

Local-Field Effects on Spontaneous Emission in a Dense Supercritical Gas

Frank J. P. Schuurmans, Dennis T. N. de Lang, Gerard H. Wegdam, Rudolf Sprik, and Ad Lagendijk

Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

(Received 9 January 1998)

We present results of experiments on the spontaneous emission rate of a europium complex in dense supercritical CO₂. The refractive index of the supercritical gas is varied from 1.00 to 1.27 by increasing the pressure up to a 1000 bars. Accordingly, the spontaneous emission rate changes. Local-field effects on spontaneous emission are clearly observed in these experiments. The empty-cavity model for the spontaneous emission rate inside dielectrics is confirmed. [S0031-9007(98)06249-8]

PACS numbers: 32.80.-t, 42.50.-p, 78.55.-m

In 1917, Einstein demonstrated that spontaneous emission must occur if matter and radiation are to achieve thermal equilibrium [1]. This picture is so fundamental, that spontaneous emission rates are often believed to be an inherent property of the atom. However, the spontaneous emission rate can be modified by changing the environment, as was noticed by Purcell [2]. In the early 1970s, Drexhage carried out pioneering experiments on the modification of the luminescence decay rate of europium complexes in front of a metallic mirror [3]. Later, many theoretical [4] and experimental [5] investigations have been devoted to the enhancement and inhibition of spontaneous emission of atoms in resonant cavities, in which case larger modifications are possible. Modifications of the spontaneous emission rate can also be induced by placing the radiator inside a spatially inhomogeneous dielectric. For example, the case of emission near a dielectric interface has been studied both experimentally [3,6] and theoretically [7]. Complete inhibition of spontaneous emission is predicted to occur in photonic band gap materials [8]. In all these approaches the rate of spontaneous emission is modified because the radiation density of states is altered.

Strikingly, the modification of spontaneous emission rate *inside* simple dielectrics has not been so extensively studied. The radiative lifetime of an atom or molecule embedded in a dielectric has been predicted by Nienhuis and Alkemade [9]

$$\tau_R(n) = \frac{\tau_R^{\text{vac}}}{n}. \quad (1)$$

Here $\tau_R(n)$ and τ_R^{vac} are the radiative lifetimes in the dielectric with refractive index n and in vacuum, respectively. However, Eq. (1) arises from quantizing the *macroscopic* Maxwell's equations, while in principle the atom couples to the *microscopic* vacuum fluctuations. To arrive from a microscopic to a macroscopic description as in Eq. (1) involves complex spatial or temporal averaging procedures. Especially the question how to treat the dielectric at and nearby the radiating atom is far from trivial. In Eq. (1) the dielectric is taken to be homogeneous over the entire space, also at the position of the radiating atom, assuming the atom is not at all present. Although the dimension of the radiating atom is much smaller than

the wavelength involved, sizable deviations from Eq. (1) are expected, since dipole radiation has a $\frac{1}{r^3}$ divergence at the origin. To incorporate these microscopic interactions local-field corrections are introduced. The approach is still macroscopic in nature, but the electric field at the radiating dipole, the *local field*, is different from the macroscopic field to incorporate local interactions. Macroscopic derivations of the local-field correction often imply the use of a cavity around the radiating dipole. The specific choice of the cavity is subtle matter [10], greatly complicating the interpretation of these models. Two limiting cases for a local-field model have been proposed. The *empty*-cavity model [11], in which the atom is inside a real empty spherical cavity in the dielectric, leads to

$$\tau_R(n) = \left(\frac{3n^2}{2n^2 + 1} \right)^{-2} \frac{\tau_R^{\text{vac}}}{n}. \quad (2)$$

In contrast, the *full* or virtual-cavity model [12] describes a cavity filled with a medium having the same average polarizability density as the surrounding dielectric. However, the dipoles *inside* the cavity do not contribute to the local field, resulting in

$$\tau_R(n) = \left(\frac{n^2 + 2}{3} \right)^{-2} \frac{\tau_R^{\text{vac}}}{n}. \quad (3)$$

The empty and full cavity models are distinct because the boundary conditions of the cavity are different.

A decisive experiment on the radiative lifetime of an atom in a dielectric, with varying refractive index, could settle the discussion on which local-field correction applies to spontaneous emission. In the few previous experiments [13], the refractive index was changed by dissolving the radiating molecule in chemically different liquids. An unfortunate aspect of this procedure is that varying the refractive index in this manner could lead to uncontrollable side effects. For example, the vacuum radiative lifetime or the quantum efficiency of the radiating molecule could well depend on the type of liquid. Experiments performed in our group on the luminescence lifetime of one molecule dissolved in 15 different liquids indeed confirm these problems. Thus we decided on a new type of experiment, in

which the refractive index is varied in a more controllable manner, circumventing these side effects.

In this Letter we present measurements on the radiative lifetime of a Eu^{3+} -complex dissolved in a supercritical gas as a function of pressure. Then, the refractive index changes because the density of the molecules in the dielectric changes. The type of molecule, CO_2 , remains the same for all refractive indices, improving on previous experiments [13]. Our experiments confirm the empty-cavity model [Eq. (2)]. It will be argued that the experimental results can be explained by a molecular cavity model based on density of state arguments.

The surrounding dielectric is supercritical CO_2 at pressures between 1 and 1000 bars. The refractive index ranges from 1.00 to 1.27. To suppress critical density fluctuations of the dielectric, the gas is kept a few degrees above the critical temperature, at $35.00 \pm 0.05^\circ\text{C}$. The experiments are performed in a pressure cell with optical access [14]. The refractive index is determined *in situ*, using a time-resolved interferometric technique [15]; see Fig. 1. A 70 fs pulse from a Ti:sapphire laser (Spectra Physics, Tsunami) with a central wavelength of 780 nm is passed through the supercritical gas in the pressure cell. To compare the transmitted pulse through the dense gas with an undistorted reference pulse, the pressure cell is placed in one of the arms of a Mach-Zehnder interferometer. This pulse pair is autocorrelated using a Fourier-transform (FT) spectrometer (BioRad FTS-60A). The high stability of FT spectrometer enables us to measure the pulse delay through the dense gas with 10 fs resolution. The optical path length of the pulse through the gas in the cylindrical pressure cell is 6.285 ± 0.005 mm, as determined by a three-point measurement. Combining the pulse delay and the optical path length readily gives the refractive index. Using this technique, we are able to determine the refractive index with an accuracy of 10^{-3} . Although the refractive index is determined at 780 nm it also applies, within the experimental

error, at the wavelengths of Eu^{3+} luminescence (around 600 nm), since CO_2 has a low dispersion in this wavelength region.

The radiating molecule is $\text{Eu}(\text{fod})_3$ [16], a β -diketone ligand complex. Eu^{3+} complexes are well suited for this experiment, as was pointed out by Rikken *et al.* [13]. The molecule is optically excited with a pulsed, tripled Nd:YAG laser at 354.7 nm. The luminescence is dispersed by a Spex 1401 double spectrometer (resolution 2 cm^{-1}) and detected with a Hamamatsu R943-02 counting photomultiplier. The radiative decay times are in the millisecond range and are recorded with a multichannel scaler (EG&G-Ortec, T914). All luminescence lifetime measurements presented are taken at $16\,360\text{ cm}^{-1}$, which corresponds to the maximum of the strongest luminescence peak of Eu^{3+} , the $^5\text{D}_0$ to $^7\text{F}_2$ transition. The found decay times hold for all Eu^{3+} transitions from the $^5\text{D}_0$ level to $^7\text{F}_i$ manifold, as the upper level is nondegenerate. A typical luminescence decay measurement is depicted in Fig. 2. As can be seen, the luminescence decay consists of two components. Both are attributed to Eu^{3+} , as is concluded from time-resolved luminescence spectra. The spectrum of the fast decaying component is much broader than the spectrum of the slowly decaying component. For the $^5\text{D}_0$ to $^7\text{F}_0$ transition the linewidths are 50 ± 5 and $17 \pm 2\text{ cm}^{-1}$, respectively. From this we conclude that the fast decaying component stems from the luminescence of a dissociating Eu complex and is therefore disregarded. The decay times are determined from the slowly decaying contribution. Furthermore, the $\text{Eu}(\text{fod})_3$ luminescence spectra are identical for all pressures. This indicates that the symmetry of the complex is independent of pressure, which means that the transition dipole moments involved are unaffected by the varying refractive index.

In these experiments the quantum efficiency of the luminescence plays an important role. The nonradiative decay rate of rare-earth ions via multiphonon relaxation [17]

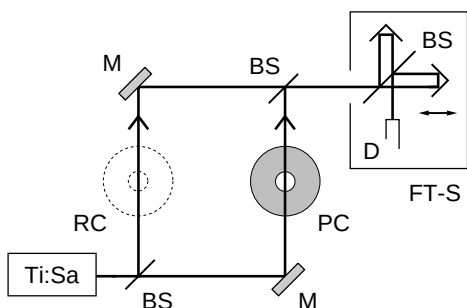


FIG. 1. A schematic overview of the interferometric time-resolved pulse transmission setup. BS: beam splitter; D: detector; FT-S: Fourier-transform spectrometer; M: mirror; RC: reference cell; PC: pressure cell; Ti:Sa: titanium sapphire laser. The 70 fs pulse train from a Ti:sapphire laser is sent through a fixed Mach-Zehnder interferometer with the pressure cell in one of the paths. The cross correlate of the transmitted and reference pulses is recorded with a scanning Fourier-transform spectrometer. In this way the refractive index change can be determined *in situ* with an accuracy of 10^{-3} .

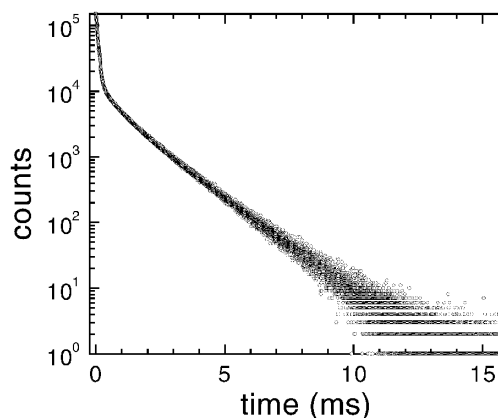


FIG. 2. Typical luminescence decay of $\text{Eu}(\text{fod})_3$ dissolved in supercritical CO_2 at 99 bars. Two different decay channels are observed, both attributed to Eu^{3+} . The fast decaying component comes from a dissociated Eu complex and is disregarded. The decay times are subtracted from the slow decay.

strongly depends on the type of host material. In this process the most energetic vibrations contribute, since the nonradiative decay rate decreases exponentially with the number of phonons involved in the transition. For supercritical CO₂, mainly the fundamental around 1388 cm⁻¹ [18] contributes to the nonradiative decay. However, this multiphonon decay process of Eu³⁺ involves approximately 12 “phonons,” making it an unlikely process. Generally, experiments [17] have shown that when six phonons are involved, the nonradiative decay rate approximately equals the radiative decay rate. For CO₂, the ratio of the radiative to the nonradiative decay rate is estimated to be at least 200, independent of the refractive index. In our experiments, long luminescence lifetimes (~1.5 ms) for Eu(fod)₃ in supercritical CO₂ indeed indicate a high quantum efficiency. Given the estimate and the long luminescence lifetimes, we conclude that the efficiency is close to unity (within 0.5%). The luminescence lifetimes obtained are also the radiative lifetimes.

The measured variation of radiative lifetime with refractive index is shown in Fig. 3. Comparison is made to the empty-cavity [Eq. (2)], full-cavity [Eq. (3)], and no-cavity [Eq. (1)] models. Clearly, the empty-cavity model applies. Furthermore, it is observed that the extrapolated vacuum lifetimes slightly depend on the excitation energy. A 10% decrease in the lifetime is found when the pumping energy is increased from 4 ± 1 to 70 ± 20 mJ/cm²; similar dependences have been observed previously [19]. This effect is probably due to the cooperative decay of europium molecules via stimulated emission at higher pump intensities. Nonetheless, the empty-cavity model is confirmed for all pumping powers, giving confidence that this is indeed the right model.

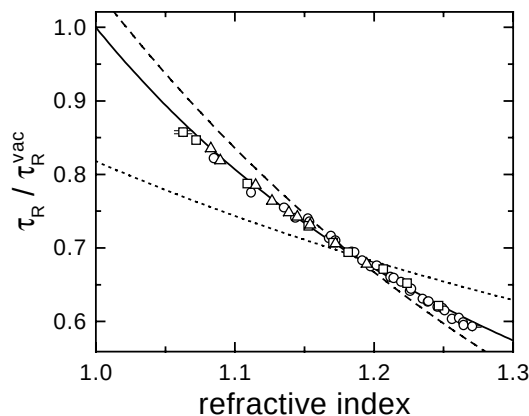


FIG. 3. The scaled radiative decay times as a function of refractive index. The decay times τ_R are scaled by the extrapolated vacuum lifetimes τ_R^{vac} . The vacuum lifetime slightly depends on the excitation energy per shot P . For $P = 4 \pm 1$ mJ/cm²: $\tau_0 = 2.04 \pm 0.01$ ms (squares); $P = 17 \pm 3$ mJ/cm²: $\tau_0 = 1.97 \pm 0.01$ ms (circles); $P = 70 \pm 20$ mJ/cm²: $\tau_0 = 1.85 \pm 0.01$ ms (triangles). For comparison, the results from the empty-cavity (full line), full-cavity (dashed line), and no-cavity models (dotted line) are plotted. The error bars for both the decay times and the refractive index are of the order of the symbol size.

Microscopically, the Eu complex is embedded in a dense gas of CO₂ molecules. These molecules sample many positions in the dielectric, except for the position of the complex. As a result, the microscopic electric field to which the radiating atom couples heavily fluctuates. Effectively, the radiating atom couples to the time-averaged microscopic field, which is equivalent to the macroscopic electric field [20], allowing for a description in terms of refractive indices. Note that the electric field at the position of the radiating atom $\mathbf{E}_{atom}$ is not the macroscopic field $\mathbf{E}_{macro}$, because the complex forms an excluded volume for the CO₂ molecules. In general, the connection between these two fields is complicated, as the dipole moment of the radiating molecule acts back on the polarizable surrounding molecules. However, the polarizability of Eu³⁺ is too small and the size of the complex too large (~1 nm) to polarize the CO₂ molecules, resulting in a simple relation between $\mathbf{E}_{atom}$ and $\mathbf{E}_{macro}$:

$$\mathbf{E}_{atom} = \frac{3n^2}{2n^2 + 1} \mathbf{E}_{macro}. \quad (4)$$

The complex is taken to be a real empty cavity [21], since it is an impenetrable region of low polarizability. For the vacuum fluctuations, which govern the radiative lifetime, a relation analogous to Eq. (4) holds. Thus the radiative lifetime of the Eu complex obeys the empty-cavity model, Eq. (2). In the case of larger transition dipole moments, deviations from Eq. (2) are expected, tending towards the full-cavity model, Eq. (3). In fact, for radiating molecules with a low polarizability density, the modification of the spontaneous emission rate can be considered due to a change in the electromagnetic mode structure, as in previous accounts [3–8]. These molecules simply form their own molecular microcavities.

The interpretation given above is still macroscopic in nature. The dielectric is not treated as a set of randomly positioned microscopic dipoles, but as a continuum up to molecular dimensions. In a microscopic derivation of the local-field effect, particle correlations in the spatial averaging procedure [22] are expected to lead to similar results. However, such a microscopic derivation for an inhomogeneous system consisting of two types of species, the radiating dipole and the dipoles of the dielectric, has not yet been done.

It would be of interest to study *stripped* rare-earth ions in dielectrics, since then the “cavity” is smaller leading to a larger modification due to dipolar interactions. However, chemical shielding by the complex is then absent, which might blur the entire effect. Another system to study local-field effects on spontaneous emission is a dense atomic gas consisting of two species, for example Na (probe atom) in Rb (dielectric). In this case, the polarizabilities involved are much larger enhancing dipole-dipole coupling, possibly leading to corrections to the empty-cavity model.

In conclusion, this Letter presents measurements on the radiative lifetime of Eu(fod)₃ in supercritical CO₂ under

varying pressure. The empty-cavity model for the modification of the spontaneous emission rate in a dielectric is confirmed in our experiments. The Eu complex is a real empty cavity in the dielectric, since its polarizability is low.

The authors acknowledge Pedro de Vries for discussions and Johan Soede, Johan van de Ridder, Huib Luigjes, and Wim Koops for valuable technical assistance with the high-pressure setup. This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie," which is financially supported by the "Nederlandse Organisatie voor Wetenschappelijk Onderzoek."

-
- [1] A. Einstein, Z. Phys. **18**, 121 (1917).
 - [2] E. M. Purcell, Phys. Rev. **69**, 681 (1946).
 - [3] K. H. Drexhage, J. Lumin. **1-2**, 693 (1970); K. H. Drexhage, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1974), Vol. XII.
 - [4] P. W. Milonni and P. L. Knight, Opt. Commun. **9**, 119 (1973); D. Kleppner, Phys. Rev. Lett. **47**, 233 (1981).
 - [5] P. Goy, J. M. Raimond, M. Gross, and S. Haroche, Phys. Rev. Lett. **50**, 1903 (1983); R. G. Hulet, E. S. Hilfer, and D. Kleppner, Phys. Rev. Lett. **55**, 2137 (1985); W. Jhe, A. Anderson, E. A. Hinds, D. Meschede, L. Moi, and S. Haroche, Phys. Rev. Lett. **58**, 666 (1987); D. J. Heinzen, J. J. Childs, J. E. Thomas, and M. S. Feld, Phys. Rev. Lett. **58**, 1320 (1987); F. De Martini, G. Innocenti, G. R. Jacobovitz, and P. Mataloni, Phys. Rev. Lett. **59**, 2955 (1987).
 - [6] C. K. Carniglia, L. Mandel, and K. H. Drexhage, J. Opt. Soc. Am. **62**, 479 (1972); R. E. Kunz and W. Lukosz, Phys. Rev. B **21**, 4814 (1980); E. Snoeks, A. Lagendijk, and A. Polman, Phys. Rev. Lett. **74**, 2459 (1995).
 - [7] C. K. Carniglia and L. Mandel, Phys. Rev. D **3**, 280 (1971); H. Khosravi and R. Loudon, Proc. R. Soc. London A **433**, 337 (1991).
 - [8] E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987); S. John and T. Quang, Phys. Rev. A **50**, 1764 (1994).
 - [9] G. Nienhuis and C. Th. J. Alkemade, Physica (Amsterdam) **81C**, 181 (1976).
 - [10] S. M. Barnett, B. Huttner, R. Loudon, and R. Matloob, J. Phys. B **29**, 3763 (1996).
 - [11] R. J. Glauber and M. Lewenstein, Phys. Rev. A **43**, 467 (1991).
 - [12] J. Knoester and S. Makumel, Phys. Rev. A **40**, 7065 (1989); S. M. Barnett, B. Huttner, and R. Loudon, Phys. Rev. Lett. **68**, 3698 (1992); S.-T. Ho and P. Kumar, J. Opt. Soc. Am. B **10**, 1620 (1993).
 - [13] G. L. J. A. Rikken and Y. A. R. R. Kessener, Phys. Rev. Lett. **74**, 880 (1995); P. Lavallard, M. Rosenbauer, and T. Gacoin, Phys. Rev. A **54**, 5450 (1996).
 - [14] H. W. L. Bruckman, A. C. Michiels, and N. J. Trappeniers, Physica (Amsterdam) **139A**, 175 (1986).
 - [15] R. H. J. Kop and R. Sprik, Rev. Sci. Instrum. **66**, 5459 (1995).
 - [16] Aldrich: Resolve-AlTM EuFOD, europium tris(6,6,7,7,8,8,8-heptafluor-2,2-dimethyl-3,5-octanedionate).
 - [17] W. T. Carnall, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneider and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 4, 171 ff; J. M. F. van Dijk and M. F. H. Schuurmans, J. Chem. Phys. **78**, 5317 (1983); B. Henderson and G. F. Imbush, *Optical Spectroscopy of Inorganic Solids* (Clarendon Press, Oxford, 1989), 1st ed., 242 ff.
 - [18] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Lancaster Press, Lancaster, 1951), 5th ed., p. 535.
 - [19] F. De Martini, M. Marrocco, P. Mataloni, L. Crescentini, and R. Loudon, Phys. Rev. A **43**, 2480 (1991).
 - [20] J. van Kranendonk and J. E. Sipe, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1977), Vol. XV.
 - [21] J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, New York, 1975), 2nd ed., p. 152.
 - [22] A. Lagendijk, B. Nienhuis, B. A. van Tiggelen, and P. de Vries, Phys. Rev. Lett. **79**, 657 (1997).