Luminescence of $Eu(fod)_3$ in a homologic series of simple alcohols

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We present measurements on the luminescence of $Eu(fod)_3$ dissolved in a series of (deuterated) alcohols and mixtures hereof, to test local-field corrections on spontaneous emission. The alcohols used are $CH_3(CH_2)_mOH$, with m ranging from 0 for methanol to 9 for 1-decanol. Accordingly, the refractive index varies from 1.33 to 1.44. To test the influence of the intrinsic molecular vibrations of the alcohols on the luminescence properties, also deuterated alcohols are used: $CH_3(CH_2)_mOD$, with $m=0,1,3$. Although the chemically homologic series of alcohols was carefully selected, small variations in the local environment of $Eu(fod)_3$ complex upon changing the host (alcohol), blur most of the local-field effect on spontaneous emission. © *2000 American Institute of Physics.* [S0021-9606(00)03332-8]

I. INTRODUCTION

In a dielectric material, the local electric field at the position of a constituting atom or molecule is different from the macroscopic one, due to the influence of the surrounding atoms (molecules) that form the dielectric.[1] This well-known difference between local and macroscopic field leads to so-called local-field corrections, which apply to a wide variety of physical quantities, like the refractive index,[2,3] the dipole–dipole coupling strength,[4] and nonlinear optical susceptibilities.[5,6] Only quite recently it was realized that local-field corrections also apply to the spontaneous emission rate of an atom or molecule embedded in a dielectric.

The modification of the radiative decay rate of a luminescent center in a dielectric was originally predicted to follow:[7]

$$\Gamma_R(n)=\Gamma_0 n. \tag{1}$$

Here $\Gamma_R(n)$ and Γ_0 are the radiative decay rate in the dielectric with refractive index n and in vacuum, respectively. However, Eq. (1) arises from quantizing the *macroscopic* Maxwell's equations, neglecting the difference between local and macroscopic field. Theoretical studies have lead to the proposition of two limiting cases for the local-field correction to spontaneous emission. The *empty*-cavity model,[8–10] in which the center is considered to be inside a real empty spherical cavity in the dielectric, results in

$$\Gamma_R(n)=\left(\frac{3n^2}{2n^2+1}\right)^2\Gamma_0 n. \tag{2}$$

Note that the local-field factor in $\Gamma_R(n)$ appears squared, as the spontaneous emission rate can be expressed in terms of an expectation value of the product of two electric field operators.[8] In contrast, the *Lorentz* or virtual-cavity model[8,9,11] 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, giving

$$\Gamma_R(n)=\left(\frac{n^2+2}{3}\right)^2\Gamma_0 n. \tag{3}$$

We would like to emphasize that the two models are distinct because the boundary conditions of the cavity are different. The majority of the researchers in the field[11] favor the Lorentz local-field correction. On the other hand, experimental results[12–14] indicate that the empty-cavity model[10] should be employed. Obviously, there is a controversy to be resolved.

Recently, De Vries and Lagendijk[9] presented a full microscopic calculation of point dipoles on a cubic lattice, forming the dielectric, plus one impurity dipole (representing the radiating atom), using a Green's function formalism. For substitutional impurity dipoles, that is a medium dipole is replaced by an impurity dipole (at a lattice position), the empty-cavity result [Eq. (2)] was found to apply. For interstitials, that is when the impurity dipole is placed in between lattice sites and no medium dipoles are removed, the Lorentz local-field correction [Eq. (3)] determines the modification of spontaneous emission. A generalization to fluids was made and it was concluded that most often the substitutional result, that is Eq. (2) applies, in agreement with experimental observations.[12,13] Furthermore, an alternative, much simpler derivation of the results of Ref. 9 has been found,[15] using the macroscopic Onsager–Böttcher approach to model both substitutional and interstitial impurities. Both a microscopic[9] and macroscopic[15] explanation for the experimentally observed empty-cavity local field correction[12,13] has been presented, solving the theoretical part of the problem.

One the major difficulties encountered when trying to measure local-field effects on spontaneous emission is found in selecting the right combination of a luminescent center and dielectric with varying refractive index. Rikken and Kessener[12] used europium complexes as the luminescent center and various polar liquids with different refractive indices as the dielectric. When we wanted to generalize their

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results, we found that the choice of solvent is crucial. The optical properties of the $4f$ intra-shell transitions in Eu^{3+}-complexes can vary enormously by dissolving it in chemically different liquids, although seemingly the complex shields the rare earth ion from the environment. For example, the emission spectra may change, indicative that the symmetry of the ligand field changes. Accordingly, the transition dipole matrix elements, or equivalently Γ_0 in Eqs. (2) and (3), change. Furthermore, the luminescence quantum efficiency depends on the type of liquid. It was found that the luminescence lifetime of a particular complex could vary over nearly an order of magnitude by only dissolving it into chemically different liquids, without changing the refractive index.[16] A change in Γ_0 and/or quantum efficiency with varying refractive index may completely blur the observation of local-field effects on spontaneous emission. Nevertheless, Rikken and Kessener[12] succeeded to confirm the empty-cavity model [Eq. (2)]. More recently, we presented measurements on the radiative lifetime of a Eu^{3+}-complex dissolved in a CO_2 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.[12] Also these experiments confirm the empty-cavity local field correction [Eq. (2)].

In this paper, we present measurements of the luminescence of a europium complex, $Eu(fod)_3$, dissolved in a carefully selected, chemically homologic series of simple alcohols. The alcohols used are $CH_3(CH_2)_mOH$, with m ranging from 0 for methanol (MeOH) to 9 for 1-decanol (DeOH). Accordingly, the refractive index varies from 1.33 to 1.44. To test the influence of the intrinsic molecular vibrations of the alcohols on the luminescence properties, also deuterated alcohols are used: $CH_3(CH_2)_mOD$, with $m=0,1,3$. Despite our careful selection of the homologic series of alcohols, local-field effects on spontaneous emission are nearly completely blurred, most likely due to subtle changes in the local symmetry of luminescent europium center.

II. EXPERIMENT

A. Choice of system

In order to observe local-field effects on spontaneous emission in full glory, the system under consideration should meet several criteria. First of all, local-field effects only modify the *radiative* decay rate, and hence the luminescence quantum efficiency should preferably be high, that is close to a 100%, or otherwise accurately known. Secondly, changes in refractive index of the surrounding dielectric should not influence the electronic wave functions involved in the luminescent transition, so that the vacuum radiative decay rate Γ_0 can be considered as a constant parameter, independent of the refractive index. The combination of these selection criteria excludes many types of systems.

Standard fluorescing organic dye molecules can be immediately discarded, as their optical properties are highly sensitive to changes in the chemical properties of the environment.[17] This is mainly due to the fact that the electronic wave functions involved in the radiative transitions have a high-electron densities close to the edges of the dye molecule, making these wave functions very susceptible to changes in the local environment. As a result, not only the transition matrix elements change, but also the resonance frequencies and fluorescence quantum efficiency. So, what is needed is a luminescent center in which the electronic wave functions involved are well shielded from the surrounding.

Lanthanide, rare-earth, ions show luminescence from $4f$ *intra*-shell transitions. These transitions are well shielded from the environment by the outer core $5s$ and $5p$ electrons. This shielding can be even enhanced by complexation with encapsulating ligands of the rare-earth ion.[20] Hence, rare-earth complexes are good candidates for the experiment. However, the luminescence quantum efficiency of lanthanide complexes can be low, posing a real drawback. Nevertheless, lanthanides are still a far better choice than organic dyes, for which chemical effects are nearly uncontrollable. Proper complexation of a suitable rare earth ion, and careful selection of the dielectric host, can result in a near ideal system.

From all lanthanides, especially Eu^{3+} is famous for its luminescence properties. For example, the red phosphor in fluorescent strip lamps is Eu^{3+}.[18,19] The main luminescence transitions of Eu^{3+} occur between the $^5D_0$ state and the ^7F_j levels ($j=0,1,\ldots,6$), of which the $^5D_0\rightarrow{}^7F_5$ and $^5D_0\rightarrow{}^7F_6$ transitions are usually very weak. The main advantage of using Eu^{3+} as an impurity dipole to test local-field effects on spontaneous emission is the nondegeneracy of the $^5D_0$ level. Consequently, the luminescence emission spectra are relatively uncomplicated and the luminescence decay rate is equal for all $^5D_0\rightarrow{}^7F_j$ transitions. Moreover, the energy gap of Eu^{3+} is relatively large, so that nonradiative decay via multi-phonon relaxation is slow.[21,22] As a result, the luminescence quantum efficiency of Eu^{3+}-complexes dissolved in liquids can be close to 100%, provided suitable ligands and solvents are used.[20]

B. Samples

The samples used are 1 mmol/l solutions[23] of $Eu(fod)_3$ (99%, Aldrich[24]) in different alcohols, in which the europium complex dissolved well. $Eu(fod)_3$ is a β-diketone ligand Complex.[20] The alcohols were all obtained from Aldrich, with a minimum purity of 99%. In the experiments a homologic series of simple alcohols was used, that is $CH_3(CH_2)_mOH$, with $m=0,\ldots,9$ (but not $m=6,8$), as also deuterated alcohols $CH_3(CH_2)_mOD$, with $m=0,1,3$, and mixtures hereof. The refractive indices of the alcohols, and its mixtures, were determined with an Abbe-refractometer (Carl Zeiss). Furthermore, in order to minimize water contamination the deuterated samples were prepared in a nitrogen purged box and readily measured after preparation (within a half hour).

C. Setup

The $Eu(fod)_3$ complex was optically excited in the absorption band of the ligand at 354.7 nm, using the 20 Hz rep. rate pulses of a tripled Nd:YAG laser (Quanta Ray, DCR 2A). The pulses duration was 10 ns, much shorter than the luminescence lifetimes to be observed. The europium-

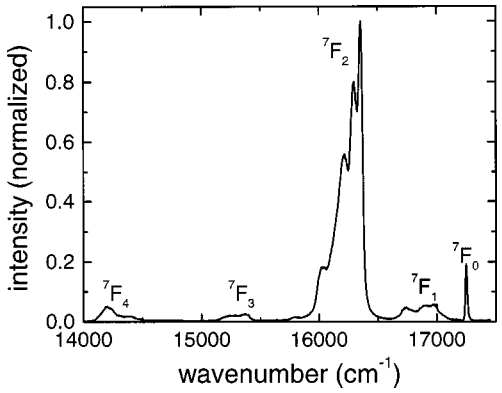

FIG. 1. The luminescence spectrum of $Eu(fod)_3$ in BuOH. The most intense decay channel is the $^5D_0 \rightarrow {}^7F_2$ transition, indicating that the Eu^{3+} ion is strongly perturbed by the fod-ligand field. Consequently, the radiative decay from the $^5D_0$ level is determined by electric dipole radiation.

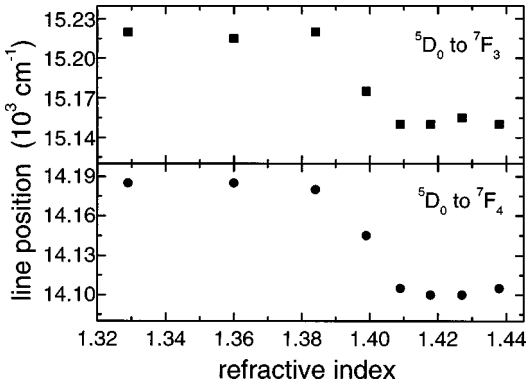

FIG. 2. The $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ line positions of $Eu(fod)_3$ dissolved in different pure OH-alcohols, here labeled with their refractive indices. The functional dependence of the line position on refractive index is remarkably similar for both transitions. With respect to the luminescence properties of $Eu(fod)_3$ in alcohols, the homologic series $CH_3(CH_2)_mOH$ can be subdivided into two groups, separated by BuOH ($m=3$). The error bars are of the order of the symbol size.

complex solutions were contained in 1×1 cm quartz cuvettes (Helma QS-series). Upon optical excitation, the Eu^{3+} ions showed luminescence, which was dispersed by a Spex 1401 double spectrometer (resolution 2 cm^{-1}) and detected with a Hamamatsu R943-02 red-sensitive single-photon counting tube. The luminescence decay rates were in the millisecond range and recorded with a multichannel scaler (EG&G-Ortec, T914); bin width 1 μs, with a maximum range of 16.4 ms (2^{14} bins). For recording luminescence spectra, the photomultiplier tube (PMT) signal was fed into the counting card of the computer, which simultaneously controlled scanning of the spectrometer.

III. RESULTS AND DISCUSSION

The luminescence spectrum of $Eu(fod)_3$ in 1-butanol, C_4H_9OH (BuOH), is presented in Fig. 1. The spectrum consists of 5 major lines, which are identified as the $^5D_0 \rightarrow {}^7F_j$ transitions of Eu^{3+}, with $j=0,\ldots,4$. Obviously, the luminescence mainly decays via the $^5D_0 \rightarrow {}^7F_2$ transition, indicating that the fod-ligand field strongly perturbs the Eu^{3+} ion.[19] A direct consequence is that the luminescence is of electric dipole character.[25,26] In general, a $^5D_0 \rightarrow {}^7F_j$ transition is $(2j+1)$-degenerate. This degeneracy can be removed by the noncentrosymmetric ligand field of the complex. A clear example of this lifted degeneracy is $^5D_0 \rightarrow {}^7F_2$ transition of $Eu(fod)_3$, for which a $(2j+1)=5$ peak structure is observed. Contrary, the $^5D_0 \rightarrow {}^7F_0$ transition is sharp [full width at half maximum (FWHM) = 15 cm^{-1}], representative for the luminescence for a transition between two nondegenerate levels.

The luminescence spectra of $Eu(fod)_3$ dissolved in different (deuterated) alcohols look all very similar. The only observable difference occurs in the weak $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions. The relative intensities of these transitions, as compared to the other $^5D_0 \rightarrow {}^7F_j$ transitions, and their line shapes are independent of the type of alcohol. However, as shown in Fig. 2, the line position does depend on the type of alcohol, with a maximum frequency shift of 70 and 80 cm^{-1} for $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$, respectively. Although these transitions only slightly contribute to the total luminescence intensity, the shift in the line positions indicates that, regarding the luminescence properties of $Eu(fod)_3$ in alcohols, the series of alcohols can be subdivided into two groups. Those alcohols with a refractive index lower than BuOH have identical luminescence spectra, as also those with a higher refractive index. The apparent subdivision will be discussed in more detail later in this section.

The luminescence decay of $Eu(fod)_3$ in BuOH measured at 16 360 cm^{-1} is displayed in Fig. 3. The decay is single exponential, as is the case for all alcohols and their mixtures, indicating that the selected system is suitable for the experiment.

The collection of luminescence lifetimes observed for $Eu(fod)_3$ in all different (deuterated) alcohols, and its mixtures, is given in Fig. 4. The lifetimes observed for the OD-alcohols are around 850 μs, much longer than $\sim$450 μs decay times for OH-alcohols. From this difference, and using the Horrocks Equation,[27] the number of O–H (O–D) oscillators in the first coordination sphere is found to be 2.1 $\pm$0.1. In other words, 1 H_2O molecule is binded to the Eu^{3+} ion in the complex, serving as an efficient quencher. Indeed, it is known that β-diketone ligand complexes usually have

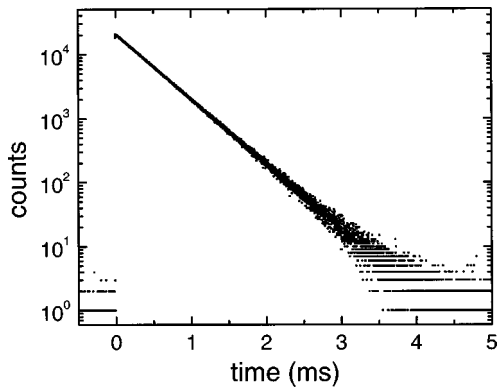

FIG. 3. The luminescence decay of $Eu(fod)_3$ in BuOH measured at 16 360 cm^{-1}. From the single exponential decay a luminescence decay time of 429 $\pm$ 2 μs is inferred.

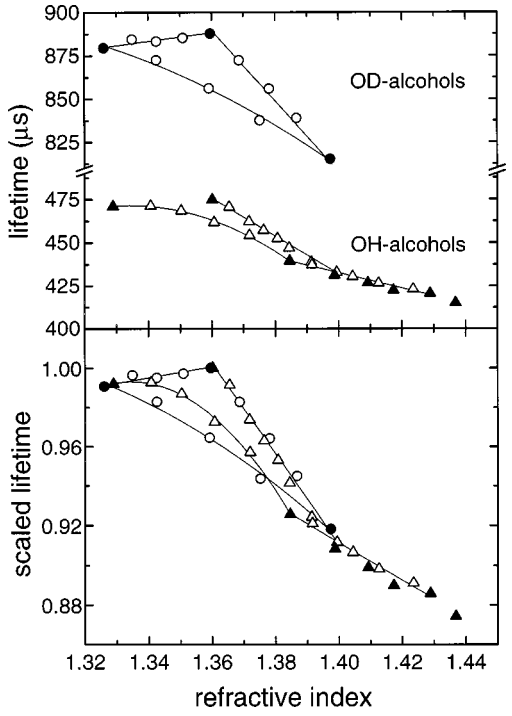

FIG. 4. *Upper figure:* The luminescence lifetimes of Eu(fod)$_3$ in normal (triangles) and deuterated (circles) alcohols. The solid symbols represent measurements on pure alcohols, the open symbols on mixtures. The following mixtures were used: MeOD–EtOD, MeOD–BuOD, EtOD–BuOD for OD-alcohols, and MeOH–PrOH, EtOH–BuOH, and PrOH–OcOH for OH-alcohols. The solid lines serve to distinguish the different alcohol mixtures. Note that the lifetimes for OD-alcohols are in the 800–900 μs range, considerably longer than the lifetimes observed for OH-alcohols (425–475 μs). *Lower figure:* The luminescence lifetimes of the upper figure scaled with the lifetimes of Eu(fod)$_3$ in pure EtOH and EtOD for the OH- and OD-alcohols, respectively. For alcohols with refractive index lower than 1.40, the luminescence lifetime is *not* solely dependent on the refractive index: For different mixtures with the same refractive index, different lifetimes are found. For alcohols with refractive index higher than 1.40, the lifetimes monotonously decrease with increasing refractive index. The error bars are of the order of the symbol size.

one water molecule positioned in the first coordination sphere,[20] which is very difficult to remove.[27]

Scaling the luminescence lifetimes of Eu(fod)$_3$ in OH- and OD-alcohols with the observed decay times for EtOH and EtOD, respectively, results in an universal curve. Conveniently, the scaled luminescence lifetimes for OH- and OD-alcohols can be discussed on the same footing. For alcohols with refractive index lower than 1.40, the luminescence lifetime strongly depends on the type of mixture, and a clear dependence on the refractive index is absent. For alcohols with a refractive index larger than 1.40, the luminescence lifetimes all fall on a single line, representing the possible functional dependence on refractive index. This clear separation was also observed in the luminescence spectrum for the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions, see Fig. 2. Note that the separation occurs at exactly the same refractive index of 1.40. Apparently, the europium complex undergoes subtle changes when dissolved in different lower alcohols, whereas these changes are absent for the higher alcohols. This is likely due to the difference in size of the alcohol molecules. Methanol is much smaller than 1-decanol, and thus penetrates more easily into the complex, modifying the local structure. This change in structure of the complex leads to a modification of the radiative and nonradiative decay, observable both in the luminescence spectra and decay measurements. For smaller solvent molecules, the variations will be larger, hence the spread in the luminescence lifetimes at low refractive indices (< 1.40), see Fig. 4.

The luminescence quantum efficiency in Eu(fod)$_3$ is higher in OD-alcohols than in OH-alcohols, as readily deduced from the difference in lifetimes, see Fig. 4. The efficiencies were independently determined by comparing to a standard solution of 1 mmol/l Eu$(NO_3)_3$ in CH_3OD, which has a known resonant quantum efficiency of 0.79 ± 0.01.[28] For this purpose, europium was resonantly excited in the $^5D_2$ level using the 465.7 nm line of an Argon laser (Spectra Physics, 165), in the case of the fod-complex by-passing excitation via the ligands. Comparing the absorption efficiencies of the different solutions, Eu(fod)$_3$ in alcohols and Eu$(NO_3)_3$ in CH_3OD, and the spectrally integrated luminescence intensities, gives the quantum efficiencies. For Eu(fod)$_3$ in OD-alcohols an efficiency of 0.82 ± 0.09 is found, and in OH-alcohols 0.43 ± 0.07; similar high efficiencies have been reported previously for europium complexes.[12,26] Within the error, the luminescence quantum efficiency is *independent* of the type of alcohol. The relatively large error is due to small amount of absorption, which is hence difficult to determine accurately. Nevertheless, the measurements prove that the quantum efficiency of europium complexes can be high, close to 1, if dissolved in suitable liquids.

IV. CONCLUSIONS

In conclusion, the change in luminescence lifetime of Eu(fod)$_3$ cannot be accounted for by considering only a change in refractive index for the lower alcohols (refractive index <1.40), even though the system was carefully selected. Most likely, this is due to subtle changes in the symmetry of the europium complex when dissolving it in different alcohols, affecting both the radiative and nonradiative luminescence decay rates. Consequently, the remaining range of refractive index variation is too small (refractive index: 1.40–1.44) to discriminate between the different theoretical models describing local-field effects on spontaneous emission (if one would, the empty-cavity model comes out best, but not very convincingly). This experiment indicates that most often the relatively small local-field correction to spontaneous emission is blurred by other, more dominant effects.

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