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Abstract

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Yu. A. VDOVIN

RADIATION OF AN EXCITED MOLECULE IN A RESONANT MEDIUM

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In the present work the radiation of an initially excited molecule, located in a system of exactly the same unexcited molecules, is considered. The presence in the system of molecules resonant with the given one has a substantial effect on the character of electromagnetic processes, on the process of photon propagation ([1]). The possibility of multiple absorption and emission of a photon in such a system leads to quenching of the radiation ([2–5]). Only in the case of a sufficiently rarefied medium can the influence of the other, unexcited, molecules be neglected. Our task is to investigate the radiation process with consistent allowance for the entire ensemble of molecules. It is assumed that the resonance is sufficiently narrow, so that only two molecular levels are essential. The energy difference of these levels (the transition frequency ω_0) is taken to be the same for all molecules. We shall proceed from the assumption of a chaotic distribution of molecules in space, which is valid for a gaseous medium and for impurities in a solid. Effects due to the finiteness of the volume occupied by the molecules will not be considered. The medium is assumed not to be very dense, i.e. $\rho\lambda^3 \ll 1$.

We write the Hamiltonian of a system of N two-level molecules and of the radiation field in the form ([1],[6])

$$H = \frac{\omega_0}{2}\sum_j \sigma_z^j + \sum_{\mathbf{k}\lambda, j}\left(Q^{j*}_{\mathbf{k}\lambda} e^{i\mathbf{k}\mathbf{x}_j} c_{\mathbf{k}\lambda}\sigma_+^j + Q^{j}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\mathbf{x}_j} c^+_{\mathbf{k}\lambda}\sigma_-^j\right) + \sum_{\mathbf{k}\lambda}\omega_k c^+_{\mathbf{k}\lambda} c_{\mathbf{k}\lambda}, \quad (1)$$

where $\mathbf{x}_j$ are the coordinates of the centers of gravity of the molecules, $\omega_k^2 = c^2k^2$, $\hbar = 1$,

$$\sigma_z^j = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_j; \qquad \sigma_+^j = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}_j; \qquad \sigma_-^j = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}_j.$$

We shall assume that at the initial time $t = 0$ there was one excited molecule in the system. The results obtained will also be applicable to the case of many excited molecules, under the condition, however, that the density of the photons formed is small, so that their interaction may be neglected.

The Hamiltonian (1) conserves the number of excitations. Therefore the state will remain one-particle at any time. Accordingly, the wave function may be represented in the form (^{1})

$$\psi(t) = \sum_{\mathbf{k}\lambda} f_\lambda(\mathbf{k}, t) c^+_{\mathbf{k}\lambda} |0\rangle e^{i\omega_0 Nt/2} + \sum_j \varphi_j(t) \sigma^j_+ |0\rangle e^{i\omega_0 Nt/2}. \tag{2}$$

(In the state $|0\rangle$ there are no photons and all molecules are unexcited.)

From the Schrödinger equation we obtain equations for the amplitudes $f_\lambda(\mathbf{k}, t)$, $\varphi_j(t)$. Passing to the Laplace representation and eliminating the amplitudes φ_j, we obtain the following equation for the function $f_\lambda(\mathbf{k}, \omega)$ $(ip = \omega,\ p- \cdots$

Laplace transform):

$$(\omega - \omega_k) f_\lambda(\mathbf{k}, \omega) = \frac{iQ^{j_0}_{k\lambda}}{\omega - \omega_0} \left(1 + \sum_{\mathbf{k}'\lambda'} Q^{j_0}_{\mathbf{k}'\lambda'} f_{\lambda'}(\mathbf{k}', \omega) \right) + \frac{1}{\omega - \omega_0} \sum_{\mathbf{k}'\lambda'} J_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}') f_{\lambda'}(\mathbf{k}', \omega), \tag{3}$$

where $J_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}') = \sum_j Q^j_{\mathbf{k}\lambda} Q^{j*}_{\mathbf{k}'\lambda'} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{x}_j}$. We have chosen the origin of coordinates at the center of mass of the excited molecule, $\mathbf{x}_{j_0} = 0$.

Our task is to find the photon distribution function with respect to ω_k for an arbitrary time t, and to find the probability $R(t)$ of detecting the excited molecule in the system,

$$n_{\mathbf{k}\lambda}(t) = |f_\lambda(\mathbf{k}, t)|^2 = \int \frac{d\omega\, d\omega'}{(2\pi)^2} K_\lambda(\mathbf{k}, \omega, \omega') e^{-i\omega' t} = \int_{-\infty + i\sigma}^{\infty + i\sigma} n_{\mathbf{k}\lambda}(\omega') e^{-i\omega' t} \frac{d\omega'}{2\pi}, \tag{4}$$

where

$$K_\lambda(\mathbf{k}, \omega, \omega') = \overline{f_\lambda(\mathbf{k}, \omega)} f^+_\lambda(\mathbf{k}, \omega' - \omega). \tag{5}$$

By the bar we denote averaging over the coordinates of the centers of mass of the molecules. This gives rise to the possibility of using the developed methods of graphical techniques. As applied to the present problems, this technique was developed in work (^{1}). It can be shown, starting from equation (3), that the function K_λ is expressed in terms of the function $K_{\lambda\lambda_0}$ introduced in (^{1}), corresponding to the presence in the initial state of the photon $\mathbf{k}_0\lambda_0$:

$$K_\lambda(\mathbf{k}, \omega, \omega') = \frac{|Q^{j_0}_{\mathbf{k}\lambda}|^2}{(\omega - \omega_0 + iW/2)(\omega - \omega_0 - \omega' - iW/2)} \sum_{\mathbf{k}0\lambda_0} K_{\lambda\lambda_0}(\mathbf{k}, \omega, \omega'; \mathbf{k}_0), \tag{6}$$

where W is the probability per unit time of spontaneous dipole emission of a photon by an isolated molecule.

Using the equation for the function $K_{\lambda\lambda_0}$, we obtain the following equation for the function K, averaged over the directions of the vector $\mathbf{k}$:

$$K(\omega_k, \omega, \omega') = K^0(\omega_k, \omega, \omega') + \frac{2}{3} N K^0(\omega_k, \omega, \omega') \int |Q_{k'}|^2 \rho_{k'} K(\omega_{k'}, \omega, \omega')\, d\omega_{k'}, \tag{7}$$

where ρ_k is the density of states in $\mathbf{k}$-space and

$$K^0(\omega_k, \omega, \omega') = \frac{1}{3} |Q_k|^2 \times$$

$$\times \frac{1}{(\omega - \omega_1 + i\gamma_1/2)(\omega - \omega_2 + i\gamma_2/2)(\omega - \omega_1 - \omega' - i\gamma_1/2)(\omega - \omega_2 - \omega' - i\gamma_2/2)}, \tag{8}$$

$$\omega_1 = \omega_0 + \frac{1}{2}\Delta + \frac{1}{2}\theta, \qquad \gamma_1 = \frac{W}{2} \frac{\theta - \Delta}{\theta},$$

$$\omega_2 = \omega_0 + \frac{1}{2}\Delta - \frac{1}{2}\theta, \qquad \gamma_2 = \frac{W}{2} \frac{\theta + \Delta}{\theta},$$

$$\theta = \frac{1}{\sqrt{2}} \left[\frac{1}{\tau^2} + \Delta^2 - \frac{W^2}{4} + \sqrt{\left(\frac{1}{\tau^2} + \Delta^2 - \frac{W^2}{4} \right)^2 + W^2 \Delta^2} \right]^{1/2}, \qquad \Delta = \omega_k - \omega_0;$$

τ is related to W by the relation

$$(W\tau)^2 = \frac{1}{2\pi\rho\lambda^3} \frac{W}{\omega_0}, \tag{9}$$

where ρ is the density of molecules of the medium, $\rho = N/V$, $\lambda = c/\omega_0$, and $\rho\lambda^3 \ll 1$.

Multiplying the left- and right-hand sides of equation (7) by $|Q_k|^2 \rho_k$ and integrating over $d\omega_k$, we obtain

$$K(\omega_k, \omega, \omega') = K^0(\omega_k, \omega, \omega') \times$$

$$\times\left(1+\frac{iW}{4\tau^2\omega'\left[(\omega-\omega_0+iW/2)(\omega-\omega_0-\omega'-iW/2)+1/4\tau^2\right]}\right). \tag{10}$$

Integrating this equation with respect to $d\omega/2\pi$ and then passing to the time representation, we finally obtain the number of photons $n(\omega_k, t)$ falling in the interval $d\omega_k$. In view of the fact that, as a rule, $W\tau \ll 1$, and only in very rarefied media $W\tau \gg 1$, we shall give the results for these limiting cases. The general expression will be given only for times $t \gg 1/W$. Namely, after the lapse of time $t \gg 1/W$ the distribution becomes stationary and has the form

$$n(\omega_k)d\omega_k = \frac{W\,d\omega_k}{\pi}\frac{1}{(1/\tau^2+\Delta^2+3/4W^2)^2+W^2\Delta^2}\left[\frac{1}{\tau^2}+\Delta^2+\frac{3}{4}W^2+\frac{1}{2}\frac{W\tau}{\sqrt{1+W^2\tau^2}}\left(\frac{1}{\tau^2}+\frac{3}{4}W^2-\Delta^2\right)\right]. \tag{11}$$

For $W\tau \gg 1$, i.e., for a very rarefied medium, in fact over the whole time region we have

$$n(\omega_k, t)d\omega_k = \frac{W\,d\omega_k}{2\pi}\frac{1}{\Delta^2+W^2/4}\left(1+e^{-Wt}-2e^{-Wt/2}\cos\Delta t\right), \tag{12}$$

i.e., we arrive at the known results for the radiation of a single molecule in vacuum (7).

We note that in the general case the distribution $n(\omega_k, t)$ receives a contribution both from the stage associated with radiation and from the stage associated with photon diffusion. However, for $W\tau \gg 1$ the diffusion stage in fact does not affect the distribution. This is in agreement with the results obtained in work (1).

For $W\tau \ll 1$, formula (12) correctly describes the process only at small times $t \ll \tau$. This means that in the present case, at first the molecule radiates as if it were isolated. However, with the passage of time the character of the process changes. The presence in the system of unexcited molecules resonant with the given one leads to the possibility of a "jump" of the excitation and of propagation of an excitation wave. The natural physical objects in this case are the quanta of the electromagnetic field of the medium, introduced in work (1), which take into account the coherent interaction of photons with the medium, corresponding to the presence of a resonant dielectric permittivity. The distribution $n(\omega_k, t)$ for $W\tau \ll 1$ and $t \gg \tau$ has the form

$$n(\omega_k, t)d\omega_k = \frac{W\,d\omega_k}{\pi}\frac{1}{\Delta^2+1/\tau^2}\left(1-\exp\left[-Wt+\frac{W|\Delta|}{2\Omega}t\right]\cos\Omega t\right), \tag{13}$$

where $\Omega = \sqrt{\Delta^2+1/\tau^2}$.

For $W\tau \ll 1$ this distribution coincides with that obtained in work (6). We see that the width of the distribution in this case is given not by the quantity W, but by the quantity $1/\tau$. The appearance of the width $1/\tau$ is due to the width of the spectrum of elementary excitations—the quanta of the medium. Expression (13) can be derived from the distributions for the quanta of the medium obtained in work (1). At times $t \gg 1/W$ distribution (13) becomes stationary, and the contribution to it is made with equal probability both by quanta of the medium of the first type (energy ω_1) and by quanta of the medium of the second type (energy ω_2):

$$n(\omega_k)d\omega_k = \frac{W\,d\omega_k}{\pi(\Delta^2 + 1/\tau^2)} = \frac{W}{2\pi}\frac{d\omega_1}{(\omega_1 - \omega_0)^2 + 1/4\tau^2} + \frac{W}{2\pi}\frac{d\omega_2}{(\omega_2 - \omega_0)^2 + 1/4\tau^2}. \tag{14}$$

We note, as follows from (11), that for $\Delta \gg 1/\tau$, $\Delta \gg W$ the function $n(\omega_k)$ is substantially different for $W\tau \gg 1$ and $W\tau \ll 1$. Namely, for $W\tau \ll 1$ it is twice as large. The latter circumstance is connected with the fact that for $W\tau \ll 1$ a nonresonance photon (large Δ) can be produced at any stage of the process, whereas for $W\tau \gg 1$ a nonresonance photon is emitted only by the initially excited molecule.

Let us find the total probability of detecting an excited molecule in the system, $R(t) = 1 - \sum_{\mathbf{k}\lambda} n_{k\lambda}$. To find this quantity it is convenient to use formula (10). Namely, integrating (10) over ω_k, then over $d\omega/2\pi$ and passing to the time representation, we obtain

$$R(t) = 1 - W\tau \int_0^{t/\tau} J_0(y)e^{-W\tau y}\,dy, \tag{15}$$

where J_0 is the Bessel function.

As follows from (15), at times $t \ll \tau$ the function $R(t)$ has the form

$$R(t) = e^{-Wt}, \tag{16}$$

i.e., the radiation proceeds as if there were a single isolated molecule. With time, however, the character of the process changes. At times $t \gg \tau$ the function R has the form

$$R(t) = 1 - \frac{W\tau}{\sqrt{1 + W^2\tau^2}}\left\{1 - \sqrt{\frac{\tau}{\pi t}}\,e^{-Wt}\left[(1 + W\tau)\cos\frac{t}{\tau} - (1 - W\tau)\sin\frac{t}{\tau}\right]\right\}. \tag{17}$$

For $W\tau \gg 1$, i.e., for a very rarefied medium, we have

$$R = \frac{1}{2W^2\tau^2} + \sqrt{\frac{2\tau}{\pi t}}\, e^{-Wt} W\tau \cos\left(\frac{t}{\tau} - \frac{\pi}{4}\right), \tag{18}$$

i.e., quenching of the radiation in fact does not occur.

For $W\tau \ll 1$,

$$R(t) = 1 - W\tau + \sqrt{\frac{2\tau}{\pi t}}\, e^{-Wt} \cos\left(\frac{t}{\tau} + \frac{\pi}{4}\right), \tag{19}$$

i.e., quenching of the radiation takes place. In this case the excitation is transmitted directly from one molecule to another.

In conclusion, we note that all the results of the work have been obtained for a system of strictly resonant molecules. In real systems there is a certain spread of energy levels, caused, for example, by the Doppler effect in gases or the Stark effect in solids. Taking this spread into account, if it is large, will lead to a certain effective replacement of the quantity W by the width of the spread δ. For example, $R(\infty)$ will have the form

$$R(\infty) = 1 - \tau\sqrt{\delta W} \,/\, \sqrt{1 + \delta W \tau^2}. \tag{20}$$

The resonance of the system will have a substantial effect for $W\delta \ll 1/\tau^2$, i.e., under the condition that the spread is not very large.

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Moscow Engineering Physics Institute

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Note: Figure translations are in progress. See original paper for figures.