Local Field Effects and Electric and Magnetic Dipole Transitions in Dielectrics

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(Received 11 March 1994)

We report measurements of the refractive index dependence of the spontaneous emission rate of electric and magnetic dipole transitions in dielectrics. Local field effects are clearly observed in the electric dipole results and discrimination between different theoretical descriptions is made. The magnetic dipole results are well described by quantum electrodynamical considerations without local field effects.

PACS numbers: 32.80.–t, 42.50.–p, 78.55.Hx

The spontaneous emission rate of an atom is determined not only by the electronic wave functions of the atomic states involved, but also by the optical density of states and the electromagnetic field strength of the optical modes at the position of the atom. The first to notice this was Purcell [1] and quantum electrodynamics (QED) now provides an elegant framework to describe such effects [2]. The basic physics is that spontaneous emission can be regarded as being stimulated by the vacuum fluctuations of the electromagnetic field. So even if the optical modes of the system are not populated in a classical sense, the local mode amplitudes affect the spontaneous emission rate. Modification of this rate has been experimentally shown for free atoms [3–5], organic molecules [6] and Eu^{3+} complexes [7] in solution, III-V semiconductor quantum wells [8], and Er^{3+}-doped SiO_2 [9] inside resonant cavities. An alternative approach towards influencing the spontaneous emission rate is placing the emitter in a spatially inhomogeneous dielectric; spontaneous emission near a dielectric interface has been studied experimentally [10–13] and theoretically [14,15]. The dielectric slab bounded by two dielectrics of lower refractive index was studied experimentally by Yablonovich *et al.* [16] and theoretically for the symmetrical case by Khosravi and Loudon [17].

Surprisingly, the most elementary case of spontaneous emission inside a *bulk* dielectric has received much less attention. The photon density of states there shows a cubic refractive index dependence [2], and the electromagnetic field at the position of the emitter is changed because of the dielectric and local field effects. Neglecting these local field effects, Nienhuis and Alkemade [18] (NA) first predicted for the electric dipole transition rate A^{ED} and the magnetic dipole transition rate A^{MD}:

$$A^{\mathrm{ED}}(n) = nA_0^{\mathrm{ED}}, \qquad A^{\mathrm{MD}}(n) = n^3A_0^{\mathrm{MD}}, \tag{1}$$

where n is the refractive index of the host dielectric. Local field effects always play an important role in the interaction of light with condensed matter [19] and constitute a critical test of our understanding of the relation between microscopic and macroscopic electromagnetic phenomena. The classical calculation of local field effects is described in many textbooks [20,21], and is based on assuming a spherical cavity inside the dielectric around the emitter. The size of the cavity is always assumed large with respect to molecular dimensions but small with respect to the wavelength involved, and the material outside the cavity is treated as a homogeneous dielectric. Agranovich and Galanin [22] have shown that the choice of the inside of such a cavity is a subtle matter; the value for the local field at the position of the emitter depending on whether the cavity is chosen to be real or virtual (Lorentz model). This difference and the case of nonspherical but still ellipsoidal cavities have been elaborated for the electrostatic case by Böttcher [23]. In the case of an empty, real spherical cavity, the result for the electric dipole transition rate A^{ED} is given by [24]

$$A^{\mathrm{ED}}(n) = \frac{9n^5}{(2n^2+1)^2}A_0^{\mathrm{ED}}. \tag{2}$$

In the case of a virtual spherical cavity, A^{ED} is given by [25]

$$A^{\mathrm{ED}}(n) = n\left(\frac{n^2+2}{3}\right)^2 A_0^{\mathrm{ED}}. \tag{3}$$

Recent calculations starting from a microscopic model for a homogeneous, high-symmetry dielectric also predict Eq. (3) [26,27]. Local field effects are not expected for magnetic dipole transitions in dielectrics, where the magnetic susceptibility equals the vacuum value. As the microscopic magnetic field operator has no refractive index dependence [27], the only effect of a surrounding dielectric on a magnetic dipole transition is through the cubic photon density of states and we therefore expect

$$A^{\mathrm{MD}}(n) = n^3A_0^{\mathrm{MD}}, \tag{4}$$

which agrees with the NA result [Eq. (1)] as it should on the basis of the correspondence principle [28].

The large difference between the results for a real or virtual cavity should allow for an experimental test. However, only very few experimental data are available; Birks [29] has reviewed some results on organic molecules but no systematic dependence on the solvent refractive index was observed. In this Letter we report on measurements of the electric and magnetic dipole transition rates of Eu^{3+} complexes in bulk dielectrics of varying refractive indices in order to discriminate between the real and

0031-9007/95/74(6)/880(4)$06.00

virtual cavity models. Eu^{3+} was chosen for several reasons. Under certain conditions it can have a radiative quantum yield close to unity; this enables determination of the absolute radiative transition rates by radiative lifetime measurements, which can be performed in the experimentally convenient μs–ms range. By embedding the Eu^{3+} ion in appropriate organic ligand cages, it can be largely isolated from the vibrational excitations of the host in which it is dissolved, thereby restricting the influence of this host to its optical properties. The inset of Fig. 1 shows the relevant levels of the Eu^{3+} complex. The $^5D_0 \rightarrow {}^7F_1$ transition has been identified as a magnetic dipole transition if the ligands do not perturb the ion very strongly [30], the $^5D_0 \rightarrow {}^7F_0$ transition is dipole forbidden, whereas the other $^5D_0 \rightarrow {}^7F_i (i = 2, 3, \ldots, 6)$ transitions are electric dipole transitions. We have studied two different Eu^{3+}-ligand complexes: One complex consists of a Eu^{3+} ion with three hexafluoroacetylacetonate ligands and two trioctylphosphine oxide molecules as synergistic agents (Eu^{3+}-hfa-topo) [31]. The ligand can be optically excited around 300 nm wavelength, after which energy is transferred to the Eu^{3+} ion in the $^5D_0$ level, followed by radiative decay to the ^7F_i levels. The other complex consists of a Eu^{3+} ion with three dipicolinic acid ligands (Eu^{3+}-dpa) [32]. This ligand can be excited around 270 nm.

Spectra of the hfa complex and lifetimes were measured on a Perkin-Elmer LS-50 spectrofluorometer (resolution 2 nm); spectra of the dpa complex were measured using a 0.85 m double monochromator (resolution 0.1 nm). Absolute quantum yield measurements were performed using a calibrated integrating sphere. The two complexes yield different luminescence spectra, as can be seen in Fig. 1. The hfa complex has a $^5D_0$ lifetime of 0.730 ms and a quantum yield ϕ of 0.95 ± 0.05 in toluene ($n = 1.495$), whereas the dpa complex has a $^5D_0$ lifetime of 3.16 ms and a quantum yield of 0.45 ± 0.05 in heavy water ($n = 1.328$). Clearly, the dpa ligand only weakly perturbs the ion and provides only partial shielding, whereas the hfa ligand strongly enhances the electric dipole transitions and gives good shielding. A small enhancement of the $^5D_0 \rightarrow {}^7F_1$ rate by this latter ligand results from the admixture of some electric dipole character, as reported by Freed and Weissman [30] and Kunz and Lukosz [33]. Therefore the $^5D_0$ lifetime of the Eu^{3+}-hfa-topo complex is almost completely determined by electric dipole transitions, whereas for the Eu^{3+}-dpa complex a significant fraction of the $^5D_0$ decay goes through the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ and through nonradiative decay. The hfa complex can be integrally dissolved in apolar hydro- and fluorocarbon solvents. The dpa complex, which is accompanied by three tetrabutylammonium ions, requires polar solvents, which may lead to partial dissociation of the complex and therefore nonradiative decay through vibrational interaction with solvent molecules, especially as the radiative rates are much lower than in the hfa case. This nonradiative decay can be reduced by using fluorinated or deuterated solvents. For both complexes, but especially for the dpa case, the presence of heavy atoms (third row to the periodic system, or heavier) in the solvent molecules may lead to a decrease of quantum yield.

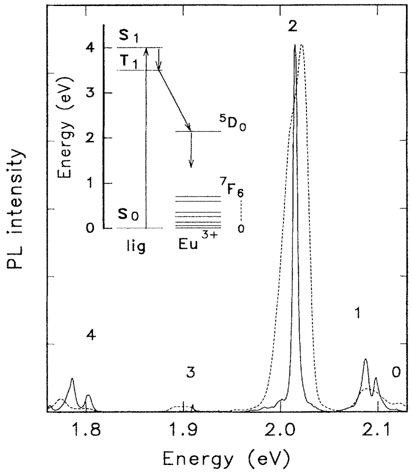

FIG. 1. Normalized luminescence from the $^5D_0$ level of 0.01 molar Eu^{3+}-hfa-topo in toluene ($n = 1.495$, dashed line, excitation 300 nm) and Eu^{3+}-dpa in deuterated dimethyl sulfoxide (DMSO-d_6, $n = 1.4775$, solid line, excitation 270 nm). Peaks are labeled with the J subscript of the final ^7F_J level. Inset shows the relevant energy levels and excitation, transfer, and luminescence processes of Eu^{3+} complexes.

Figure 2 shows the $^5D_0$ radiative lifetime of the Eu^{3+}-hfa-topo complex as a function of the refractive indices of the solvents, all apolar hydro- and fluorocarbons. The experimental data were fitted to

$$\tau(n) = [A^{\mathrm{ED}}(n) + A^{\mathrm{NR}}]^{-1}, \tag{5}$$

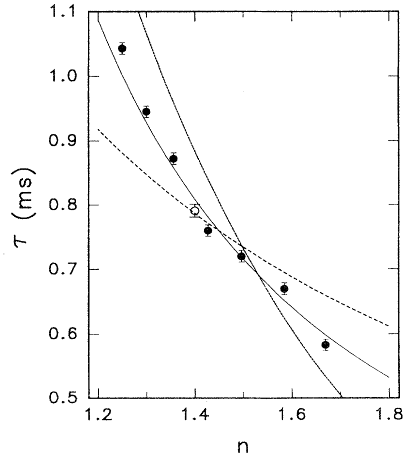

FIG. 2. Radiative lifetime of Eu^{3+}-hfa-topo in apolar hydro- and fluorocarbons, as a function of the solvent refractive index. Lines are fits to Eq. (5), using $A^{\mathrm{ED}}(n)$ from Eq. (1) (dashed line), $A^{\mathrm{ED}}(n)$ from Eq. (2) (solid line), and $A^{\mathrm{ED}}(n)$ from Eq. (3) (dotted line). Open symbol comes from Ref. [30].

where A^{NR} is the nonradiative decay rate, assumed to be independent of n. Using Eq. (2) for $A^{\mathrm{ED}}(n)$ gives the solid line as fit, which shows good agreement. It yields $A_0^{\mathrm{ED}} = 620 \pm 20\ \mathrm{s}^{-1}$ and $A^{\mathrm{NR}} = 30 \pm 30\ \mathrm{s}^{-1}$. This implies a quantum yield [which equals $A^{\mathrm{ED}}/(A^{\mathrm{ED}} + A^{\mathrm{NR}})$] in toluene ($n = 1.495$) of 0.98 ± 0.02, in agreement with the direct measurement. Using Eq. (3) for $A^{\mathrm{ED}}(n)$ (dotted line) clearly gives a poor fit when the parameters are restricted to comply with the experimental quantum yield. Also shown is a fit to the NA result for A^{ED} [Eq. (1)] which shows very poor agreement with the data. This clearly proves that local field effects play an important role in determining the spontaneous emission rate, and that they can be adequately described in a local field approximation using a *real* cavity.

Having established the refractive index dependence of the electric dipole transition rate, it is now possible to determine the refractive index dependence of the magnetic dipole transition rate for the Eu^{3+}-dpa complex by determining the fraction of the $^5\mathrm{D}_0$ population that decays radiatively into the $^7\mathrm{F}_1$ level as a function of the refractive index of the host, from the areas under the luminescence peaks. This magnetic dipole branching ratio R^{MD} is defined as

$$R^{\mathrm{MD}} \equiv \frac{A(^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1)}{\sum_i A(^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_i)} = \frac{A^{\mathrm{MD}}}{A^{\mathrm{MD}} + A^{\mathrm{ED}}}, \tag{6}$$

and does not depend on nonradiative decay. Rearrangement, using Eq. (2), gives

$$A^{\mathrm{MD}}(n) = \frac{R^{\mathrm{MD}}(n)}{1 - R^{\mathrm{MD}}(n)} A^{\mathrm{ED}}(n) = \frac{R^{\mathrm{MD}}(n)}{1 - R^{\mathrm{MD}}(n)} \frac{9n^5 A_0^{\mathrm{ED}}}{(2n^2 + 1)^2}. \tag{7}$$

$A^{\mathrm{MD}}(n)$ is now determined apart from the multiplicative constant A_0^{ED}. This constant can be obtained from the lifetime and quantum yield measurements in $\mathrm{D_2O}$, using $\tau^{-1} = A^{\mathrm{ED}} + A^{\mathrm{MD}} + A^{\mathrm{NR}}$ and $\phi = (A^{\mathrm{ED}} + A^{\mathrm{MD}})/(A^{\mathrm{ED}} + A^{\mathrm{MD}} + A^{\mathrm{NR}})$, yielding $A_0^{\mathrm{ED}} = 64 \pm 6\ \mathrm{s}^{-1}$ and $A^{\mathrm{NR}}(\mathrm{D_2O}) = 180 \pm 20\ \mathrm{s}^{-1}$. The lower radiative and higher nonradiative rates as compared to the hfa results agree with the weaker complexing and shielding properties of the dpa ligands. Figure 3 shows R^{MD} (inset) and A^{MD} as a function of refractive index of the hosts. The lowest refractive index ($n = 1.05$) measurement was obtained by absorbing a Eu^{3+}-dpa solution in a $\mathrm{SiO_2}$ xerogel and evaporating the solvent. The other hosts are common deuterated solvents. R^{MD} clearly increases with n, which means that A^{MD} increases more rapidly with n than A^{ED}. Using Eq. (7), we find a refractive index dependence of A^{MD} (Fig. 3, closed symbols) that is well described by $A^{\mathrm{MD}}(n) = A_0^{\mathrm{MD}} n^q$, with $q = 3.1 \pm 0.2$, which agrees very well with Eq. (4), and $A_0^{\mathrm{MD}} = 10 \pm 1\ \mathrm{s}^{-1}$. Performing the same analysis, but now using Eq. (3) (virtual cavity model) again yields $A^{\mathrm{MD}}(n) = A_0^{\mathrm{MD}} n^q$ (Fig. 3, open symbols), but now with $q = 3.9 \pm 0.25$. As this value has no theoretical justification, we conclude also from these magnetic dipole results that the *real* cavity model gives the proper description of our experiment.

The good fits in Figs. 2 and 3 clearly prove that an accurate and consistent description of the refractive index dependences of electric and magnetic dipole transition rates of Eu^{3+} complexes in dielectrics is given by the real cavity model, as expressed by Eqs. (2) and (4). A microscopic explanation as to why this model applies here instead of the more generally accepted virtual cavity (Lorentz) model is not straightforward. Some insight can be gained from considering the more appropriate case of a cavity of radius a inside a dielectric with refractive index n, and inside that cavity an emitter with polarizability α, as described by Böttcher [23]. For this more general case it can be shown that

$$A^{\mathrm{ED}}(n) = \frac{9n^5}{[2n^2 + 1 - (2\alpha/a^3)(n^2 - 1)]^2} A_0^{\mathrm{ED}}. \tag{8}$$

One immediately sees that for an empty cavity ($\alpha = 0$) or a very large radius, Eq. (2) (real cavity model) follows. For the virtual cavity case, the polarizability density inside the cavity, given by $\alpha/(4\pi a^3/3)$, has to equal that in the dielectric, given by $N_{\mathrm{DIEL}}\alpha_{\mathrm{DIEL}}$ (where N_{DIEL} and α_{DIEL} are the number density and polarizability of the constituents of the dielectric) in order

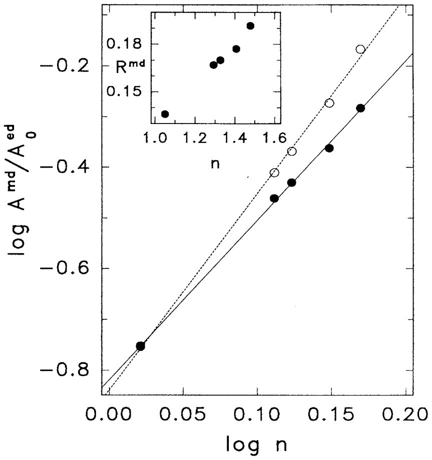

FIG. 3. Calculated normalized magnetic dipole transition rate $A^{\mathrm{MD}}/A_0^{\mathrm{ED}}$ of Eu^{3+}-dpa as a function of host refractive index. Use of Eq. (2) (real cavity) yields closed symbols; Eq. (3) (virtual cavity) yields open symbols. Straight lines are least squares fits to the data. Inset shows the magnetic dipole branching ratio R^{MD}.

for an externally applied electric field not to be affected by the presence of the cavity. $N_{\rm DIEL}$ and $\alpha_{\rm DIEL}$ are related to the refractive index of the dielectric through the well-known Clausius-Mossotti relation, valid for the virtual cavity case $4\pi N_{\rm DIEL}\alpha_{\rm DIEL}/3 = (n^2 - 1)/(n^2 + 2)$. Substituting these two relations into Eq. (8) yields Eq. (3), the virtual cavity result.

In view of the very different character of the Eu^{3+} complexes and the host constituents in this experiment, it should not be surprising that the condition for the derivation of Eq. (3) from Eq. (8) of homogenous polarizability density is not fulfilled. One should expect that the relatively large and rigid Eu^{3+} complexes represent a region in which the polarizability density is much lower than in the surrounding dielectric. In that case, i.e., $\alpha/(4\pi a^3/3) \ll N_{\rm DIEL}\alpha_{\rm DIEL}$, the predictions of Eq. (8) will, at least numerically, be close to those of Eq. (2). Therefore Eq. (2) could be expected to give a good description, as observed in our experiment.

In conclusion, we have reported for the first time the refractive index dependences of electric and magnetic dipole transition rates of Eu^{3+} complexes in dielectrics. The electric dipole results are well described in a local field approximation using a real cavity, whereas the magnetic dipole results are well described by elementary quantum electrodynamical considerations without local field effects.

We gratefully acknowledge M. J. Kraan for synthesizing the Eu^{3+} complexes, M. van Bommel for supplying the xerogel, T. Brandsma and J. Jans for technical assistance, and H. v. Houten, N. Pulsford, and P. Sharma for critical reading of the manuscript and stimulating discussions.

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[1] E. M. Purcell, Phys. Rev. **69**, 681 (1946).

[2] E. A. Power, *Introductory Quantum Electrodynamics* (Longmans, London, 1964); P. Meystre and M. Sargent III, *Elements of Quantum Optics* (Springer, Berlin, 1990).

[3] R. G. Hulet, E. S. Hilfer, and D. Kleppner, Phys. Rev. Lett. **55**, 2137 (1985).

[4] W. Jhe, A. Anderson, E. A. Hinds, D. Meschede, L. Moi, and S. Haroche, Phys. Rev. Lett. **58**, 1320 (1987).

[5] D. J. Heizen and M. S. Feld, Phys. Rev. Lett. **59**, 2623 (1987).

[6] F. De Martini, G. Innocenti, G. R. Jacobovitz, and P. Mataloni, Phys. Rev. Lett. **59**, 2955 (1987).

[7] F. De Martini, M. Marrocco, P. Mataloni, L. Crescentini, and R. Loudon, Phys. Rev. A **43**, 2480 (1991).

[8] Y. Yamamoto, S. Machida, Y. Horikoshi, K. Igeta, and G. Björk, Opt. Commun. **80**, 337 (1991).

[9] A. M. Vredenberg, N. E. J. Hunt, E. F. Schubert, D. C. Jacobson, J. M. Poate, and G. J. Zydzik, Phys. Rev. Lett. **71**, 517 (1993).

[10] K. H. Drexhage, J. Lumin. **1–2**, 693 (1970).

[11] C. K. Carniglia, L. Mandel, and K. H. Drexhage, J. Opt. Soc. Am. **62**, 479 (1972).

[12] K. H. Drexhage, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1974), Vol. XII.

[13] W. Lukosz and R. E. Kunz, J. Opt. Soc. Am. **67**, 1607 (1977).

[14] C. K. Carniglia and L. Mandel, Phys. Rev. D **3**, 280 (1971).

[15] H. Khosravi and R. Loudon, Proc. R. Soc. London A. **433**, 337 (1991).

[16] E. Yablonovitch, T. J. Gmitter, and R. Bhat, Phys. Rev. Lett. **61**, 2564 (1988).

[17] H. Khosravi and R. Loudon, Proc. R. Soc. London A **436**, 373 (1992).

[18] G. Nienhuis and C. Th. J. Alkemade, Physica (Amsterdam) **81C**, 181 (1976).

[19] D. E. Aspnes, Am. J. Phys. **50**, 704 (1982); C. Tarrio and S. E. Schnatterly, Mod. Phys. Lett. B **5**, 1479 (1991); I. I. Shaganov, Sov. J. Opt. Technol. **59**, 1 (1992).

[20] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).

[21] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976).

[22] V. M. Agranovich and M. D. Galanin, *Electronic Excitation Energy Transfer in Condensed Matter* (North Holland, Amsterdam, 1982).

[23] C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973), Vol. I.

[24] R. J. Glauber and M. Lewenstein, Phys. Rev. A **43**, 467 (1991).

[25] A. von Hippel, *Dielectrics and Waves* (Wiley, New York, 1954).

[26] J. Knoester and S. Mukamel, Phys. Rev. A **40**, 7065 (1989).

[27] S.-T. Ho and P. Kumar, J. Opt. Soc. Am. B **10**, 1620 (1993).

[28] In Ref. [24], a linear refractive index dependence for $A^{\rm MD}$ was predicted. This is because of an incorrect transformation between the electric and magnetic field.

[29] J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley, London, 1970).

[30] S. Freed and S. I. Weissman, Phys. Rev. **60**, 440 (1941).

[31] F. Halverson, J. S. Brinen, and J. R. Leto, J. Chem. Phys. **41**, 157 (1964).

[32] D. H. Metcalf, J. M. Stewart, S. W. Snyder, C. M. Grisham, and F. S. Richardson, Inorg. Chem. **31**, 2445 (1992).

[33] R. E. Kunz and W. Lukosz, Phys. Rev. B **21**, 4814 (1980).