

SCALING OF SPONTANEOUS EMISSION AND INTERMOLECULAR INTERACTIONS IN A DIELECTRIC MEDIUM USING POLARITONS

Jasper Knoester and Shaul Mukamel

Department of Chemistry
University of Rochester
Rochester, NY 14627

The theoretical description of the excited state dynamics of molecules embedded in a condensed phase is of great interest in view of the numerous optical experiments that are currently carried out on, for instance, mixed crystals, glasses and solutions. The excited state evolution of the molecules studied is affected by the host medium. Not only does the medium induce dephasing processes, also properties which seem to be intrinsic to the molecules may be altered by the environment. For example, the spontaneous decay rate of an excited molecule embedded in a dielectric differs from the rate for the same molecule in vacuum.^[1-3] This phenomenon ties to a much more general current field of interest, in which the problem is addressed how the spontaneous emission of a molecule is affected by both the nature and the geometry of the surrounding space. Systems which draw considerable experimental and theoretical attention within this framework are molecules (dipoles) near dielectric or metallic surfaces,^[4] in high Q cavities,^[5] in or near small dielectric particles,^[6,7] or in an artificial superlattice with a spatial periodicity in the dielectric constant.^[8] The common principle underlying all these cases is that the density of states of the eigenmodes of the radiation field depends on the nature and the geometry of the medium considered, and that this density of states is one of the important factors in the Fermi golden rule for the radiative decay rate:

$$\gamma = \frac{2\pi}{\hbar} |\text{coupling}|^2 \times \text{density of states.} \quad (1)$$

Total absence of spontaneous decay may be achieved if the molecular transition frequency falls inside a gap in the density of states. Another example of the influence of the medium is that it may change the intermolecular forces. A well-known consequence of this is the dependence of the Förster rate of energy transfer between two molecules on the index of refraction of the host medium.^[1,3]

For molecules in vacuum the excited state dynamics may be described in an elegant way using the master equation of Lehmborg.^[9] This equation describes the evolution of the molecular system, while accounting for single molecule decay, dispersive intermolecular interactions and superradiant interactions. Using heuristic arguments, this equation may be altered to account for the dielectric constant of an infinite host medium. It is the purpose of this work, however, to include the effect of the frequency dependent dielectric function on this equation from first principles. In particular, our theory yields the dependence of the dispersive and superradiant intermolecular forces and of the single molecule spontaneous decay rate on the dielectric function.

Our model system consists of two-level molecules substituted in an atomic host crystal. The impurity transition frequency is Ω_0 ; for the atoms we consider explicitly one sp-transition with frequency Ω . Our starting point is the multipolar Hamiltonian in the dipole

approximation,^[10] which consists of a molecular, an atomic, and a radiation part, and moreover contains a radiation-molecule coupling and a radiation-atom coupling. As is well-known, it is possible to diagonalize the Hamiltonian for the crystal and the radiation field, which leads to the definition of polaritons as new elementary excitations.^[11] After transforming from the atomic and radiation operators to polariton operators, we obtain the Hamiltonian in a form which is formally equivalent to Lehmborg's starting Hamiltonian, namely:

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{pol}} + \hat{H}_{\text{int}}. \quad (2)$$

Here \hat{H}_{mol} represents the two-level molecules and \hat{H}_{pol} is the Hamiltonian of the polaritons, which is harmonic like the usual radiation field Hamiltonian. Finally, \hat{H}_{int} is the interaction between the impurities and the polaritons. The only difference with Lehmborg's formalism is that the vacuum photons are replaced by polaritons, which are the proper eigenmodes of the space surrounding the molecules. The derivation of the equation of motion for an arbitrary molecular operator may now be carried out along the lines presented by Lehmborg. Additional complications met in this derivation are technical and due to the much more complicated dispersion relation for the polaritons than for photons [Figure 1], and the complexity of the coupling coefficients of the molecules to the polaritons. In short, the derivation involves formally solving the Heisenberg equation of motion for the polariton creation and annihilation operators and substituting this solution into the Heisenberg equation of motion for the impurity operator Q that one is interested in. This leads to an equation of motion for Q at time t which contains other impurity operators at times $t' \leq t$ and the initial conditions of the polariton operators. Making the Markov approximation, we obtain a final time-local equation which has the same structure as Lehmborg's master equation (all operators are taken at time t):^[12]

$$\begin{aligned} \frac{d\hat{Q}}{dt} = & i\Omega_0 \sum_{\alpha} [\hat{b}_{\alpha}^{\dagger} \hat{b}_{\alpha}, \hat{Q}] - \frac{i}{\hbar} \sum_{\alpha} [\hat{b}_{\alpha}^{\dagger}, \hat{Q}] \vec{\mu}_{\alpha} \cdot \hat{D}_{+}(\vec{r}_{\alpha}, t) - \frac{i}{\hbar} \sum_{\alpha} \vec{\mu}_{\alpha} \cdot \hat{D}_{-}(\vec{r}_{\alpha}, t) [\hat{b}_{\alpha}, \hat{Q}] \\ & + i \sum_{\alpha \neq \beta} \Omega_{\alpha\beta} [\hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta}, \hat{Q}] + \sum_{\alpha, \beta} \gamma_{\alpha\beta} [\hat{b}_{\alpha}^{\dagger} \hat{Q} \hat{b}_{\beta} - \frac{1}{2} (\hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta} \hat{Q} + \hat{Q} \hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta})]. \end{aligned} \quad (3)$$

Here $\hat{b}_{\alpha}^{\dagger}$ and \hat{b}_{α} denote the creation and annihilation operators for an excitation on molecule α , which obey the Pauli anti-commutation relations

$$[\hat{b}_{\alpha}^{\dagger}, \hat{b}_{\beta}]_{+} = \delta_{\alpha\beta} + 2 \hat{b}_{\alpha}^{\dagger} \hat{b}_{\beta} (1 - \delta_{\alpha\beta}),$$

and $\vec{\mu}_{\alpha}$ is the transition dipole of molecule α . The first term in the equation of motion is the usual evolution due to the isolated molecule Hamiltonian. The second and third terms arise from the interactions of the molecules with the positive and negative frequency parts of the crystal electric displacement field. This field is derived from the initial condition of the polariton operators and is not perturbed by the presence of the impurities. It propagates with the dispersion relation of the perfect crystal and, assuming a coherent initial state for the polaritons, it may be considered a classical external field.^[12] In situations in which the polariton field is initially in the vacuum (spontaneous emission problems), these terms may be omitted from Eq.(3).^[9] Finally, the last two terms in the equation of motion are the most interesting, because they represent polariton mediated (self)interactions between the molecules. They arise from the emission of a polariton by one molecule and its subsequent absorption by another, analogous to the way the vacuum dipole-dipole interaction may be obtained by emission and absorption of photons. The coefficients $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ are given by

$$\Omega_{\alpha\beta} = -\frac{1}{\hbar} \left(\frac{\Omega_0}{c} \right)^3 \sqrt{\epsilon(\Omega_0) \left(\frac{\epsilon(\Omega_0) + 2}{3} \right)^2} \vec{\mu}_{\alpha} \cdot \left(\hat{u} \frac{\cos x}{x} - \hat{v} \frac{\sin x}{x^2} - \hat{w} \frac{\cos x}{x^3} \right) \cdot \vec{\mu}_{\beta}, \quad (4a)$$

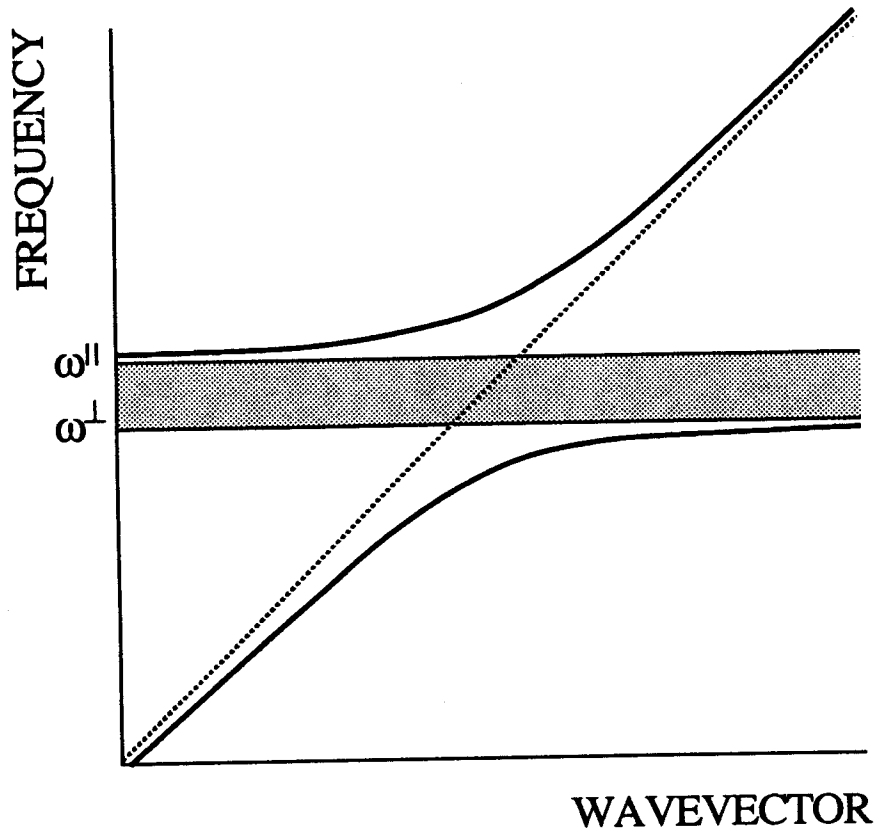


Figure 1. Typical polariton dispersion curves in the optical region (thick solid lines). The diagonal line represents the pure photon dispersion curve. The shaded region between the transverse (ω^\perp) and the longitudinal (ω^\parallel) crystal exciton frequencies is the stopgap, where no polariton modes exist.

$$\gamma_{\alpha\beta} = \frac{2}{\hbar} \left(\frac{\Omega_0}{c} \right)^3 \sqrt{\epsilon(\Omega_0)} \left(\frac{\epsilon(\Omega_0) + 2}{3} \right)^2 \vec{\mu}_\alpha \cdot \left(\vec{u} \frac{\sin x}{x} + \vec{v} \frac{\cos x}{x^2} - \vec{v} \frac{\sin x}{x^3} \right) \vec{\mu}_\beta, \quad (4b)$$

with

$$\vec{u} = 1 - \vec{r}_{\alpha\beta} \vec{r}_{\alpha\beta} / r_{\alpha\beta}^2, \quad \vec{v} = 1 - 3 \vec{r}_{\alpha\beta} \vec{r}_{\alpha\beta} / r_{\alpha\beta}^2, \quad x = \sqrt{\epsilon(\Omega_0)} \Omega_0 r_{\alpha\beta} / c$$

[$r_{\alpha\beta} \equiv |\vec{r}_{\alpha\beta}| = |\vec{r}_\alpha - \vec{r}_\beta|$]. The frequency dependent transverse dielectric function $\epsilon(\omega)$ of the atomic crystal is obtained within our calculation from the dispersion relation of the polaritons and reads

$$\epsilon(\omega) = 1 + \frac{4\pi\beta\Omega^2}{-\omega^2 + \Omega^2(1 - 4\pi\beta/3)}. \quad (5)$$

Here $\beta \equiv 2\rho\mu^2/\hbar\Omega$ is the oscillator strength of the host crystal per unit volume [ρ is the average atomic density and μ is the magnitude of the transition dipoles between the atomic ground state and the three-fold degenerate excited state]. The function $\epsilon(\omega)$ has a pole at the transverse dipolar exciton frequency in the infinite effective mass approximation; this approximation has been used in the derivation of the above results.^[12] We note that if $\epsilon(\Omega_0)$ is set equal to unity in Eqs.(4), we indeed recover Lehmborg's form for $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$.^[9] The significance of these coefficients is clear: $\Omega_{\alpha\beta}$ represents the real (dispersive) retarded dipole-dipole interaction between molecules α and β , and $\gamma_{\alpha\beta}$ is the superradiant interaction

for $\alpha \neq \beta$ and the single molecule spontaneous decay rate if $\alpha = \beta$. Our calculation shows from a fully microscopic starting point how these quantities are affected by the dielectric host medium.

We proceed by investigating in more detail the single molecule decay rate

$$\gamma_{\alpha\alpha} = \gamma_{\alpha\alpha}^{\text{vac}} \sqrt{\epsilon(\Omega_0)} \left(\frac{\epsilon(\Omega_0)+2}{3} \right)^2, \quad (6)$$

where $\gamma_{\alpha\alpha}^{\text{vac}} = 4\mu_0^2 \Omega_0^3 / 3\hbar c^3$ stands for the decay rate in vacuum (μ_0 is the magnitude of the impurity transition dipole). We note that with respect to $\gamma_{\alpha\alpha}$ our calculation is equivalent to evaluating the Fermi golden rule Eq.(1), if the coupling is taken between the molecule and the polaritons, and the polariton density of states is used. In the crystal the molecule loses its electronic energy by emitting polaritons instead of photons. We note that the scaling with ϵ in Eq.(6) may be derived from macroscopic arguments, provided that Ω_0 is separated well enough from Ω , so that the frequency dispersion of the dielectric function may be neglected [$\epsilon(\omega) = \epsilon$]. In this derivation we also use the Fermi golden rule, but now we consider the molecule to be coupled to an effective radiation field with a modified velocity of light given by $c/\epsilon^{1/2}$. In the frequency domain, the density of states of this field scales as $\epsilon^{3/2}$. Furthermore, the coupling scales as $\epsilon^{-1/2}$, because the plane wave amplitude of the macroscopic electromagnetic field scales like this. Combining these two effects in Eq.(1), leads to a decay rate proportional to $\epsilon^{1/2}$, which is commonly given as the only dependence on the dielectric constant.^[2] The appearance of the last factor in Eq.(6) may be interpreted as the rescaling of the molecule's transition dipole due to the reaction field or local field from the environment. Using electrostatics, there is a dilemma of how to account for this effect. A rescaling of the dipole with a factor $(\epsilon+2)/3$ is obtained by considering the impurity as residing within in a *virtual* cavity inside a continuous dielectric, whereas consideration of a *real* cavity leads to a factor $3\epsilon/(2\epsilon+1)$.^[3] In our microscopic calculation, we do not face this ambiguity; the factor $(\epsilon+2)/3$ emerges naturally. Moreover, our theory properly accounts for the frequency dispersion. It must be noted that in the presence of frequency dispersion, the density of states does not simply scale like $\epsilon^{3/2}$, but also contains the derivative of $\epsilon(\omega)$. The apparent simplicity of Eq.(6) is a consequence of delicate cancellations of factors in the polariton density of states and the coupling.^[12] The phenomenological arguments for the scaling given here may be extended to explain the complete dependence of $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ on $\epsilon(\Omega_0)$.

We now concentrate on the near zone result for $\Omega_{\alpha\beta}$, which reads

$$\Omega_{\alpha\beta}^{\text{near}} = \frac{1}{\epsilon(\Omega_0)} \left(\frac{\epsilon(\Omega_0)+2}{3} \right)^2 \vec{\mu}_\alpha \cdot \vec{v} \cdot \vec{\mu}_\beta / \hbar r_{\alpha\beta}^3 \quad (7)$$

This is easily recognized as the instantaneous dipole-dipole interaction scaled by the screening factor $1/\epsilon(\Omega_0)$ and the local field factor $[(\epsilon(\Omega_0)+2)/3]^2$. This scaling has also been obtained by Agranovich,^[3] who starts out with vacuum instantaneous intermolecular interactions (minimal coupling Hamiltonian) and accounts for the lattice by exchange of dipolar excitons instead of polaritons. In this approach, retardation is completely neglected. The fact that this still yields a result identical to our fully retarded theory can be understood, because the near zone real interaction is by definition insensitive to retardation. By contrast, the coefficients $\gamma_{\alpha\beta}$ can never be obtained without explicitly accounting for retardation, not even in the near zone. A well-known consequence of the result Eq.(7) is that the Förster rate of energy transfer between two molecules, which is proportional to the square of their interaction, scales like $[(n^2+2)/3]^4 n^{-4}$, with $n = \epsilon^{1/2}$ the index of refraction of the surrounding medium.^[1,3]

An important question is how our results are limited by the position of the molecular transition frequency Ω_0 with respect to the atomic transition at Ω . One restriction arises from using the infinite effective exciton mass approximation in the derivation. This approximation affects the polariton density of states in and close to the stopgap, which ranges from the transverse to the longitudinal dipolar exciton frequencies, given by $\omega^\perp = \Omega(1-4\pi\beta/3)^{1/2}$ and $\omega^\parallel = \Omega(1+8\pi\beta/3)^{1/2}$, respectively [see Figure 1]. Thus, our results are not valid within this

frequency region. In fact, within this approximation, the polariton density of states vanishes completely inside the stopgap, leading to total inhibition of spontaneous decay for $\omega^\perp \leq \Omega_0 \leq \omega^\parallel$. A finite effective mass would lead to a finite decay rate. Another restriction is imposed by the fact that our calculation does not account for delocalization of the impurity excitations when Ω_0 approaches Ω . The reason is that, as a consequence of the Markov approximation, the effective interactions $\Omega_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ are calculated only to second order in the molecule-impurity interaction. Delocalization can only be taken into account in a non-perturbative theory. In his calculation of the near zone dipole-dipole coupling mentioned above,^[3] Agranovich did go beyond second order perturbation theory in the molecule-exciton coupling, and he therefore obtained extra scaling factors which are important near the exciton frequencies. These extra factors do not simply depend on $\epsilon(\Omega_0)$; the universal scaling with the dielectric function must be expected to break down when delocalization sets in. Obviously, our results are most interesting in the frequency region where delocalization is not important and the dielectric function shows a clear dispersion. A measure for the importance of delocalization is given by $\rho\mu_0\mu/\hbar|\omega^\perp - \Omega_0|$, the ratio of the molecule-lattice coupling and the energy mismatch. On the other hand, it follows from Eq.(5) that the frequency dispersion of the dielectric function behaves like $4\pi\rho\mu^2/\hbar|\omega^\perp - \Omega_0|$. We thus observe that the frequency dispersion may still be appreciable while the delocalization is negligible as long as $\mu \gg \mu_0$, i.e., for a host crystal with a relatively large oscillator strength.

Finally, we comment on recent supersonic beam experiments, in which it was observed that the radiative lifetime of 9,10-dichloroanthracene embedded in Ar clusters does not reach its bulk value even for cluster sizes of a few thousand Ar atoms.^[13] This may be understood as follows. The radiation field plays a crucial role in spontaneous emission. In order to account for the effect of the material environment on the spontaneous emission of a molecule, the radiation field must be coupled to this environment. In bulk media this gives rise to polaritons, as used above; in system smaller than an optical wavelength, however, polaritons cannot possibly play a role. Therefore, the lifetime can only be expected to reach its bulk value in clusters with sizes is of the order of an optical wavelength.

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