On the theory of the luminescence of isolated molecules

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The luminescence decay law for isolated molecules is investigated. It is shown that luminescence decay is described by an exponential law only in certain cases: 1) the adiabatic-level spectrum of the molecule in the excitation-energy region is quasicontinuous (i.e., in the case of polyatomic molecules or of broad-band excitation); 2) the adiabatic-level spectrum is discrete and nondense, when only one eigenstate of the total Hamiltonian of the molecule gets excited (i.e., in the case of molecules with few atoms or of a quasimonochromatic excitation field). In the remaining cases the excited states do not decay according to an exponential law. Special attention is given to the description of quantum beats in the luminescence decay law. The dependence of the observed excited-state decay law on the duration and spectral composition of the exciting electromagnetic-field pulse is discussed. It is shown that quantum beats can be observed only when the pulse duration of the exciting source is shorter than the oscillation period. The importance for spectroscopy inside radiative lines of the investigation of the fine characteristics of the luminescence decay law is stressed.

1. INTRODUCTION

Molecular luminescence is the most direct and information-yielding method of investigating the structure and decay modes of electronically excited molecules. These data, in their present form, can be obtained in the study of the luminescence of isolated molecules, which explains the large number of experimental investigations that have been carried out on this problem[1-4]. The investigation of the characteristics of luminescence is also important in itself, in view of the use of molecules as the working medium of lasers.

The theoretical methods of describing the temporal characteristics of molecular luminescence amounted, until recently, only to the use of the standard expressions of formal kinetics, which allowed us to obtain these characteristics in a highly averaged form. The use of short exciting pulses and of detecting equipment with a high time resolution[5] allows us to investigate the finer features of molecular luminescence, features which cannot be described in the framework of classical kinetics and have to be quantum-mechanically treated to be understood. To such characteristics pertain first and foremost quantum beats in the luminescence decay law, which yield, as in the case of atomic luminescence[6,7], a wealth of information about the energy levels of molecules. This problem has been investigated with the aid of simplified models in several recent papers[8,11].

The use of models in these papers is due to the extreme complexity of the system of energy levels of molecules. In molecular systems, in the Born-Oppenheimer approximation, we can, as is well known, distinguish three types of degrees of freedom: electronic, vibrational, and rotational. The combination of these three types of states leads to an energy spectrum that, even in the case of molecules composed of a few atoms, is incomparably richer than atomic spectra. The problem is further complicated by the fact that there are located in the region of electronic-excitation energies in molecules energy levels belonging to different electron states, and the application of the adiabatic approximation in this energy region is not only unjustified, but also leads to the loss of important features of the behavior of the system (e.g., the nonradiative transitions[8]). This impels us, in describing molecular luminescence, to take into account in the Hamiltonian of the system the nonadiabatic operator. This leads to the mixing of the functions of the adiabatic approximation, which is entirely analogous to the level-anticrossing effect in atomic spectroscopy. In spite of the indicated difficulties, as will be shown below, we can derive and analyze the expressions necessary for the description of the time dependence of luminescence decay without recourse to excessive schematization of the energy spectrum of the system.

There is another reason that makes a more careful investigation of molecular luminescence necessary. Until very recently, not much attention was paid to the analysis of the preparation of the initial excited state. It was usually assumed without proof that a molecule falls, on excitation, into an adiabatic state. It was not until very recently that Rhodes, Henry, and Kasha[12,13] and Jortner et al.[9,14] showed that this is, in fact, the case if the spectrum of the exciting field is continuous and sufficiently broad. When the excitation is effected by an electromagnetic field with a narrow spectral distribution, the characteristics of the luminescence will depend on the properties of this distribution[15,16]. Below we consider the problem, as applied to the case of isolated molecules, of the preparation of excited states and the dependence of the characteristics of the luminescence on the conditions under which the excitation takes place.

The theoretical investigation of the law of decay of electronically excited molecules (the luminescence decay law) is also of interest in view of the fact that molecules are an example of quantum systems with nonexponential laws of decay of the excited states.

We shall consider the case of a single isolated molecule that during its lifetime in the excited state does not undergo collisions. We shall consider only one-photon transitions, assuming that they are the most probable.

2. THE HAMILTONIAN AND THE GREEN FUNCTIONS OF THE SYSTEM

The Hamiltonian H of the molecule and the radiation field can be represented as the sum of the Hamiltonian H_1 of the molecule, the Hamiltonian H_2 of the radiation field, and their interaction operator W. The Hamiltonian of the molecule can, in its turn, be represented as the sum of the Hamiltonian H_1^0 of the adiabatic approximation and the nonadiabatic operator V. Usually, in the case of L-S coupling, the operator V also includes the spin-orbit interaction operator. We therefore have

$$H=H_0+V+W, \quad H_0=H_1^0+H_2. \tag{1}$$

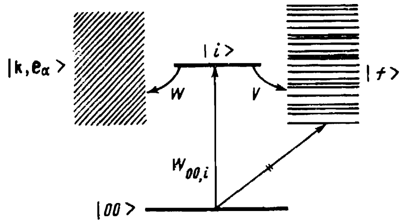
The explicit forms of the operators are well known, and have been thoroughly described (see, for example,[17-19]). The operator V acts only on the (electronic, vibrational, and spin) wave functions of the molecule and the operator W depends on the coordinates of the electrons of the molecule and the coordinates of the field.

The eigenfunctions $|nf\rangle$ of the Hamiltonian H_1^0 have the form of a product of the electronic (and spin) wave function $|n\rangle$ and the vibrational wave function $|f\rangle^{1)}$. The indices n and f denote the corresponding sets of quantum numbers. The function $|n\rangle$ determines the given electronic state (term) of the molecule.

The eigenvalue spectrum E_{nf} for fixed n and small values of f has a low density, and the level spacing ($\gtrsim 100$ cm^{-1}) significantly exceeds the radiation widths of the levels ($\ll 1$ cm^{-1}). As the value of f increases, the spectrum—even for few-atom molecules—very rapidly becomes dense, becoming, for polyatomic molecules, quasicontinuous at energies of the order of the electron-excitation energy[8,11]. Thus, a typical situation is one in which the low-density region of the spectrum of some electronically excited term i contains a much denser vibrational-level spectrum below the energy level of the f term.

Usually, the optical dipole transition from the ground state $|00\rangle$ is allowed when it is to a state of the term i, but forbidden (or has a low probability) either by multiplicity or on account of the Franck-Condon principle when it is to a state of the other terms located in the same energy region. The dipole transitions from the state $|00\rangle$ to the states $|ig\rangle$ usually have a high probability when the values of g are not high, i.e., in the relatively sparse region of the spectrum of the term i. In view of this, we shall consider only one level of the term i and denote its energy and wave function by E_i and $|i\rangle$. The state $|i\rangle$ is often coupled by a relatively strong nonadiabatic interaction to the vibrational levels of some other term. We shall consider only the states of this term. Let us denote their functions and energies by $|f\rangle$ and E_f. This limitation on the model has a purely formal character, since the functions $|f\rangle$ can be taken to be nonadiabatic functions constructed from the functions of all the terms, with the exception of the term i. No additional restrictions will be imposed in the general treatment on the spectrum of the system and the matrix elements of the operators V and W. The model that considers one level of the i term is used extensively at present[8-14], since it embraces many important features of the problem. The possibility of extending it and the effects that such an extension gives rise to are discussed at the end of the paper.

The eigenfunctions $|\mathbf{k}, \mathbf{e}_\alpha\rangle$ of the operator H_2 describe the field's one-photon states with momentum k and polarization $\mathbf{e}_\alpha$. The eigenstates of the operator H_2 form a continuous spectrum that is degenerate with respect to the polarization values and the directions of the vector k. The spectrum of the Hamiltonian H_0 is shown in the figure. The eigenfunctions $|nf\mathbf{k}\mathbf{e}_\alpha\rangle$ of the Hamiltonian H_0 have the form of products of the functions $|nf\rangle$ and $|\mathbf{k}\mathbf{e}_\alpha\rangle$. These functions are not eigenfunctions of the operator H, but they can be used as basis functions for the construction of the eigenfunctions. For this purpose it is necessary to compute the matrix elements of the operators V and W and to diagonalize the Hamiltonian H.



Diagrammatic representation of the spectrum of the Hamiltonian H_0.

Using the properties of the operators, we have

$$\begin{aligned}
&\langle nf\mathbf{k}\mathbf{e}_\alpha|V|n'f'\mathbf{k}'\mathbf{e}_{\alpha'}\rangle=\delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}V_{nf,\,n'f'}(1-\delta_{nn'}),\\
&\langle nf\mathbf{k}\mathbf{e}_\alpha|W|n'f'\mathbf{k}'\mathbf{e}_{\alpha'}\rangle=W_{nf,\,n'f'}(|\mathbf{k}|,\mathbf{e}_\alpha) \text{ and } \mathbf{k}'=0,\\
&\langle nf\mathbf{k}\mathbf{e}_\alpha|W|n'f'\mathbf{k}'\mathbf{e}_{\alpha'}\rangle=W_{nf,\,n'f'}(|\mathbf{k}'|,\mathbf{e}_{\alpha'}) \text{ and } \mathbf{k}=0.
\end{aligned} \tag{2}$$

Furthermore, for the above-described model we have

$$W_{00,\,i}\neq 0, \quad W_{00,\,f}=0, \quad V_{if}\neq 0, \; V_{ff'}=0.$$

The diagonalization of the Hamiltonian H is extremely complicated, and can be accomplished only for very simplified models[8,9]. Remembering, however, that the ground state $|00\rangle$ of the system is separated from the excited states by a wide energy gap whose magnitude is considerably greater than the matrix elements of the operators V and W, we can assume that the state $|00\rangle$ of the Hamiltonian H_0 and the ground state Ψ_0 of the Hamiltonian H coincide to a high degree of accuracy[8,9].

The matrix elements of the dipole transitions from the ground state of the Hamiltonian H_0 to the excited states have the form

$$\langle nf\mathbf{k}\mathbf{e}_\alpha|\hat{p}|00\rangle=p_{nf,\,00}\delta_{0,\,|\mathbf{k}|}, \quad p_{i,\,00}\neq 0, \quad p_{f,\,00}=0, \tag{3}$$

where $\hat{p}$ is the momentum operator of the electrons of the molecule. The $k \neq 0$ states of the Hamiltonian H_0 will be denoted below by $|k_\mu(E)\rangle$, the $k = 0$ states by Ψ_0, $|i\rangle$, and $|f\rangle$. All these functions are assumed to be orthonormal.

Let us introduce the Green functions:

$$\begin{gathered}
G_0=\frac{1}{z-H_0}, \quad G=\frac{1}{z-H}=\frac{1}{z-H_0-V-W},\\
G_0=\frac{|\Psi_0\rangle\langle\Psi_0|}{z-E_0}+\frac{|i\rangle\langle i|}{z-E_i}\\
+\sum_f\frac{|f\rangle\langle f|}{z-E_f}+\sum_\mu\int\frac{|k_\mu(E')\rangle\langle k_\mu(E')|}{z-E'}dE',
\end{gathered} \tag{4}$$

where $z = E + i\delta$ for the retarded Green functions G^+ and $z = E - i\delta$ for the advanced functions G^-. (We shall not indicate the explicit E dependence of the Green functions.)

Let us introduce the operator

$$P=|i\rangle\langle i|+\sum_f|f\rangle\langle f|$$

of projection onto the eigenfunctions of the Hamiltonian H_1^0 and let us define the reduced Green functions:

$$G_1=PGP, \quad G_2=(1-P)GP. \tag{5}$$

Using the Dyson equation $G = G_0 + G_0(V + W)G$ and the completeness condition for the basis functions, we can derive the expressions[19,20]

$$G_1=g_0+g_0RG_1, \quad G_2=g_1RG_1, \tag{6}$$

where $g_0 = PG_0$, $g_1 = (1 - P)G_0$, and the operator R is determined by the expression

$$R=V+W+(V+W)g_1R. \tag{7}$$

As will be seen below, we only need to know the matrix element $\langle i|G|i\rangle = \langle i|G_1|i\rangle$. From the first expression in (6) we obtain the system of equations

$$\begin{gathered} G_{ii}(E-E_i-R_{ii})-\sum_f R_{if}G_{fi}=1, \\ -R_{fi}G_{ii}+G_{fi}(E-E_f-R_{ff})-\sum_{f'\neq f} R_{ff'}G_{f'i}=0, \end{gathered} \tag{8}$$

where we have introduced the notation: $G_{ii} = \langle i|G|i\rangle$, $G_{fi} = \langle f|G|i\rangle$, etc., and E should be taken to stand for $E + i\delta$.

Let us proceed to the computation of the matrix elements of the operator R. Taking (2) into account, we have

$$R_{if}=\langle i|V|f\rangle=v_f, \quad R_{fi}=v_f^*.$$

For the matrix element R_{ii} we can write:

$$R_{ii}=\sum_\mu \int \frac{\langle i|W|k_\mu(E')\rangle\langle k_\mu(E')|W|i\rangle}{E-E'+i\delta}dE'=\int \frac{\rho(E')|W_i(E')|^2}{E-E'+i\delta}dE', \tag{9}$$

where $\rho(E')$ is the density of the states $|k_\mu(E')\rangle$. Evaluating the integral in (9), we obtain

$$R_{ii}=d(E)-i\pi\rho(E)|W(E)|^2, \tag{10}$$

where d(E) is the real part of the integral (9) and leads, owing to radiative decay, to a shift of the level i. We shall neglect it. The second term in (10) depends weakly on E[19], and can be taken to be equal to its value at $E = E_i$. This is half the radiation width Γ of the level i. Thus, $R_{ii} = -i\Gamma/2$. In view of the large value of $E_0 - E_i$ in comparison with the matrix elements of the operators V and W, we neglect the terms that the function Ψ_0 gives rise to.

The determinant of the system (8) has the form

$$D(E)=\begin{vmatrix} E+{}^1\!/_2\, i\Gamma & v_1 & v_2 & \cdots & v_N \\ v_1^* & E-\Delta_1 & & & \\ v_2^* & & E-\Delta_2 & & \\ \cdot & & & \cdot & \\ \cdot & & & & \cdot \\ v_N^* & & & & E-\Delta_N \end{vmatrix}. \tag{11}$$

Here and below the energies are measured from the energy of the level i and $\Delta_n = E_n - E_i$. The matrix element G_{ii} is equal to the ratio of the determinant $D_1(E)$ obtained from (11) by deleting the first column and the first row (see (8)) to the determinant D(E).

In deriving (11), we have assumed that the states $|f\rangle$ have zero radiation width and, therefore, $R_{ff'} = 0$. In real systems, the widths of these states are smaller than Γ by several orders of magnitude. Allowance for these widths in (11) is important for times much longer than the lifetime of the state $|i\rangle$. For certain cases (not considered here) it is necessary and leads to the appearance in the diagonal and off-diagonal terms in (11) of small imaginary corrections $\Gamma_{ff'}$ [21,22].

3. THE POLES OF THE FUNCTION G_{ii} FOR SOME PARTICULAR CASES

The poles of the function G_{ii} determine the energies of the quasistationary states and their widths[19]. Knowledge of the locations of the poles is necessary for the description of the time evolution of the excited states. Let us consider a few physically different cases.

A. The statistical limit. This is the case when the levels of the term f form a dense spectrum, Δ_n and v_n are smooth functions of n, $\Delta_n - \Delta_{n-1} \sim 1/N$, and $v_n - v_{n-1} \sim 1/N$. Such a model is justified for polyatomic molecules and is used (in a simplified form) in a number of papers[8,22]. Let us consider the locations of the poles of G_{ii} in the limit as $N \to \infty$. Expanding the determinant (11), and dividing the numerator and denominator in the expression for G_{ii} by D_1, we obtain

$$G_{ii}=\left(E+i\frac{\Gamma}{2}-\sum_{n=1}^N \frac{|v_n|^2}{E-\Delta_n}\right)^{-1}. \tag{12}$$

We obtain for the determination of the poles the equation

$$E+i\frac{\Gamma}{2}=\sum_{n=1}^N \frac{|v_n|^2}{E-\Delta_n}, \tag{13}$$

which has N + 1 roots. N roots of this equation for real Δ_n lie between Δ_n and Δ_{n+1}, and one root lies outside the spectrum of the levels f_n[23] (for the case of complex Δ_n, see[24]).

We shall seek the roots of the first type. Let us set $E_n = \Delta_n + x_n$, x_n being ~1/N. (We denote the poles by the same symbols E_n used to denote the eigenvalues of the Hamiltonian H_1^0, since this does not lead to any confusion). We have

$$\Delta_n+x_n+i\frac{\Gamma}{2}=\sum_{n'=1}^N \frac{|v_{n'}|^2}{\Delta_n-\Delta_{n'}+x_n}=\frac{|v_n|^2}{x_n}+\sum_{n'\neq n}^N \frac{|v_{n'}|^2}{(n-n')d\Delta/dn+x_n}. \tag{14}$$

At large values of N the dominant contribution to this sum is made by the terms in the region $n \sim n'$. According to the original assumption of the model, v_n and $d\Delta/dn$ are slowly varying functions of n. Replacing them in the vicinity of n by constants, we obtain for (14) the expression

$$\Delta_n+i\frac{\Gamma}{2}=\frac{|v_n|^2}{\varepsilon_n}\left(\frac{1}{\lambda_n}+2\lambda_n\sum_{k=1}^\infty \frac{1}{\lambda_n^2-k^2}\right)=\pi\frac{|v_n|^2}{\varepsilon_n}\operatorname{ctg}(\pi\lambda_n). \tag{15}$$

Here we have introduced the notation $\lambda_n = x_n/\epsilon_n$ and have extended the sum over k to infinity, in view of the fact that the dominant contribution to it is made by the terms with small $k = n - n'$. Furthermore, we have neglected x_n on the left-hand side of (15), since $x_n \sim N^{-1}$.

From (15) we obtain

$$x_n=\frac{\varepsilon_n}{\pi}\operatorname{arcctg}\frac{(\Delta_n+i\Gamma/2)\varepsilon_n}{\pi|v_n|^2}+O\left(\frac{1}{N}\right). \tag{16}$$

The singular root E_0 of Eq. (13) for $N \to \infty$ is, in the case of real Δ_n, determined by the equation

$$E_0+i\frac{\Gamma}{2}=\int_1^N \frac{|v(n)|^2}{E_0-\Delta(n)}dn. \tag{17}$$

In this formula we have replaced the sum over n by an integral in accordance with the Euler-Maclaurin formula. Since either $E_0 > \max\Delta(n)$ or $E_0 < \min\Delta(n)$, the integration can be carried out along the real axis.

B. The quasi-resonance case. Let us now consider the interesting case when one level of the term f is located near the level i, the other levels of the f term being separated from the level i by a wide (in the sense indicated below) energy gap. The poles of G_{ii} can then be determined, using perturbation theory[25]. The poles in the zeroth approximation are determined with allowance for only the interaction of the level i with the nearest level of the term f (the interaction matrix element v and the difference Δ between the level energies). Then from (11) we find

$$E_1{}^0={}^1/_2\{\Delta-i\Gamma/2+[(\Delta-i\Gamma/2)^2+4|v|^2]^{1/2}\}=a-ib, \tag{18}$$

$$E_2{}^0={}^1/_2\{\Delta-i\Gamma/2-[(\Delta-i\Gamma/2)^2+4|v|^2]^{1/2}\}=c-id, \tag{19}$$

$$E_n{}^0=\Delta_n, \quad 3\leqslant n\leqslant N+1. \tag{20}$$

The influence of the interaction of the level i with the remaining N − 1 levels of the term f on the locations of the poles of G_{ii} is determined with the aid of perturbation theory[25]. We obtain up to second order the expressions

$$E_1=E_1{}^0+\frac{|v|^2}{|v|^2+(a+id)^2}\sum_n\frac{|v_n|^2}{E_1{}^0-\Delta_n}, \tag{21}$$

$$E_2=E_2{}^0+\frac{|v|^2}{|v|^2+(c+ib)^2}\sum_n\frac{|v_n|^2}{E_2{}^0-\Delta_n}, \tag{22}$$

$$E_n=\Delta_n+|v_nv|^2\left\{\frac{1}{(\Delta_n-E_1{}^0)[|v|^2+(a+id)^2]}+\frac{1}{(\Delta_n-E_2{}^0)[|v|^2+(c+ib)^2]}\right\} \tag{23}$$

It can be seen from (21)–(23) that the condition of applicability of these formulas is the usual requirement that $|E_1^0-\Delta_n|\gg|v_n|$ and $|E_2^0-\Delta_n|\gg|v_n|$, or, if $|v|$ and $|\Delta|$ are small compared to $|\Delta_n|$, that $|\Delta_n|\gg|v_n|$. In the particular case when Γ = 0, (23) assumes the form

$$E_n=\Delta_n+|v_n|^2\left(|\Delta_n+\frac{|v|^2}{\Delta-\Delta_n}\right)^{-1}. \tag{24}$$

C. The Fermi resonance. For reasons that will become clear below, it is of interest to consider the case of Fermi resonance, when two of the f-term levels are quasi-degenerate ($\Delta_1=\Delta+\epsilon$ and $\Delta_2=\Delta-\epsilon$ with arbitrary Δ, v_1, and v_2), while the condition $|\Delta_n|\gg|v_n|$ is satisfied for the remaining levels. Let us again use perturbation theory to find the poles of G_{ii}. Setting $\epsilon=0$ and $v_n=0$ for $n\neq1, 2$, we find in the zeroth approximation that

$$\begin{gathered}E_{1,2}^0=\frac{1}{2}\{\Delta-i\Gamma/2\pm[(\Delta-i\Gamma/2)^2+4|v_1|^2+4|v_2|^2]^{1/2}\},\\ E_3{}^0=\Delta,\quad E_n{}^0=\Delta_n,\quad 3\leqslant n\leqslant N+1.\end{gathered} \tag{25}$$

The positions of the poles of G_{ii} can then be determined up to second-order perturbation theory, using standard formulas[25]. The results of the computations are, however, rather unwieldy, and we shall not give them here. Let us only note that for $|\Delta|\gg|v_1|$, $|v_2|$, and ε, the real parts of the roots E_1, E_2, and E_3 are respectively equal to Δ ± ε and ~0, while the imaginary parts are equal to

$$-i\frac{|v_1|^2}{\Delta^2}\frac{\Gamma}{2},\quad -i\frac{|v_2|^2}{\Delta^2}\frac{\Gamma}{2}\ \text{and}\ -i\frac{\Gamma}{2}.$$

D. The nondense intermediate case. This is the case when $|v_n|>|\Delta_n-\Delta_{n-1}|$ and $\Gamma\ll|\Delta_n-\Delta_{n-1}|$, and can be realized in molecules composed of a few (~5) atoms when there is sufficiently strong nonadiabatic coupling between the terms. Bixon and Jortner[8] found for the case when v_n = const = v and $\Delta_n=n\epsilon$ that

$$E_n\approx n\varepsilon-i\frac{\Gamma}{2\pi N}\left[1+\left(\frac{n}{N}\right)^2\right]^{-1}, \tag{26}$$

where $N=\pi|v|^2/\epsilon$.

In the general case, it follows from Eq. (11) that $|\operatorname{Im}E_n|\leq\Gamma/2$, since

$$\sum_n\operatorname{Im}E_n=-\frac{\Gamma}{2}$$

and all the poles of G_{ii} lie in the lower half-plane[19]. This seemingly trivial result is of great importance for the understanding of the luminescence properties of molecules (see below).

4. PREPARATION OF THE EXCITED STATES AND THEIR EVOLUTION

Let the system at the initial moment of time (t = 0) be in the state Ψ_0, and let an electromagnetic radiation of electric-field intensity $\mathscr{E}(t')$ begin to act on the system at this instant. If the time of action of the field is equal to τ, then for the wave function of the excited state we can write, correct to first order in the interaction of the molecule with the exciting field, the expression[20]:

$$\Psi(t)=\frac{1}{2\pi}\int dE\,e^{-iEt}\int_0^\tau e^{iEt'}\mathscr{E}(t')\,dt'\,G^+\hat{p}|\Psi_0\rangle, \tag{27}$$

where $\hat{p}$ is the momentum operator for the electrons of the molecule. Taking into account the selection rules (3), we have

$$\Psi(t)=\frac{p_i}{2\pi}\int dE\,e^{-iEt}\int_0^\tau e^{iEt'}\mathscr{E}(t')\,dt'G^+|i\rangle, \tag{28}$$

where $p_i=\langle i|\hat{p}|\Psi_0\rangle$. We assume, for simplicity, that the polarization of the exciting field and the dipole moment of the transition have the same direction. The probability amplitude for finding the system in a given state after the emission of a photon is equal to

$$\langle k_\mu(E_k)|\Psi(t)\rangle=\frac{p_i}{2\pi}\mathscr{N}^{-1/2}\int dE\,e^{-iEt}\langle k_\mu(E_k)|G^+|i\rangle\int_0^\tau\mathscr{E}(t')\,e^{iEt'}\,dt',$$

where $\mathscr{N}$ is the normalization factor, which is equal to $\langle\Psi(\tau)|\Psi(\tau)\rangle$.

It has previously[15] been shown that

$$\mathscr{N}=\pi^{-1}\tau p_i^2\int\operatorname{Im}G_{ii}I(E)\,dE,$$

where I(E) is the spectral distribution function of the field intensity.

Taking the second expression in (6) into account, we obtain for the photon-emission probability the expression

$$\begin{gathered}W_{k\mu}=\frac{p_i^2}{4\pi^2}\mathscr{N}^{-1}\iint dE\,dE'\exp[-i(E-E')t]\frac{W_\mu(E)W_\mu^*(E')G_{ii}^+G_{ii}^-}{(E-E_k+i\delta)(E'-E_k-i\delta)}\\ \times\int_0^\tau\int_0^\tau\exp[i(Et'-E't'')]\mathscr{E}(t')\mathscr{E}(t'')\,dt'\,dt''.\end{gathered} \tag{29}$$

To find the total emission probability, we must integrate $W_{k\mu}$ over E_k and sum over μ. Introducing the density $\rho_k(E)$ of the states $|k_\mu(E)\rangle$, neglecting the dependence of $W_k(E)$ and $\rho_k(E)$ on the energy (i.e., taking their values at $E=E_i$), and introducing the notation $\Gamma=2\pi\rho_k|W_k|^2$, we obtain after integrating (29) over E_k the expression

$$\begin{gathered}W(t)=K\frac{\Gamma}{\tau}\iint dE\,dE'\exp[-i(E-E')t]G_{ii}^+G_{ii}^-(E'-E+i\delta)^{-1}\\ \times\int_0^\tau\int_0^\tau\exp[i(Et'-E't'')]\mathscr{E}(t')\mathscr{E}(t'')\,dt'\,dt'',\end{gathered} \tag{30}$$

where K is a constant.

The quantity W(t) should be averaged over the states of the exciting field, i.e., the product $\mathscr{E}(t')\mathscr{E}(t'')$ should be replaced by the correlation function of the field $\Phi(t', t'')$, which, for stationary fields, depends only on the difference $t' - t''$. Then for the rate of change of the emission probability—a quantity which yields the luminescence decay law—we have

$$\mathscr{P}(t)=\frac{dW}{dt}=K\frac{\Gamma}{\tau}\iint dE\,dE'\exp[-i(E-E')t]G_{ii}^{+}G_{ii}^{-} \tag{31}$$
$$\times\int_0^\tau\int_0^\tau\exp[i(Et'-E't'')]\Phi(t'-t'')dt'\,dt''.$$

If the width of the spectral distribution of the exciting field exceeds the width of the state $|i\rangle$, then the function $\Phi(t' - t'')$ can be replaced by a delta function. We then have from (31) the expression

$$\mathscr{P}(t)=K\frac{\Gamma}{\tau}\int_0^\tau dt'\left|\int G_{ii}^{+}\exp[-iE(t-t')]dE\right|^2. \tag{32}$$

The E integral can be evaluated with the aid of the theory of residues, closing the contour of integration for $t - t' \geq 0$ in the lower half-plane. If the poles of the function G_{ii} are located at the points $E_n - i\gamma_n$ ($\gamma_n > 0$), then we obtain$^{2)}$

$$\mathscr{P}(t)=K\frac{\Gamma}{\tau}\sum_{n,n'}A_nA_{n'}^{*}\exp[-(\gamma_{nn'}+i\Delta_{nn'})t]\frac{\exp[(\gamma_{nn'}+i\Delta_{nn'})\tau]-1}{\gamma_{nn'}+i\Delta_{nn'}} \tag{33}$$

where we have introduced the notation $\gamma_{nn'} = \gamma_n + \gamma_{n'}$ and $\Delta_{nn'} = E_n - E_{n'}$.

The formula (33) gets simplified if the irradiation time is short (i.e., if $\tau \ll \Delta_{nn'}^{-1}$, $\tau \ll \gamma_{nn'}^{-1}$):

$$\mathscr{P}(t)=K\Gamma\sum_{nn'}A_nA_{n'}^{*}\exp[-(\gamma_{nn'}+i\Delta_{nn'})t]. \tag{34}$$

It can be seen from (34) that $\mathscr{P}(t)$ attenuates in time, oscillating with frequencies equal to the difference between the real parts of the poles of G_{ii}, which are equal in order of magnitude to the difference between the energies of the levels i and f. If some of the poles of G_{ii} are degenerate, then instead of the oscillating factors in the terms of the sum (34) that correspond to these poles, there appear power factors. In the presence of a pole of order n, the factor with the highest power is $t^{2(n-1)}$.

The beats in the luminescence decay law can be divided into the following three types: high-frequency beats, when $\Delta_{nn'} \gg \gamma_{nn'}$, low-frequency beats, when $\Delta_{nn'} \ll \gamma_{nn'}$, and beats with intermediate frequencies, when $\Delta_{nn'} \sim \gamma_{nn'}$. The experimental observation of the high-frequency beats requires the use of high-time-resolution equipment. The observation of the low-frequency oscillations is difficult, in view of the fact that the oscillating factor corresponding to a given excited state of the molecule varies little during the lifetime of the molecule in that state. The beats most accessible for experimental investigation are those with the intermediate frequencies $\Delta_{nn'} \sim \gamma_{nn'}$.

Let us proceed to discuss the luminescence decay law for excitation by short pulses in the particular cases considered in Sec. 3.

A. The statistical limit. In this case the expression for $\mathscr{P}(t)$ can be represented in the form

$$\mathscr{P}(t)=K\Gamma\left|\int_{-\infty}^{\Delta_1}e^{-iEt}\left(E+i\frac{\Gamma}{2}-\sum_n\frac{|v_n|^2}{E-\Delta_n}\right)^{-1}dE\right.$$
$$\left.+\int_{\Delta_1}^{\Delta_N}e^{-iEt}\left(E+i\frac{\Gamma}{2}-\sum_n\frac{|v_n|^2}{E-\Delta_n}\right)^{-1}dE\right|^2. \tag{35}$$

Let us, for definiteness, assume that $\mathrm{Re}\,E_0 < \Delta_1$. Taking, moreover, into account the fact that the difference between the energies of the ground state and the state $|i\rangle$ significantly exceeds the width of the level i, we have set the lower limit of the range of integration equal to $-\infty$; $\Delta_N \to \infty$, since the spectrum is not bounded from above. The integrand has one pole E_0 in the region $-\infty < \mathrm{Re} < \Delta_1$, and the first integral in (35) is equal to

$$\left(1+\int\frac{|v(n)|^2}{E_0-\Delta(n)}dn\right)^{-1}e^{-iE_0t}.$$

In the interval $\Delta_1 - \Delta_N$ the integrand has very many close poles, and the evaluation of the second integral in (35) with the aid of the theory of residues is difficult. Calculating, as in (15), the sum over n, we obtain

$$\mathscr{P}(t)=K\Gamma\left|C_0e^{-iE_0t}+\int_{\Delta_1}^{\Delta_N}e^{-iEt}\left[E+i\frac{\Gamma}{2}-\pi\frac{|v(E)|^2}{\varepsilon(E)}\mathrm{ctg}\frac{\pi E}{\varepsilon(E)}\right]^{-1}dE\right|^2 \tag{36}$$

The integral in (36) can be represented in the form

$$\int_{\Delta_1}^{\Delta_N}e^{-iEt}\left[E+i\frac{\Gamma}{2}+i\frac{\gamma(E)}{2}\right]^{-1}$$
$$\times\left\{1+\gamma(E)\left[i+\mathrm{ctg}\frac{\pi E}{\varepsilon(E)}\right]\Big/\left[E+i\frac{\Gamma}{2}-\frac{\gamma(E)}{2}\mathrm{ctg}\frac{\pi E}{\varepsilon(E)}\right]\right\}dE, \tag{37}$$

where $\gamma(E) = 2\pi|v(E)|^2/\epsilon(E)$. The second term in (37) is a rapidly oscillating function with an oscillation period $\sim 1/\epsilon(E = 0)$. At times $t \ll 1/\epsilon(E)$, the second term in (37) can be replaced by its mean value, which when evaluated over the period of oscillation of the cotangent turns out to be equal to zero. Then

$$\mathscr{P}(t)=\left|C_0e^{-iE_0t}+\int_{\Delta_1}^{\Delta_N}e^{-iEt}\left[E+i\frac{\Gamma}{2}+i\frac{\gamma(E)}{2}\right]^{-1}dE\right|^2. \tag{38}$$

Since the poles of the Green function are located in the lower half-plane, $\mathscr{P}(t)$ is a decreasing function of the time. If $\Delta_1 \to -\infty$ and $\gamma(E) = \mathrm{const}$, then we arrive at the Bixon-Jortner model[8]. In the limit $\Delta_1 \to -\infty$, the first term in (38) is, as can be shown, using a procedure similar to the one used in[26], exponentially small. Then for $\mathscr{P}(t)$ we have

$$\mathscr{P}(t)=\Gamma e^{-(\Gamma+\gamma)t}. \tag{39}$$

Notice that this result is valid for times $t \ll \epsilon^{-1}$, and, consequently, the energy spectrum of polyatomic molecules can be considered to be continuous only for these times. It is also clear that the quantum yield for these times is less than unity[15,16].

B. The quasi-resonance case. Neglecting in this case terms of order $|v_n|^2/\Delta^2$, we obtain

$$\mathscr{P}(t)=\frac{K\Gamma}{|E_1-E_2|^2}\{|E_1-\Delta|^2\exp(-2\,\mathrm{Im}\,E_1t)+|E_2-\Delta|^2\exp(-2\,\mathrm{Im}\,E_2t)$$
$$-2(\alpha^2+\beta^2)\exp[-\mathrm{Im}(E_1+E_2)t]\cos(\omega t+\delta)\}; \tag{40}$$
$$\alpha=\mathrm{Re}\,(E_1^{*}-\Delta)(E_2-\Delta),\quad \beta=\mathrm{Im}\,(E_1^{*}-\Delta)(E_2-\Delta),$$
$$\delta=\arccos\alpha(\alpha^2+\beta^2)^{-1},\quad \omega=\mathrm{Re}\,(E_1-E_2),$$

and E_1 and E_2 are given by the formulas (21) and (22).

It is evident from (40) that the decay law for the state $|i\rangle$ is characterized by three terms, two of which decay exponentially and the third oscillates in time while decaying exponentially. The beat frequency ω may become small upon the variation of the parameters Δ and v, and the beats can then be experimentally observed. Because of the decreasing exponential function in front of the cosine, these beats will appear at times of the order of Γ^{-1}. At times $t \gg \Gamma^{-1}$ the function $\mathscr{P}(t)$ will be determined by the poles E_n with $n > 2$. Since the difference $\mathrm{Re}(E_n - E_{n'}) \gg \Gamma$, the beats given by these terms (not given in (40) for the sake of simplifying the expression for $\mathscr{P}(t)$) will be high-frequency beats, and it will be difficult to observe them. The decay law in this time region cannot be even approximately described by an exponential function. Luminescence decay with two exponential functions has been experimentally observed[2-4], and, moreover, beats have been observed by Busch et al.[3] (see, however,[4]).

C. The Fermi resonance. In this case, retaining, as in (40), the terms that contribute to $\mathscr{P}(t)$ at small and intermediate times, we have

$$\mathscr{P}(t)=K\Gamma\left|\frac{1}{E_1-E_2}\left[\frac{(E_1-\Delta)^2-\varepsilon^2}{E_1-E_3}e^{-iE_1t}-\frac{(E_2-\Delta)^2-\varepsilon^2}{E_2-E_3}e^{-iE_2t}\right]+\frac{(E_3-\Delta)^2-\varepsilon^2}{(E_3-E_1)(E_3-E_2)}e^{-iE_3t}\right|^2, \tag{41}$$

where E_1, E_2, and E_3 can, as was noted in Sec. 3, be found with the aid of perturbation theory. It follows from (41) that $\mathscr{P}(t)$ will contain the term

$$\sim\exp[-\mathrm{Im}(E_1+E_2)t]\cos(\omega' t+\delta'), \quad \omega'=\mathrm{Re}(E_1-E_2),$$

which, for $|\Delta| \gg |v_1|, |v_2|$, assumes quite a simple form:

$$\mathrm{Im}(E_1+E_2)\approx\frac{\Gamma}{2}\frac{|v_1|^2+|v_2|^2}{\Delta^2}, \quad \omega'=2\varepsilon.$$

Thus, at times

$$\sim\frac{2}{\Gamma}\frac{\Delta^2}{|v_1|^2+|v_2|^2}$$

in view of the smallness of ϵ, the oscillations can be experimentally observed. The discussion in the preceding section on the contribution of the poles E_n with $n > 2$ applies also in the Fermi-resonance case.

D. As was pointed out at the end of Sec. 3, $\mathrm{Im}\, E_n < \Gamma$ and consequently in any model, with the exception of the statistical limit, the observable luminescence-decay time will be greater than the inverse radiation width of the state $|i\rangle$. For the case when $v_n = \mathrm{const} = v > \epsilon$, $\Delta_n = n\epsilon$, and $\Gamma \ll \epsilon$, Bixon and Jortner [8] found that

$$\mathrm{Im}\, E_n \sim \frac{\Gamma}{N}\left[1+\left(\frac{n}{N}\right)^2\right]^{-1}, \quad N=\pi|v|^2/\varepsilon.$$

The increase of the lifetime of the excited states of triatomic molecules has been experimentally observed[27].

Let us now discuss the dependence of the excited-state decay law on the conditions of excitation. It can be seen from (33) that in the case of broad-band excitation the luminescence decay law will depend on the irradiation time (see apropos of this also[13,28]). The various terms in (33) depend on τ differently. The diagonal elements for fixed t increase monotonically ($\Delta_{nn} = 0$), while the off-diagonal elements are modulated by the oscillating factor $\exp(i\Delta_{nn'}\tau)$. This should lead to the decrease of the contribution of the off-diagonal elements (as compared to the contribution of the diagonal elements) as τ increases and to some decrease in the beat amplitude. It should also be borne in mind that what is experimentally observed is the luminescence from many excited molecules. The phases of the oscillating terms in the decay law for the individual molecules are uniformly distributed over an interval of τ, and for $\tau \gtrsim \Delta_{nn'}^{-1}$ the beats will average out and vanish. The most optimum conditions for beat observation are therefore attained when exciting sources with long pulses are used and when the beat period is short.

In narrow-band excitation, when the line width of the radiation source is less than $\Delta_{nn'}$, individual nonadiabatic states will be excited. It was shown in[15] that the probability of finding the system in an excited state is equal to

$$W(t)=K\left|\int \mathrm{Im}\, G_{ii}I(E)e^{-iEt}dE\right|^2. \tag{42}$$

If the spectral energy distribution function of the exciting field $I(E)$ is different from zero only in the region of some pole $E_n - i\gamma_n$ of the function G_{ii}, then the decay law will have an exponential character, and the decay constant will be equal to $\gamma_n < \Gamma$. In excitation by a source of band width less than γ_n, the lifetime of the system will be determined by the band width[15]. Notice that a narrow-band excitation can be realized only for irradiation times very much exceeding the reciprocal of the exciting-line width. It follows from this that the observation of the beats under these conditions is difficult.

The excitation of those individual nonadiabatic levels of few-atom molecules that have large $\Delta_{nn'}$ values is possible, and has already been carried out[27], using ordinary (not laser) light sources. It was shown that the luminescence-decay time is indeed very much greater than the lifetime (for a radiative transition) of the state $|i\rangle$, i.e., that $\gamma_i \ll \Gamma$. Similar experiments can, apparently, be performed in the case of polyatomic molecules only with laser light sources; they would be highly desirable if they could be done.

5. THE ROLE OF THE ROTATIONAL STATES

The entire analysis carried out above is based on a model in which it is assumed that the rotational quantum numbers do not change in the nonadiabatic-transition process and that only one electronic vibrational-rotational state of the term i is excited. We can, in principle, derive, with allowance for an arbitrary number of the states of the i term and without limitations on the matrix elements of the operators V and W, an expression of the type (11). Qualitatively, the results do not change. There arises in the expression for $\Psi(t)$ in this case a sum over the states $|i\rangle$, which leads to the appearance in the expression for $\mathscr{P}(t)$ of additional oscillating terms with frequency of oscillation of the order of the energy spacing between the levels of the term i. In the case when the vibrational-rotational level spacing is large compared to the radiation width of the levels (small molecules), the beats will be high-frequency beats and difficult to observe experimentally. In the case when the indicated oscillations are of intermediate frequency the beats also manifest themselves in an experimentally determined decay law. If the rotational states are degenerate and the molecule has a dipole (magnetic) moment, then the degeneracy can be removed in an electric (magnetic) field. This will lead to a change in the function $\mathscr{P}(t)$, i.e., to the dependence of the luminescence decay law on the external field. The latter pertains, of course, to the vibrational levels as well if their locations change in the external field. Experiments of this kind will, possibly, allow the measurement of the dipole (magnetic) moments of molecules in the excited state.

The foregoing analysis shows that isolated molecules can have diverse excited-state decay laws. The exponential law can be observed only in certain cases, which are indicated above. The investigation of the beats in the luminescence decay law for molecules allows us, in principle, to determine the locations of those levels of the molecules whose spacings are less than their radiation widths (spectroscopy within a radiative-decay line). The determination of the locations of the levels by other means is difficult in this case.

Notice that quantum beats in the luminescence decay law are also possible for molecules in the condensed phase[29]. These beats decay in a period of time that depends on the vibrational-relaxation time of the molecule. The experimental investigation of them will allow the determination of the relaxation times of the highly-excited vibrational states of the molecule.

[1)] The functions $|f\rangle$ should, generally speaking, be taken to be vibrational-rotational functions (see Sec. 5).

[2)] In deriving this expression, we used the fact that the width of the level i (the interval in which G_{ii} is different from zero) is considerably less than E_0-E_i, and we took the lower limit of the integration to be equal to $-\infty$. If the lower limit of the range of integration is finite, then there appears in (33) a term that decreases with time according to a power law [19].

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201