

Spontaneous emission in absorbing dielectrics: A microscopic approach

Gediminas Juzeliūnas*

State Institute of Theoretical Physics and Astronomy, A. Goštauto 12, Vilnius 2600, Lithuania

(Received 13 January 1997)

Decay of an excited molecule (atom) has been considered in an absorbing dielectric. The decay rate has been derived calculating the total rate of excitation transfer to the surrounding species. The contribution due to the far-zone energy transfer yields the rate of photon emission in the absorbing medium. The analysis is based on a microscopic QED theory of energy transfer in condensed phases. As a result, effects due to discreteness of the medium (such as the local field effects) are reflected intrinsically in the decay rates. The microscopic approach supports the previous introduction of the local field factors on a phenomenological basis. [S1050-2947(97)50306-4]

PACS number(s): 42.50.Ct, 42.50.Lc, 32.80.-t, 33.80.-b

Spontaneous emission is a phenomenon that has played an important role in establishing concepts of modern quantum theory [1]. Over the past years there has been a great deal of interest in modified spontaneous emission by atoms (molecules) in various environments, such as in photonic band-gap crystals [2], and in the vicinity of metal surfaces [3] or dielectric interfaces [4]. Spontaneous emission is altered in homogeneous dielectrics as well [5–11]. The rate of the process reads, in the case of photon emission into transparent areas of a dielectric [5,8–12],

$$\Gamma_A^{sp-em} = \frac{|\mu^A|^2 \omega^3}{3\hbar \pi \epsilon_0 c^3} n \left(\frac{n^2 + 2}{3} \right)^2. \quad (1)$$

The rate (1) may be obtained through a standard procedure that involves summation over the modes of emitted photons. The emitted photons are “dressed” by polarization of the medium, the effects due to the dielectric medium being described in terms of the refractive index (see, e.g., Refs. [9–11]): Such an approach is relevant to the case where only the long-wavelength modes (with $ka \ll \pi$) are involved in the emission process, a being a characteristic distance between the species constituting the medium. Consequently, Eq. (1) does not generally hold in the case where the emission takes place into absorbing areas of the dielectric: In the latter absorbing case, an important role may be played by excitonlike modes of the medium with larger values of k [13].

Spontaneous emission in lossy dielectrics may be considered in a number of ways. The phenomenon might be dealt with analyzing the macroscopic Maxwell equations for a classical dipole in an absorbing medium [14,15]. Quantum-mechanical analysis has also been carried out [6,7]. Specifically, in a recent paper by Barnett *et al.* [7], the decay rate has been calculated for an excited atom embedded in an absorbing dielectric. The rate was separated into the “transverse” and “longitudinal” components: These correspond, respectively, to the rate of emission of a transverse photon and the rate of nonradiative decay via longitudinal coupling of the atom to the dielectric [7]. The absorbing medium has been described macroscopically [6,7], so that effects due to

discreteness of the medium (such as the local field effects) have not been intrinsically reflected: The local field corrections have been introduced phenomenologically at later stages [6,7]. Yet, a fully microscopic approach is desired. It is the purpose of the present Rapid Communication to give such a microscopic analysis of the phenomenon.

We shall deal with the decay of the excited state of a molecule (atom) A situated in the absorbing molecular medium. Consider the decay rate Γ_A due the energy transfer from A to the surrounding species:

$$\Gamma_A = \sum_{X \neq A} W_{XA}, \quad (2)$$

the summation being over all the molecules X constituting the medium. Here W_{XA} is the pair rate of excitation transfer between the species A and X :

$$W_{XA} = \frac{2\pi}{\hbar} \sum_{\gamma} |\langle X_{\gamma} | T | A \rangle|^2 \delta(\hbar \omega_{\gamma}^X - \hbar \omega), \quad (3)$$

$|A\rangle$ and $|X_{\gamma}\rangle$ are the state vectors for which either A or X are excited (T being the appropriate transition operator); ω ($\equiv \omega^A$) and ω_{γ}^X are the excitation frequencies of the species A and X , the index γ labeling the excited-state sublevels (electronic, vibrational, rotational, etc.) of the molecule X . For large organic molecules, these sublevels form dense spectra, so that the contributions due to the energy conservation δ functions are smoothed in the pair rates (3).

We shall invoke the formalism of quantum electrodynamics (QED) [16] in which the energy transfer emerges as the second-order process mediated by a virtual photon. The QED approach treats on equal grounds the energy transfer at distances belonging to both near and far zones [17]. The latter far-zone transfer may be viewed [18] as spontaneous emission of a photon followed by its subsequent recapture by a distant acceptor. Adopting such a concept, we shall regard the contribution to the decay rate (2) due to the far-zone energy transfer, $\Gamma_A^{far-zone}$, as the rate of spontaneous emission in the absorbing medium. The approach is in a certain relationship to the absorber theory [19] in which the spontaneous emission is seen to be the result of the direct interac-

*Electronic address: gj@itpa.lt

tion between the emitting atom and the Universe, the latter acting as a perfect absorber at all emitted frequencies. In our situation, the surrounding medium does act as a perfect absorber even at extremely low concentration of absorbing molecules (or as an alternative for almost transparent condensed medium), as long as the system dimensions are large enough to ensure eventual recapture of the emitted photon. For such a weakly absorbing medium, the rate $\Gamma_A^{far-zone}$ will be demonstrated to reproduce completely the usual rate (1) for emission of a photon in the transparent dielectric. This includes *inter alia* the case of the free space corresponding to the limit where $n \rightarrow 1$.

To obtain the proper decay rate using Eq. (2), the pair transfer rates W_{XA} should not only reflect effects due to retardation [16], but also incorporate influences of the surrounding medium. A microscopic QED theory has been developed recently [20,21] that takes into account both effects. The approach treats the energy transfer to be mediated by ‘‘medium-dressed’’ photons (i.e., virtual polaritons), rather than by the conventional vacuum photons, as considered in Ref. [16]. Applying the microscopic theory [20], one can write the following transition matrix element for energy transfer between the initially excited molecule A and the one belonging to the medium:

$$\langle X_\gamma | T | A \rangle = \frac{\mu_\gamma^X \mu^A e^{i\omega r/c}}{4\pi\epsilon_0} n \left(\frac{n^2+2}{3} \right)^2 \times \left[\eta_3 \left(\frac{1}{n^3 r^3} - \frac{i\omega}{n^2 c r^2} \right) - \eta_1 \frac{\omega^2}{n c^2 r} \right], \quad (4)$$

where μ^A and μ_γ^X are the transition dipole elements (chosen to be real) for the molecules A and X ; $\mathbf{r} = \mathbf{r}_X - \mathbf{r}_A$ is the distance of the $A-X$ separation, and

$$\eta_j = \hat{\mu}_\gamma^X \cdot \hat{\mu}^A - j (\hat{\mu}_\gamma^X \cdot \hat{\mathbf{r}}) (\hat{\mu}^A \cdot \hat{\mathbf{r}}) \quad (j=1,3) \quad (5)$$

are the orientational factors. Here also n is the refractive index for the medium comprising the molecules X :

$$n^2 = 1 + \frac{\alpha \rho \epsilon_0}{1 - \alpha \rho / 3 \epsilon_0}, \quad (6)$$

ρ is a number of molecules per unit volume, and α is the molecular polarizability (calculated at the excitation frequency ω):

$$\alpha \equiv \alpha^X = \frac{1}{\hbar} \sum_\gamma \left[\frac{(\mu_\gamma^X)^2 / 3}{\omega_\gamma^X - \omega - i\sigma} + \frac{(\mu_\gamma^X)^2 / 3}{\omega_\gamma^X + \omega + i\sigma} \right], \quad (7)$$

σ being a small parameter that makes smooth the contributions due to the densely spaced (quasidiscrete) molecular levels γ of vibrational, rotational, etc., origin in the absorbing areas of the spectrum. As a result, Eqs. (6) and (7) yield the complex refractive index:

$$n = n' + i n''. \quad (8)$$

In deriving the transition matrix element (4), the molecules were considered to be of the same type (so that $\mu_\gamma^X \equiv \mu_\gamma$ and $\omega_\gamma^X \equiv \omega_\gamma$), placed regularly to form a simple cubic lattice, and characterized by isotropic polarizabilities $\alpha \equiv \alpha^X$ [20].

Such a model may also represent a common situation where the nonisotropic species are randomly oriented in their sites. The result (4) seems to be not sensitive to the possible lack of translational symmetry as well, as long as the widths of molecular lines exceed the characteristic energies of resonance coupling between the species comprising the medium [22]. It is therefore expected that the transition matrix element (4) should describe adequately the energy transfer in a variety of amorphous media constituted of randomly situated and oriented molecules. For such systems, the quantity α entering Eqs. (4) and (6), is to be understood as an averaged polarizability for all the species X constituting the medium:

$$\alpha = \bar{\alpha}^X = N^{-1} \sum_X \alpha^X, \quad (9)$$

N being the total number of molecules X in the system. The subsequent analysis is consistent with both definitions (7) and (9) for α .

We shall separate the full decay rate (2) into the far-zone contribution and that due to the near-zone energy transfer:

$$\Gamma_A = \Gamma_A^{far-zone} + \Gamma_A^{near-zone}. \quad (10)$$

The former $\Gamma_A^{far-zone}$ (to be regarded as the rate of spontaneous emission) corresponds to the r^{-2} term in the pair rates (3)-(4):

$$\Gamma_A^{far-zone} = \frac{3 |\mu^A|^2 \omega^4}{8 \hbar \pi^2 \epsilon_0^2 c^4} \left| \frac{n^2+2}{3} \right|^4 \times \sum_{X \neq A} (\alpha^X)'' |\eta_1|^2 \frac{e^{-2n'' \omega r/c}}{r^2}, \quad (11)$$

with $(\alpha^X)'' \equiv \text{Im} \alpha^X$. The decay rate $\Gamma_A^{far-zone}$ is built of a large number of pair transfer rates operating predominantly in the far zone. Hence, the sum over r can be changed by the integral (accompanied by the replacement $\text{Im} \alpha^X \rightarrow \text{Im} \bar{\alpha}^X \equiv \alpha''$) to yield

$$\Gamma_A^{far-zone} = \frac{|\mu^A|^2 \omega^3}{3 \hbar \pi \epsilon_0 c^3} n' \left| \frac{n^2+2}{3} \right|^2, \quad (12)$$

where use has been made of the following:

$$n'' = \frac{1}{2n'} \left| \frac{n^2+2}{3} \right|^2 \alpha'' \rho / \epsilon_0. \quad (13)$$

The result (12) representing the rate of spontaneous emission in the absorbing medium manifestly accommodates contributions due to the dielectric medium, including the local field factor. It is noteworthy that the present analysis is based on a microscopic theory [20], the relationship (12) supporting the previous introduction of the local field correction by Barnett *et al.* [6,7] on a phenomenological basis. In the limit $\alpha'' \rightarrow 0$, $n'' \rightarrow 0$, the far-zone rate (12) reduces smoothly to the usual result (1) for the spontaneous emission in the transparent medium, there being a vanishing contribution due to the near-zone decay (to be discussed later): $\Gamma_A^{near-zone} \rightarrow 0$. In other words, the present analysis reproduces in full the rate

of the spontaneous emission in the transparent dielectrics ($n''=0$), including *inter alia* that in the free space ($n'=1$, $n''=0$). Here the free space is viewed as a limit where the density of absorbing species goes to zero, while the size of the system goes to infinity to ensure eventual recapture of the emitted photon somewhere in the system. Note also that, in order to arrive at a sensible result for $\Gamma_A^{far-zone}$, the influences of the medium are to be necessarily reflected in the pair transfer rates comprising the decay rate (11). In fact, it is the exponential factor $\exp(-2n''\omega r/c)$ representing the absorption losses at the intervening medium that helps avoid the potentially infinite decay rate $\Gamma_A^{far-zone}$ due to the r^{-2} factor featured in Eq. (11).

The latter $\Gamma_A^{near-zone}$ corresponds to the remaining terms in the pair rates (3)-(4). Here the pair rates are governed predominantly by the near-zone r^{-6} range dependence, so that

$$\Gamma_A^{near-zone} = \frac{3|\mu^A|^2}{8\hbar\pi^2\varepsilon_0^2} \sum_{X \neq A} \frac{(\alpha^X)'' |n^2 + 2|^4 |\eta_3|^2}{|n|^4 r^6}. \quad (14)$$

The rate $\Gamma_A^{near-zone}$ represents the contribution to the decay rate Γ_A by the near-zone (nonradiative) energy transfer. A cautionary note should be made concerning the straightforward use of the above equation (14) in the case where most of the surrounding species X are efficient energy acceptors. Then the major contribution to $\Gamma_A^{near-zone}$ comes from the energy transfer to the closest species X (up to a few configurational spheres around A). At such small distances, a description of the pair rates in terms of the refractive index is questionable. Yet, one can make use of a certain ‘‘effective’’ index of refraction n_{eff} in Eq. (14). The quantity $n_{eff} \equiv n_{eff}(r)$ approaches the true refractive index n as $r \gg a$ [23], where a is a characteristic distance between the species comprising the medium. On the other hand, since the decay rate $\Gamma_A^{far-zone}$ is built of a macroscopically large number of pair rates, it may be described quite legitimately through the refractive index in Eqs. (11) and (12). The same applies to the near-zone rate (14) in the case where the medium comprising the transparent background species X_1 is diluted with a small fraction of the absorbing acceptor mol-

ecules X_2 . In such a case, the space between the molecule A and any acceptor X_2 is filled with a large number of background molecules X_1 , the latter providing the major contribution to the refractive index n . The acceptors X_2 contribute much more weakly to n , yet ensuring the existence of some imaginary part n'' that plays an important role in the far-zone through the exponential factor featured in Eq. (11).

It is to be pointed out that the separation of the full decay rate into the far- and near- zone components corresponds to a division of the rate into its ‘‘transverse’’ and ‘‘longitudinal’’ parts adopted in Ref. [7]. The present partition into the far- and near-zone rates goes along with the multipolar formulation of the QED employed in Ref. [20]: In such a multipolar QED [24], the coupling between the molecules is mediated exclusively via the transverse photons, there being no instantaneous (longitudinal) contribution to the intermolecular coupling. Finally, the above analysis yields the exponential decay of the excited-state population for a selected molecule A , as long as the backtransfer of the excitation energy is negligible from the surrounding species X . Yet, the near-zone contribution $\Gamma_A^{near-zone}$ may depend markedly on a specific distribution of acceptors around the donor in the case of a somewhat inhomogeneous medium. At short times, this leads to the well-known [25] nonexponential decay of the excited-state population averaged over the ensemble. On the other hand, the rate of radiative decay ($\Gamma_A^{far-zone}$) depends much more weakly on a specific site of the emitter A , yielding an exponential contribution to the decay of the excited-state population in the ensemble. The exponential decay becomes the dominant kinetics at sufficiently large times.

In summary, decay rates have been derived for an excited molecule (atom) through the calculation of the total rate of excitation transfer to the surrounding species. The contribution due to the far-zone energy transfer represents the rate of photon emission in the absorbing medium. The analysis is based on a microscopic QED theory of energy transfer in condensed phases, so that effects due to discreteness of the medium (such as the local field effects) are reflected intrinsically in the decay rates. The microscopic approach supports the previous introduction of the local field factors on a phenomenological basis.

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