Spontaneous emission rates of a single-impurity molecule in birefringent host crystals for electric quadrupole transitions

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Abstract

In a birefringent host crystal, the spontaneous emission rate of zero-phonon line of a single-impurity molecule depends on the angles between the transition dipole moment and the principal axes of the dielectric (permittivity) tensor and also on the main dielectric constants of a host crystal. In this paper, the spontaneous emission rate of the electric quadrupole transition of a single-impurity molecule is calculated for uniaxial host crystals with the ordinary reflective indices $n_o = 1.5, 2, 3$ and a variable extraordinary reflective index, and for seven biaxial host crystals (anthracene, chrysene, diphenyl, fluorine, naphthalene, phenanthrene, terphenyl). For the above-mentioned biaxial crystals, differences in the values of spontaneous emission rate of the quadrupole transition in the same host crystal are up to 11%.
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Different widths of a purely electronic zero-phonon line appear for chemically identical single molecules embedded in the same host crystal [1–6]. An anisotropy of the birefringent host crystal leads to the dependence of the spontaneous emission rate and, consequently, the dependence of the radiative linewidth of a single-impurity molecule on the orientation of the electron position vector (or the transition dipole moment vector in the dipole transition) in the crystal. The dependences of the density of the emitted photon final states (expressed through the phase and the ray velocities of the photons) and the local and the average electric field strengths on the orientation of the wave vector of the photon in the host crystal and on principal refractive indices are taken into account.

The theory of the spontaneous emission rate for the electric dipole transition of a single-impurity molecule is presented in Ref. [7], and for the electric quadrupole transition in Ref. [8]. The relative spontaneous emission rate of the electric dipole emission in uniaxial crystals are calculated in Ref. [7] and in biaxial crystals in Ref. [9].

Here, the dependence of the coefficients A_i, which determine the relative spontaneous emission rate of the quadrupole transition, on the extraordinary reflective index n_e are calculated for uniaxial host crystals with the ordinary reflective indices $n_o = 1.5, 2, 3$. Also the coefficients A_i are found for seven biaxial host crystals.

As a model, we consider a two-level single molecule in a host crystal. The levels $|1>$ and $|2>$ are coupled by radiation modes in the dipole approximation. Each mode is characterized by the wave vector $\boldsymbol{k}$ and the polarization index $\lambda \, (+, -)$ and is treated as a quantum oscillator with the frequency $\omega_{\boldsymbol{k}}$. The spontaneous emission rate of the electric quadrupole transition $|2> \rightarrow |1>$ in a birefringent host crystal is described by the following equation [8]:

$$\gamma_q = \frac{1}{2\pi\varepsilon_v} \frac{\omega_{21}^3}{2\pi\hbar c^3} \sum_{\lambda=+,-} \int \frac{(\boldsymbol{e}_{\boldsymbol{k}\lambda}\mathbf{M}_{21}\mathbf{k})^2 n_{\boldsymbol{k}\lambda}^2 s_{\boldsymbol{k}\lambda}}{(\boldsymbol{e}'^0_{\boldsymbol{k}\lambda}\varepsilon\boldsymbol{e}'^0_{\boldsymbol{k}\lambda})} \, \mathrm{d}\Omega, \qquad (1)$$

where the tensor $\mathbf{M}_{21} \equiv e<1|\boldsymbol{r}\bullet\boldsymbol{r}|2>$ for the transition $|2> \rightarrow |1>$, $\boldsymbol{r}$ is the electron position vector, e is the electric charge, the dot $\bullet$ denotes the direct (Cartesian) product, $\boldsymbol{e}_{\boldsymbol{k}\lambda}$ are the two transverse (polarization) vectors of the electric field strength at the site of the impurity molecule

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(effective or local field vectors), $e'_{k\lambda}{}^0$ are the polarization unit vectors of the average electric field in the medium (the field in a bulk crystal), ε is the dielectric (permittivity) tensor, $n_{k\lambda} = c/v_{k\lambda}$ and $s_{k\lambda} = c/u_{k\lambda}$ are the phase and the ray refraction indices, $v_{k\lambda}$ and $u_{k\lambda}$ are absolute values of the phase and the ray velocities, $d\Omega$ is the space angle element, ω_{21} is the atomic transition frequency, c is the velocity of the light, and ε_v is the dielectric constant in the vacuum.

Let the basic vectors of the coordinate system coincide with the principal axes of the dielectric (permittivity) tensor ε. Then the tensor ε is diagonal $\varepsilon_{jk} = \varepsilon_j \delta_{jk}$ ($j, k = 1, 2, 3$) (for a uniaxial crystal $\varepsilon_1 = \varepsilon_2 \neq \varepsilon_3$ and for a biaxial crystal $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$), where ε_j are the main dielectric constants, the corresponding principal refractive indices are $n_j = \varepsilon_j^{1/2}$. Let us represent the unit tensor $\mathbf{M}_{21}^0$ as $M_{ij}^0 = x_i x_j$, where x_i are the components of the electron position unit vector r^0. Then the relative spontaneous emission rate of the electric quadrupole transition in a biaxial crystal reads

$$F_q(x_1, x_2, x_3) \equiv \gamma_q(x_1, x_2, x_3)/\gamma_q(0, 0, 1)$$
$$= A_1 x_1^4 + A_2 x_2^4 + A_3 x_1^2 x_2^2 + A_4 x_1^2 x_3^2$$
$$+ A_5 x_2^2 x_3^2 + x_3^4. \quad (2)$$

In uniaxial crystals $A_1 = A_2 = A_3/2$ and $A_4 = A_5$. In Eq. (2), the coefficients A_i can be found from Eq. (1) after integrating over $d\Omega$ when the model which determines the local electric field vectors $e_{k\lambda}$ is specified. In Ref. [7], it was found how the components of the effective field $e_{k\lambda}$ are expressed through the components of the average field $e'_{k\lambda}{}^0$. For an interstitial impurity located in the center of the crystal cell, $e'_{k\lambda}{}^0$, $n_{k\lambda}$ and $s_{k\lambda}$ were found by using formulas from Ref. [10]. In the case of an isotropic crystal ($\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \varepsilon$) $e_{k\lambda} = (2 + \varepsilon)e'_{k\lambda}{}^0/3$, which coincides with the results of Ref. [11], and the spontaneous emission rate of the electric quadrupole transition reads

$$\gamma_q = \frac{8\pi}{15}\left(\frac{2 + \varepsilon}{3}\right)^2 n^3 \frac{1}{2\pi\varepsilon_v} \frac{\omega_{21}^5 M^2}{2\pi\hbar c^5}. \quad (3)$$

For uniaxial crystals in the above model, Fig. 1 demonstrates the dependence of the coefficients A_1 and A_4 which determine the relative spontaneous emission rate F_q of the electric quadrupole transition (see Eq. (2)) on the extraordinary principal refractive index $n_e = n_3$ for three different ordinary principal refractive indices $n_o = n_1 = n_2 = 1.5, 2, 3$. In Fig. 2, the dependence of the relative spontaneous emission rate F_q on the coordinate x_3 for six pairs of the ordinary and extraordinary refractive indices is presented. As an example, we see that for the first pair ($n_o = 3$, $n_e = 2.5$) γ_q has a minimum value if r is directed along the third principal axis of the tensor ε ($x_3 \equiv z = 1$, $F_q = 1$) and a maximum value if r is perpendicular to the third principal axis ($x_3 \equiv z = 0$, $F_q = 1.37$).

In Table 1, the values of the coefficients A_i are calculated for seven biaxial crystals (anthracene, chrysene, diphenyl, fluorine, naphthalene, phenanthrene, terphenyl; the principal refractive indices were taken from Ref. [12] for $\lambda = 546.1$ nm, and room temperature). Let us introduce
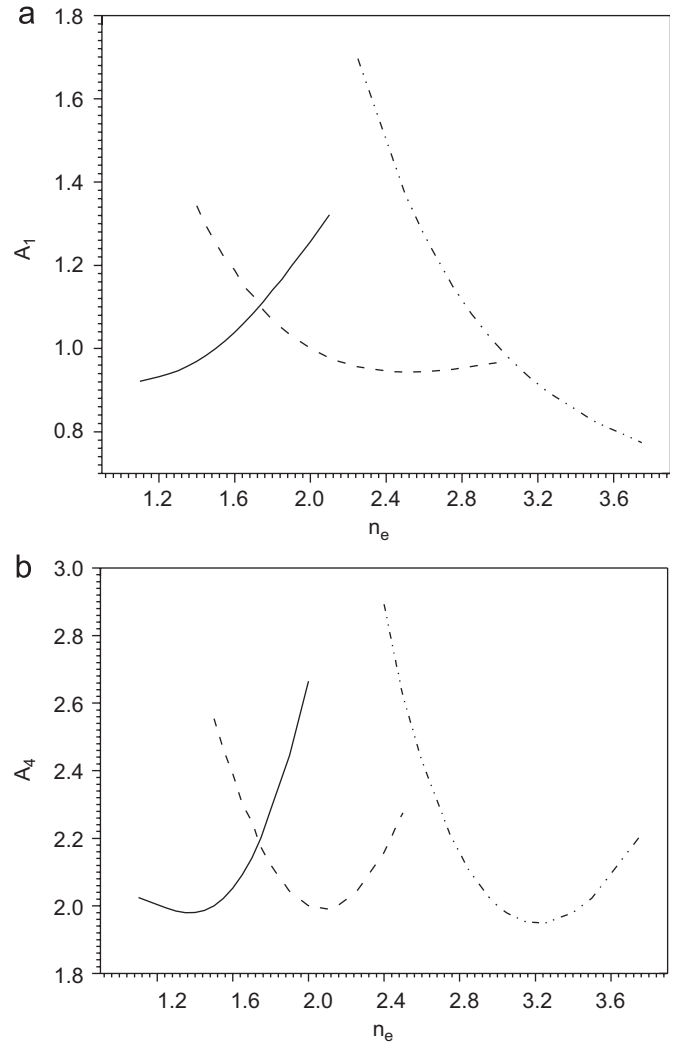

Fig. 1. The dependence of the coefficients A_1 and A_4 on the extraordinary refractive index n_e for different ordinary refractive indices $n_o = 1.5$ (solid line), $n_o = 2$ (dash line) and $n_o = 3$ (dash dot–dot line) for uniaxial crystals.
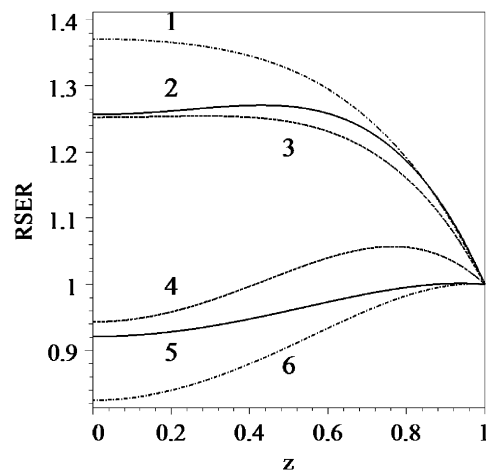

Fig. 2. The dependence of the relative spontaneous emission rate of the quadrupole transition F_q on the coordinate $x_3 \equiv z$ for following pairs: 1—$n_o = 3$, $n_e = 2.5$; 2—$n_o = 1.5$, $n_e = 2$; 3—$n_o = 2$, $n_e = 1.5$; 4—$n_o = 2$, $n_e = 1.5$; 5—$n_o = 1.5$, $n_e = 1.1$; 6—$n_o = 3$, $n_e = 3.5$.