Dependence of fluorescence characteristics on the spectral distribution of the intensity of the exciting electromagnetic field

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The dependence of the evolution characteristics of the excited states of polyatomic molecules and condensed media on the spectral distribution of the exciting electromagnetic field intensity is investigated. It is shown that in one-photon excitation by a field with a narrow spectral distribution the lifetime of the excited states and their decay law depend on the width and shape of the spectral distribution. With decrease of the spectral width of the excitation line the lifetime increases. For such excitation, the fluorescence quantum yield of all real systems depends on the width and position of the center of the exciting light line. Examples are given of systems for which one may expect a particularly strong dependence of the fluorescence quantum yield on the parameters mentioned above.

INTRODUCTION

The first investigation of the dependence of the characteristics of the evolution of excited states on the spectral distribution of the intensity of the exciting electromagnetic field was carried out back in the 30's by Weisskopf, using resonant fluorescence of isolated atoms as an example [1]. The results of this study are universally known and reduce to the following. When the atom is excited by a field with a broad spectral intensity distribution, the fluorescence line shape coincides with the absorption line shape (the line has natural width and shape). But if the excitation is effected by a narrow line, whose width is smaller than the natural width of the excited state of the atom, then the fluorescence line has the frequency distribution of the exciting-line intensity. These results were obtained under the assumption that the natural line width of the fluorescence is due only to radiative damping of the excited state. For isolated atoms, this decay channel of the excited states is indeed the only one, if we disregard the relatively rare cases of the Auger effect.

The situation is entirely different when condensed systems (for example, impurity crystals) and polyatomic molecules are excited. In this case, as is well known, the decay of the electron-excited states proceeds via two channels: 1) radiative decay; 2) nonradiative decay, when the energy of the electronic excitation is transformed into the energy of vibrational motion (and translational motion in the case of photochemical reactions) of the system atoms. The state decay rate constant K, which is connected with the natural width of the state Γ by the relation $K=\Gamma\hbar^{-1}$, is equal in this case to the sum of the rate constants of the radiative (k_r) and nonradiative (k_{nr}) transitions, and the quantum yield of the radiation is determined by the expression $Q=k_rK^{-1}$.

In molecular spectroscopy and in solid-state spectroscopy it is usually assumed that the lifetimes of the excited states and the value of Q are determined by the properties of the system and do not depend on the conditions of the preparation of the excited state. It has been shown only recently [2] that this is indeed the case if the system is excited by an electromagnetic field containing all the frequencies. Until now, however, the dependence of the fluorescence characteristics of polyatomic molecules and condensed media on the spectral composition of the exciting field has not yet been investigated. This question is the topic of the present paper.

We note that Weisskopf's results cannot be directly transferred to molecules and condensed media, since the perturbation responsible for the nonradiative transitions can cause the system to "forget" the method by which its excited states were prepared. The results of the present paper show, however, that this is not so, and that the fluorescence characteristics of isolated atoms and molecules, as well as those of condensed media, depend on the excitation conditions. This is a consequence of the time-independent interaction operators that lead to the radiative and non-radiative decay of the excited states.

We shall assume that the system, which we shall call for brevity a molecule, is at low temperature. Strictly speaking, the temperature should be set equal to zero, but the results are also valid at finite temperatures when the thermal energy is lower than the molecule vibration energy. Most luminescence investigations are carried out precisely at such temperatures. The exciting field will be assumed stationary and weak enough, and consequently only spontaneous radiative transitions will be considered.

HAMILTONIAN AND GREEN'S FUNCTIONS OF THE SYSTEM

The Hamiltonian of the molecule and of its radiation field can be represented in the form of the molecule Hamiltonian H_1', the field Hamiltonian H_2, and their interaction operator W. The Hamiltonian H_1' can, in turn, be written in the form of the sum of the adiabatic-approximation Hamiltonian H_1 and the nonadiabaticity operator V, which includes (in the case of L-S coupling) also the spin-orbit interaction operator. Thus,

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

The explicit form and the properties of the operators V and W are well known and described in [3,4]. The operator V acts only on the wave (electronic, vibrational, and spin) functions of the molecule, and the operator W depends on the coordinates of the molecule electrons and on the coordinates of the field.

The eigenfunctions $|nf\rangle$ of the Hamiltonian H_1 can be represented in the form of the product of the electronic wave function $|n\rangle$ by the vibrational function $|f\rangle$.1) The index n denotes the set of quantum numbers characterizing the given electronic state (term) of the system, and the index f denotes the set of vibrational quantum numbers. The spectrum of the eigenvalues E_{nf} of the Hamiltonian H_1 has the following two characteristic properties: 1) the distance between neighboring electronic states is usually much larger than the vibrational quanta of the system; the distance between the ground and the first electron-vibrational state is particularly large in this case; 2) in the case of condensed systems, the distance between neighboring vibrational levels is negligibly small and the spectrum is quasicontinuous; in the case of polyatomic molecules this distance decreases rapidly with increasing reserve of vibrational energy, so that at energies on the order of the electron-excitation energy the spectrum becomes likewise quasicontinuous[2].

The Hamiltonian H_2 describes single-photon states of the photon field, with wave functions $|\mathbf{k}, e_\alpha\rangle$, where $\mathbf{k}$ is the wave vector and e_α is the photon polarization 2). The lower state corresponds to the vacuum function $|0\rangle$. The functions $|\mathbf{k}, e_\alpha\rangle$ are obtained from $|0\rangle$ by applying to the latter the production operator $a^+_{\mathbf{k},e_\alpha}$. The states of the Hamiltonian H_2 form a continuous spectrum and are degenerate in the wave vector and in the polarization. The wave functions $|n, f, \mathbf{k}, e_\alpha\rangle$ of the Hamiltonian H_0 take the form of a product of the functions $|n,f\rangle$ and $|\mathbf{k}, e_\alpha\rangle$, and the corresponding energies are equal to the sum of the energies E_{nf} and $\hbar|\mathbf{k}|c$.

The wave functions $\psi_\nu(E)$ of the total Hamiltonian H can be represented in the form of an expansion in the set of the functions of the Hamiltonian H_0, for which purpose it is necessary to diagonalize the matrix H expressed in the representation of the function $|n, f, \mathbf{k}, e_\alpha\rangle$. (The quantum numbers ν characterize different functions of states that are degenerate in energy.) The functions $\psi_\nu(E)$ are normalized by the relation $\langle\psi_\nu(E)|\psi_{\nu'}(E')\rangle = \delta(E-E')\delta_{\nu\nu'}$. The matrix elements of the operators V and W have the following properties, which follow from the definition of V and W and from the orthonormal character of the functions of the Hamiltonian H_1 and H_2:

$$\langle n, f, \mathbf{k}, e_\alpha|V|n', f', \mathbf{k}', e_{\alpha'}\rangle = V_{nfn'f'}\delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'}; \tag{2}$$

$$\begin{gathered}\langle n, f, \mathbf{k}, e_\alpha|W|n', f', \mathbf{k}', e_{\alpha'}\rangle = W_{nfn'f'}(|\mathbf{k}|, e_\alpha) \quad \text{at} \quad k'=0,\\ \langle n, f, \mathbf{k}, e_\alpha|W|n', f', \mathbf{k}', e_{\alpha'}\rangle = W_{nfn'f'}(|\mathbf{k}'|, e_\alpha) \quad \text{at} \quad k=0.\end{gathered} \tag{3}$$

The explicit form of the matrix elements (2) and (3) is given in [4,5]. We shall neglect the diagonal matrix elements of the operators V and W, since they lead only to a renormalization of the energy levels of the Hamiltonian H_0.

The problem of the diagonalization of H, even for simple models, is very complicated [2]. For most real systems, however, it is known that the matrix elements of the operators V and W on the wave functions $|n, f, \mathbf{k}, e_\alpha\rangle$ and $|0, 0, 0\rangle$ constitute a small fraction of the energy difference between these states or, equivalently, the widths of the excited states are much smaller than their energies [3-5]. This enables us to state that the wave function of the ground state of the Hamiltonian H can be replaced with very good accuracy by the function $|0,0,0\rangle$ of the Hamiltonian H_0. We note also that the quantity $|\langle\psi_\nu(E)|n, f, 0\rangle|^2$ differs noticeably from zero for the functions $\psi_\nu(E)$ for which E lies in the interval $E_{nf} \pm \Delta E$, where ΔE is of the order of the half-width of the state $|nf\rangle$.

The operator of the interaction of the system with an external electromagnetic field whose electric component has an intensity $\mathscr{E}(t)$ is equal to $\hat{P}\mathscr{E}(t)$, where $\hat{P}$ is the operator of the momentum of the system electrons. (We assume that the dimensions of the molecule are much smaller than the wavelength of the exciting light.) The matrix elements of the transition from the ground state to the excited state are

$$\langle n, f, \mathbf{k}, e_\alpha|\hat{P}|0, 0, 0\rangle = P_{nf}\delta_{0,|\mathbf{k}|}. \tag{4}$$

For simplicity it is assumed that the external field is linearly polarized and that the polarization direction coincides with the direction of the dipole moment of the electron transition.

The matrix elements P_{nf} satisfy certain selection rules, along which we list the following: The value of P_{nf} is zero if the multiplicity of the states $|n\rangle$ and $|0\rangle$ differ. The probability of the transition is usually maximal if the values of f are small, and decreases rapidly with increasing value of f by virtue of the Franck-Condon principle [2,3,6]. The probability of an optical transition from the state $|0, 0, 0\rangle$ into states $|0, f, 0\rangle$ at large f is very small [5].

The typical arrangement of the states of the Hamiltonian H_0 is such that many states that form a continuous spectrum are located in the region of a certain electron-vibrational state $|i\rangle$, the optical transition to which is allowed, and the optical transitions to these states are either strongly or fully forbidden [2]. Thus, for example, in the case of molecules, the state $|i\rangle$ is the zeroth vibrational state of the first singlet excited term. (The ground states of most molecules are singlets.) The continuous spectrum of the energy levels in the region of the energy level $|i\rangle$ form states $|0, f, \mathbf{k}, e_\alpha\rangle$, states $|0, f, 0\rangle$ with large values of f, states of triplet terms located below the state $|i\rangle$, and, finally, states of possible photoproducts of the initial system. Under conditions when energy can be transferred away from the molecule, contributions to the continuous spectrum are also made by the energy-acceptor levels. (The operator V must include in this case the operator of interaction of the energy donor and acceptor molecules.) In the case of isolated atoms, the continuous spectrum of the energy levels in the region of the excited level $|i\rangle$ is much poorer and is made up of only states $|n, \mathbf{k}, e_\alpha\rangle$, where the energy E_n is smaller than the energy E_i.

For convenience in the subsequent manipulations, we shall designate the wave function of the ground state of the Hamiltonian H (and H_0) by ψ_0, the wave functions of the excited states by $\psi_\nu(E)$, those of the function $|n, f, \mathbf{k}, e_\alpha\rangle$ with $|\mathbf{k}| = 0$ by $|f_\lambda(E)\rangle$, and those of the functions $|n, f, \mathbf{k}, e_\alpha\rangle$ with $|\mathbf{k}| \neq 0$ by $|k_\mu(E)\rangle$. The subscripts λ and μ denote the sets of quantum numbers characterizing different functions of energy-degenerate states.

Replacement of the quasicontinuous set of states $|n, f, 0\rangle$ by the continuous set $|f_\lambda(E)\rangle$ is possible if the reciprocal of the average distance between the states $|n, f, 0\rangle$ in the pertinent electron-excitation energy region of the system greatly exceeds the time of observation of the system, which is equal in the case of isolated molecules to the free-path time. This condition is satisfied with great accuracy [2] for condensed systems at all times, and for polyatomic molecules with rare exceptions [6]. For molecules with a small number of atoms, the spectrum of the levels E_{nf} cannot be replaced by a quasicontinuous spectrum, and this case will be considered separately.

We introduce the Green's functions

$$G_0 = 1/(z - H_0), \quad G = 1/(z - H), \tag{5}$$

$$G_0 = \frac{|\psi_0\rangle\langle\psi_0|}{z-E} + \sum_\lambda \int \frac{|f_\lambda(E')\rangle\langle f_\lambda(E')|}{z-E'} dE' + \sum_\mu \int \frac{|k_\mu(E')\rangle\langle k_\mu(E')|}{z-E'} dE' \tag{6}$$

$$G = \frac{|\psi_0\rangle\langle\psi_0|}{z-E_0} + \sum_\nu \int \frac{|\psi_\nu(E')\rangle\langle\psi_\nu(E')|}{z-E'} dE', \tag{7}$$

where $z = E + i\delta$ for retarded Green's functions G^+ and $z = E - i\delta$ for advanced Green's functions G^-. We shall not indicate explicitly the energy dependence of the functions G (or R, see below) if there is no danger of misunderstanding. In the case of isolated molecules, it is necessary to include in the second term of (6) also the sum over the discrete lower vibrational states, but we need not write it out in explicit form. The functions G and G_0 are connected by the Dyson equation $G = G_0 + G_0(V + W)G$. We introduce the projection operator $|i\rangle\langle i|$, where $|i\rangle$ is the eigenfunction of H_0, and define the reduced Green's functions by the relation

$$G_1 = |i\rangle\langle i|G|i\rangle\langle i|, \quad G_2 = (1 - |i\rangle\langle i|)G|i\rangle\langle i|. \tag{8}$$

Using Dyson's equation and the completeness of the set of the functions of the operator H_0, we can show [7] that

$$G_1 = g_0 + g_0 R G_1, \quad G_2 = g_1 R G_1, \tag{9}$$

where $g_0 = |i\rangle\langle i|G_0$, $g_1 = (1 - |i\rangle\langle i|)G_0$, and the operator R is defined by the relation

$$R = (V + W) + (V + W)g_1(V + W) + (V + W)g_1(V + W) \times g_1(V + W) + \ldots = (V + W) + (V + W)g_1 R. \tag{10}$$

TIME AND LAW OF DECAY OF EXCITED STATES

Assume that an external electromagnetic field begins to act at a time $t = 0$ on a system situated in a state ψ_0. Then, after the field has acted for a time τ, we have for the wave function of the excited state, in the first order of the perturbation theory in the molecule interaction with the external field [3],

$$\Psi(t) = -i \sum_\nu \int dE\, e^{-iEt} \int_0^\tau \mathscr{E}(t') e^{iEt'} \langle\psi_\nu(E)|\hat{P}|\psi_0\rangle \psi_\nu(E)\, dt'. \tag{11}$$

Here and below we assume $\hbar = 1$ and $E_0 = 0$. For the probability amplitude of finding the system with the wave function $\Psi(\tau)$ we have

$$\langle\Psi(\tau)|\Psi(t)\rangle = A(t) = \\ = N^{-1} \sum_\nu \int dE |P_\nu(E)|^2 e^{-iE(t-\tau)} \int_0^\tau\int_0^\tau \mathscr{E}(t')\mathscr{E}(t'') e^{iE(t'-t'')}\, dt'\, dt'', \tag{12}$$

where $P_\nu(E) = \langle\psi_\nu(E)|\hat{P}|\psi_0\rangle$, and N is a normalization coefficient equal to $\langle\Psi(\tau)|\Psi(\tau)\rangle$.

Expression (12) must be averaged over all the states of the radiation field, to which end the product $\mathscr{E}(t')\mathscr{E}(t'')$ should be replaced by the correlation function of the field $\Phi^{(1)}(t', t'')$, which in the case of a stationary source depends only on the difference $t' - t''$ [8]. In this case, the double integral in (12) with respect to t′ and t″ can be calculated in part:

$$\int_0^\tau\int_0^\tau e^{iE(t'-t'')}\Phi^{(1)}(t' - t'')\, dt'\, dt'' = \tau \int_{-\tau}^{\tau} e^{iEx}\Phi(x)\, dx. \tag{13}$$

At values of τ greatly exceeding the field correlation time, the integral (13) is proportional to the intensity I(E) of light of frequency E [8]. (The proportionality coefficient will be omitted.) Then

$$A(t) = \Big[\sum_\nu \int dE\, |P_\nu(E)|^2 I(E)\Big]^{-1} \sum_\nu \int dE\, e^{-iE(t-\tau)} |P_\nu(E)|^2 I(E). \tag{14}$$

We assume further that I(E) differs from zero in a certain energy interval $E_i \pm \Delta E$. Assume that in this interval there is located one state $|i\rangle$ ($|i, f, 0\rangle$) of the Hamiltonian H_0, the optical transition to which from the state ψ_0 is allowed, and that the remaining states of this type are located far from $|i\rangle$ in energy, so that their contribution to the functions $\psi_\nu(E)$ can be neglected in the indicated energy interval. In the case of isolated molecules, this situation is always observed if f is small and if the state $|i\rangle$ is not degenerate. We can then write

$$|P_\nu(E)|^2 = |\langle\psi_\nu(E)|i\rangle\langle i|\hat{P}|\psi_0\rangle|^2 = |P_i|^2 |\langle\psi_\nu(E)|i\rangle|^2. \tag{15}$$

The quantity

$$\sum_\nu |\langle\psi_\nu(E)|i\rangle|^2,$$

as is well known, is equal to

$$\sum_\nu |\langle\psi_\nu(E)|i\rangle|^2 = -\frac{1}{\pi} \operatorname{Im} \langle i|G^+|i\rangle = -\frac{1}{\pi} \operatorname{Im} G_{ii}. \tag{16}$$

From the first relation of (9) we have

$$G_{ii}^+ = (E - E_i - \langle i|R^+|i\rangle + i\delta)^{-1}. \tag{17}$$

The value of the matrix element $\langle i|R^+|i\rangle$ can be obtained from (10). In the first order we have

$$\langle i|R^+|i\rangle = \sum_\lambda \int \frac{|\langle i|V|f_\lambda(E')\rangle|^2}{E + i\delta - E'} dE' \\ + \sum_\mu \int \frac{|\langle i|W|k_\mu(E')\rangle|^2}{E + i\delta - E'} dE' = D(E) - i\pi\rho_f(E)|V_{if}(E)|^2 - i\pi\rho_k(E)|W_{ik}(E)|^2. \tag{18}$$

Here D(E) is the real part of the integrals 3) and $\rho_f(E)$ and $\rho_k(E)$ are the densities of the corresponding states. Neglecting D(E), which leads to a shift of the level $|i\rangle$, assuming the imaginary part of (18) to be independent of E, and introducing the notation

$$k_r = 2\pi\rho_k|W_{ik}|^2, \quad k_{nr} = 2\pi\rho_f|V_{if}|^2, \quad K = k_r + k_{nr}, \tag{19}$$

we obtain

$$G_{ii} = (E - E_i + iK/2 + i\delta)^{-1}. \tag{20}$$

It is seen from (19) that k_r is a constant of the radiative-decay rate of the state $|i\rangle$, and k_{nr} are constants of the nonradiative decay, which are calculated in first-order perturbation theory.

If the excitation line has a Lorentz contour $I(E) = [(E - E_i)^2 + \gamma^2/4]^{-1}$ with a half-width $\gamma/2$, we obtain for A(t)

$$A(t) = (\gamma - K)^{-1}(\gamma e^{-Kt/2} - K e^{-\gamma t/2}). \tag{21}$$

In the calculation of the integral it was assumed that $E_i \gg K$ and γ, and consequently the lower integration limit was taken to be $-\infty$. In (21) we have omitted the nonessential parameter τ, on which only the probability of formation of the initial state $\Psi(\tau)$ is dependent, but not the law governing the variation of the probability $|A(t)|^2$ that the system will stay in this state.

It is seen from (21) that in the case of a broad excitation line, when the line width γ greatly exceeds the natural width of the level K, the rate of decay of the excited state depends only on the properties of the system and is equal to K. In the case when $\gamma \ll K$, the decay rate constant becomes equal to γ ($\gamma\hbar^{-1}$ in ordinary units), and does not depend on the system properties. In the limit as $\gamma \to 0$, a stationary state of the system is excited and $|A(t)|^2 = \text{const}$.

All the foregoing is valid not only for the special case when we confine ourselves to the first approximation (18). Indeed, if the imaginary parts of the poles of G^+_{ii} are equal to $-iK_m/2$, and the half-width of the Lorentz excitation line is $\gamma/2$, then we can obviously write for the amplitude A(t)

$$A(t) = \sum_m A_m(t) e^{-K_m t/2} + B(t) e^{-\gamma t/2}. \tag{22}$$

Here $A_m(t)$ and B(t) are periodic functions of the time. It is seen from (22) that at small γ the rate of decay of the excited state does not depend on the properties of the system and is equal to γ. If all the values of K_m are close, then at $\gamma \gg K_m$ the decay is not exponential.

The spectral composition of the exciting field governs not only the rate of decay of the excited state, but also the law of the decay, if the excitation line width is small enough. If the excitation is produced by a line with a Gaussian contour $I(E) = \exp[-(E - E_i)^2\gamma^{-2}]$ and the quantity γ is small, so that the interval in which I(E) varies appreciably is much smaller than the interval of variation of G^+_{ii} (i.e., $\gamma \ll K$ in the case of applicability of formula (20)), then the integral (14) varies with t like $\exp(-\gamma^2 t^2/2)$. Thus, the law governing the decay ceases to be exponential, and the half-life time, equal to $\hbar(\ln 2)^{1/2}/\gamma$, does not depend on the properties of the system and can be made arbitrarily large with decreasing γ. In the case of excitation of a line having a nonzero and constant intensity only in a certain energy interval that is so small that one can neglect the variation of G^+_{ii} in it, the decay obeys a power law: $|A(t)|^2 \sim t^{-2}$.

Let us examine finally one more case in which the contour of the excitation band consists of a number of equidistant Lorentz lines with half-width $\gamma/2$, and with distances ϵ between their maxima:

$$I(E) = \sum_n I_n[(E - E_0 - n\varepsilon)^2 + \gamma^2/4]^{-1}, \tag{23}$$

where E_0 is a certain constant. A contour of this type can be of interest in the investigation of the fluorescence excited by radiation from a multimode laser. The poles of I(E) are located at the points $E_0 + n\epsilon \pm i\gamma/2$. If the modulus of the imaginary parts of the poles of G^+_{ii} greatly exceed γ, then the law governing the variation of A(t) with I(E), defined by (23), takes the form

$$A(t) \cong e^{-\gamma t/2} e^{-iE_0 t} \sum_n A_n e^{-in\varepsilon t}, \tag{24}$$

where A_n are certain constants. It is seen from (24) that the probability of the system staying in the excited state has an exponential attenuation that is modulated by a periodic cofactor with period $2\pi\epsilon^{-1}$. Thus, the multimode character in the spectral distribution of the intensity of the exciting field leads to a modulation of the decay law by a periodic factor. It is easy to see that an analogous statement holds true also in the case when I(E) can be represented in the form of the sum of equidistant lines with Gaussian contour.

We note that all the cited results are in essence independent of the assumptions used to derive (15). Indeed, allowance for other states that contribute to $P_\nu(E)$, with the exception of the state $|i\rangle$, leads only to a shift of the poles of $|P_\nu(E)|^2$ and perhaps to the appearance of new poles, but does not change the general structure of the expression for A(t). The described dependence of the rate and law of decay of the excited state on the spectral composition of the exciting electromagnetic field has, consequently, a general character.

If we put V = 0, then the Hamiltonian H will correspond to the case of an isolated atom. It follows therefore that the dependence of the lifetime and of the decay law of isolated atoms on the form of I(E) has the same character as for the considered systems. The dependence of the lifetimes of isolated atoms on the width of the function I(E) follows, of course, even from Weisskopf's results [1], if the connection between the lifetime and the width of the radiated line is taken into account.

The different behavior of the dependence of the rate (and law) of the decay of the excited state on γ at large and small widths of the spectral-distribution function of the intensity of the exciting electromagnetic field is connected with the differences in the nature of the states excited in these limiting cases. When $\gamma \gg K$ we have $\Psi(\tau) \equiv |i\rangle$ [2], and the state $|i\rangle$ decays with a constant K independently of the value of γ. If $\gamma \ll K$, the state $\Psi(\tau)$ is not a state of the Hamiltonian H_1, but is a superposition of states of the molecule and of the photon field. The weights of the different functions in this superposition depend on the spectral width of the exciting field, which leads in final analysis to a dependence of the rate of evolution of $\Psi(t)$ on γ. In [9] it has been proposed to call such states electrodynamic.

An increase of the lifetime of the excited states following excitation with a field having a small spectral width may help obtain states with inverted population.

FLUORESCENCE QUANTUM YIELD

We proceed to consider the dependence of the fluorescence quantum yield on the spectral composition of the exciting field. Expression (11) can be rewritten in the form [7]

$$\Psi(t) = \frac{1}{2\pi}\int dE\, e^{-iEt}\int_0^\tau \mathscr{E}(t')\, e^{iEt'}\, dt'\, G^+\hat{P}|\psi_0\rangle. \tag{25}$$

Using the same assumptions as in the derivation of (15), we obtain

$$\Psi(t) = \frac{1}{2\pi}\int dE\, e^{-iEt}\int_0^\tau \mathscr{E}(t')\, e^{iEt'}\, dt'\, G^+|i\rangle\langle i|\hat{P}|\psi_0\rangle. \tag{26}$$

The amplitude of the probability of observing the system in the state $|k_\mu(E')\rangle$ when a photon is emitted is equal to

$$\langle k_\mu(E')|\Psi(t)\rangle = N^{-1/2}(2\pi)^{-1}P_i\int dE\, e^{-iEt}\int_0^\tau \mathscr{E}(t')\, e^{iEt'}\, dt'\, \langle k_\mu(E')|G^+(E)|i\rangle, \tag{27}$$

where N is the normalization factor of the function $\Psi(\tau)$ and is equal, as before, to $-\pi^{-1}\tau P_i^2 \int I(E) \operatorname{Im} G^\pm_{ii}\, dE$.

From the second expression of (9) we get

$$\langle k_\mu(E')|G^+(E)|i\rangle = \langle k_\mu(E')|R^+(E)|i\rangle\langle i|G^+(E)|i\rangle(E - E' + i\delta)^{-1}. \tag{28}$$

The total probability of the transition of $(q_\mu(E'))$ to the state $|k_\mu(E')\rangle$ is equal to the square of the modulus of (27), taken at infinite t. When t tends to infinity, only the pole $E = E' - i\delta$ makes a nonvanishing contribution to the integral with respect to E in (27), inasmuch as $\delta \to 0$. We then obtain, replacing E′ by E after the integration

$$q_\mu(E) = N^{-1}P_i^2|\langle k_\mu(E)|R^+|i\rangle\langle i|G^+|i\rangle|^2 \int_0^\tau\int_0^\tau \mathscr{E}(t')\mathscr{E}(t'')e^{iE(t'-t'')}\,dt'\,dt''. \tag{29}$$

Averaging (29) over the states of the exciting field and assuming the quantity τ to be much larger than the field correlation time, we obtain

$$q_\mu(E) = -\pi|\langle k_\mu(E)|R^+|i\rangle|^2|G_{ii}|^2 I(E)\left[\int \operatorname{Im} G_{ii}^+ I(E)\,dE\right]^{-1} \tag{30}$$

The fluorescence quantum yield is obtained upon integration of (30) with respect to E and summation over μ. Introducing the density $\rho_k(E)$ of the states $|k_\mu(E)\rangle$, which is equal to the product of the density of the states $|n, f\rangle$, and $|\mathbf{k}, e_\alpha\rangle$, we get

$$Q = -\pi\int \rho_k(E)|R_{ki}G_{ii}|^2 I(E)\,dE\left[\int \operatorname{Im} G_{ii}\, I(E)\,dE\right]^{-1}. \tag{31}$$

Expression (31) can be simplified. The main contribution of (31) is made by an energy region smaller than or of the order of the natural width of the level $|i\rangle$. By virtue of the weak dependence of the matrix elements W_{ki} (and R_{ki}) and the density of states $\rho_k(E)$ on the momentum of the radiated photon [3], and under conditions when the main contribution to (31) is made by final molecule states the energy of which is close to the energy of the group state (narrow fluorescence band), the functions $\rho_k(E)$ and $R_{ki}(E)$ can be replaced by their values at $E = E_i$. The quantity $2\pi\rho_k(E_i)|R_{ki}(E_i)|^2$ is equal to the rate constant k_r of the radiative decay of the state $|i\rangle$, and we obtain for Q

$$Q = -\frac{k_r}{2}\int |G_{ii}|^2 I(E)\,dE\left[\int \operatorname{Im} G_{ii}^+ I(E)\,dE\right]^{-1}. \tag{32}$$

Recognizing that $\operatorname{Im} G_{ii}^+ = -\operatorname{Im}(G_{ii}^+)^{-1}|G_{ii}^+|^2$, and that according to (17) we have $\operatorname{Im}(G_{ii}^+)^{-1} = -\operatorname{Im} R_{ii}^+$, we obtain for the fluorescence quantum yield

$$Q = -\frac{k_r}{2}\int |G_{ii}|^2 I(E)\,dE\left[\int \operatorname{Im} R_{ii}^+\,|G_{ii}|^2 I(E)\,dE\right]^{-1}. \tag{33}$$

We see therefore that if $\operatorname{Im} R_{ii}^+ = \text{const}$, then the value of Q does not depend (under the assumptions made concerning the functions $\rho_k(E)$ and $R_{ki}(E)$) on the form of I(E). The simplest example of such a case is formula (20), with the aid of which we obtain the usual expression $Q = k_r K^{-1}$, regardless of the form of I(E).

For real systems, the expression given for G_{ii}^+ by formula (20) can be employed in rare cases or else only for approximate estimates, since it is obtained under the assumption that the density of the states $|n, f, 0\rangle$ and $|n, f, \mathbf{k}, e_\alpha\rangle$ and the matrix elements of the operators V and W do not depend on the energy and the quantum numbers of the states. Strictly speaking, this condition is never satisfied.

For isolated molecules, the matrix elements of the operator V change very strongly (by several orders of magnitude) with changing vibrational numbers f [6]. In the case of impurity molecular crystals, the matrix elements of the operator V for the vibrational states of the impurity molecules are largest, and those for the crystal vibrations are much smaller. In impurity crystals containing rare-earth ions, the matrix elements of the nonadiabaticity operator are also very strongly dependent on the type of the states $|nf\rangle$ [10]. It follows therefore that $\operatorname{Im} R_{ii}$ is in the general case a function of the energy, and that Q will depend on the form of I(E) if the intensity distribution I(E) is not constant in the interval where the functions $|G_{ii}|^2$ and R_{ii} change appreciably, i.e., at sufficiently narrow excitation lines 4).

If the distribution I(E) differs from zero in a narrow energy interval near the energy E_0, which is so small that its value is much smaller than the interval of the significant change of the functions R_{ii} and G_{ii}, then we can put $I(E) \approx \delta(E_0 - E)$, and we get for Q

$$Q = -{}^1\!/_2 k_r[\operatorname{Im} R_{ii}^+(E_0)]^{-1}. \tag{34}$$

It follows from (34) that if the function $\operatorname{Im} R_{ii}^+$ changes significantly with energy, then Q also depends strongly on the position of the center of the narrow exciting line.

The simplest example of a Green's function different from (20) can be found for the three-level system of states ψ_0, $|i\rangle$, and $|f\rangle$ in which the state $|i\rangle$ is optically active with a radiative width k_r, and the state $|f\rangle$ is connected by a nonadiabatic interaction with the state $|i\rangle$ and relaxes with a relaxation width λ. Such a system is frequently realized experimentally, and its behavior was considered in [10-12]. The Green's function of a three-level system is

$$G_{ii}^+ = \left(E + \Delta + i\frac{\lambda}{2}\right)\left[\left(E + i\frac{k_r}{2}\right)\left(E + \Delta + i\frac{\lambda}{2}\right) - |v|^2\right]^{-1} \tag{35}$$

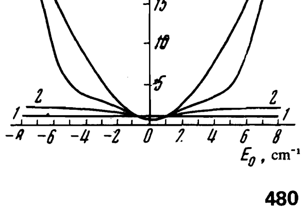
where Δ is the energy difference between the states $|i\rangle$ and $|f\rangle$, while $v = \langle i|V|f\rangle$ and the energies are reckoned from the energy of the level $|i\rangle$.

The figure shows the dependence of the quantum yield Q of the fluorescence of a three-level system (referred to its value at I(E) = const) on the parameters E_0 and γ of a Lorentz line of an exciting field $[(E - E_0)^2 + \gamma^2]^{-1}$. The value of E_0 is reckoned from the energy level $|i\rangle$. The following values of the parameters were chosen: $k_r/2 = 10^{-2}$ cm^{-1}, $\lambda/2 = v = 1$ cm^{-1}, and $\Delta = 0$, which are realized, for example, in the case of certain molecules placed in a solvent [5,6]. We see that at small γ the quantity Q changes very strongly (by one order of magnitude) depending on the position of the excitation line center E_0. At small γ, the dependence of Q on E_0 is described by formula (34), which in this case takes the form 5)

$$Q = \frac{k_r}{2}\left\{\frac{k_r}{2} + \frac{\lambda|v|^2}{2}\left[(E_0 + \Delta)^2 + \frac{\lambda^2}{4}\right]^{-1}\right\}^{-1}. \tag{36}$$

When E_0 tends to infinity, Q tends to unity, but in this case the probability of energy absorption by the system vanishes, and the fluorescence gives way to Raman scattering.

Calculations show that when v decreases and Δ increases, the dependence of Q on E_0 becomes less strong, for in this case R_{ii}^+ depends little on E and the quantum yield tends to unity. It follows therefore that a significant dependence of Q on the form of I(E) should be expected in those cases when the fluorescence quantum yield in the case of broadband excitation is small and the function R_{ii}^+ changes strongly with energy. This statement can be justified not only for a three-level system, but also in the general case.



Dependence of the quantum yield Q of the fluorescence of a three-level system on the parameters of the Lorentz excitation line E_0 and γ: 1) $\gamma = 10$, 2) $\gamma = 0.5$; 3) $\gamma = 10^{-1}$; 4) $\gamma = 10^{-2}$ cm^{-1}.

Let us cite a few examples for which one can expect a strong increase of the fluorescence quantum yield following excitation with a line having a narrow spectral width in comparison with the quantum yield in the case of broadband excitation.

1) Fluorescence from vibrationally excited states of an electron-excited state of a condensed system at low temperature (the so-called hot fluorescence).

2) Emission from highly excited electronic states of condensed systems.

3) Fluorescence from excited states of molecules that become rapidly deactivated as a result of singlet-triplet conversion or photochemical decay.

We note that in those cases when several states of the type $|i\rangle$ are located in the energy interval where I(E) differs from zero, an additional cause appears for the dependence of Q on the form of I(E). This case will be considered separately.

It can be shown that a dependence of Q on the form of I(E) is possible also in the case of inhomogeneously broadened lines.

Experimental observation of the dependence of the quantum yield of the fluorescence on the excitation conditions is of great importance for spectroscopy, since it uncovers the possibility of investigating the emission of systems that produce no luminescence under broadband excitation. In addition, such investigations help explain details of intramolecular interactions (the form of the function R_{ii}), which is important for the theory of molecular structure.

FLUORESCENCE LINE SHAPE

Formula (30) can be used to find the spectral distribution of the radiated photons $\Phi(h\nu)$. To determine $\Phi(h\nu)$ it is necessary to return to the initial notation $|k_\mu(E)\rangle = |nf\rangle |k, e_\alpha\rangle$, and to sum (30) over the possible final states of the photons (over the polarizations and projections of the vector **k**) and the possible states $|nf\rangle$, the energy of which satisfies the relation $E_{nf} + h\nu = E$. Introducing the densities $\rho(h\nu)$ and $\rho(E_{nf})$ of the states $|\mathbf{k}, e_\alpha\rangle$ and $|nf\rangle$, respectively, we obtain

$$\Phi(h\nu) = \Phi_0 \rho(h\nu) \rho(E_{nf}) |R_{nfi}(E) G_{ii}(E)|^2 I(E), \tag{37}$$

where Φ_0 is constant and R_{nfi} is the matrix element of the operator R, averaged over the polarizations and directions of **k**.

Expression (37) coincides in structure with Weisskopf's expression [1] for isolated atoms. The first factor $\rho(h\nu)\rho(E_{nf})|R_{nfi}(E)G_{ii}(E)|^2$ determine the natural form of the fluorescence band of the molecule (fluorescence following excitation with a field having I(E) = const). When the system is excited by a field the width of whose spectral distribution of intensity is smaller than the natural width of the fluorescence lines the fluorescence line shape depends on the form of I(E).

Experimental observations of the dependence of the fluorescence line width on the form of the function I(E) should be carried out under conditions that exclude inhomogeneous broadening.

We emphasize in conclusion that the results pertain to the case of an isolated molecule or impurity center of a crystal, and consequently are valid at a very low concentration of the latter, when one can neglect Green's-function matrix elements of the type $\langle i|G|i'\rangle$, where $|i\rangle$ and $|i'\rangle$ are the excited states of different centers. (The matrix elements $\langle i|G|i'\rangle$ are proportional to the matrix element $\langle i|R|i'\rangle$, which determines the rate of energy transfer between the centers, and are small in the case of large distance between the centers.) The described effects should also be observed at higher impurity-center concentrations, but an investigation of this case calls for taking into account the spatial coherence of the exciting field and the collective effects in the study of the system, and will be the subject of a separate paper.

For molecules in the gas phase, it is necessary to satisfy conditions whereby the average distance between the molecules is large and changes insignificantly during the lifetime of the excited state, so that the change of the energy of their interaction does not exceed the width of the excited state.

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(1) For isolated molecules, the function $|f\rangle$ should be taken to mean a vibrational-rotational function. This refinement is not reflected in any manner in the results obtained below, since allowance for the rotational degrees of freedom of the system leads only to an inessential change in the values of the matrix elements V and W, and to a change in the density of states.

(2) By the same token, we shall take into account only the single-photon transitions, since they are the most probable.

(3) The isolated-molecule discrete states discussed following formula (6) contribute in the approximation (18) only to D(E).

(4) It also follows from this that the expression $Q = k_r K^{-1}$ for the quantum yield is only approximate.

(5) Formula (36) coincides with the expression obtained in [11] for the luminescence quantum yield following excitation with monochromatic light.

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