon_3}{|\epsilon_2^2 - \epsilon_3^2|} \frac{4 \hat{k}_{//}' \hat{k}_{//}''}{|k_{//} - \hat{k}_{//} - \Delta \hat{k}_{//}|^2}, \quad (5.2.5)$$

where K_{out} is the ratio of the intensity in the glass substrate to the intensity of the "outward-going" radiation in medium 3.

As an example I will calculate the intensity enhancement for two Kretschmann configurations, for optimum film thickness $(\hat{k}_{//}'' - \Delta \hat{k}_{//}'')$ and optimum angle of incidence (the plasmon angle), using the "literature value" of $\epsilon_{Ag} = -16 + 0.6i$ ($\lambda=600$ nm). For the BK7-Ag-Air system, on which the measurements in chapter 4 are performed, one finds the following values

$$\epsilon_1=2.30, \quad \epsilon_3=1.00, \quad (c/\omega) \hat{k}_{//}'=1.033, \quad (c/\omega) \hat{k}_{//}''=0.00129, \quad \ell_{mfp}=18.5 \mu m, \\ K_{in}=142, \quad (K_{out}/K_{in})=0.124, \quad K_{out}=18.$$

Excitation of SP at the metal-medium 3 interface is only possible when the glass substrate that carries the metal film has a larger index of

refraction than medium 3. To study CS₂ and CCl₄ we have used a heavy soft glass, denoted as SF57 and produced by Schott. Its index of refraction ($n_1=1.82$) sufficiently exceeds the index of refraction of CS₂ ($n_3=1.62$) and of CCl₄ ($n_3=1.46$). For the SF57-Ag-CCl₄ system I find the following values $\epsilon_1=3.404$, $\epsilon_3=2.13$, $(c/\omega)\hat{k}_{//}=1.567$, $(c/\omega)\hat{k}_{//}''=0.00451$, $\ell_{mfp}=5.3 \mu\text{m}$, $K_{in}=64$, $(K_{out}/K_{in})=0.54$, $K_{out}=35$.

5.3 Stimulated Raman scattering (SRS) studied with surface plasmons

On coupling light into the Kretschmann configuration a huge EM field builds up at the metal-medium 3 interface. As the EM field, associated with SP, is basically two-dimensional and has an evanescent character in the direction perpendicular to the interface, only molecules very close to the interface can join in nonlinear optical processes. In this chapter the effects of the optical nonlinearity of medium 3 are evaluated and the (minor) optical nonlinearities of the metal are neglected. Because the effects are expected to be weak, the optical nonlinearity of medium 3 can be interpreted as a two-step process: the incident radiation creates a third-order polarization in medium 3, which then acts as a source term in Maxwell's equations and emits radiation. In this section a new formalism will be presented to calculate the efficiency with which radiation created in medium 3 is coupled through the metal film into the glass substrate.

The coherence of the laser light results in a phase relation between the induced dipoles and the radiation emitted by $P^{(3)}(\vec{r}, t)$ is coherent and directional. For many nonlinear processes, and for SRS in particular, the phase relation parallel to the surface is such ($k_{//} > \epsilon_3^{1/2}(\omega/c)$) that radiation emitted directly into medium 3 interferes destructively and can not propagate there. Constructive interference can occur for radiation moving through the metal into the glass substrate. This path is a very efficient one, when the frequency and parallel momentum of the emitted radiation fit the energy-impulse relation of the SP. The generated light is then emitted into the glass substrate approximately at the plasmon angle with the silver film. Instead of saying radiation is transmitted through the metal film, one might just as well say that excited molecules couple to SP, which then decay radiatively and emit into the prism.

In ref.16 a nice calculation is presented on the amount of radiation that is generated close to the interface of two semi-infinite media, one responding linear and one (medium 3) responding nonlinear to a driving EM field. Given the local EM fields, the nonlinear polarization induced in medium 3 is calculated with the help of the bulk nonlinear susceptibility of medium 3. This nonlinear polarization acts as a source term in Maxwell's equations and generates new EM radiation, which is purely TM-polarized, when the incident radiation is. In short equations (5.3.1) and (5.3.2), which are presented below together with a trial solution, have been solved in ref.16.

$$(\nabla \cdot \nabla) \vec{E} - \nabla(\nabla \cdot \vec{E}) + (\epsilon \omega^2 / c^2) \vec{E} = -\omega^2 / (\epsilon_0 c^2) \vec{P}_{NL} , \quad (5.3.1)$$

$$\nabla \cdot (\epsilon \epsilon_0 \vec{E} + \vec{P}) = 0 , \quad (5.3.2)$$

$$\vec{P}_{NL} = (1/2) \vec{P}_p \exp(i \vec{k}_p \vec{r} - i \omega t) + c.c. ,$$

$$\text{Medium 2 } (z < 0): \vec{E}_2 = (1/2) \vec{E}_2 \exp(i \vec{k}_2 \vec{r} - i \omega t) + c.c. ,$$

$$\text{Medium 3 } (z > 0): \vec{E}_3 = (1/2) \vec{E}_3 \exp(i \vec{k}_3 \vec{r} - i \omega t) + \vec{E}_p \exp(i \vec{k}_p \vec{r} - i \omega t) + c.c. ,$$

where $k_{p,x} = k_{2,x} = k_{3,x} = k_{//}$ and ∇ is the vector derivative.

The incident radiation is not explicitly presented in the trial solution as our only concern is the evaluation of the generated EM field. On mathematical grounds this generated EM field has been separated into a particular solution, having the same wave vector $\vec{k}_p$ as the nonlinear polarization and existing only in the nonlinear medium, and a homogeneous solution, having wave vectors $\vec{k}_2$ and $\vec{k}_3$ in medium 2 and medium 3 respectively.

The boundary conditions, requiring that the parallel component of $\vec{E}$ and $\vec{B}$ (non-magnetic media) be continuous at the interface, make this set of equations rigorously solvable, as has been done by DeMartini and Shen¹⁶. They derive expressions for the field amplitudes of the particular ($\vec{E}_p$) and the homogeneous ($\vec{E}_2$ and $\vec{E}_3$) solution.¹⁷

A description of the nonlinear interaction in the Kretschmann system is more difficult than the one given in ref.16, because it involves three media instead of two. In this thesis a Green's function approach will be used to derive the EM fields generated by a given nonlinear polarization in medium 3. For this purpose medium 3 is mentally divided in layers parallel

to the metal surface and the radiation emitted by each layer is evaluated separately. Due to coherence, the sheets of dipole densities thus formed, can radiate only in two directions, "upward" and "downward". Moreover part of the downward-propagating radiation will be reflected by the metal into the upward direction. Solving the equations (5.3.1) and (5.3.2) for a driving nonlinear polarization concentrated in a plane ($z=\xi$), as $\vec{P}_{NL} = (1/2)(p_x \vec{e}_x + p_z \vec{e}_z) \delta(z-\xi) e^{i(k_{//}x - \omega t)} + \text{c.c.}$, the following Green's function can be found for the generated electric field

$$\begin{aligned} \vec{E}(\vec{r}, \xi, t) = e^{-i(\omega t - k_{//}x)} \left\{ \frac{1}{4\epsilon_3\epsilon_0} \right\} \times [& (-k_{\perp} p_x - ik_{//} p_z) (\vec{e}_x + i(k_{//}/k_{\perp}) \vec{e}_z) \theta(z-\xi) e^{-k_{\perp}(z-\xi)} \\ & + (-k_{\perp} p_x + ik_{//} p_z) (\vec{e}_x - i(k_{//}/k_{\perp}) \vec{e}_z) \theta(-z+\xi) e^{+k_{\perp}(z-\xi)} \\ & + (-k_{\perp} p_x + ik_{//} p_z) (\vec{e}_x + i(k_{//}/k_{\perp}) \vec{e}_z) r_{321} e^{-k_{\perp}(z+\xi)} \\ & - 2p_z(\xi) \delta(z-\xi) \vec{e}_z] + \text{c.c.}, \end{aligned} \quad (5.3.3)$$

where $k_{\perp} = \{k_{//}^2 - \epsilon_3(\omega/c)^2\}^{1/2}$ is the inverse penetration depth of the EM field into medium 3. The various terms of equation (5.3.3) denote, in order of occurrence, the upward, the downward, the reflected and a non-propagating wave. The first three waves propagate and have an associated magnetic field. The latter non-propagating wave does not have an associated magnetic field. Recently Felderhof and Marowsky^{18,19} have extended the existing theory on the behavior of polarization sheets. They have derived expressions for the intensity of the emitted radiation similar to our equation (5.3.3). The advantage of the Green's function method over the theory explicated in ref.16 is that the boundary conditions appear quite naturally and the (known) expressions for reflection and transmission of a plane wave from a Kretschmann configuration can be used.

Only the downward-propagating EM field is transmitted through the metal and couples out of the system into the glass. Integrating over the continuum of layers of nonlinear polarization the strength of the total downward-propagating wave at the metal-medium 3 interface can be evaluated

$$\begin{aligned} \vec{E}_{\text{downward}}(z=0, t) = & \left\{ \frac{1}{4\epsilon_3\epsilon_0} \right\} (\vec{e}_x - i(k_{//}/k_{\perp}) \vec{e}_z) e^{-i(\omega t - k_{//}x)} \\ & \times \int_0^{\infty} d\xi \{ -k_{\perp} p_x(\xi) + ik_{//} p_z(\xi) \} e^{-k_{\perp}\xi} + \text{c.c.} \end{aligned} \quad (5.3.4)$$

Having derived this general formula, we will now consider the specific case of stimulated Raman scattering. In this situation two laser beams of different colors are aligned to create SP in the Kretschmann geometry, resulting in strong local EM fields. When the two lasers are focused on the same spot and their frequency difference equals the frequency of a Raman-active mode of medium 3 a strong third-order polarization in this medium results. The amount of emitted radiation can be calculated from equation (5.3.4), keeping in mind that the wave vector of the induced polarization is equal to: $\vec{k}_p = \vec{k}_\ell - \vec{k}_\ell^* + \vec{k}_s$.

Close to the SP resonance E_z is larger than E_x . As a consequence the induced nonlinear polarization vector also points sharply towards the z-direction. Combining this with the fact that close to the SP resonance $k_{//}$ is much larger than $k_\perp$ it should be clear that $\{-k_\perp p_x(\xi)\}$ can be neglected with respect to $\{ik_{//} p_z(\xi)\}$ in equation (5.3.4).

As the frequency difference between both lasers used in the SRS experiment is usually relatively small, their evanescent fields will stretch to comparable distance into the nonlinear medium. The third-order nonlinear polarization, being proportional to E^3 , consequently decreases also exponentially into medium 3, but penetrates only one third of this distance. When the integral in (5.3.4) is performed it yields

$$\vec{E}(\vec{r}, t) = (1/2)\vec{E}_\ell(z)e^{-i(\omega_\ell t - k_{//}x)} + (1/2)\vec{E}_s(z)e^{-i(\omega_s t - k_{//}x)} + c.c.,$$

$$\vec{E}_i(z) = \vec{E}_i(0) e^{-k_\perp z} \quad (i=\ell, s),$$

$$\vec{P}_{NL}(\vec{r}, t) = (1/2)\vec{P}_s(\vec{r})e^{-i\omega_s t} + c.c. + \text{terms with other frequencies},$$

$$P_{s,z}(\vec{r}) = (3/2)\epsilon_0 \chi_{zzzz}^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s) |E_{\ell,z}(z)|^2 E_{s,z}(z) e^{ik_{//}x},$$

$$E_{s, \text{downward}, x} = \frac{ik_{//}}{4k_\perp} \frac{3}{4\epsilon_3} \chi_{zzzz}^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s) |E_{\ell,z}(0)|^2 E_{s,z}(0) e^{ik_{//}x}, \quad (5.3.6)$$

where all macroscopic EM fields appearing in equation (5.3.6) have to be evaluated at the metal-medium 3 interface ($z=0$). Notice once more the difference between the (smooth) envelope of the electric field, denoted with an extra subscript s or ℓ , and the field itself. Equation (5.3.6) specifies the x-component of the (downward-propagating) electric field in medium 3. Its z-component is a factor $-i(k_{//}/k_\perp)$ times larger and the absolute value of

the electric field is a factor $(1+(k_{//}/k_{\perp})^2)^{1/2}$ larger than this x-component.

To compare the Raman gain signal obtainable in the Kretschmann geometry with that in a bulk sample, the equations that describe "three-dimensional" Raman gain (equation (1.8.7) and (2.6.2) combined) are reproduced below.

$$E_{s,extra} = ikL (3/4\epsilon_3) \chi_{zzzz}^{(3)}(-\omega_s, \omega_l, -\omega_l, \omega_s) |E_{l,z}|^2 E_{s,z}, \quad (5.3.7)$$

$$I_{extra} = kL (3/2\epsilon_3) \text{Re}\{i\chi_{zzzz}^{(3)}(-\omega_s, \omega_l, -\omega_l, \omega_s)\} |E_{l,z}|^2 I_{in}, \quad (5.3.8)$$

where L is the length of the sample and $k = \epsilon_3^{1/2}(\omega/c)$ $(= (k_{//}^2 + k_{\perp}^2)^{1/2})$.

Comparing the equations (5.3.6) and (5.3.7) one notices three differences. Firstly in equation (5.3.7) a factor k is used, instead of a factor $k_{//}$ in equation (5.3.6) ($k_{//} \approx k$). Secondly the effective sample length in the surface-enhanced SRS experiment is $(1/4k_{\perp})$. Thirdly the electric fields appearing in equation (5.3.6) are enhanced as a result of the SP resonance.

In a surface-enhanced SRS experiment E_z at the metal-medium 3 interface is enhanced by a factor $(k_{//}/(k_{//}^2 + k_{\perp}^2)^{1/2})/K_{in}$ with respect to the absolute value of E_{in} in a bulk SRS experiment, for both colors, because the intensity enhancement of the incident radiation is K_{in} and the intensity present in the z-component of the electric field is a fraction $k_{//}^2/(k_{//}^2 + k_{\perp}^2)$ of the total intensity. With this knowledge $P_z^{(3)}(\vec{r}, t)$ can be evaluated as well as the generated field $E_{s,downward,x}$, being specified by equation (5.3.6). In this calculation the x-component of $P^{(3)}$ is neglected. When the generated light is coupled out of the Kretschmann system an extra enhancement of $((k_{//}^2 + k_{\perp}^2)^{1/2}/k_{\perp})/K_{out}$ is obtained. Summarizing: comparing SRS in the Kretschmann configuration with SRS in the bulk the effective interaction length is only half the penetration depth of the intensity into the nonlinear medium $\{1/(4k_{\perp})\}$, but the signal from this thin layer is enhanced, purely through trapping of radiation, by a factor

$$\text{Enhancement (without consideration of phase)} = \frac{\text{Extra field ATR}}{\text{Extra field bulk}} =$$

$$\frac{k_{//}}{k_{\perp}} \frac{k_{//}^3}{[(k_{//}^2 + k_{\perp}^2)(k_{//}^2 - k_{\perp}^2)^{1/2}]} K_{in}/(K_{in}K_{out}). \quad (5.3.9)$$

5.4 Phase of stimulated Raman scattering in the ATR configuration

This seems to be the right moment to take into consideration the phase of the coherent Stokes light created through stimulated Raman scattering in the Kretschmann configuration. Does the generated Stokes beam really result in an amplification of the light reflected from the Kretschmann system, or is it optically out of phase with the reflected light? In this section the phase relation between the generated Stokes beam and the reflected beam will be determined. For this purpose the reflected beam is divided into a beam that is directly reflected from the glass-metal interface, and a beam that represents the multiple reflected light and that can be associated with the radiative decay of SP. As the three plane waves have an identical $k_{//}$, they indeed have a fixed phase relation.

The phase relation between the three outgoing EM waves is determined by the ratio of their complex amplitudes (E_x) at the metal-medium 3 interface. These phase relations will be determined as a function of the angle incidence ($k_{//}$ real).

The (complex) field amplitude of the multiple-reflected light can be easily extracted from equation (4.4.1)a. To determine the amplitude of the generated Stokes light I will once more trace its generation, giving special attention to the phase of the radiation. The x-component of the incoming wave gains a factor t_{123} when it is coupled into medium 3. The induced nonlinear polarization points strongly towards the z-direction and its amplitude is proportional to $\chi^{(3)} |E_{\ell,z}|^2 E_{s,z}$, where $(E_z/E_x) = i(k_{//}/k_{\perp})$. Finally the x-component of the radiation emitted into the glass is proportional to $t_{321} i k_{//} p_z$. This completes the generation and results in: $E_{out} \propto -t_{123} t_{321} \chi^{(3)} E_{in}$. Rewriting the product $t_{123} t_{321}$ in a more appropriate form one finds

$$t_{123} t_{321} = r_{12} \frac{|\epsilon_2| \epsilon_3}{|\epsilon_2^2 - \epsilon_3^2|} \frac{-4i k_{//} \Delta k_{//}''}{((k_{//} \hat{k}_{//}' \Delta k_{//}') - i(\hat{k}_{//}'' + \Delta k_{//}''))^2}, \quad (5.4.1)$$

$$\text{Direct reflection} : E_{out} = r_{12} E_{in} \quad (5.4.2)a$$

$$\text{Multiple reflections} : E_{out} = r_{12} \left[\frac{2i \Delta k_{//}''}{(k_{//} \hat{k}_{//}' \Delta k_{//}') - i(\hat{k}_{//}'' + \Delta k_{//}''))} \right] E_{in} \quad (5.4.2)b$$

$$E_{\text{out}} = r_{12} \chi^{(3)} \left[\frac{4i \hat{k}_{\parallel}' \Delta \hat{k}_{\parallel}''}{\{(\hat{k}_{\parallel}' - \hat{k}_{\parallel}' - \Delta \hat{k}_{\parallel}') - i(\hat{k}_{\parallel}'' + \Delta \hat{k}_{\parallel}'')\}^2} \right] \frac{3}{4\epsilon_3} \frac{|\epsilon_2| \epsilon_3}{|\epsilon_2^2 - \epsilon_3^2|} \frac{k_{\parallel}^2}{4k_{\perp}^2} |E_{\ell, z}(0)|^2 E_{\text{in}}$$

In fig.(5.4.1) the ratio of the amplitude of the total reflected light, with respect to the amplitude of the direct reflection, is plotted in the complex plane. The curves 1,2 and 3 correspond to three metal films with different thicknesses. As the angle of incidence is varied the total reflectivity traces one of the curves.

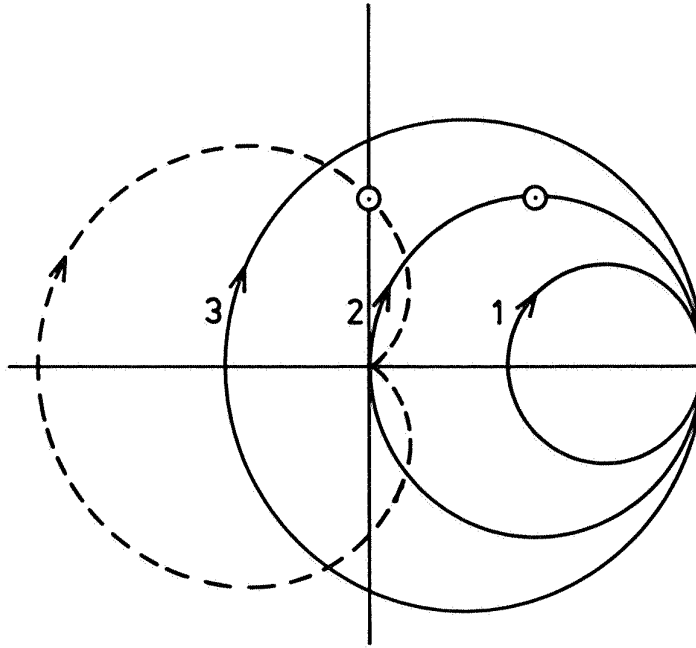


Fig.5.4.1 The complex amplitude of light reflected from a Kretschmann configuration plotted in the complex plane. This amplitude traces one of the drawn curves when the angle of incidence is scanned through the SP resonance. Curve 2 represents the complex ATR curve for a film of optimum thickness, whereas curve 1 belongs to a thicker film and curve 3 belongs to a thinner film. The dashed curve represents the amplitude of the coherent Stokes radiation, created in medium 3 when $\{\text{Re}\chi^{(3)}=0\}$, for a film of optimum thickness and for various angles of incidence. The arrows indicate in which "direction" both amplitudes evolves when the angle of incidence is increased. The dots show which situation corresponds to $\{(\hat{k}_{\parallel}' - \hat{k}_{\parallel}' - \Delta \hat{k}_{\parallel}') = (\hat{k}_{\parallel}'' + \Delta \hat{k}_{\parallel}'')\}$.

The graphs allows for an easy visualization of equation (5.4.2)b and they can be interpreted as complex ATR curves (see section (4.4)). Curve 2 represents the ATR curve for a film of optimum thickness. Curve 1 represents the ATR curve for a thicker film, whereas curve 3 is for a thinner film (more multiple-reflected light). At the plasmon angle the total reflection of the Kretschmann system reaches its minimum, because the multiple-reflected light is 180° out of phase and interferes destructively with the direct reflection. Complete cancellation results when the metal film has the optimum thickness ($\hat{k}_{//}'' = \Delta \hat{k}_{//}''$) and both contributions are equally strong. At the plasmon angle the phase change on reflection on a thick film is identical to the phase change on reflection from bulk metal, while the phase flips an extra 180 degrees on reflection from a film thinner than the optimum thickness. This property leads to an very accurate ellipsometric method to determine the optimum thickness (chapter 4 ref.7).

When the angle of incidence is tuned away from the plasmon angle, the amplitude of the multiple-reflected light decreases and is not 180° out of phase with the direct reflection anymore. A physical explanation is that the propagating SP, which are related to the multiply-reflected light, can experience e.g. a phase lag with respect to the direct reflection when the angle of incidence is larger than the plasmon angle ($k_{//} > (\hat{k}_{//}' + \Delta \hat{k}_{//}')$). As a consequence the phase of the total reflection depends critically on the angle of incidence. The arrow in fig.(5.4.1) indicates in which "direction" (E_{out}/E_{in}) changes when the angle of incidence is increased.

The phase of the SRS light as a function of the angle of incidence is plotted as the dashed curve in fig.(5.4.1), under the assumption that $i\chi^{(3)}$ is real and positive ($\chi^{(3)}$ purely imaginary). When $\chi^{(3)}$ is not purely imaginary the dashed graph has to be rotated in the complex plane. The two dots in fig.(5.4.1) show the amplitudes at an angle of incidence that corresponds to $(\hat{k}_{//}' - \Delta \hat{k}_{//}') = 2\Delta \hat{k}_{//}''$.

In our experiment the expected intensity of the coherently-generated Stokes light is typically 10^{-12} of the intensity of the incident radiation and this light can thus only be detected through its interference with the total reflection. Using straight-forward algebra the expressions (5.4.2)a,b and c immediately yield the equations (5.4.3) and (5.4.4) that quantitatively describe surface-enhanced Raman gain or loss in a general situation

$$I_r/I_{in} = \frac{\{(k_{//} \hat{k}'_{//} - \Delta \hat{k}'_{//})^2 + (\hat{k}''_{//} - \Delta \hat{k}''_{//})^2\}}{\{(k_{//} \hat{k}'_{//} - \Delta \hat{k}'_{//})^2 + (\hat{k}''_{//} + \Delta \hat{k}''_{//})^2\}} \quad (5.4.3)$$

$$\Delta I_r/I_{in} = \frac{8 \Delta \hat{k}''_{//} \hat{k}'_{//}}{\{(k_{//} \hat{k}'_{//} - \Delta \hat{k}'_{//})^2 + (\hat{k}''_{//} + \Delta \hat{k}''_{//})^2\}^2} \frac{3 |\epsilon_2| \epsilon_3}{4 \epsilon_3 |\epsilon_2^2 - \epsilon_3^2|} \frac{k_{//}^2}{4 k_1^2} |E_{\ell, z}(0)|^2$$

$$\times [\text{Re} \chi^{(3)} \{-2 \hat{k}''_{//} (k_{//} \hat{k}'_{//} - \Delta \hat{k}'_{//})\} + \text{Im} \chi^{(3)} \{-(k_{//} \hat{k}'_{//} - \Delta \hat{k}'_{//})^2 - (\Delta \hat{k}''_{//})^2 + (\hat{k}''_{//})^2\}], \quad (5.4.4)$$

where I_r is the intensity of the reflected light, I_{in} is the intensity of the incident light, ΔI_r is the variation in reflected intensity due to $\chi^{(3)}$, and $\chi^{(3)}$ is a short-hand notation for $\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$.

The equations (5.4.3) and (5.4.4) give a complete description of the surface-enhanced stimulated Raman effect. One of the factors appearing in equation (5.4.4) is $|E_{\ell, z}(0)|^2$. The signal is proportional to the intensity of the ω_ℓ -beam at the metal-medium 3 interface and is largest when the "yellow" beam is tuned for optimum generation of surface plasmons. Although the amount of generated SRS has an optimum when the red beam is also tuned for optimum generation of SP, the largest variation in reflected intensity is obtained at an angle of incidence that differs from the plasmon angle, as the change in intensity of the red-beam results from interference between the SRS and the reflected beam.

When a Raman-active mode is excited on resonance in a material without electronic contribution $i\chi^{(3)}$ is real and positive ($\text{Im} \chi^{(3)} < 0$). When the angle of incidence of the red beam equals the plasmon angle equation (5.4.4) predicts that the interference between the SRS light and the total reflection will result in a loss for thick films ($\Delta \hat{k}''_{//} < \hat{k}''_{//}$) and a gain for thin films. This is consistent with the idea that the number of SP increases through SRS causing an increase in multiple-reflected light.

For a film of optimum thickness the Raman gain signal will be extremely low and the angle of incidence has to be mistuned from the plasmon angle to make the variations in reflected intensity detectable. When $i\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$ is real and positive one can show that the reflectivity of a film of optimum thickness will increase as a result of stimulated Raman scattering, for any angle of incidence. The induced variation in reflected intensity is maximized when $\{(k_{//} \hat{k}'_{//} - \Delta \hat{k}'_{//}) - (\Delta \hat{k}''_{//} + \hat{k}''_{//})\}$ and $I_r = (1/2)I_{in}$. Notice that we keep on assuming that the "yellow" beam is tuned for optimum

SP generation. Under this condition and under this angle the amplitude of the generated Stokes field has half the value it has at the plasmon angle. The dots in fig.(5.4.1) show that the SRS light is 45° out of phase with the total reflected light. Combining these numbers one finds that the surface-enhancement at $((k_{//} \hat{k}_{//}' - \Delta \hat{k}_{//}') = (\Delta \hat{k}_{//}'' + \hat{k}_{//}''))$ is given by equation (5.4.5). This equation differs by a factor (1/2) from equation (5.3.9), being explained by the fact that the optical phase of the emitted light was not taken into account in equation (5.3.9)

$$\text{Surface-enhancement} = (1/2) \frac{k_{//}}{k_{\perp}} \frac{k_{//}^3}{[(k_{//}^2 + k_{\perp}^2)(k_{//}^2 - k_{\perp}^2)^{1/2}]} K_{in} \sqrt{(K_{in} K_{out})}, \quad (5.4.5)$$

where K_{in} and K_{out} are maximum values, to be calculated at the plasmon angle and the presented surface-enhancement is derived in the wings of the ATR curve at $I_r = (1/2)I_{in}$ and $((k_{//} \hat{k}_{//}' - \Delta \hat{k}_{//}') = (\Delta \hat{k}_{//}'' + \hat{k}_{//}''))$.

The angle-dependent phase of the generated Stokes beam is a considerable complication in surface-enhanced SRS. This complication does not arise when one performs a surface-enhanced CARS experiment. The intensity of the anti-Stokes radiation simply reaches an optimum at the plasmon angle and decreases monotonically when the angle of incidence of the red beam is detuned from this angle. A complication that does arise in surface-enhanced CARS is the phase-matching condition that has to be fulfilled. The theory developed in this chapter is equally well suited to describe results from other surface-enhanced experiments. A beautiful surface-enhanced CARS experiment has been performed by Chen et al.²

5.5 Surface-enhanced SRS from a different point of view

In chapter 4 it is shown that the parameters $\hat{k}_{//}$ and $\Delta \hat{k}_{//}$ completely determine the angle dependence of the reflectivity from the Kretschmann system, or the shape of the ATR curve. Any change in the index of refraction of the metal film or of medium 3 is reflected in a change in these two parameters. In section (4.9) the effect of a variation of the dielectric constant of the metal has been evaluated to explain the pump-probe measurements on the reflectivity of a BK7-Ag-air system. In this section the optical nonlinearity of medium 3 will be captured in the form of an effective change of its dielectric constant ϵ_3 . This change affects $\hat{k}_{//}$ and

$\hat{\Delta k}_{//}$ and results in a change in the shape of the ATR curve, and the reflectivity at fixed angle of incidence. The model introduced in this section is an alternative to the model, evaluated in section (5.4), that described surface-enhanced stimulated Raman scattering as coherent Stokes radiation emitted through the metal film by the dipoles created in medium 3.

It is rather easy to determine the influence of a homogeneous change in the index of refraction of medium 3 on the reflectivity. However, as the EM fields are evanescent in medium 3, only the index of refraction close to the metal film will be affected and an inhomogeneous dielectric constant results. One can show (chapter 4, ref.24) that this inhomogeneity can be corrected for afterwards, dividing by a factor 2. An uniform change in ϵ_3 equal to the change induced at the metal-medium 3 interface will simply result in a modification of $\hat{k}_{//}$ and $\hat{\Delta k}_{//}$ that is twice as large as the modification induced by the exponentially-decreasing ϵ_3 profile.

A second point of worry might be the fact that the stimulated Raman effect induces birefringence in medium 3 and the change in effective dielectric constant, due to optical nonlinearity, is anisotropic, being the strongest for light polarized perpendicular to the metal film (as $E_{\ell,z} > E_{\ell,x}$). This birefringent character of ϵ_3 is expected to be hardly of importance, because the electric field of the ω_s beam in medium 3 points dominantly perpendicular to the metal film and is mainly sensitive to changes in the dielectric constant for light polarized in that direction.

Simple calculus immediately shows that $\hat{k}_{//}$ is affected far stronger by a change in the index of refraction ϵ_3 than $\Delta k_{//}$ is. The formulas necessary to calculate the effect of SRS on the reflectivity of the Kretschmann configuration, for any film thickness and any angle, are

$$\epsilon_3(z) = \epsilon_3(I=0) + (3/2)\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s) |E_{\ell,z}(z)|^2, \quad (5.5.1)$$

$$\epsilon_{3,\text{eff}} = (1/2)\epsilon_3(z=0),$$

$$(c/\omega) \frac{d\hat{k}_{//}}{d\epsilon_3} = (\hat{k}_{//})^3 (c/\omega)^3 \frac{1}{2\epsilon_3^2} - \frac{1}{2\epsilon_3^{3/2}} \left[\frac{\epsilon_2}{(\epsilon_2 + \epsilon_3)} \right]^{(3/2)}, \quad (5.5.2)$$

$$I_{\text{reflected}} = \left(1 - \frac{4\hat{k}_{//}^n \hat{\Delta k}_{//}^n}{(\hat{k}_{//} - \hat{k}'_{//} - \hat{\Delta k}'_{//})^2 + (\hat{k}_{//} + \hat{\Delta k}_{//})^2} \right) I_{\text{in}}, \quad (5.5.3)$$

$$\frac{dI_{\text{ref}}}{dk_{\parallel}'} = \frac{-8\hat{k}_{\parallel}''\Delta\hat{k}_{\parallel}''(\hat{k}_{\parallel}''\hat{k}_{\parallel}'\Delta\hat{k}_{\parallel}')}{\{(k_{\parallel}''\hat{k}_{\parallel}'\Delta\hat{k}_{\parallel}')^2 + (\hat{k}_{\parallel}'' + \Delta\hat{k}_{\parallel}'')^2\}^2} I_{\text{in}}, \quad (5.5.4)$$

$$\frac{dI_{\text{ref}}}{d\hat{k}_{\parallel}''} = \frac{4\Delta\hat{k}_{\parallel}''\{- (\hat{k}_{\parallel}''\hat{k}_{\parallel}'\Delta\hat{k}_{\parallel}')^2 - \Delta\hat{k}_{\parallel}''^2 + \hat{k}_{\parallel}''^2\}}{\{(k_{\parallel}''\hat{k}_{\parallel}'\Delta\hat{k}_{\parallel}')^2 + (\hat{k}_{\parallel}'' + \Delta\hat{k}_{\parallel}'')^2\}^2} I_{\text{in}}. \quad (5.5.5)$$

Equations (5.5.1)-(5.5.5) describe the change in reflectivity due to third-order nonlinearity of medium 3, at any angle of incidence. As a result of stimulated Raman scattering ($\text{Im } \chi^{(3)} < 0$) the imaginary part of the dielectric constant ϵ_3 at the frequency ω_s decreases and a more narrow ATR curve results. The electronic contribution, when present, usually results in a positive real part of $\chi^{(3)}(-\omega_s, \omega_\ell, -\omega_\ell, \omega_s)$ and will effectively shift the whole ATR curve to larger angles of incidence. In conclusion: when a yellow beam is aligned to create SP at the interface of a metal film and a Raman-active medium 3 (with $\text{Re}\chi^{(3)} > 0$), one expects the ATR curve for the red beam to become more narrow and shift to larger angles of incidence. The changes in reflectivity resulting from both effects add when $(\hat{k}_{\parallel}''\hat{k}_{\parallel}'\Delta\hat{k}_{\parallel}') < 0$.

Comparing the equations (5.5.4) and (5.5.5) with equation (5.4.4) one can show that there is quantitative agreement between both models, apart from minor corrections of the order of a few percent, arising from the fact that the electric field is not completely perpendicular to the metal film. In this paragraph the agreement between the result obtained with the "emitting dipole" model and the result obtained with the "effective dielectric constant" model will be checked quantitatively for the particular situation that $(\text{Re}\chi^{(3)} = 0)$. For that situation the change in ϵ_3 at the metal-medium 3 interface is $\Delta\epsilon_3 = (3/2)i\text{Im}\chi^{(3)}|E_{\ell,z}(z=0)|^2$. The change in the effective dielectric constant of medium 3 is just half as big ($\Delta\epsilon_{3,\text{eff}} = (1/2)\Delta\epsilon_3$). The resulting change in $\hat{k}_{\parallel}''$ can be determined with the help of equation (5.5.2). Substituting this result in equation (5.5.5) one arrives at

$$\Delta I_{\text{ref}} = \frac{4\Delta\hat{k}_{\parallel}''\{- (\hat{k}_{\parallel}''\hat{k}_{\parallel}'\Delta\hat{k}_{\parallel}')^2 - \Delta\hat{k}_{\parallel}''^2 + \hat{k}_{\parallel}''^2\}}{\{(k_{\parallel}''\hat{k}_{\parallel}'\Delta\hat{k}_{\parallel}')^2 + (\hat{k}_{\parallel}'' + \Delta\hat{k}_{\parallel}'')^2\}^2} \frac{3c^2(\hat{k}_{\parallel}')^3}{8\omega^2 \epsilon_3^2} \text{Im}\chi^{(3)}|E_{\ell,z}(z=0)|^2 I_{\text{in}}. \quad (5.5.6)$$

Let us now try to calculate the changes in reflectivity induced through stimulated Raman scattering in the SF57-Ag-CS₂ system. In bulk CS₂ we have measured an effective gain of about 6.5×10^{-4} when a yellow beam with an (unmodulated) intensity of 12.8 mW was focused with a 50 mm lens ($w_0 = 9.5 \mu\text{m}$). The peak power of this laser is 30 W and its peak intensity is about $1.0 \times 10^{11} \text{ W m}^{-2}$. From equation (2.5.2) an effective $g_{\text{SS}} = 2.5 \times 10^{-12} \text{ W}^{-1} \text{ m}$, or a gain of 0.27 m^{-1} can be derived. Using this experimentally-determined gain coefficient the expected surface-enhanced SRS signal for the SF57-Ag-CS₂ system can be evaluated to be

$$\epsilon_1 = 3.404, \quad \epsilon_2 = -16 + 0.6i, \quad \epsilon_3 = 2.64, \quad (c/\omega) \hat{k}'_{\parallel} = 1.778, \quad (c/\omega) k_{\perp} = 0.772$$

$$K_{\text{in}} = 28, \quad K_{\text{out}} = 75,$$

$$\text{Enhancement (equation (5.4.5))} : 1.5 \times 10^3,$$

$$\text{Sample length} : \{1/(4k_{\perp})\} = 33 \text{ nm},$$

$$\text{Equivalent length bulk sample} : 49 \mu\text{m},$$

$$\text{Expected gain (due to } \text{Im}\chi^{(3)}) : 1.3 \times 10^{-5}.$$

From the effective bulk gain an effective $\text{Im}\chi^{(3)} = -5.6 \times 10^{-22} \text{ J}^{-2} \text{ C}^2 \text{ m}^2$ can be determined. Substituting the relevant numbers in equation (5.5.6) the gain predicted by the "effective dielectric constant" model is calculated to be 1.5×10^{-5} , being in reasonable agreement with the value determined from the "emitting dipole" model. The discrepancy is mainly due to our neglect of the birefringence induced in medium 3.

Performing the same calculations for the BK7-Ag-air system one notices that the enhancement factor is approximately a factor 10 larger, an enhancement of 1.4×10^4 has been calculated for the BK7-Ag-air system, and the field penetrates deeper into the gaseous medium (93 nm instead of 33 nm). On first sight the equivalent length of a gaseous bulk sample seems to be almost as large as the length of the focus in a real bulk sample. Unfortunately the width of the ATR curve for the BK7-Ag-air system is far smaller than the opening angle of the focused beam and the expected enhancement is greatly reduced, to a value only slightly more than that obtainable for liquid samples.

The effect of the imaginary part of $\chi^{(3)}(-\omega_s, \omega_l, -\omega_l, \omega_s)$ being determined one can easily estimate the effect of the Real part of $\chi^{(3)}$. In the case of CS₂ it is known, from a comparison between ordinary SRS and

time-resolved SRS, that the effective real part of $\chi^{(3)}$ is about three times larger than its imaginary part (at $\nu_L - \nu_S = 656 \text{ cm}^{-1}$). In the wings of the "red" ATR curve ($(k_{//} - k'_{//} - \Delta k'_{//}) = (\Delta k''_{//} + k''_{//})$) the change in the reflectivity resulting from the real part of $\chi^{(3)}$ will thus be about three times larger than the change resulting from its imaginary part. Experimentally the former effect is extremely hard to detect, as it is practically independent of the frequency difference between both dye lasers, whereas the latter effect has a clear signature, as it is peaked around ($\nu_L - \nu_S = 656 \text{ cm}^{-1}$).

Under experimental conditions our ATR curves were always a factor 2-3 wider than the literature value of ϵ_{Ag} would allow for. This discrepancy is probably a result of roughness of the silver layer and results in a decrease in K_{in} as well as in K_{out} . The surface-enhancement expected under experimental conditions is probably about a factor 4-9 smaller than the enhancement just calculated. In conclusion an experimental gain of about 2×10^{-6} , due to $\text{Im}\chi^{(3)}$, should be feasible.

5.6 Preliminary experiments on CS_2 and CCl_4

The enhancement of the local intensity obtainable in the Kretschmann configuration lead us to the study of SRS on CS_2 and CCl_4 in this setup. As the optimum thickness of the silver film is hardly sensitive to the index of refraction of medium 3, we kept on using silver films of about 45 nm thickness. For the SF57-Ag- CS_2 the measured plasmon angle of 74° agreed with theory, but the measured FWHM of the ATR curve (2.8°) was about a factor 2 wider than the theory predicts ($\epsilon_{Ag} = -16 + 0.6i$). The ATR curves obtained for a SF57-Ag-air system (FWHM 0.5°) as well as for the SF57-Ag- CCl_4 system ("FWHM" 1.8°) were also roughly a factor 2 too wide.

Although the first experiments were performed with CS_2 as medium 3 we soon decided to work with CCl_4 , primarily because boiling of CS_2 could be observed, even at moderate laser power (10 mW). At $1.0 \times 10^5 \text{ Pa}$ (1 Bar) the boiling point of CCl_4 (77°C) is considerably higher than that of CS_2 (46°C). We have studied the 460 cm^{-1} symmetric C-Cl stretch of carbon-tetrachloride. Although the strength of this Raman-active mode, specified as the gain measured with laser pulses similar to ours, is only 30 % of the strength of the 656 cm^{-1} mode of CS_2 the larger surface-enhancement, resulting from the lower index of refraction of CCl_4 , should just compensate for this difference.

The measured ATR curve for the SF57-Ag-CCl₄ shifted almost 0.8° per day to larger angles of incidence and seemed to broaden simultaneously. This gradual shift and widening must reflect a slow chemical reaction between CCl₄ and silver. Monitoring the time-dependent change of the ATR curve allowed us to determine the reaction rate of this process. Using equation (4.5.1) in combination with a dielectric constant of AgCl of 4.3 ($\lambda=600$ nm)²⁰ one can show that the formation of AgCl takes place at a rate of a few nm per day. I deliberately say "a few", instead of the 4 nm/day one determines from equation (4.5.1), because it is unlikely that the AgCl layer is smooth and equation (4.5.1) is only valid for smooth upper layers. Roughness of the upper layer will lead to bigger shifts and to a widening of the ATR curve, something that was experimentally confirmed.

The chemical reaction is prevented by evaporating a glassy layer on top of the Ag film. A 3 nm layer did not give full protection, but it did slow down the reaction by a factor 3. A 8 nm layer of evaporation glass was needed to stop the formation of AgCl completely. An extra 2 nm layer of NiCr was evaporated between the silver film and the SF57 substrate to insure better attachment of the silver to the prism. The configuration actually used in the experiments described in the sections (5.7) and (5.8) thus consisted of a SF57 glass substrate - 2 nm NiCr - 45 nm Ag - 8 nm "evaporation" glass - and bulk CCl₄ on top.

5.7 The average increase in temperature

Measurements on the SF57-Ag-CCl₄ system showed that the ATR curve recorded with focused light differed drastically from results obtained with unfocused light, while both methods gave similar results for the BK7-Ag-air system. This effect, which will be denoted as the deformation of the ATR curve, is clearly shown in fig.(5.7.1). The deformation of the ATR curve depends strongly on the focused intensity and can be attributed to a rise of the average temperature of the liquid CCl₄. An increase in temperature of the liquid results in a decrease of its dielectric constant ϵ_3 . The reflectivity of the system and the absorption of heat due to SP generation and SP decay are directly related to this dielectric constant. A change of the reflectivity will in its turn influence the average temperature, which closes the feedback loop. Talking about "the average temperature" I always have in mind the temperature of a very thin (100 nm)

layer of liquid close to the metal. Simulations show that the temperature rise is limited to a region comparable to the size of the focused spot (radius 10 μm) and decreases approximately as $(1/r)$ far from this focus. The temperature of the bulk liquid is hardly influenced by the input of heat.

The nonlinear dependence of the reflectivity on ϵ_3 is the basic reason for the observed bistability at laser powers higher than 10 mW (focused with a 50 mm lens). At some fixed angles of incidence the reflectivity can be either high (65-70%) or low (25-30%). The state of high reflectivity corresponds to a low average temperature of the liquid and the liquid stays cold, because little radiation is absorbed. The state of low reflectivity corresponds to a high average temperature of the liquid and the liquid stays hot, because a lot of radiation is absorbed. The system acts as a kind of optical switch, having a "cold" phase and a "hot" phase. Temporal blockade

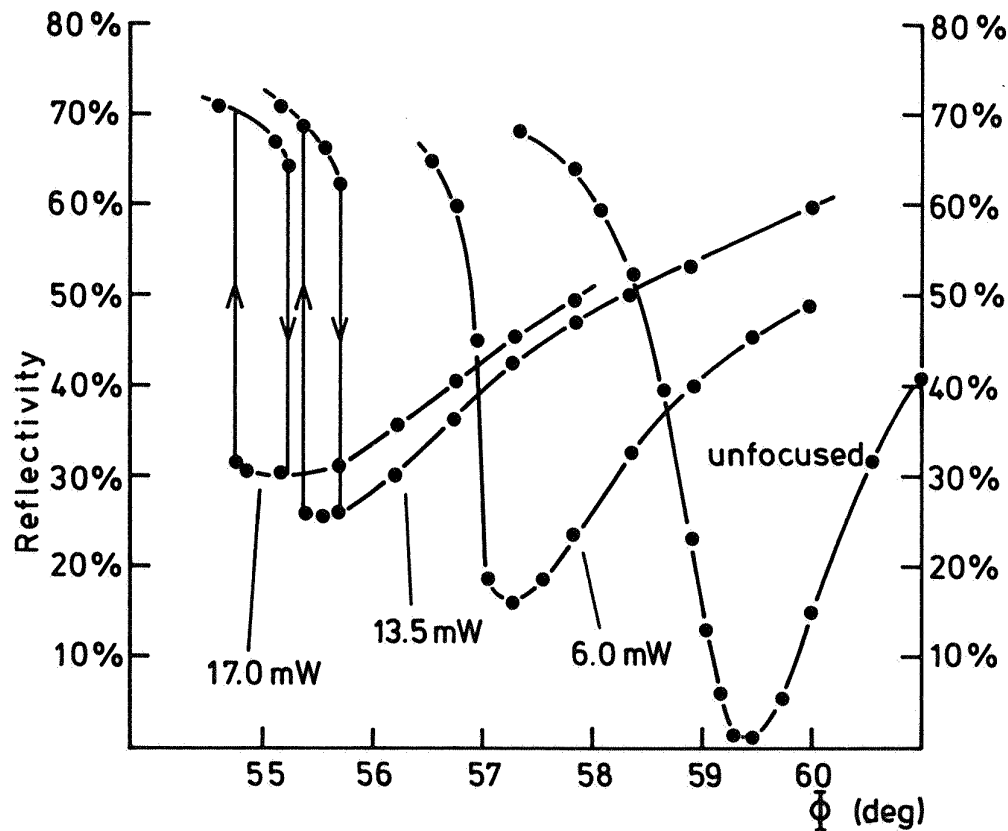


Fig.5.7.1 The reflectivity from a SF57-Ag-CCl₄ Kretschmann system as a function of the angle of incidence. The ATR curves found for focused light are strongly deformed with respect to the ATR curve found for unfocused light. This deformation arises from an increase in temperature of the liquid.

of the incident light switches the system from the hot phase to the cold phase. Introducing an extra beam to heat up the system and removing this beam afterwards switches the system from the cold phase to the hot phase. Because the effects are based on an average temperature increase, or decrease, the switching times are rather long (10-100 ms).

The observation of similar optical switching behavior has been reported in ref.21 and 22, where the reflectivity of an interface between two media is measured and hysteresis is observed. In both articles the dependence of the index of refraction of one of the two media on the temperature is mentioned as the origin of the hysteresis. Hysteresis of the reflectivity as a function of the incident power can also be observed when the dielectric constant of one of the media depends strongly on the density²³ or directly on the light intensity^{24,25}, through third-order optical nonlinearity. Although both effects should be present in the SF57-Ag-CCl₄ system, one expects changes in reflectivity resulting from compression of the liquid to be of minor importance, while the intensity dependence of the index of refraction is one of the effects arising from $\text{Re}\chi^{(3)}$, and is already accounted for in the equations.

It might seem strange that the minimum of the ATR curve for focused light is far higher than the minimum reflectivity observed for unfocused light. This is due to a combined effect of SP propagation and the local nature of the rise in temperature. At low intensity a dark stripe is visible in the transverse profile of the reflected beam, indicating that hardly any light is reflected at the plasmon angle, while light incident at other angles is partly reflected. This light is thus filtered out of the cone of reflected radiation. The measured reflectivity for focused light is averaged over the whole range of available incident angles, and thus is higher than the reflectivity of an unfocused beam at the plasmon angle. An equivalent interpretation can be formulated in terms of SP propagation. When the incident beam is focused too strongly the SP move out of the focal region and the interference between the light emitted through radiative decay of SP and the direct reflection results in a stripe in the transverse profile of the reflected beam.

At higher intensities the dark stripe becomes distorted. For 17 mW of incident power the dark structure inside the profile of the reflected beam is a stripe at large angles of incidence. When the angle of incidence is decreased the dark structure curves, starts looking like a sickle and

finally changes into a small dark ring with a hole of intense light in the middle. During this angle scan the outer perimeter of the reflected beam increases slowly. On further increase of the angle of incidence the system suddenly switches to the cold state, the dark ring disappears and the outer perimeter shrinks back to "normal" again. To explain the observed changes in the shape of the reflected beam one should recall that the dielectric constant of CCl_4 is only locally changed. These local variations can be interpreted as a lens producing "self-focusing" and "self-deformation" of the reflected beam. An equivalent interpretation in terms of SP is that the SP are reflected at the edge of the "bubble" of hot liquid. Their propagation is limited and they are confined inside the hot region. The "self-confinement of SP" will certainly change the surface-enhancement calculated in section (5.3).

A rough estimate of the increase in average temperature can be obtained from the shift of the minimum of the ATR curve, which determines a kind of effective index of refraction of the bulk liquid. As the inhomogeneity introduced by the hot bubble of liquid is neglected, this will probably lead to an underestimate of the temperature increase at the center of the focal

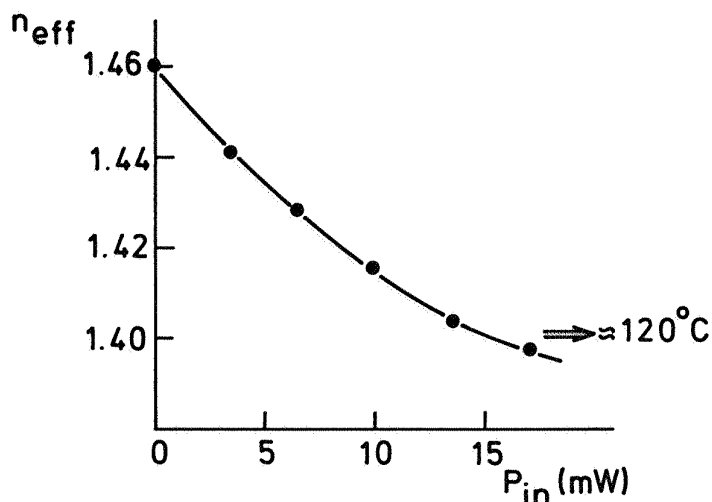


Fig.5.7.2 The effective index of refraction of liquid CCl_4 , as derived from the minima of the recorded ATR curves, as a function of the incident laser power. The effective index of refraction can be converted into an effective temperature via $(dn/dT) = -6.2 \times 10^{-4} \text{ K}^{-1}$. At a laser power of 17 mW the estimated temperature of the liquid is 120 °C, which is more than 40 °C above its "natural" boiling point (at 1 Bar).

region. Our results are presented in fig.(5.7.2). Changes of the effective index of refraction of a few percent are observable for laser powers as low as 10 mW. These changes can be transformed into an effective temperature via the relation $(dn/dT) = -6.2 \times 10^{-4} \text{ K}^{-1}$. The linear dependence of the dielectric constant of CCl_4 as a function of temperature, up to 70°C has been checked with great accuracy.²⁶ At 17 mW of incident laser power the effective temperature thus derived is 120°C , while bulk CCl_4 boils at 77°C at a pressure of $1.0 \times 10^5 \text{ Pa}$! Our experiment demonstrates that the small volume of hot liquid CCl_4 is superheated by at least 40°C .

At least two reasons can be found to explain this extreme case of superheating. First of all the heated volume is extremely small. What will happen when a liquid is heated above the boiling point at one position and is below the boiling point a few μm away? Does the heated liquid form microscopic bubbles that condensate in the colder region? It is energetically unfavourable to form microscopic bubbles. For very small bubbles the pressure resulting from surface tension cannot be neglected²⁷ and leads to a considerable increase in boiling temperature. A second argument to explain the superheating is lack of roughness on a μm scale. This roughness is needed to start the boiling process. The glassy upper layer, situated on top of the silver film in our Kretschmann system, is probably also connected to the huge superheating, as superheating of bulk liquid is most easily observed when it is heated in a smooth and clean glass container.

When the power of the focused beam was raised beyond 20 mW and the angle of incidence was scanned a third phase could be observed, beside the "cold liquid" phase and the "hot liquid" phase. In this "third phase" the reflectivity of the system is about 72 %. When the third phase is reached the laser power can be largely reduced before the system switches to the "cold liquid" phase. Observation of the focal region with a microscope showed that the third phase should be associated with the formation of a gas bubble at the Ag-CCl_4 interface. Once the gas bubble is formed the laser power can be greatly reduced without destruction of the bubble. The size of the gas bubble is related to the incident intensity, but typically extends to slightly beyond the focal region. Every now and then the bubble detaches from the substrate, rises and a new bubble is formed.

5.8 Time-resolved experiments on the glass-Ag-CCl₄ system

We have performed two-beam pump-probe experiments on the SF57-Ag-CCl₄ system described in section (5.6). Two collinear laser beams are focused, with a 50 mm lens, through the glass substrate onto the silver film at approximately the plasmon angle. The frequency difference between both lasers was tuned to a Raman-active mode in CCl₄ at $\nu=460\text{ cm}^{-1}$. The angle of incidence was tuned slightly above the plasmon angle. Actually we did not really have much choice, because the ATR curves were heavily deformed and the other slope of the ATR curve was unstable, something that has been described in section (5.7). Unfortunately for this angle of incidence the optical crosstalk resulting from $\text{Im}\chi^{(3)}$ and from $\text{Re}\chi^{(3)}$ have negative signs and counteract. The double-modulation technique presented in section (2.4) was used to accurately measure the optical crosstalk between the yellow pump pulse and the red probe pulse. For the surface-enhanced SRS measurements it is advisable to place the 500 Hz chopper in front of the detection photodiode instead of in the yellow pump beam, because the heat input, which determines the DC temperature of the system and the behavior of the SP, is kept constant that way.

Very strong signals were observable. The optical crosstalk was a factor 5-10 larger than that measured for the BK7-Ag-air system. Two striking differences with the latter experiment, described in chapter 4, were observable. First of all the gain on the red probe beam was about 90° out of phase with the 8.4 MHz modulation imposed on the yellow pump beam. Secondly the measured signal was practically independent of the overlap in time between the yellow and the red pulse. The signal was a mere 5 % higher when the yellow pulse arrived before the red pulse instead of after this pulse. The phase shift of the gain on the red beam as well as the insensitivity to the pulse overlap both suggest that the measured optical crosstalk results from a relative slow process, probably thermal in nature. The reflectivity of a given red pulse is apparently not exclusively determined by the previous yellow pulse, but many preceding yellow pulses (12 ns, 24 ns, 36 ns ... earlier) probably influence this reflectivity.

Far more information can be obtained from measurements of the change in reflectivity of the red pulse when it is detected in phase with the 8.4 MHz modulation. A measurement of the "in phase" variation in reflectivity as a function of the time delay between the yellow pump pulse and the red probe

pulse is plotted in fig.(5.8.1). The fast effects, resulting from the previous pump pulse only, are better represented in this "in phase" measurement, while the measurement is less sensitive to the slower effects, which tend to be out of phase with the modulation. When the delay T between probe and pump pulse changes from negative to positive, the yellow pulse starts acting as a "pump" and the reflectivity decreases suddenly. After this sudden decrease the reflectivity gradually increases almost linearly in time. We could trace this increase over a limited time, due to the length of the delay line, but even for a delay as short as 0.5 ns the gradually increase already compensated for the stepwise decrease. The magnitude of the stepwise change in reflectivity is identical to that observed for the BK7-Ag-air system ($\Delta R/R \approx -1 \times 10^{-4}$). It is therefore attributed to sudden heating of the silver film. As the angle of incidence was larger than the plasmon angle heating of the metal should indeed induce loss in the reflected intensity (see section (4.9)).

The energy dissipated in the metal will diffuse into the glass substrate and into the liquid CCl_4 . Heating of the CCl_4 will result in a decrease of its dielectric constant, which will be reflected in a shift of

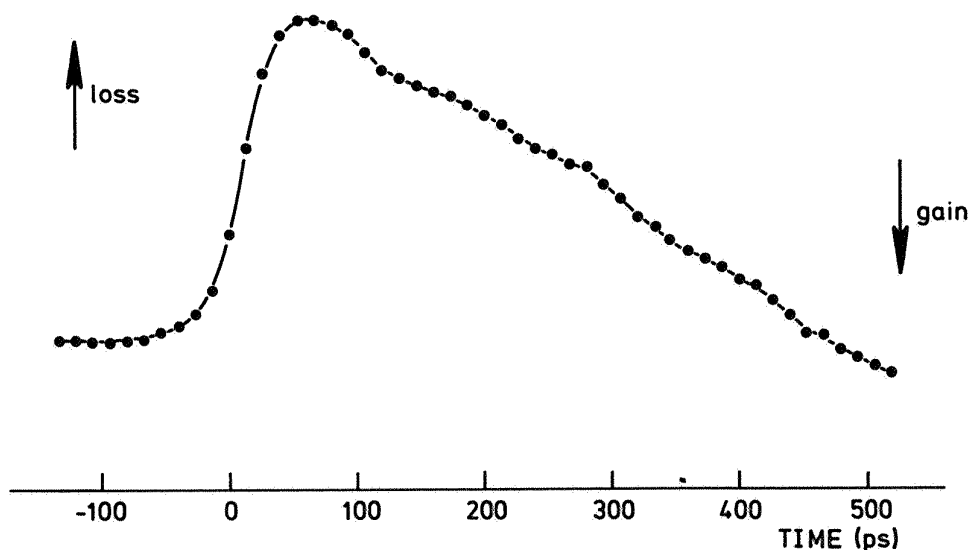


Fig.5.8.1 The "in-phase" change in reflectivity of the probe beam as a function of the time delay between the pump and the probe pulse, for the SF57-Ag- CCl_4 Kretschmann system. The stepwise decrease in reflectivity can be attributed to the heating of the silver film, while the gradual increase in reflectivity that follows shows the diffusion of heat into the CCl_4 liquid.

the ATR curve to smaller angles of incidence. The gradual increase in reflectivity pictured in fig.(5.8.1) is probably associated with diffusion of heat, on a ns timescale, into the liquid CCl_4 . The "out of phase" optical crosstalk can be that strong, because a temperature change of the liquid CCl_4 has far more influence on the reflectivity of the system than the corresponding temperature change of the silver has. A more detailed study of the change in reflectivity, as a function of the time delay between pump and probe, would allow for a very accurate determination of the transport of energy in a liquid on a microscopic scale (typically 10 nm).

Somewhere on top of these two thermal signals, one arising from the metal and one arising from the liquid, the surface-enhanced stimulated Raman signal should be present. In the "in-phase" time-resolved measurement presented in fig.(5.8.1) SRS should lead to a peak around zero delay. None of our measurements showed this peak, which thus poses an upper limit for the strength of the SRS signal. Unfortunately the measurements had a rather poor signal to noise ratio, as a result of variations in the large thermal background signal. The upper limit for the total SRS signal, resulting from $\text{Re}\chi^{(3)}$ as well as $\text{Im}\chi^{(3)}$, set by these measurements, is about 3×10^{-6} .

Another approach to search for surface-enhanced SRS is to perform a scan of the frequency difference between both lasers for zero time delay. In this situation the SRS signal should give rise to a sharp structure around the Raman frequency (460 cm^{-1} for CCl_4). We have tried this technique without result. The amount of optical crosstalk did depend on the frequency difference ($\nu_p - \nu_s$), but no signal was observed around 460 cm^{-1} . The upper limit that this technique gave for the observable relative change in reflected intensity was about 10^{-5} .

Two-beam stimulated Raman measurements are negatively influenced by the presence of large thermal signals, which have to be suppressed. The variations in these thermal signals introduce extra noise in the measurements. For this reason we decided to try a time-resolved four-beam SRS experiment on the system. In a four-beam measurement, where the yellow pump beam is amplitude modulated with 8.4 MHz and the path length of the yellow probe beam is modulated with 500 Hz, none of the thermal signals should have the double modulation, whereas the TSRS signal has. The time-resolved four-beam experiment gave a strong signal around zero delay and absolutely no signal when the time delay was tuned far beyond pulse overlap. Unfortunately the strength of this signal was practically independent of the

frequency difference between both lasers. Measurements on bulk SF57 glass confirmed our suspicion that the signal arose from the instantaneous contribution to $\chi^{(3)}$ of SF57 glass. The observed instantaneous contribution of SF57 glass is about 40 % of the value found for bulk CS₂. Even though the instantaneous contribution of the substrate will mask the SRS signal around zero delay the SRS signal should be observable for larger delays. As this was not the case our detection accuracy once again poses an upper limit for the strength of the TSRS signal of about 10^{-5} .

5.9 Conclusions

Calculations on the basis of the theory developed in the first part of this chapter show that a surface-enhanced stimulated Raman experiment with the present laser powers should be visible. The expected signal strength is not huge, but the signal should be detectable ((S/N)≈10, RC=1 s).

Experimentally surface-enhanced SRS has not yet been observed. Many interesting effects have been measured and these effects might partially frustrate the observability of the surface-enhanced SRS signal. The effects that have been measured are summed up below. Apart from a time-resolved study of the temperature variations of the silver film, which formed the key issue in chapter 4, heat diffusion into the CCl₄ on top of the silver could be observed in a time-resolved way. The steady-state increase in temperature of the liquid led to two striking results. First of all the shape of the ATR curve depended on the intensity of the incident beams. The curves shifted to lower angles of incidence and were heavily deformed. Secondly hysteresis could be observed in measurements of the reflectivity as a function of the angle of incidence, or as a function of the incident intensity. Superheating of CCl₄ by more than 40 °C could be observed.

The deformation of the ATR curve, resulting from a DC rise in temperature, might have really devastating effects on the strength of the surface-enhanced SRS. It is yet unknown how the change in behavior of the SP (and possible trapping of the SP), which is directly related to the deformation of the ATR curve, is reflected in a change in the enhancement of the fields coupled in and out of the silver-medium 3 interface. K_{in} and K_{out} are likely to decrease as a result of the inhomogeneity in temperature of the liquid. If this is the case the surface enhancement will decrease as well.

DC temperature variations can be excluded through the use of a low repetition rate system that makes use of amplified light pulses. Chen et al.² have demonstrated the feasibility of such an experiment. They were the first to demonstrate the existence of surface enhancement in a CARS experiment for a glass-silver-benzene system with the use of unfocused 20 mJ pulses at a repetition rate of 10 pulses per minute.

A point of worry for further studies is the form of the ATR curves of the prepared Kretschmann system, as measured with unfocused light. Practically all the ATR curves are roughly a factor 2-3 wider than the theory predicts for flat films. This discrepancy is almost certainly caused by roughness of the glass substrate and of the evaporated silver film. If an experimental technique could be found to reduce this roughness and diminish the width of the ATR curve the surface-enhancement would certainly benefit strongly from it.

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SUMMARY

Spontaneous Raman scattering is an inelastic light scattering process that is characterized by the fact that the frequency difference between the incident and scattered radiation is independent on the frequency of the incident radiation. The energy difference between the incident and scattered photons is used for the excitation of one (or several) degrees of freedom (modes) of the material under study, which are then said to be Raman-active.

Since the invention of the laser the related technique of stimulated Raman scattering (SRS) became experimentally available. For a stimulated Raman experiment two laser beams are focused in a (transparent) sample. When the frequency difference between both lasers matches the eigenfrequency of a Raman-active mode, the beam with the lowest frequency, here denoted as "red", gains in intensity while the intensity of the beam with the highest frequency, denoted as "yellow", decreases after passage through the sample.

In chapter 1 several different theoretical approaches to stimulated Raman scattering and other nonlinear optical techniques are presented to give our experiments a broad theoretical basis.

In all our experiments we make use of two mode-locked dye lasers, which are synchronously pumped by one actively-mode-locked Argon-ion laser. The two dye lasers, which are tunable in frequency, produce pulses of typically 5 ps pulse width with a repetition rate of 82 MHz. After splitting and recombining the two laser beams, synchronized pairs of pulses are formed each consisting of one red pulse and one yellow pulse. When the frequency difference between the lasers fits the eigenfrequency of a Raman-active mode, each of these pairs can excite this mode. Using one pair to pump and a second pair to probe the Raman-active excitation, after a variable delay, its dynamics can be studied directly in the time domain. This technique is called time-resolved stimulated Raman scattering (TSRS). All materials studied up to now (CS_2 , C_6H_6 , diamond) showed an exponential decay in time, being related to the transverse relaxation time T_2 . Spontaneous Raman scattering yields similar information, the techniques are complementary and both have their pros and cons.

In chapter 2 stimulated Raman scattering is treated from an experimental point of view. As there are only a few TSRS setups in the whole world and I was the first in our group to develop this optical experiment, the technique itself gets a lot of attention. The interpretation of the

time-resolved measurements is not simple because other nonlinear effects, besides TSRS, are observable. They are denoted as the electronic contribution and the Kerr effect and result both in an intensity-dependence of the index of refraction of the material under study.

In chapter 3 the possible saturation of a Raman transition is considered. For this purpose the excited-state population is calculated and the intensities necessary for a "Raman echo" experiment are evaluated.

Although TSRS is reasonably well suited for the study of thin dielectric layers, signals produced by layers thinner than $0.1\text{-}1\text{ }\mu\text{m}$ are hardly detectable with our setup. One of the reason we started investigating surface plasmons (SP) is their capability to enhance this signal strength.

A surface plasmon is an electro-magnetic (EM) excitation bound to a metal-dielectric interface that travels almost at the speed of light along the interface. SP can be excited with the so-called Kretschmann geometry, consisting of a thin metal film evaporated onto a (glass) substrate with a dielectric, denoted as medium 3, on top. At certain angles, a light beam, coming through the glass, can excite SP at the metal-medium 3 interface.

In chapter 4 some characteristics of SP are described as well as an experiment we have performed to study their dynamics. In this "pump-probe" experiment a (first) yellow pulse creates SP and the metal film is heated due to SP decay resulting in a change in reflectivity of a (second) red probe pulse. The possibility to measure changes in reflectivity of 10^{-7} enabled us to observe the 50 fs decay of the SP, the subsequent (ns) diffusion of heat into the substrate and the (ps) acoustic oscillations that were produced by the acoustic phonons generated through SP decay.

The local EM field associated with SP can be far greater than the incident EM field. One therefore expects the stimulated Raman scattering, as well as other nonlinear effects to be "surface-enhanced" when these effects are observed with the help of SP. In the first part of chapter 5 calculations are presented to determine the signal strength in a surface-enhanced SRS experiment. While trying to perform this experiment we observed a number of new and interesting effects, being described in the second part of chapter 5. Apart from (local) superheating ($>40\text{ }^{\circ}\text{C}$), bistability of the reflectivity, self-trapping of SP and (ns) diffusion of heat into medium 3 could be observed. In conclusion SP are very sensitive local probes of all kind of properties at metal-dielectric interfaces.

SAMENVATTING

Spontane Raman-verstrooiing is een inelastisch licht-verstrooiings proces dat gekenmerkt wordt door het feit dat het frequentieverschil tussen het inkomende en het verstrooide licht onafhankelijk is van de frequentie van eerstgenoemde. Het energieverval tussen de inkomende en verstrooide fotonen wordt benut voor de excitatie van één (of meerdere) vrijheidsgraden (modes) van het te onderzoeken materiaal, die dan Raman-actief genoemd worden.

De aanverwante techniek van gestimuleerde Raman-verstrooiing (SRS) werkt als volgt: In een SRS experiment worden twee laserbundels gefocusseerd in een transparant materiaal. Wanneer het frequentieverschil tussen beide lasers overeenkomt met de eigenfrequentie van een Raman-actieve mode, zal de intensiteit van de bundel met de laagste frequentie, hier "rood" genoemd, toenemen en zal de intensiteit van de bundel met de hoogste frequentie, hier "geel" genoemd, afnemen bij doorgang door het preparaat.

In hoofdstuk 1 worden, om onze experimenten theoretisch te ondersteunen, verschillende beschrijvingswijzen besproken van zowel gestimuleerde Raman-verstrooiing als van andere niet-lineaire optische technieken.

Alle experimenten zijn gedaan m.b.v. twee "fase-gekoppelde" kleurstoflasers, die gelijktijdig door één fase-gekoppelde Argon-ion laser gepompt worden. Beide kleurstoflasers zijn verstembaar in kleur en produceren pulsen met een typische pulsbreedte van 5 ps en een herhaalfrequentie van 82 MHz. Hiermee maken we gesynchroniseerde pulsparen die bestaan uit een rode puls en een gele puls. Indien het frequentieverschil tussen beide lasers overeenkomt met de eigenfrequentie van een Raman-actieve mode, kan elk pulspaar deze mode aanslaan. Door met één paar deze mode te exciteren en vervolgens met een tweede paar de mate van excitatie te observeren kan men de dynamica van deze mode rechtstreeks meten. Deze techniek heet "tijdsopgeloste gestimuleerde Raman-verstrooiing" (TSRS). In de tot nu toe bestudeerde materialen (CS_2 , C_6H_6 , diamant) bleek het verval steeds exponentieel en kon het beschreven worden met de zogenoemde transversale relaxatietijd T_2 . Soortgelijke informatie kan verkregen worden uit spontane Raman-metingen. Beide technieken vullen elkaar aan en hebben hun eigen voor- en nadelen.

In hoofdstuk 2 wordt de experimentele kant van de gestimuleerde Raman-verstrooiing besproken. Er wordt veel aandacht besteed aan de techniek zelf, aangezien er slechts enkele TSRS opstellingen in de wereld zijn en ik de eerste in onze groep ben die deze techniek ontwikkelt heeft. De tijdsopge-

loste metingen zijn soms moeilijk te interpreteren aangezien, behalve TSRS, ook andere niet-lineaire effecten bijdragen. Deze worden aangeduid als de "electronische bijdrage" en het "Kerr-effect" en resulteren beide in een intensiteits-afhankelijkheid van de brekingsindex van het bestudeerde medium.

In hoofdstuk 3 wordt de mogelijkheid van verzadiging van de Raman-overgang behandeld. Hiervoor wordt zowel de bezetting van het aangeslagen niveau als de intensiteit nodig voor het maken van een "Raman echo" berekend.

Hoewel TSRS redelijk geschikt is om de dynamica van dunne diëlectrische lagen te bestuderen, blijkt onze opstelling ongeschikt voor de detectie van lagen dunner dan $0.1\text{--}1\text{ }\mu\text{m}$. Dit was één van de redenen waarom we oppervlakte-plasmonen (SP) zijn gaan bestuderen.

Een oppervlakte-plasmon is een electro-magnetische (EM) golf die gebonden is aan de grenslaag tussen een metaal en een diëlectricum en bijna met de lichtsnelheid langs deze grenslaag beweegt. SP kunnen gecreëerd worden in de Kretschmann-geometrie, bestaande uit een dunne metaallaag opgedampt op een (glazen) ondergrond met een diëlectricum, aangeduid als "medium 3", er bovenop. Onder de zogenoemde "plasmonhoek" kan een lichtbundel vanuit het glas SP aanslaan op de (metaal-medium 3) grenslaag.

Hoofdstuk 4 behandelt enkele eigenschappen van SP. Hier wordt ook een "excitatie-observatie" experiment beschreven dat als volgt werkt: Een (eerste) gele puls creëert SP die vervallen en het metaal verhitten. Als gevolg hiervan zal een (tweede) rode observatie puls op een iets andere manier worden gereflecteerd. De mogelijkheid om veranderingen van 10^{-7} in reflectiviteit te meten stelde ons in staat om zowel het 50 fs verval van de SP te bestuderen als de daaropvolgende (ns) warmtediffusie in de glazen ondergrond en de (ps) geluidsgolf, beide geproduceerd via SP verval.

Het locale EM veld behorende bij de SP kan veel groter zijn dan het inkomende EM veld. Hierdoor verwacht men dat gestimuleerde Raman verstrooiing en andere niet-lineaire effecten op de grenslaag versterkt zullen worden. Het eerste deel van hoofdstuk 5 beschrijft een berekening van de verwachte "oppervlakte-versterking". Het tweede deel van hoofdstuk 5 beschrijft de nieuwe interessante verschijnselen die we gemeten hebben toen we een oppervlakte-versterkt SRS experiment uitvoerden. Deze omvatten (locale) oververhitting ($>40\text{ }^{\circ}\text{C}$), bistabiliteit van het reflectievermogen, "zelf opsluiting" van SP en (ns) warmtediffusie naar medium 3. Ik concludeer dat m.b.v. oppervlakte-plasmonen allerlei eigenschappen van een metaal-diëlectricum grenslaag op zeer gevoelige wijze kunnen worden gemeten.

POPULAIRE SAMENVATTING

Spectroscopie is de tak van de natuurkunde die de wisselwerking tussen licht en moleculen bestudeert. Moleculen zijn de bestanddelen waaruit elk materiaal is opgebouwd. Vroeger werden bij optisch onderzoek lampen als lichtbron gebruikt. Sinds de uitvinding van de laser in 1960 gebruikt men meestal laserlicht, omdat dit geconcentreerd is in een nauwe bundel van meestal hoge intensiteit. Bovendien heeft het laserlicht meestal 'één' kleur die met geen enkele andere kleur is vermengd.

Bij een lage lichtintensiteit is het gedrag van de moleculen lineair. Dit betekent dat een verdubbeling van de lichtintensiteit een twee maal zo grote reactie geeft. Bij hoge intensiteiten blijkt dit niet meer het geval te zijn en treden de zogenoemde niet-lineaire optische effecten op. Deze effecten zijn om twee redenen interessant.

Natuurkundig gezien zijn niet-lineaire optische effecten interessant vanwege het simpele feit dat ze optreden en nog niet nauwkeurig zijn bestudeerd. Wetenschappelijk onderzoek is altijd gericht op het bestuderen van verschijnselen die nog niet volledig begrepen zijn. Onderzoekers proberen, door middel van experimenten, kennis te vergaren over de optredende processen. Zuiver wetenschappelijk onderzoek is enkel en alleen gericht op het vergaren van kennis. Toepassing van de verkregen resultaten is niet noodzakelijk om het onderzoek te rechtvaardigen.

Een tweede reden voor de interesse in de niet-lineaire optica is toch de duidelijke aanwezigheid van toepassingsgebieden, bijvoorbeeld het toenemende gebruik van glasvezels voor communicatie-doeleinden. De hoge lichtintensiteiten in deze glasvezels, en de optredende niet-lineaire effecten, kunnen aanleiding geven tot storing en vervorming van de verzonden berichten. Dit vraagt nader onderzoek. Een ander toepassingsgebied betreft de ontwikkeling van optische computers. Deze kunnen berekeningen uitvoeren op basis van niet-lineaire optische effecten. Zulke computers kunnen in principe veel sneller werken dan de huidige elektronische computers.

Het onderzoek dat in dit proefschrift staat beschreven is zuiver wetenschappelijk gericht. De doelstelling was meer inzicht te krijgen in niet-lineaire optische processen. Onze kennis is na 4 jaren onderzoek inderdaad sterk toegenomen. Dit blijkt onder andere uit verschillende publikaties in internationale natuurkundige tijdschriften. Via deze publikaties kunnen onze resultaten ook door andere natuurkundigen

worden gebruikt.

Voor mijn onderzoek heb ik gebruik gemaakt van lasers die zeer korte lichtpulsen geven. Met deze pulsen, die een pulsduur hebben van slechts 5 picoseconde (één picoseconde is een miljoenste van een miljoenste seconde), heb ik geprobeerd om de relaxatie van verschillende "vrijheidsgraden" te bestuderen. De vrijheidsgraden die ik heb bestudeerd zijn moleculaire vibraties in vloeistoffen en vaste stoffen en roostertrillingen in diamant.

De gebruikte techniek is steeds dezelfde en is een "aanslag-opvraag"-procedure. De eerste lichtpuls geeft de te onderzoeken vrijheidsgraad een tik. De aangeslagen trilling zal na verloop van tijd in sterkte verminderen. We noemen dit de relaxatie van de trilling. Als we net na de eerste puls een tweede lichtpuls door het materiaal sturen zal deze lichtelijk verstoord worden door de nog aanwezige trilling. Door nu het tijdsverschil tussen de eerste "aanslagpuls" en de tweede "opvraagpuls" te variëren kunnen we de relaxatie van de aangeslagen vrijheidsgraad direct meten. We noemen zo'n experiment dan tijds-opgelost.

De methode die we gebruiken om trillingen aan te slaan heet "gestimuleerde Raman verstrooiing". Als je een gele laserbundel op een materiaal richt blijkt er meestal niet alleen verstrooid geel licht maar ook een klein beetje rood licht af te komen. Als je een groene laserbundel gebruikt blijkt meestal ook een beetje geel licht geproduceerd te worden. De lichtenergie die via deze verstrooiing verdwijnt veroorzaakt de trillingen in het materiaal. Dit effect is genoemd naar zijn ontdekker, de Indiër Sir Chandradekhara Raman. Het woord "gestimuleerd" houdt verband met het feit dat het Raman effect ook optreedt wanneer je zowel geel als rood licht aanbiedt. In dat geval resulteert het Raman effect in een versterking van de doorgelaten rode bundel en een verzwakking van de doorgelaten gele bundel. Bij gestimuleerde Raman verstrooiing bestaan zowel de eerderbeschreven aanslagpuls als de opvraagpuls feitelijk uit een "pulspaar" van een gele en een rode puls.

In hoofdstuk 1 worden diverse niet-lineaire optische theorieën behandeld, waarbij de nadruk natuurlijk op gestimuleerde Raman verstrooiing ligt. In hoofdstuk 2 worden de gebruikte apparaten en meettechnieken globaal beschreven. Tevens worden hier de belangrijkste tijdsopgeloste resultaten, verkregen met de "aanslag-opvraag" procedure, gepresenteerd. Behalve het

Raman effect zijn nog twee andere effecten zichtbaar: de "electronische bijdrage" en het "Kerr-effect". In hoofdstuk 3 wordt nader ingegaan op de vraag hoe sterk het systeem bij gestimuleerde Raman verstrooiing door de lichtpulsen wordt verstoord. Bovendien staat in hoofdstuk 3 de aanverwante techniek van "coherente anti-Stokes Raman verstrooiing (CARS)" beschreven. De resultaten verkregen met deze techniek worden vergeleken met de resultaten verkregen met behulp van gestimuleerde Raman verstrooiing.

Voor het bestuderen van optische verschijnselen op of in de buurt van oppervlakken blijkt het gebruik van oppervlakte-plasmonen van essentieel belang. Een oppervlakte-plasmon kan beschouwd worden als licht dat gevangen is op de grenslaag van een metaal en een ander materiaal. Voor de experimenten maken we gebruik van een glazen prisma, waarop we een zeer dunne laag (met een dikte van 50 miljoenste millimeter) zilver dampen. Oppervlakte-plasmonen kunnen nu geproduceerd worden met een laserbundel die onder een bepaalde hoek door het glas heen op de zilverlaag gericht staat. De details van zo'n experiment zijn beschreven in hoofdstuk 4. Bovendien worden in hoofdstuk 4 enkele experimenten genoemd die we verricht hebben om het gedrag van oppervlakte-plasmonen nader te bestuderen.

Allereerst hebben we geprobeerd de levensduur van deze oppervlakte-plasmonen te meten. Omdat ze korter leven dan onze lichtpulsen konden we jammer genoeg geen gebruik maken van de aanslag-opvraag techniek. Toch konden we hun levensduur bepalen. Oppervlakte-plasmonen staan niet stil, maar reizen bijna met de lichtsnelheid langs het zilveroppervlak. Door de laserbundels heel scherp te focuseren (tot op 5 duizendste van een millimeter) en de opvraagbundel te verplaatsen ten opzichte van de aanslagbundel konden we kijken hoe groot de afstand is die de oppervlakte-plasmonen gemiddeld aflegden voordat ze uiteenvielen. Omdat we hun snelheid kunnen berekenen konden we zo hun gemiddelde levensduur bepalen.

Bij vertraging van de opvraagpuls ten opzichte van de aanslagpuls bleek het signaal toch zwakker te worden. Onze interpretatie is dat we, in dat experiment, met de aanslag-opvraag techniek keken naar de vervalsprodukten van de oppervlakte-plasmonen. Dit verval bleek onder andere een schokgolf in de zilverlaag te produceren. Verder bleek de zilverlaag gedurende korte tijd iets opgewarmd te worden door de aanslagpuls. Deze warmte lekte echter snel (5 miljardste van een seconde) weg naar het glazen prisma.

Oppervlakte-plasmonen kunnen prima gebruikt worden voor het bestuderen van optische effecten op of in de buurt van een oppervlak. Ze zitten als het ware vast aan dit oppervlak en hebben een hele sterke wisselwerking met moleculen in de buurt van dit oppervlak. In het eerste deel van hoofdstuk 5 wordt de sterkte van deze wisselwerking uitgerekend. In het tweede deel van hoofdstuk 5 wordt een experiment beschreven waarmee we geprobeerd hebben gestimuleerde Raman verstrooiing met behulp van oppervlakte-plasmonen te meten. Dit is tot nog toe niet gelukt, maar we hebben wel diverse andere nog onbekende en interessante effecten ontdekt. Onze metingen wijzen onder andere uit dat de temperatuurstijging ten gevolge van het verval van oppervlakte-plasmonen aanzienlijk is en kan oplopen tot 100 °C. Deze temperatuursverhoging blijkt grote invloed te hebben op het gedrag van de oppervlakte-plasmonen. Ook blijkt dat de vloeistof die we voor deze metingen boven het zilver hadden aangebracht veel heter kan worden dan de temperatuur waarop het doorgaans kookt. De vloeistof kan zelfs tot meer dan 40 °C boven het normale kookpunt worden oververhit!

Het onderzoek dat in dit proefschrift staat beschreven is uitgevoerd in het kader van een beleidsruimte van de stichting "Fundamenteel Onderzoek der Materie (FOM)". Dit is een landelijke stichting die met overheidsgelden het wetenschappelijk onderzoek in Nederland stimuleert. Iedereen kan in principe een aanvraag voor financiering van een project indienen, maar een commissie van "wijze" natuurkundigen beslist uiteindelijk welke aanvragen gehonoreerd worden. Ons onderzoek past goed in het Nederlandse natuurkundebeleid. In 1983 kreeg het een financiële bijdrage van de stichting FOM toegewezen. Gelukkig betekent mijn promotie niet het einde van dit onderzoek. Het wordt (zelfs nu al) voortgezet door een "nieuwe" assistent in opleiding (a.i.o.), te weten Rogier Groeneveld.

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Met veel plezier denk ik terug aan de 4 jaar die ik als promovendus op het Natuurkundig Laboratorium heb doorgebracht in de groep "Spectroscopie van de gecondenseerde materie". Wat ik altijd enorm op prijs heb gesteld is de vrijheid die je hier als experimentator hebt. Deze vrijheid werd nog vergroot doordat het onderzoek met ultra-korte laserpulsen kort voor mijn komst was opgestart. Experimentele vrijheid vormt volgens mij de basis van fundamenteel onderzoek. Hoewel we (intern) wel eens geringschattend doen en experimenteren beschrijven in termen als "prutsen", "spelen" en "knoppen draaien", blijkt achteraf dat met het begrip ook de grote lijn en de schoonheid van het onderzoek zichtbaar wordt.

Na de voltooiing van dit proefschrift wil ik graag mijn dank uitspreken aan iedereen die betrokken is geweest bij het onderzoek dat ik de afgelopen jaren heb uitgevoerd. Allereerst gaat mijn dank uit naar mijn promotor Ad Lagendijk, die me de afgelopen jaren met zijn informele en hartstochtelijke aanpak op zo'n geslaagde wijze heeft begeleid, me van de wetenschap heeft laten proeven en me haar smaak heeft leren waarderen. Zonder hem zou dit proefschrift er niet gekomen zijn. Verder gaat mijn dank naar alle collega's die voor zo'n gezellige werksfeer zorgden en met wie ik zo prettig heb samengewerkt. Vooral met Mick Baggen heb ik vaak geëxperimenteerd. Het opzetten van de tijdopgeloste gestimuleerde Raman-metingen in een diamantcel, zie sectie (2.9), was zijn idee. Ook de tijdopgeloste CARS metingen die beschreven zijn in sectie (3.3) hebben we samen uitgevoerd. Rogier Groeneveld, die begonnen is als doctoraal-student en nu AIO is, dank ik voor zijn medewerking aan een deel van de "oppervlakteplasmon" experimenten zoals beschreven in secties (5.6)-(5.8). Erik Spaans heeft als doctoraal-student bijdragen geleverd aan de secties (2.8) and (2.12). Ook wil ik Martine de Mazière en Martin van der Mark bedanken voor hun aandeel in het onderzoek, evenals de doctoraal-studenten Han Saft en Daniëlla Vischjager. Verder heb ik nuttige en interessante discussies gehad met: Jook Walraven, Rudolf Sprik, Rob Vreeker, Meint van Albada, Pedro de Vries, Raymond van Roijen, Jaap Berkhout, Juleon Schins en vele anderen.

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hebben gebogen. Voor glaswerk en vacuumononderdelen was Bert Zwart altijd paraat. Op de afdeling metallurgie hebben Ton Riemersma en Hugo Schlatter mij uitgelegd hoe opdampen en sputteren in de praktijk gaat. Zij zorgden tevens voor een groot deel van de benodigde chemicaliën. Ben Leonards maakte alle tekeningen in dit proefschrift, waarvoor mijn dank. Als laatste wil ik nog Wim Koops noemen, die nu sinds een jaar lasertechnicus is bij onze groep.

Ik overdrijf niet als ik onze groep beschrijf als fanatiek en dynamisch. Dit kwam o.a. tot uiting in het werkoverleg en de wetenschappelijke groepsbesprekingen op vrijdagmiddag. Vooral deze laatstgenoemde deden voor een buitenstaander nogal vreemd aan. De discussie liep steevast hoog op en deze middagen vormden een ideale training in "spreken voor aggressief publiek". Ja, misschien mis ik die vrijdagmiddagen nog wel het meest.