Nonexponential fluorescence decay of polyatomic molecules

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Organic molecules with a small electronic gap between the S_1 and T_1 states (2000–4000 cm^{-1}) exhibit deviations from the exponential law of fluorescence attenuation associated with violation of the balance equation in the absence of collisions. This survey provides an exhaustive classification of all physical situations which arise in various correlations between parameters. Dephasing processes and the attenuation of molecular states, biexponential attenuation, and chaotic and periodic quantum beats in the limits of strong and weak coupling are discussed. The predictions of the strong coupling theory are compared with experimental data for pyrazine. Rotational effects are interpreted as a narrowing of a band of strongly coupled states with an increase in the rotational quantum number. Periodic quantum beats at the weak coupling limit arise due to a reversible energy exchange among vibrational sublevels.

1. INTRODUCTION

The unusual luminescence properties of some azines and carbonyl compounds in rarified vapors and supersonic flows in nano- and picosecond excitation attracted attention after the discovery of the biexponential fluorescence attenuation of pyrazine.[1] This attenuation was later detected in pyramidine and its methyl derivatives,[2-6] *s*-triazine,[7] quinoxaline,[8] diacetyl,[9,10] glyoxyl,[11] methylglyoxyl,[9b,11,12] acetyldehyde,[13] acetone,[14] and other organic[15-17] and inorganic[18] polyatomic molecules, as well as cations[19] and triatomic molecules.[20,21] Yet another deviation from simple exponential attenuation is exhibited in the form of chaotic or regular quantum beats in the fluorescence intensity of these molecules in a magnetic field and when there is no magnetic field.[10,16,17,21-34] These beats are also seen in more complex anthracene-like compounds,[35,36] in which biexponential fluorescence attenuation from higher vibrational states has also been detected recently.[35b]

Interest in these phenomena increased especially when their dependence on molecular rotation was detected.[37-40] This dependence has been studied in rather great detail.[7,10,22-34,40-56] Also studied were the polarization properties,[52,56] the effect of the magnetic field,[17,21b,30,33,47,52-54,56] the length of the pulse of exciting light,[8a,32,47] its wavelength, and gas pressure. The results have been summarized in surveys.[24,26,57-61]

Recently a communication has appeared on the observation of quantum beats in femtosecond excitation. These beats are caused by vibrational-rotational motion of excited molecules in stable[62] and transition short-lived[63] states. A theoretical interpretation of these[64] and the aforementioned phenomena is based on general physical ideas.

The law of luminescence attenuation is associated with the dynamics of the excited state, and the latter is defined by the structure of the energy spectrum and the excitation conditions. In atoms, the isolated electronic states that interact with the continuum of states of the electromagnetic field decay according to an exponential law. The exception is degenerate levels, because they may be split by an external field, and, by using coherent excitation, one can observe reversible transitions between a small number of close sublevels from beats in radiation intensity.[65] In polyatomic molecules the luminescence kinetics are richer because the nuclear degrees of freedom make the spectrum more complex, and open channels for intramolecular redistribution of energy. In isolated molecules this is mainly electronic radiationless transitions, intramolecular vibrational relaxation in one electronic state, and reversible energy exchange between electronic and/or vibrational degrees of freedom.

This survey classifies possible types of behavior depending on the correlations between parameters, and, where possible, makes a comparison with experimental data. The difficulty lies in the need to order a large number of different situations and not lose sight of the essentially simple picture of physical phenomena due to the abundance of details. It is easy to represent this picture on the basis of the following general concepts.

In the area of the spectrum which is significant for luminescence, an isolated polyatomic molecule has a set of quasi-steady states which attenuate due to spontaneous radiation, radiationless transition, and vibrational relaxation. Depending on the spectral width and pulse length used to excite the molecules, one can excite individual states or coherent and incoherent superpositions of these states. Thus, in the general case the evolution of the excited state includes the processes of population relaxation and the coherence of molecular states.

If one excites an individual quasi-steady state, the entire process is reduced to the population relaxation of this state, and is described by a balance equation. According to this equation, the increase in the population of the luminescence state per unit time is equal to the difference between the number of incoming (due to excitation) and outgoing (due to radiation and relaxation) molecules. In this case, in rapid excitation, radiation is attenuated according to an exponential law at a rate equal to the rate of population relaxation. If the rate of excitation is comparable to the latter, the attenuation curve is a convolution of this exponent with an excitation function and, consequently, depends on the shape of the excitation pulse. If a group of states is excited, but there is an effective mechanism for rapid loss of phase memory, then these states are combined into one quasi-steady state with a large width (actually, because a new channel of intramolecular relaxation is opened) and the kinetics is again described by the balance equation.

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A different situation arises if there is coherent excitation of a group of molecular states, and phase memory is retained in the course of the characteristic time of evolution. Then, in addition to the relatively slow population relaxation, more rapid processes take place which are associated with two types of coherence effects. And if a sufficiently large number of quasi-steady states participates, then relaxation of the initial coherence occurs in a pure form, or, as it is said, there is dephasing of the initially prepared "optically light" state, which is expressed in the appearance of a rapid component on the radiation attenuation curve. If a small number of states participates (for example, a total of two), then coherence is expressed in the appearance of regular beats. As the number of states increases the beats become chaotic and gradually disappear due to averaging, giving way to the rapid exponential decay mentioned above.

From what has been said it is clear that the fundamental cause of nonexponential radiation attenuation is the violation of the balance equation due to the appearance of coherence effects. Thus, after one defines a quantum model of levels and the basic parameters in section 1.1, an examination of the balance equation in section 1.2 is the natural point of departure for subsequent analysis. The goal of this analysis is, first, the establishment of the limits of applicability of this equation based on solution of the basic equations of the model (see sections 2, 3, 4.5, and 5.1) and, second, classification of the types of nonexponential behavior in cases where the equation is not applicable.

1.1. Quantum model

The theory of radiationless transition[66,67] examines a scheme of levels (Fig. 1) which includes one "optically light" (Φ_s) and many "optically dark" (Φ_l) states in absorption and radiation with the participation of the ground state (Φ_0). This corresponds to the conditions of typical experiments. The portion of molecules $P_s(t)$ in state Φ_s at time t is calculated for a given initial value $P_s(0)$ (and $P_l(0) = 0$). The intensity of luminescence is

$$I_s(t) = \tau^{-1}_{\mathrm{rad}(s)} P_s(t), \tag{1.1}$$

where $\tau_{\mathrm{rad}(s)}$ is the radiation lifetime of state Φ_s.

The dynamics of the system are defined by the following parameters: the matrix element of interaction v_{sl}, the average distance between levels ρ_l^{-1}, the half-width of levels γ_s and γ_l, the resonance defect $\Delta = E_s - E_{l=0}$ ($E_{l=0}$ is the level E_l closest to E_s) and the pulse length τ_{pulse} of the exciting monochromatic radiation. The correlations between them affect the characteristics of the initially prepared state and its subsequent evolution.

Jumping ahead for easier orientation in the presentation and clearer representation of the results of analysis, we present in Fig. 2 a scheme which encompasses the most interesting cases. Within the limits of this scheme the examination is conducted from the top down. At the very top is the object of investigation, polyatomic molecules.

Following Robinson and Jortner, the statistical limit, the intermediate case, and the case of small molecules are differentiated. According to Ref. 67 these situations may be described in the framework of the Bixon–Jortner model if instead of the true steady states one examines (as is suggested by Robinson) the so-called effective states with the same

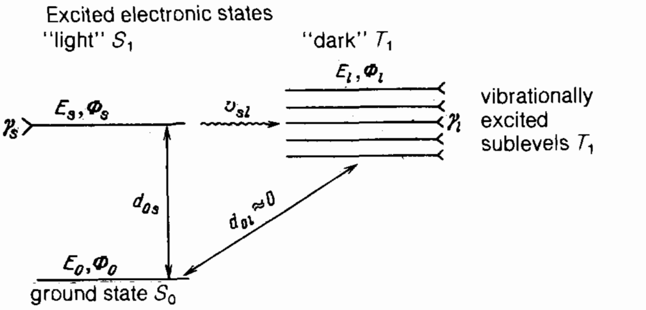

FIG. 1. Model of energy levels d_{0s} and d_{0l} are the matrix elements of the dipole moment.

v_{sl} equal to its maximum value. Then the statistical limit is realized in the limit of a large $\gamma_l\rho_l$, and the intermediate case and the case of small molecules are realized in the opposite limit (an accurate condition is obtained in section 2, see Fig. 2). For molecules in an inert gas medium (according to Robinson) γ_l depends linearly on pressure p; thus, at the limit of zero pressure $\gamma_l^0 = 0$ in the case of small molecules, and $\gamma_l^0 \neq 0$ in the intermediate case (broadening of the levels in an isolated molecule is a consequence of the Freed–Jortner principle of practical irreversibility[66,67]). Since, formally, the case of small molecules is a special case of the intermediate case, the case of small molecules need not be examined individually (thus, the intermediate case and the case of small molecules are placed on a common base in Fig. 2).

1.2. Balance equation

In the statistical limit, and in specific conditions in the intermediate case as well (see Fig. 2 and section 5.1), the following balance equation holds true

$$\dot{P}_s(t) = -(\tau^{-1}_{\mathrm{rad}(s)} + k_s + \tau^{-1}_{\mathrm{RT}(s)} + \tau^{-1}_{\mathrm{VR}(s)})P_s(t) + F(t), \tag{1.2}$$

where k_s is the rate of radiationless transition $\Phi_s \rightsquigarrow \Phi_l$, $\tau^{-1}_{\mathrm{RT}(s)}$ is the rate of radiationless transition $\Phi_s \rightsquigarrow \Phi_0$, $\tau^{-1}_{\mathrm{VR}(s)}$ is the rate of vibrational relaxation (dissociation and other processes are taken into account by adding the corresponding rates), $F(t)$ is an excitation function which is nonzero in an interval of τ_{pulse} near $t = 0$. Integrating it and substituting it into Eq. (1.1) we obtain the law of radiation attenuation

$$I_s(t) = \tau^{-1}_{\mathrm{rad}(s)} \int_{-\infty}^{t} \exp[(t - t')\tau^{-1}_{\mathrm{obs}(s)}]F(t')dt', \tag{1.3}$$

where

$$\tau_{\mathrm{obs}(s)} = (\tau^{-1}_{\mathrm{rad}(s)} + k_s + \tau^{-1}_{\mathrm{RT}(s)} + \tau^{-1}_{\mathrm{VR}(s)})^{-1} \tag{1.4}$$

is the observed lifetime for instantaneous excitation of the state Φ_s at time $t = 0$, that is, for the condition

$$\tau_{\mathrm{pulse}} \ll \tau_{\mathrm{obs}(s)}. \tag{1.5}$$

Actually, in this case the exponent changes slowly compared to the excitation function and it may be taken outside the integral sign at $t' = 0$. In the remaining integral at $t > 0$ the upper can be allowed to go to infinity, so the integral is equal to the total number of absorbed photons per molecule, that is, $P_s(0)$ (this is equivalent to making $F(t) = P_s(0)\delta(t)$). As a result, we obtain, as for a free atom, exponential attenuation

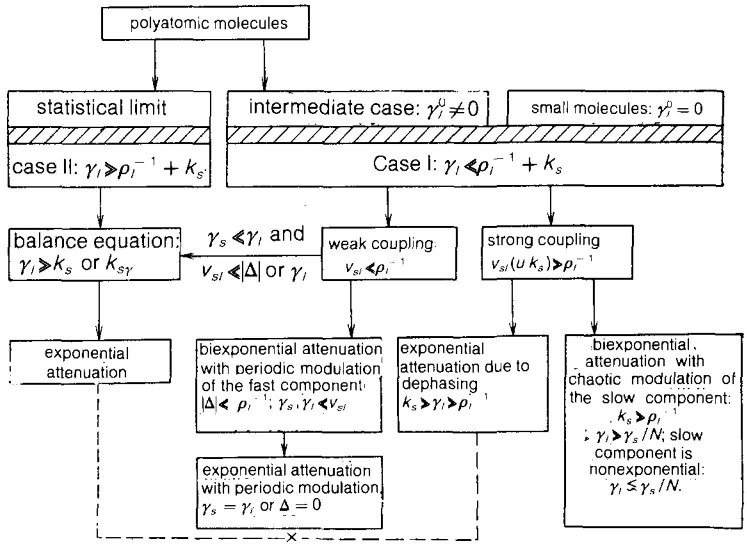

FIG. 2. Basic types of temporal behavior of fluorescence intensity from the initial prepared state Φ_s depending on the correlations between parameters γ_s, γ_l, ρ_l^{-1}, Δ, and v_{sl} (or $k_s = 2\pi v_{sl}^2 \rho_l$). In situations connected by the crossed out dashed line, exponential attenuation has a different physical nature.

$$I_s(t) = I_s(0) e^{-t/\tau_{\mathrm{obs}(s)}} \qquad (1.6)$$

with a lifetime (Eq. (1.4)), but now the quantum yield φ is less than unity. We recall that φ is the ratio of the total number of emitted photons to the total number of absorbed photons:

$$\varphi = \int_{-\infty}^{+\infty} I_s(t)\,\mathrm{d}t \left(\int_{-\infty}^{+\infty} F(t)\,\mathrm{d}t \right)^{-1}. \qquad (1.7)$$

Substituting Eq. (1.3) and changing the order of integration (or directly integrating Eq. (1.2) over time), we obtain the well-known formula

$$\varphi = \frac{\tau_{\mathrm{obs}(s)}}{\tau_{\mathrm{rad}(s)}}. \qquad (1.8)$$

It holds true for any ratio between τ_{pulse} and $\tau_{\mathrm{obs}(s)}$.

From what has been stated it is clear that deviation from exponential attenuation (Eq. (1.6)) when Eq. (1.2) is applicable can occur only when inequality (1.5) is violated, when the attenuation kinetics begins to be affected by the shape of the excitation pulse. For example, at $\tau_{\mathrm{pulse}} \gg \tau_{\mathrm{obs}(s)}$, on taking the slow function $F(t)$ outside the integral sign in Eq. (1.3), we obtain

$$I_s(t) = \varphi F(t), \qquad (1.9)$$

that is, the radiation reproduces the shape of the excitation pulse. This situation is characteristic, for example, for reverse electronic transitions[68] when the vibrational energy is slowly accumulated in the ground electronic state in infrared multiphoton excitation, and is then transferred into an excited electronic state with rapid de-excitation.

As already stated, this survey discusses the nonexponential kinetics of fluorescence attenuation due to the violation of the balance equation (1.2) in the intermediate case. The theory which is presented refers not only to radiationless transitions, but also to the processes of intramolecular vibrational relaxation and vibrational reversible energy exchange in cases where one can create experimental conditions in which one light state is excited that interacts with several dark states.[35b]

A feature of intramolecular vibrational relaxation and vibrational reversible energy exchange is that the states Φ_l, which are dark in absorption due to small Franck–Condon factors or due to symmetry violations, are light in radiation. Thus, radiation from these states is spectrally distinguishable from radiation from Φ_s, since the corresponding transitions into various vibrational sublevels of the ground electronic state are permitted. Thus, one can obtain additional information on the dynamics of the excited state by measuring the intensity

$$I_l(t) = \tau_{\mathrm{rad}(l)}^{-1} P_l(t). \qquad (1.10)$$

2. INITIAL EQUATIONS AND THEIR SOLUTION. CRITERIA OF THE STATISTICAL LIMIT AND OF THE INTERMEDIATE CASE

In the absence of broadening of levels, the wave functions of molecular states are written in the form $\Phi_n = a_{sn}\Phi_s + \Sigma_l a_{ln}\Phi_l$, and the normalized probability of detecting a molecule in the light state in the case of instantaneous excitation (Eq. (1.5)) (with $\hbar = 1$) is equal to[66,67]

$$P_s(t) = \Big| \sum_n a_{sn}^2 e^{-iE_n t} \Big|^2, \qquad (2.1)$$

$$a_{sn}^2 = \left[1 + \sum_l \frac{v_{sl}^2}{(E_n - E_l)^2} \right]^{-1}; \quad \sum_n a_{sn}^2 = 1; \qquad (2.2)$$

the energies of the molecular levels E_n are the roots of the equation

$$E_n - E_s = \sum_l \frac{v_{sl}^2}{E_n - E_l}. \qquad (2.3)$$

In the approximation of the effective Hamiltonian, which is based on the Green's function method[66,67] and corresponds to the assumption about the statistical character of the decay of zero states, the widths of the levels are introduced by substitution of the real energies with complex energies:

$$E_\nu \to \tilde{E}_\nu = E_\nu - i\gamma_\nu \quad (\nu = s,\, l,\, n), \qquad (2.4)$$

and a_{sn}^2 is replaced in Eq. (2.1) by the residue g_{sn} of the Green's function in band $\tilde{E}_n$; the residue is given by Eq. (2.2) after substitution of Eq. (2.4) (the notation a_{sn}^2 is retained for Eq. (2.2) for real energies). In the Bixon–Jortner model we assume that $E_l = E_s - \Delta + l\varepsilon$ $(l = 0, \pm 1, \pm 2, \ldots)$, $v_{sl} = \text{const}$, $\rho_l = 1/\varepsilon$, $\gamma_l = \text{const}$. Substituting this into Eqs. (2.1)–(2.3) and separating the real and imaginary parts in Eq. (2.3) we obtain[1,69]

$$P_s(t) = \left|\sum_n g_{sn} \exp(-iE_n t - \gamma_n t)\right|^2, \qquad (2.5)$$

$$g_{sn} = \{[1 + \pi^2 v_{sl}^2 \rho_l^2 \sin^{-2}[\pi(x_n + iy_n)]\}^{-1}, \qquad (2.6)$$

$$E_n - E_s = \frac{1}{2} k_s \frac{\sin(2\pi x_n)}{\mathrm{ch}(2\pi y_n) - \cos(2\pi x_n)}, \qquad (2.7)$$

$$\gamma_n - \gamma_s = \frac{1}{2} k_s \frac{\mathrm{sh}(2\pi y_n)}{\mathrm{ch}(2\pi y_n) - \cos(2\pi x_n)}, \qquad (2.8)$$

where the following notations are adopted

$$k_s = 2\pi v_{sl}^2 \rho_l, \qquad (2.9)$$

$$x_n = \rho_l(E_n - E_s + \Delta), \quad y_n = \rho_l(\gamma_l - \gamma_n). \qquad (2.10)$$

It follows from Eq. (2.8) that γ_n is between γ_s and γ_l, since y_n always has the same sign as $\gamma_n - \gamma_s$.

Depending on the quantity y_n one can isolate three cases.

I. $|2\pi y_n| \ll 1$. In an approximation which is linear relative to y_n there are no corrections to E_n associated with the attenuation of levels, $g_{sn} = a_{sn}^2$ and

$$\gamma_n = \gamma_l + a_{sn}^2(\gamma_s - \gamma_l), \qquad (2.11)$$

where

$$a_{sn}^2 = \frac{v_{sl}^2}{(E_n - E_s)^2 + (\pi v_{sl}^3 \rho_l)^2 + v_{sl}^2}. \qquad (2.12)$$

Substituting Eq. (2.11) into Eq. (2.10) we write the condition of smallness of y_n in the form $|\gamma_s - \gamma_l| \ll (2\pi\rho_l)^{-1} a_{sn}^{-2}$. This condition will be satisfied for all n if we replace a_{sn}^{-2} with its minimal value $(\pi v_{sl}\rho_l)^2 + 1$. Then, either

$$\gamma_s < \gamma_l \ll \frac{1}{4} k_s + (2\pi\rho_l)^{-1}, \qquad (2.13a)$$

or

$$\gamma_l < \gamma_s \ll \frac{1}{4} k_s + (2\pi\rho_l)^{-1}, \qquad (2.13b)$$

where it is assumed that $|\gamma_s - \gamma_l| \sim \gamma_s + \gamma_l$, and on the right sides the small terms are eliminated.

II. $2\pi y_{n_0} \gg 1$ for some n_0. Many levels coalesce into one quasi-steady level $E_{n_0} = E_s$, with $g_{sn_0} = 1$, and

$$\gamma_{n_0} = \gamma_s + \frac{1}{2} k_s. \qquad (2.14)$$

The condition on y_{n_0} is satisfied when

$$\gamma_l \gg \gamma_s + \frac{1}{2} k_s + (2\pi\rho_l)^{-1}. \qquad (2.15)$$

We note that in addition to $n = n_0$ there are other quasi-steady levels $n \neq n_0$, which differ only slightly from the zero levels $\tilde{E}_l$, and their contribution to radiation disappears as $\gamma_l \to \infty$, since the contribution of the ground level does not depend on γ_l.

III. $2\pi y_{n_0} \ll -1$. Again there is coalescing of the levels $E_{n_0} = E_s$ with $g_{sn_0} = 1$ and

$$\gamma_{n_0} = \gamma_s - \frac{1}{2} k_s. \qquad (2.16)$$

The coalescence condition

$$\gamma_s \gg \gamma_l + \frac{1}{2} k_s + (2\pi\rho_l)^{-1} \qquad (2.17)$$

shows that the second term in Eq. (2.16) is small and it should be dropped (see following section).

3. MONOEXPONENTIAL ATTENUATION WITH GREAT BROADENING OF LEVELS

Let E_s be a vibrational sublevel of a singlet state S_1, E_l is a sublevel of the triplet T_1 lying at an energy ΔE below S_1. Of the processes causing the broadening of levels we will consider only radiation attenuation, vibrational relaxation, and radiationless transition into S_0 (other possible processes are dealt with by a simple addition of the corresponding widths). Then

$$\gamma_s = \gamma_{\mathrm{rad}(s)} + \gamma_{\mathrm{RT}(s)} + \gamma_{\mathrm{VR}(s)} \equiv \frac{\tau_s^{-1}}{2},$$

$$\gamma_l = \gamma_{\mathrm{RT}(l)} + \gamma_{\mathrm{VR}(l)} \equiv \frac{\tau_l^{-1}}{2},$$

$$\tau_s^{-1} = \tau_{\mathrm{rad}(s)}^{-1} + \tau_{\mathrm{RT}(s)}^{-1} + \tau_{\mathrm{VR}(s)}^{-1},$$

$$\tau_l^{-1} = \tau_{\mathrm{RT}(l)}^{-1} + \tau_{\mathrm{VR}(l)}^{-1}, \qquad (3.1)$$

where the vibrational relaxation widths depend linearly on pressure, and the radiationless transition widths are present only in the intermediate state or the statistical limit. Radiation broadening is absent in final states, thus, in the small molecule state, with $p \to 0$, we have $\gamma_s (\to \gamma_{\mathrm{rad}(s)}) \gg \gamma_l (\to 0)$. On the other hand, one usually chooses the ground state or a weakly-excited vibrational state in S_1 as Φ_s so that γ_s is small. At large γ_s it would be difficult to prepare the initial state Φ_s, since at small $\tau_{\mathrm{obs}(s)}$ Eq. (1.5) cannot be satisfied. This means that at final pressures (and in the intermediate case, at any pressures) it should be true that $\gamma_l \gg \gamma_s$, since in the final state the supply of vibrational energy is larger (by ΔE) and the rate of vibrational relaxation increases as vibrational excitation increases. Thus, the ratio of γ_s to γ_l, can have any value and if the contribution of radiationless transition to S_0 is not too large, it may be regulated by a change in pressure.

We begin our examination of the kinetics of fluorescence with case III of the previous section, which, according to Eq. (2.17), corresponds to low pressures and a rapid radiation attenuation. Obviously, the intensity of fluorescence (Eq. (1.1)) attenuates according to an exponential law since the sum in Eq. (2.5) contains one term corresponding to the quasi-steady molecular state $n = n_0$ with the half-width of Eq. (2.16). We note, however, that in the absence of relaxation, that is, in the limit $\gamma_s = \gamma_{\mathrm{rad}(s)}$ and $\gamma_l = 0$, Eq. (2.16) formally gives a quantum yield greater than unity. This apparent contradiction is removed if one considers the contribution of weakly-excited levels $\tilde{E}_l$, which interferes with the contribution of the ground quasi-steady state. It then follows that consideration of the small second term in Eq. (2.16) is excessive accuracy; in fact, as it should be in this case, the quantum yield is equal to unity. Thus, *for rapid radiation decay the interaction between the singlet and triplet is in no way exhibited* and the rate of radiation attenuation is equal to the rate of attenuation of the zero level E_s, so $\gamma_{n_0} \simeq \gamma_s$.

In case II, intensity attenuates according to an exponential law (Eq. (1.6)) with an observed lifetime (Eq. (1.4)), a rate of radiationless transition $S_1 \rightsquigarrow T_1$ (Eq. (2.9)), which does not depend on γ_s and γ_l, and a quantum yield (1.8). In contrast to case III, Eq. (2.15) does not limit the relative value of terms in Eq. (2.14), thus, φ may have any value less than unity. From what has been stated it is clear that case II corresponds to the statistical limit (see Fig. 2; the less interesting case III is not shown in the figure).

The applicability of balance equation (1.2) stems from the fact that, according to Eq. (2.14), the total rate of attenuation of the fluorescent state is the sum of rates of transitions with and without radiation.

The statistical limit condition is usually written in the form[50] $\gamma_l \rho_l \gg 1$, where ρ_l is the density of all[66] or only of the effective[67] states. In the examined model this condition is more rigorous than inequality (2.15), which is especially important in the case of strong coupling (see below).

The most interesting, from the point of view of the subject of this survey, is case I, when not one, but several quasi-steady states participate in the dynamics. In case I it is necessary to differentiate the limits of strong and weak coupling.[70–73] From a formal point of view, the difference between them is that in the first limit case a large number $N \gg 1$ of final levels E_l yield a contribution to the dynamics of the initially excited state, while in the second case, basically only one level $E_{l=0}$ makes a contribution (when there is a large broadening of levels the situation can change, see section 5.1). Physically these cases differ in the appearance of the effects of coherence, relaxation, and the resonance defect.

4. FLUORESCENCE KINETICS WITH SLIGHT BROADENING IN THE LIMIT OF STRONG COUPLING: $v_{sl} \gg \rho_l^{-1}$

The number of triplet levels E_l which strongly interact with the singlet level E_s is proportional to the ratio of the width of the Lorentz distribution (Eq. (2.12)), which is approximately equal to k_s, to the distance between levels ρ_l^{-1}. This number (the so-called dilution factor) can be conveniently defined by the formula[11]

$$N = \pi k_s \rho_l = 2\pi^2 v_{sl}^2 \rho_l^2, \tag{4.1}$$

which differs from the definitions[1,61,68,71] by a numerical factor.[1)]

The features of the system dynamics and the observed fluorescence kinetics in the examined situation are determined by the following factors:

1) Participation of a large number of levels: $N \gg 1$. An additional aspect is that fluorescence is attenuated differently when $1 \ll N \ll N_0$ ("not too large N") and $N \gg N_0$ ("very large N"), where N_0 is determined by the experimental ability to observe weak radiation transitions from molecular states Φ_n with an oscillator strength $\sim 1/N_0$ from the strength of the oscillator for radiation from a light zero state Φ_s.

2) The difference in widths of molecular states γ_n according to Eq. (2.11). This leads, generally speaking, to a rather complex kinetics, but this occurs only in a narrow region of parameters. Actually, it is clear from Eq. (2.12) that $a_{sn}^2 \lesssim 1/N$; consequently, the variable second term in Eq. (2.11) will be a small addition to the constant first term when

$$\gamma_s \ll N \gamma_l, \tag{4.2}$$

then one can replace γ_n with the average value $\bar{\gamma}_n = \gamma_l + \bar{a}_{sn}^2 (\gamma_s - \gamma_l)$, where $\bar{a}_{sn}^2 = 1/(N+1)$ in accordance with normalization equation (2.2). Thus, in this approximation all levels have the same width

$$\bar{\gamma}_n = \frac{N}{N+1}\gamma_l + \frac{1}{N+1}\gamma_s \approx \gamma_l + \frac{1}{N}\gamma_s. \tag{4.3}$$

Equation (4.2) is violated only in the limit $\gamma_l \to 0$, that is, in the case of small molecules when $p \to 0$; nonetheless, this limit is also interesting, and will be examined in section 4.4.

3) The ability to prepare various initial states, namely Φ_s or Φ_n. This ability is due to the fact that at large v_{sl} the condition for preparation of a zero nonsteady state Φ_s can be violated.[67] In particular, since the strong coupling condition and inequality (2.13) may be satisfied at rather small ρ_l, the coherent width of pulse $\Delta\omega_{\text{coh}} = 1/\tau_{\text{pulse}}$ may be smaller than the distance between zero levels ρ_l^{-1}, and thus between molecular levels ρ_n^{-1}, since[67] $\rho_n \approx \rho_l$. Then the excitation prepares the molecular quasi-steady state Φ_n, which leads to a change in the law of fluorescence attenuation (see section 4.5).

Let us examine in order all the possibilities which arise in the limit of the strong coupling case I.

4.1. Rapid monoexponential attenuation in the case of dephasing of an optically light zero state

Let the state Φ_s be initially prepared (in the case of strong coupling in the Bixon–Jortner model the corresponding conditions[67] are reduced to Eq. (1.5)) and let Eq. (4.2) hold true. We write the probability (Eq. (2.5)) in the form

$$P_s(t) = P_s^0(t)\, e^{-2\bar{\gamma}_n t}, \tag{4.4}$$

$$P_s^0(t) = \sum_{n,\,n'} a_{sn}^2 a_{sn'}^2 e^{i(\delta_n - \delta_{n'})}. \tag{4.5}$$

At time $t = 0$, the phases $\delta_n = -E_n t$ are correlated, since they all equal zero (this is a consequence of coherent excitation), and $P_s^0(0) = 1$. At $t > 0$ there is a loss in initial coherence or dephasing, in the sense that there appear phase differences $\delta_n - \delta_{n'} \neq 0$, which increase with t and become random to a greater degree. According to Refs. 66 and 67, at $t \ll T = 2\pi\rho_l$, $P_s^0(t) = \exp(-k_s t)$, so the characteristic time of dephasing is $\tau_{\text{deph}(s)} = 1/k_s$. Substituting this into Eq. (4.4) and using Eqs. (4.3) and (3.1) we find that in the first, fast stage of fluorescence the dephasing leads to an exponential attenuation of intensity at a rate[1]

$$\tau_{\text{fast}}^{-1} = k_s + 2\bar{\gamma}_n = k_s + \tau_l^{-1} + \frac{1}{N}\tau_s^{-1}. \tag{4.6}$$

At $t \gg \tau_{\text{deph}(s)}$ the attenuation curve deviates more and more from the exponent, since oscillations in individual terms of the sum in Eq. (4.5) begin to appear. As t increases the amplitude of oscillations increases, but at $t = T$ in the Bixon–Jortner model they cease, and there is full restoration of coherence ("optical echo"), that is, $P_s^0(t)$ returns to its initial value, 1. In a more realistic model of nonequidistant randomly distributed levels (with the same average density ρ_l) the coherence is not even partially restored,[57,73,74,82] that is, there is a full irreversible loss of coherence, and $P_s^0(t)$ fluctuates near the average value

$$\overline{P_s^0} = \sum_n a_{sn}^4,$$

which is obtained from Eq. (4.5) by averaging over arbitrary phases. Once we have determined the density of molecular states $\rho_1(E) = \Sigma\delta(E - E_n)$ and substituting Eq. (2.12), we obtain

$$\overline{P_s^0} = \int_{-\infty}^{+\infty} \left[\frac{v_{sl}^2}{(E - E_s)^2 + \left(\frac{1}{2}N + 1\right) v_{sl}^2} \right]^2 \times \rho_1(E)\, dE = \frac{N^{1/2}}{(N+2)^{3/2}} \approx \frac{1}{N}. \quad (4.7) \tag{4.7}$$

where, when we calculate the integral, we replace the density $\rho_1(E)$ with the average value ρ_l, since it fluctuates in intervals $\sim\varepsilon$. The width of the Lorentz function $\sim N\varepsilon \gg \varepsilon$. Due to the gradual increase in the amplitude of chaotic oscillations with an increase in t the arrival of $P_s^0(t)$ at the constant in Eq. (4.7) in the region $1/k_s < t < T = 2N/k_s$ occurs smoothly, without a dip to $P_s^0(T) = \exp(-2N) \ll \overline{P}_s^0$ at $t = T$, which can be seen from the results of numerical calculations.[73,74]

We stress that this holds true for an arbitrary arrangement of levels. In Ref. 17b a dip in the fluorescence intensity of butanol is observed, which is associated with the existence of correlations in the arrangement of levels (the so-called correlation dip[17c]).

The final result of the dephasing process is a uniform "smearing" of the initial population of state Φ_s into N Φ_n states; the oscillator strength for transition into Φ_s is also distributed along all Φ_n; thus, after dephasing the intensity of radiation from each molecular state will be $\sim 1/N^2$, and the total intensity, which now is a simple sum of partial intensities, will be of the order of $1/N$.

For very large N the intensity after dephasing is virtually equal to zero, and it can be assumed that radiation ceases completely. If we select the maximum observation time[66,67] $\tau_{\max} \gg \tau_{\text{deph}(s)}$, then the attenuation process is described by one exponent with lifetime τ_{fast} from Eq. (4.6).

Equation (4.6), with a consideration of the definitions in Eq. (3.1), contrasts sharply with the usual kinetic formula, Eq. (1.4), which follows from the balance equation (1.2), and this should be specially considered. First, instead of the radiation lifetime of the fluorescent state Φ_s the lengthened radiation lifetime of the molecular states[71] Φ_n enters: $\tau_{\text{rad}(n)} = N\tau_{\text{rad}(s)}$. Second, the contribution of relaxation to the initial electronic state has decreased by a factor of N, but a relaxation contribution appears in the final state. Third, the addition to k_s is small, since, according to Eqs. (4.3) and (2.13), the fastest process is dephasing. Thus, $\tau_{\text{fast}} \approx \tau_{\text{deph}(s)}$ and the quantum yield is small:

$$\varphi_{\text{fast}} = \frac{\tau_{\text{fast}}}{\tau_{\text{rad}(s)}} \ll 1. \tag{4.8}$$

In the typical formula, Eq. (1.4), there are no restrictions on the relative contribution of radiation and relaxation processes, thus, φ may take on any value less than unity.

The considerations presented above show that, despite the purely exponential character of fluorescence attenuation when N quasi-steady states Φ_n participate, *the balance equation* (1.2) *and formula* (1.4) *are not applicable* (this situation is marked in Fig. 2 by a crossed out dashed line). They are applicable only in the statistical limit, when molecular states coalesce into one quasi-steady state level (case II in section 2). In Refs. 3, 9b, 20, 28b, 49, 51, and 61, Eq. (1.4) is used instead of Eq. (4.6), but this should not lead to large errors, since in both formulas the addition to k_s should be small if Eq. (2.13) is satisfied. In Ref. 14b it is proposed that the estimate of $\tau_{\text{rad}(s)}$ from Eq. (1.4) for acetone yields an incorrect result, precisely because of the inapplicability of the balance equation (not as a result of the nonstatistical nature of decay, but rather because of the simultaneous excitation of several levels).

4.2. Biexponential attenuation: fast and slow stages

In the case of values of N which are not very large and a low rate of relaxation processes (vibrational relaxation and radiationless transition into S_0) radiation does not cease with the completion of dephasing at $t \approx T$; a second slow stage begins, in which, in contrast to the first stage, relaxation processes play a decisive role. Replacing $P_s^0(t)$ in Eq. (4.4) with the average value (4.7), we obtain exponential attenuation at a rate

$$\tau_{\text{slow}}^{-1} \equiv 2\overline{\gamma}_n = \tau_l^{-1} + \frac{1}{N}\tau_s^{-1}, \tag{4.9}$$

which coincides with the average observed rate of decay of molecular states $\tau_{\text{obs}(n)}^{-1}$. Since the second term is small due to Eq. (4.2), we have

$$\tau_{\text{slow}}^{-1} \equiv \tau_{\text{obs}(n)}^{-1} \approx \tau_{\text{VR}(l)}^{-1} + \tau_{\text{RT}(l)}^{-1}. \tag{4.10}$$

To observe the second stage, the maximum time of the experiment must be large, $\tau_{\max} \gg T$, and the intensity of fluorescence by the beginning of the second stage must be greater than the minimal intensity $I_{\min}$ resolvable by the equipment, that is, according to Eqs. (1.1), (4.4), and (4.7) the following should hold true: $(\tau_{\text{rad}(s)}^{-1}/N)\exp(2\overline{\gamma}_n T) \gg I_{\min}$. Defining $N_0 = (I_{\min}\tau_{\text{rad}(s)})^{-1}$, we write the latter in the form of two inequalities: $1 \ll N \ll N_0$ and

$$\overline{\gamma}_n \lesssim (4\pi\rho_l)^{-1} \ln\frac{N_0}{N} \equiv \alpha\rho_l^{-1}. \tag{4.11}$$

Since $\overline{\gamma}_n \approx \gamma_l$ this is a limitation on γ_l, namely $\gamma_l \lesssim \alpha\rho_l^{-1}$. This is more rigorous than Eq. (2.13) since in the strong coupling limit we have $\rho_l^{-1} \ll k_s$. Simultaneously, one can reach the following conclusion: *when there is fast relaxation in a final electronic state, and Eq. (4.11) is violated, there is no slow component and a fast component alone is observed.*

When two stages are observed, the intensity of radiation from the initially prepared state Φ_s can be purely formally written in the form of the sum of two exponents, the fast and the slow (coherent and incoherent components[1]):

$$I_s(t) = \tau_{\text{rad}(s)}^{-1}\left(e^{-t/\tau_{\text{fast}}} + \frac{1}{N}e^{-t/\tau_{\text{slow}}}\right). \tag{4.12}$$

Actually, at each moment we have only one component. Actually, taking Eqs. (4.6) and (4.9) we obtain

$$\frac{\tau_{\text{slow}}}{\tau_{\text{fast}}} = \frac{k_s}{2\overline{\gamma}_n} + 1 \approx \frac{k_s}{2\gamma_l} \gg 1. \tag{4.13}$$

Thus, in the interval $0 \leqslant t \lesssim \tau_{\text{fast}}$ we have one fast component (the constant $\sim 1/N$ can be ignored), and in the interval $\tau_{\text{fast}} \ll t < \tau_{\max}$, we have one slow component. Simultaneous observation of the two components in a relatively large time interval would require $\tau_{\text{fast}} \approx \tau_{\text{slow}}$, but then since $N \gg 1$, the incoherent component could be ignored.

4.3. Quantum yield and the number of strongly coupled states

Substituting Eq. (4.12) into Eq. (1.7), where the denominator is equal to 1 due to the normalization, for the total quantum yield we obtain $\varphi = \varphi_{\text{fast}} + \varphi_{\text{slow}}$, where φ_{fast} is given by Eq. (4.8), and

$$\varphi_{\text{slow}} = \frac{\tau_{\text{slow}}}{N\tau_{\text{rad}(s)}} \equiv \frac{\tau_{\text{obs}(n)}}{\tau_{\text{rad}(n)}}. \tag{4.14}$$

The right equality agrees with the fact that by the time the dephasing is completed an incoherent superposition of Φ_n states is prepared. Each of these states has a population $\sim 1/N$. Since neither $\tau_{\text{obs}(n)}$ nor $\tau_{\text{rad}(n)}$ depend on n, this ensemble of N states is equivalent to one state with a population of 1. Then, as in Eq. (1.8), φ_{slow} is a ratio of the observed and radiation lifetimes of this state. Substituting Eq. (4.9) and taking Eq. (4.2) into consideration, we obtain

$$\varphi_{\text{slow}} = \frac{\gamma_{\text{rad}(s)}}{N\gamma_l + \gamma_s} \approx \frac{\gamma_{\text{rad}(s)}}{N\gamma_l} \ll 1. \tag{4.15}$$

Thus, *when there is biexponential attenuation, the quantum yields of radiation of the fast and slow components are small*, and their ratio $\varphi_{\text{fast}}/\varphi_{\text{slow}} = 2N\gamma_l/k_s = 2\pi\gamma_l\rho_l$ may be arbitrary. Taking Eq. (2.15) into consideration, one can formulate the experimental criterion for transition from the intermediate state to the statistical limit in the form

$$\frac{\varphi_{\text{fast}}}{\varphi_{\text{slow}}} \gg 1 + \pi k_s \rho_l = 1 + N,$$

which differs substantially from the criterion presented in Ref. 50: $\varphi_{\text{fast}}/\varphi_{\text{slow}} > 1$, which is based on a weaker condition than in Eq. (2.5), $\gamma_l \rho_l \gg 1$.

The number of strongly coupled states may be determined from experimental data either as a ratio of the amplitudes of fast (C_{fast}) and slow (C_{slow}) components in Eq. (4.12) or through the lifetimes and quantum yields of Eqs. (4.8) and (4.14):

$$N = \frac{C_{\text{fast}}}{C_{\text{slow}}} = \frac{\tau_{\text{slow}}\varphi_{\text{fast}}}{\tau_{\text{fast}}\varphi_{\text{slow}}}. \tag{4.16}$$

Equations (4.12) and (4.16) hold true only under ideal conditions of excitation and detection, when τ_{pulse} and the response time of the detecting system are small compared to τ_{fast} (see section 6.4).

4.4. Nonexponential attenuation in the slow stage with chaotic quantum beats

Let us examine now the case of extremely slow relaxation when Eq. (4.2) is not satisfied and it is necessary to consider various widths γ_n. In the dephasing stage, obviously, nothing changes, since, as before, $\gamma_n \ll k_s/4$ due to Eq. (2.13), and for the slow stage, we obtain the following instead of Eq. (4.4) from Eq. (2.5)

$$P_s(t) = \sum_n a_{sn}^4 e^{-2\gamma_n t}. \tag{4.17}$$

We transform this sum into an integral as in Eq. (4.7), and replace $\rho_1(E)$ with the constant ρ_l, which is allowed when $t \ll N^2/|\gamma_s - \gamma_l|$, when the index of the exponent changes slowly as energy changes by ε. As a result we obtain the formula[1]

$$P_s(t) = \frac{1}{N} e^{-2\gamma_l t} f(2a\gamma_l t), \qquad a = \frac{2(\gamma_s - \gamma_l)}{N\gamma_l},$$

$$f(\tau) = \frac{2}{\pi}\int_0^1 \left(\frac{x}{1-x}\right)^{1/2} e^{-x\tau}\,dx, \quad f(0) = 1, \tag{4.18}$$

which is valid over a wide range of change in t and a. In particular, when $a \ll 1$ we obtain, as above, an exponent with a characteristic time (Eq. (4.10)), and when $a \gg 1$ intensity attenuates by a factor of $t^{-3/2}$ faster. Integrating Eq. (4.17) we obtain the quantum yield of the slow component

$$\varphi_{\text{slow}} = \gamma_{\text{rad}(s)} \sum_n \frac{a_{sn}^4}{\gamma_n},$$

which now may take any values. In particular, in the absence of relaxation we have[71] $\gamma_n = a_{sn}^2 \gamma_{\text{rad}(s)}$ and $\varphi_{\text{slow}} = 1$.

If N is not large enough, *the slow stage of attenuation may be modulated by irregular quantum beats* caused by incomplete averaging of the cross terms in Eq. (4.5). The spectrum of such oscillations consists of lines whose positions are defined by energy differences $E_n - E_{n'}$. Their intensities are defined by the products $a_{sn}^2 a_{sn'}^2$, or in the general case[22-26,30-32] $g_{sn} g_{sn'}$.

4.5. Slow monoexponential attenuation in the excitation of a molecular state

Let us now examine the situation when a state Φ_n is initially prepared. As has already been stated, this requires that $\Delta\omega_{\text{coh}} \ll \rho_l^{-1}$ and that N not be too large, otherwise the oscillator strength will be small for absorption $\Phi_0 \to \Phi_n$. Yet another limitation stems from the condition of instantaneous excitation $\tau_{\text{pulse}} \ll \tau_{\text{obs}(n)}$, analogous to Eq. (1.5). Uniting this with the foregoing, and using Eq. (4.10), we obtain $\rho_l^{-1} \gg \tau_{\text{pulse}}^{-1} \gg \gamma_l$. Then it is obvious that it is possible to excite Φ_n only when $\rho_l^{-1} \gg \gamma_l$, when Φ_s attenuates in two stages. In this case the first stage is absent, since there is no coherent excitation of many molecular states; for the slow stage the formulas obtained above hold true.

If $\tau_{\text{pulse}}^{-1} \lesssim \gamma_l$, then excitation is not instantaneous and the decay is nonexponential. Since the decay of molecular states, according to the assumption, corresponds to the statistical limit (see section 2), violation of exponentiality is linked with the effect of the shape of the exciting pulse, and is described by Eqs. (1.3) and (1.9).

4.6. Summary of results

We summarize the results obtained in sections 3 and 4 of the analysis of the fluorescence kinetics in relation to the correlation between four parameters, γ_s, γ_l, ρ_l^{-1}, and k_s with a restriction on the limit of strong coupling $k_s \gg \rho_l^{-1}$ and with instantaneous excitation.

1) If the largest parameter is γ_s, then the triplet state is "cut off," that is, everything occurs as in the case $v_{sl} = 0$: radiation attenuates exponentially at a rate $2\gamma_s$ and a quantum yield $\varphi = \gamma_{\text{rad}(s)}/\gamma_s$. This may be explained as in Ref. 67, section 3.1: the observed lifetime $\tau_{\text{obs}(s)} = 1/(2\gamma_s)$ is so short that the interaction of v_{sl} does not have time to affect noticeably the dynamics of the excited state.

2) If the largest parameter is γ_l, then the statistical limit occurs, for which the balance equations (1.2), as well as Eqs. (1.4), (1.6), and (1.8) which stem from it.

3) If the largest parameter is k_s, then two cases are possible.

A. At $\rho_l^{-1} \ll \gamma_l \ll k_s$ fluorescence attenuates exponentially, and the main reason for decay is dephasing. The rate of attenuation (Eq. (4.6)) is approximately equal to the rate of dephasing of k_s, and the contribution of radiation and radiationless channels is small, and is not described by the sum of the rates of all the processes, that is, Eq. (1.2) is not applicable. The quantum yield (Eq. (4.8)) is small. The slow stage is not observable due to its weak intensity.

B. At $\gamma_l \ll \rho_l^{-1} \ll k_s$ it becomes possible to excite Φ_s or Φ_n depending on τ_{pulse}. *When Φ_s is excited*, attenuation has two stages, and the fast stage is exactly as in case A. In the slow stage, fluorescence attenuation is due to the decay of Φ_n molecular states. It can be observed if N is not too large; otherwise the radiation will have too small an intensity. The slow stage may be modulated by chaotic quantum beats. The characteristics of the smooth component of the slow stage differ in the two cases: a) for $\gamma_s/N \ll \gamma_l$ and for instantaneous excitation, attenuation is exponential, the time of attenuation (Eq. (4.10)) is approximately equal to the time of decay of the zero triplet levels due to vibrational relaxation, radiationless transition into S_0 and, possibly, other processes, and the quantum yield (Eq. (4.15)) is small; b) for $\gamma_l \lesssim \gamma_s/N \ll \rho_l^{-1}$ attenuation is nonexponential, and the quantum yield may have any value. Finally, *in the excitation of* Φ_n one observes only one slow stage with the characteristics described here.

To conclude the examination of the limit of strong coupling, let us formulate the following basic conclusions.

The kinetics of fluorescence attenuation are characterized by two processes: rapid decay of the fluorescent state, whose rate is determined only by the intramolecular parameters v_{sl} and ρ_l, and slow attenuation of molecular states. This attenuation is sensitive to relaxation processes, in particular, vibrational relaxation. Depending on the conditions of excitation and the system parameters, the fast process has a different physical nature: dephasing of the set of molecular quasisteady states or attenuation of one united state. In an experiment time $t < \tau_{\max}$ one can observe either one (attenuation in one stage) or both (attenuation in two stages). Attenuation in the first (fast) stage is always purely exponential, and the quantum yield is small; this also occurs in the second stage when there is sufficiently rapid relaxation in a final electronic state; however, when relaxation is slowed, exponentiality is violated more and more, and the quantum yield rises. Vibrational relaxation may also be linked with intramolecular intermode redistribution of energy[68,75] and intermolecular interactions. In the latter case the form and rate of fluorescence attenuation in the gas phase will depend on pressure if the contribution of radiationless transition to S_0 is not very large. The resonance defect Δ is not a significant parameter, since in strong coupling the levels push apart and resonance (if it existed) disappears.

5. THE WEAK-COUPLING LIMIT: $v_{sl} \ll \rho_l^{-1}$

We list the basic features of the weak-coupling limit.

1) The role of relaxation in the final electronic state increases. As we saw in the previous section, in the strong-coupling limit relaxation appears only in the second stage, and only if the number of strongly coupled levels N is not too large. It is clear that with a weakening of the coupling and a decrease in N, the role of relaxation should increase. Actually, in weak coupling, Eq. (2.13) is reduced to $\gamma_s, \gamma_l \ll \rho_l^{-1}$, that is, the widths of the levels are less than the distances between them. But then the attenuation kinetics depend on the correlation between γ_l, v_{sl}, and Δ, and the rate of radiationless transition $S_1 \rightsquigarrow T_1$ (when it can be introduced) depends not only on intramolecular parameters, but also on γ_l.

For comparison we recall that a very fast relaxation (Eq. (2.15)) (case II from section 2, which corresponds to the statistical limit) has no effect on the kinetics and no effect on the rate of fluorescence attenuation at any coupling strength (the notion of coupling strength generally lacks scope because, due to coalescence of molecular levels into one quasi-steady state level, only the radiationless width k_s of this united level has physical sense, and not the parameters v_{sl} and ρ_l by themselves). However, we examine case I from section 2.

2) The effect of a dephasing-type coherence effect is absent, since only two levels, E_s and $E_{l=0}$ mainly interact.

3) The effect of a different type of coherence may appear. This effect is associated with the presence of two near levels. It leads to periodic beats in intensity due to quantum transitions between these levels.

4) Attenuation may be biexponential, despite the absence of dephasing.

When the conditions of instantaneous excitation (Eq. (1.5)) are satisfied and $\tau_{\text{pulse}} \ll 2\pi/v_{sl}$ (see Ref. 67 section 3.1), Φ_s is the initially prepared state and the fluorescence intensity is described by Eqs. (1.1) and (2.5). To find the molecular levels $\widetilde{E}_n$ one can use Eq. (2.3) (in which the substitution of Eq. (2.4) was performed), without turning to the Bixon–Jortner model. As is clear from what has been stated, the largest parameter is ρ_l^{-1}, since the correlations between the remaining parameters are arbitrary.

Let us denote by $\widetilde{E}_+$ and $\widetilde{E}_-$ the molecular levels which change into $\widetilde{E}_s$ and $\widetilde{E}_{l=0}$, respectively, when $v_{sl} \to 0$. These levels may be strongly perturbed at small Δ and γ_l. The remaining levels $\widetilde{E}_n$ are always weakly perturbed and do not contribute to Eq. (2.5).

5.1. Monoexponential attenuation: radiationless transition in the intermediate case

Let us assume that all levels are weakly perturbed. Then, only one term remains in the sum in Eq. (2.5). This term corresponds to $\widetilde{E}_+$, since $g_{s+} \approx 1$, and for the remaining terms $g_{sn} \approx 0$. Thus, $P_s(t) = \exp(-\Gamma t)$ with $\Gamma = -2\,\mathrm{Im}\,\widetilde{E}_+$. Finding $\widetilde{E}_+$ from perturbation theory, we find $\Gamma = 2\gamma_s + k_{s\gamma}$, where the rate of radiationless transition $S_1 \rightsquigarrow T_1$ is given by the formula[67]

$$k_{s\gamma} = 2\sum_l \frac{v_{sl}^2(\gamma_l - \gamma_s)}{(E_l - E_s)^2 + (\gamma_l - \gamma_s)^2} \tag{5.1}$$

with a dependence on γ_l which is characteristic of the intermediate case (as we will see below, here we must discard γ_s). Obviously in this case Eq. (1.2) holds true, as well as the equations which stem from it, Eqs. (1.4)–(1.8), where $k_{s\gamma}$ must be substituted for k_s. The conditions for the realization of monoexponential decay, which is described by the balance equation, include, first, the condition of applicability of perturbation theory $v_{sl} \ll |\widetilde{E}_s - \widetilde{E}_l|$, which for $l \neq 0$ is satisfied automatically (weak coupling) and for $l = 0$ further requires

$$v_{sl} \ll |\Delta| \quad \text{or} \quad v_{sl} \ll \gamma_l. \tag{5.2}$$

This, however, is insufficient, and it is further required that $\gamma_l \gg \gamma_s$.

In order to understand the sense of the latter, we assume in Eq. (3.1) for simplicity that $\gamma_{\mathrm{VR}(s)} = \gamma_{\mathrm{RT}(s)} = 0$, and examine the situation when $\gamma_l \lesssim \gamma_s$. We define $\lambda = v_{sl}^2/(\Delta^2 + \gamma_l^2) \ll 1$; from Eq. (5.1) we obtain the estimate $k_{s\gamma} \sim \lambda\gamma_s \ll \gamma_s$. It then follows that $k_{s\gamma}$ yields only a small correction to the total width Γ, and the quantum yield φ is close to 1. Moreover, when $\gamma_l < \gamma_s$, it is found that $k_{s\gamma} < 0$ and $\varphi > 1$. This contradiction is permitted by the fact that (compare with case III in sections 2 and 3) if Γ contains a small term $k_{s\gamma}$, then one must simultaneously consider analogous terms in the sum in Eq. (2.5) and in the coefficients g_{sn} (for example, $g_s \sim \lambda$). As a result decay becomes weakly nonexponential and $k_{s\gamma}$ is no longer the rate of radiationless transition $S_1 \rightsquigarrow T_1$; Eq. (1.2) is not applicable either. It is easy to verify by direct calculation that the total quantum yield (Eq. (1.7)), considering all contributions $\sim\lambda$ goes to 1 as $\gamma_l \to 0$. In the opposite limit case $\gamma_l \gg \gamma_s$ we have $k_{s\gamma} \sim \lambda\gamma_l$, and if the contributions of transitions with and without radiation are comparable in value (that is, $k_{s\gamma} \sim \gamma_s$, $\gamma_l \sim \gamma_s/\lambda$ and φ is substantially less than unity), then in Eq. (2.5) one can ignore all terms $\sim\lambda$, which leads to the balance equation, which was discussed at the beginning of this section. Thus, the second condition of applicability of the balance equation reads

$$\gamma_l \gg \gamma_s,\ k_{s\gamma}, \tag{5.3}$$

that is, relaxation in the final state should be faster than radiation attenuation and the radiationless transition $S_1 \rightsquigarrow T_1$. When this condition is violated decay becomes purely radiative (that is, $\Gamma = 2\gamma_s$ and $\varphi = 1$), since the deviations are small and are not of physical interest.

If for all l the second inequality of Eq. (5.2) is satisfied, perturbation theory is applicable independently of the strength of the coupling, since the true expansion parameter is v_{sl}/γ_l, and not $v_{sl}\rho_l$; in the transition to strong coupling, Eq. (5.3) corresponds to Eq. (2.15), and γ_l, due to Eq. (5.2), becomes larger than ρ_l^{-1}. Thus, the second inequality of Eq. (5.2), together with Eq. (5.3), insures the applicability of the balance equation for any coupling strength; the difference lies only in the fact that at the strong coupling limit the dependence of $k_{s\gamma}$ on γ_l disappears, since Eq. (5.1) changes to[67] $2\pi v_{\text{eff}}^2 \rho_{\text{eff}}$, that is, the intermediate case changes into the statistical limit.

As can be seen from Eq. (5.1), when there is weak perturbation of two levels, $\tilde{E}_s$ and $\tilde{E}_{l=0}$, the contribution to relaxation of the light state Φ_s yields, generally speaking, many dark states Φ_l. In strong perturbation one cannot examine the level $l \neq 0$ at all, and one is limited to the two-level Trifonov–Shekhtman model[67] in which the perturbed levels have the form

$$E_\pm = \frac{1}{2}(\tilde{E}_s + \tilde{E}_l) \pm \left[\frac{1}{4}(\tilde{E}_s - \tilde{E}_l)^2 + v_{sl}^2\right]^{1/2}, \tag{5.4}$$

where the sign in front of the square root is selected in accordance with the rule indicated at the beginning of this section; l means $l = 0$. Strong perturbation arises when there is a small resonance defect $|\Delta| \ll \rho_l^{-1}$ and small widths (see the preceding section).

5.2. Periodic quantum beats appear in the case which is the opposite of Eq. (5.2), when

$$\gamma_s,\ \gamma_l \ll v_{sl}. \tag{5.5}$$

Expanding Eq. (5.4) in powers of $(\gamma_s - \gamma_l)/v_{sl}$ and limiting ourselves to first-order terms, we obtain

$$E_\pm = E_s - \frac{1}{2}\Delta \pm \frac{1}{2}R\Delta, \quad R = \left(1 + \frac{4v_{sl}^2}{\Delta^2}\right)^{1/2}, \tag{5.6}$$

and for $\gamma_\pm$ Eq. (2.11) is obtained with $n = \pm$ and

$$a_{s\pm}^2 = \frac{R \pm 1}{2R}. \tag{5.7}$$

Let us calculate the probability $P_s(t)$ using Eq. (2.5) in which $g_{s\pm} \approx a_{s\pm}^2$. Using the notation $\tau_\pm = 1/(2\gamma_\pm)$, $\tau = (\gamma_s + \gamma_l)^{-1}$ and $\Omega = R\,|\Delta|$, we obtain

$$P_s(t) = a_{s+}^4 e^{-t/\tau_+} + a_{s-}^4 e^{-t/\tau_-} + 2a_{s+}^2 a_{s-}^2 e^{-t/\tau} \cos \Omega t. \tag{5.8}$$

The first two terms describe monotonic attenuation, and the third describes quantum beats which modulate the monotonic decay. The frequency and depth of modulation depend on the strength of the coupling and the resonance defect, and the relationship between them can be quite arbitrary.

Quantum beats are theoretically examined in the publication of Zewail *et al.*[35] when $\gamma_s = \gamma_l$, which leads to a degeneracy of relaxation times $\tau_\pm = \tau$ (degeneracy also takes place when $\Delta = 0$). Taking Eq. (5.7) into account, Eq. (5.8) may be converted into the form[35]

$$P_s(t) = e^{-t/\tau}[1 - 2a_{s+}^2 a_{s-}^2 (1 - \cos \Omega t)]. \tag{5.9}$$

This formula corresponds to cases (1) and (2) in Zewail's classification, when Φ_s is optically light in absorption and radiation, and Φ_l is dark. In case (1) Φ_s and Φ_l are vibrational sublevels of different electronic states (S_1 and T_1 or S_1 and S_0), and in case (2) they belong to one state S_1. The state Φ_l is dark due to the electronic or vibrational rules of selection. In case (2) this is insured by special selection of those spectral regions of absorption or radiation where the oscillator strength for transitions $\Phi_0 \leftrightarrow \Phi_l$ is negligibly small compared to the transitions $\Phi_0 \leftrightarrow \Phi_s$.

For the precise resonance $\Delta = 0$, the depth of modulation is equal to 100%:

$$P_s(t) = e^{-t/\tau} \cos^2 (v_{sl} t). \tag{5.10}$$

As $|\Delta|$ increases, the frequency of modulation increases and depth falls, and at the limit $|\Delta| \gg v_{sl}$ it becomes negligibly small; simultaneously one of the exponents in Eq. (5.8) disappears, and monoexponential decay is again obtained, as in section 5.1.

5.3. Quantum yield may be defined if one substitutes Eq. (5.8) into Eqs. (1.1) and (1.7)

In integration over time one must ignore the contribution of the oscillating term, which is of the same order of smallness as the terms dropped in the derivation of Eqs. (5.6) and (2.11). Then, $\varphi = \varphi_+ + \varphi_-$, where

$$\varphi_\pm = \frac{\gamma_{\text{rad}(s)}}{\gamma_s + (a_{s\pm}^{-2} - 1)\gamma_l} a_{s\pm}^2. \tag{5.11}$$

Taking into consideration the fact that $a_{s\pm}^{-2} > 1$ and $\gamma_s > \gamma_{\text{rad}(s)}$ due to the definitions in Eqs. (5.7) and (3.1), we obtain $\varphi \leqslant 1$; the equality occurs only in the absence of relaxation when $\gamma_s = \gamma_{\text{rad}(s)}$ and $\gamma_l = 0$.

Although in the general case the quantum yield is less than unity, here it is impossible to introduce the concept of the radiationless transition $S_1 \rightsquigarrow T_1$ in any other way. There is no other sensible way to determine its rate, as the balance equation does not hold true.

5.4. Biexponential attenuation

Let the ratio $\varkappa = v_{sl}^2/\Delta^2 \ll 1$ be small, but let the intensity be of the order of $\varkappa^2$ with respect to the total observed intensity (in section 5.1 we ignored these contributions).

If γ_s and γ_l differ greatly, then Eq. (5.8) predicts biexponential attenuation with modulation of the *fast* component by quantum beats. Let us examine this situation in more detail from the point of view of a comparison with biexponential decay at the limit of strong coupling (see section 4.2).

Let us assume that insufficient temporal resolution of the equipment δt does not make it possible to observe beats. We will specifically assume that $\tau_{\pm} \gg \delta t \gg \Omega^{-1}$. Then after averaging Eq. (5.8) over intervals of width δt, the beats disappear and the fluorescence intensity acquires the form

$$I_s(t) = \tau_{\mathrm{rad}(s)}^{-1} (a_{s+}^4 e^{-t/\tau_+} + a_{s-}^4 e^{-t/\tau_-}). \tag{5.12}$$

We obtain the following from Eqs. (5.6), (5.7), and (2.11) with an accuracy up to terms $\sim \varkappa$:

$$\begin{aligned} a_{s+}^2 &= 1 - \varkappa, \qquad a_{s-}^2 = \varkappa, \\ \gamma_+ &= \gamma_s + \varkappa\gamma_l, \qquad \gamma_- = \varkappa\gamma_s + \gamma_l. \end{aligned} \tag{5.13}$$

Which of the two components of (5.12) will be fast and which will be slow depends on the correlation between γ_s and γ_l. Let us examine the two extreme cases.

I. Relaxation is absent, that is, $\gamma_s = \gamma_{\mathrm{rad}(s)}$ and $\gamma_l = 0$. Substituting Eq. (5.13) into Eq. (5.12) we obtain a biexponential law (Eq. (4.12)), where one can formally define the parameters

$$N \equiv \frac{C_{\mathrm{fast}}}{C_{\mathrm{slow}}} = \frac{a_{s+}^4}{a_{s-}^4} = \frac{1}{\varkappa^2} \gg 1 \tag{5.14}$$

(but not $N = 1/\varkappa$ as in Refs. 20 and 57) and

$$\tau_{\mathrm{fast}} \equiv \tau_+ = \tau_{\mathrm{rad}(s)}, \quad \tau_{\mathrm{slow}} \equiv \tau_- = \tau_{\mathrm{rad}(s)} N^{1/2}, \tag{5.15}$$

and the quantum yields (Eq. (5.11) are equal to

$$\varphi_{\mathrm{fast}} \equiv \varphi_+ = 1 - \varkappa, \quad \varphi_{\mathrm{slow}} \equiv \varphi_- = \varkappa. \tag{5.16}$$

Taking into consideration the definition equations (5.14)–(5.16), the observed values satisfy Eq. (4.16).

The case of weak coupling I may be differentiated from the case of strong coupling I (sections 2 and 4.2) in two ways.

1) According to Eq. (5.15) the ratio of the attenuation times of the slow and fast components in the case of weak coupling, case I, is equal to $N^{1/2}$, and when there is strong coupling with $\gamma_l = 0$, we obtain from Eqs. (4.13) and (4.3) $\tau_{\mathrm{slow}}/\tau_{\mathrm{fast}} = Nk_s\tau_{\mathrm{rad}(s)} + 1 \gg N$. Thus, if N is defined from experiment according to Eq. (4.16) and if $N \gg 1$, then the relaxation time ratios will greatly differ in the two cases.

2) According to Eqs. (4.8), (4.15), and (5.16), the quantum yields of the two components also differ greatly: $\varphi_{\mathrm{fast}} \approx 1$, $\varphi_{\mathrm{slow}} = 1/N^{1/2} \ll 1$ for weak coupling, case I, $\varphi_{\mathrm{fast}} \ll 1$, $\varphi_{\mathrm{slow}} \leqslant 1$ for strong coupling. In other words, for weak coupling, case I, the main luminescence is due to the fast component, and in strong coupling, it is due to the slow component.

II. There is fast vibrational relaxation, so that $\gamma_l \gg \gamma_s$. From Eq. (5.13) we obtain

$$\begin{aligned} \tau_{\mathrm{fast}} &\equiv \tau_- \approx \frac{1}{2\gamma_l}, \\ \tau_{\mathrm{slow}} &\equiv \tau_+ = \frac{1}{2(\gamma_s + \varkappa\gamma_l)}, \\ \frac{\tau_{\mathrm{fast}}}{\tau_{\mathrm{slow}}} &= \frac{\gamma_s}{\gamma_l} + \varkappa \ll 1. \end{aligned}$$

To bring Eq. (5.12) into the form of Eq. (4.12), we must again define N as $C_{\mathrm{fast}}/C_{\mathrm{slow}}$. In this case we obtain

$$N \equiv \frac{a_{s-}^4}{a_{s+}^4} = \varkappa^2 \ll 1. \tag{5.17}$$

The quantum yields (Eq. (5.11)) are equal to

$$\begin{aligned} \varphi_{\mathrm{fast}} &\equiv \varphi_- = \frac{\varkappa^2\gamma_{\mathrm{rad}(s)}}{\gamma_l} = \frac{\varkappa^2\tau_{\mathrm{fast}}}{\tau_{\mathrm{rad}(s)}} \ll 1, \\ \varphi_{\mathrm{slow}} &\equiv \varphi_+ = \frac{\gamma_{\mathrm{rad}(s)}}{\gamma_s + \varkappa\gamma_l} = \frac{\tau_{\mathrm{slow}}}{\tau_{\mathrm{rad}(s)}} \leqslant 1. \end{aligned}$$

It is easy to verify that Eq. (4.16) is again satisfied. As in the case of strong coupling, the quantum yield of the fast component is small, and the slow component may have any value. The main difference is found in the inequality (5.17), since in strong coupling the following should be true: $N \gg 1$. Obviously, in the case of weak coupling, case II, decay is mainly monoexponential, since the fast component, which exists only for small periods of time, has the same small amplitude and small quantum yield (see section 5.1).

5.5. Periodic quantum beats of radiation from the final state

Equation (5.8) continues to hold true if the state Φ_l also has a nonzero oscillator strength for a radiation transition to Φ_0 (in particular, this may be vibrational sublevel[35] S_1; it is necessary only that the radiation from $\Phi_l \to \Phi_0$ can be spectrally differentiated from the radiation of $\Phi_s \to \Phi_0$. Then, along with Eq. (1.1) it makes sense to examine Eq. (1.10), assuming as before that state Φ_s is initially prepared (that is, $P_l(0) = 0$). Acting as in the deduction of Eq. (2.1) in Ref. 67 and using Eqs. (2.4), (5.6), and (5.7), we come to the formula

$$P_l(t) = a_{s+}^2 a_{s-}^2 (e^{-t/\tau_-} + e^{-t/\tau_+} - 2e^{-t/\tau} \cos \Omega t). \tag{5.18}$$

Detection of radiation from an optically dark (in absorption) state Φ_l, which is indirectly populated in the absorption of a photon, and as a result of a link with the optically light state Φ_s, may yield quantum beats with a 100% amplitude modulation, if the rates of relaxation of states Φ_s and Φ_l are identical ($\gamma_s = \gamma_l$) or if there is precise resonance ($\Delta = 0$); in both cases

$$P_l(t) = 2a_{s+}^2 a_{s-}^2 e^{-t/\tau} (1 - \cos \Omega t). \tag{5.19}$$

For identical relaxation rates this expression corresponds to case (3) in Zewail's classification.

Comparing Eqs. (5.18) and (5.8) we see that both types of radiation oscillations have the same frequency and amplitude, but are phase-shifted by π. The total population of states Φ_s and Φ_l

$$P_s(t) + P_l(t) = a_{s+}^2 e^{-t/\tau_+} + a_{s-}^2 e^{-t/\tau_-}$$

attenuates monotonically. However, the total intensity $I_s(t) + I_l(t)$ may retain beats due to the difference in radiation times, $\tau_{\mathrm{rad}(s)}$ and $\tau_{\mathrm{rad}(l)}$. When there are identical radiation times, beats may occur if, instead of the right inequality (5.5), a weaker condition is satisfied,[76] $2v_{sl} > |\gamma_s - \gamma_l|$.

5.6. Summary of results

All five parameters, $\gamma_s, \gamma_l, \rho_l^{-1}, v_{sl}$ and Δ, are important at the limit of weak coupling. The following limitations are placed on them: a) the limitation of weak coupling $v_{sl} \ll \rho_l^{-1}$; b) the limitation of the intermediate case, inequality (2.13), which acquires the form γ_s, $\gamma_l \ll \rho_l^{-1}$; c) the limitation of instantaneous excitation. Moreover, $|\Delta| \leqslant (1/2)\rho_l^{-1}$ according to the definition of Δ. Thus, the largest parameter is ρ_l^{-1}.

1) If $\gamma_s \ll \gamma_l$ and $v_{sl} \ll \gamma_l$ or $v_{sl} \ll |\Delta|$ (any Δ), then the balance equation holds true and the decay of the light state is monoexponential. Radiation from the dark states is of weak intensity.

2) If $\gamma_s, \gamma_l \ll v_{sl}$ and $0 < |\Delta| \ll \rho_l^{-1}$, then decay of the light and dark states is biexponential (monoexponential when $\gamma_s = \gamma_l$ or $\Delta = 0$) with modulation of the fast component by periodic beats. The radiation from the two states is of equal intensity, and the oscillations are phase-shifted by π.

This situation corresponds to the physical process of redistribution of vibrational energy E_{vib} in S_1. At the limit of weak coupling, when the interaction of only two vibration states is significant, this redistribution leads to periodic beats in fluorescence intensity. To observe beats experimentally one must separate bands in the radiation spectrum which are responsible for the transitions $\Phi_s \to \Phi_0$ and $\Phi_l \to \Phi_0$. The change in the intensity of these bands over time is described, respectively, by Eqs. (5.8) and (5.18). As noted above, the two types of beats are phase-shifted by π and differ in the depth of modulation; for example, in the case of different relaxation rates, the radiation from the optically dark state has a 100% modulation (see Eq. (5.19)), while the modulation of radiation from the light state is less than 100% and depends on the strength of coupling (see Eq. (5.9)).

As E_{vib} increases, the distances between vibrational levels are decreased and the condition for weak coupling is violated; the interaction encompasses an ever greater number of levels, and the picture of beats becomes more complicated, since their spectrum includes the frequencies of transitions between any pairs of levels. At large values of E_{vib} there is a transition to the intermediate case and the statistical limit, at which point the intramolecular redistribution of vibrational energy becomes irreversible, and the fluorescence intensity attenuates according to a biexponential or monoexponential law in full analogy with an electronic radiationless transition (see section 7).

6. DISCUSSION OF EXPERIMENTAL DATA FOR PYRAZINE

To realize the mechanisms of nonexponential fluorescence attenuation described in section 4 the electronic gap ΔE must not be too large, otherwise attenuation will be monoexponential due to the great density of states ρ_l in T_1 near the potential minimum S_1, which leads to the balance equation (1.2) (see section 2). For many of the molecules listed in the Introduction, values of $\Delta E = 2000$–4000 cm^{-1} are typical. In particular, for pyrazine, $\Delta E = 4055$ cm^{-1}. The experiments which have been discussed involve the $0_0^0 S_1$-S_0 transition (frequency $\nu_{00} = 30876$ cm^{-1}) of pyrazine molecules cooled in a free supersonic stream to a rotational temperature $T_{\text{rot}} \sim 30$ K and below.

Figure 3 shows the typical picture of biexponential fluorescence attenuation of pyrazine. The slow component is modulated by chaotic quantum beats whose shape changes when a magnetic field H is switched on. Fourier analysis of beats in Ref. 30 shows that when H changes in the interval 0–150 G there is a shift in lines and a redistribution of intensity between them with a tendency toward saturation. The effect of the magnetic field may be explained only by the influence of spin-orbital interaction between S_1 and T_1.

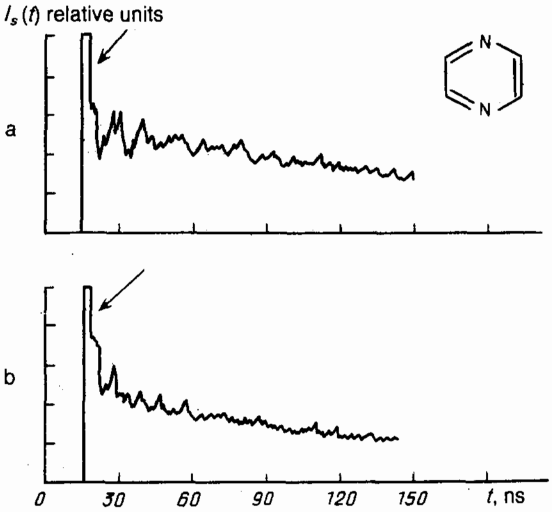

FIG. 3. Attenuation of fluorescence intensity emitted from the ground vibrational level of state S_1 in the pyrazine molecule (transition $0_0^0 S_1 \to S_0$, $\nu_{00} = 30876$ cm^{-1}) in a free supersonic stream in picosecond excitation ($\tau_{\text{pulse}} = 15$ ps) without a magnetic field (a) and with $H = 50$ G (b). The spectral resolution is $\Delta\nu = 3$ cm^{-1} and the observation time[30] is $\tau_{\max} = 300$ ns. The arrows indicate the fast component whose intensity is cut off.

In the time scale which was used, the fast component appears in the form of a sharp maximum in the initial part of the attenuation curve. This section can be resolved on the picosecond scale. One difficulty is that the response time of the fluorescence detection systems used is of the order of τ_{fast}. Thus the experimental curve approximates the convolution of the exponential with the response function,[31,48] which introduces an additional error into the definition of τ_{fast}. Reference 32 suggests an alternative method of determining τ_{fast} (Fig. 4), the temporal resolution of which is limited only by the length of the exciting pulse.

These experiments proved the existence of a fast intramolecular process which may be linked with dephasing. However, the fast component also exists in nanosecond excitation (Fig. 5), when there can be no dephasing (see section 6.4). Other mechanisms of fast decay have been proposed with regard to this (see section 6.5).

6.1. The effect of rotation

In pyrazine one observes a strong dependence of the kinetics and the quantum yield of fluorescence on the initial-

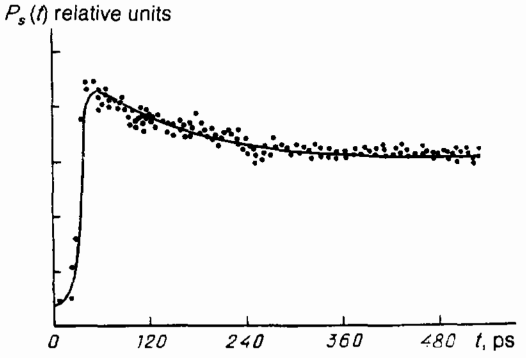

FIG. 4. Direct observation of the fast component of the decrease in the population of the ground vibrational level of state S_1 by two-photon ionization, with $\tau_{\text{pulse}} = 2$ and 10 ps. The solid line is an approximation of the exponent with $\tau_{\text{fast}} = 118 \pm 16$ ps. The ratio of the fast and slow components depends on the efficiency of ionization, and comparison with fluorescence data requires a detailed knowledge of the kinetics.[32]

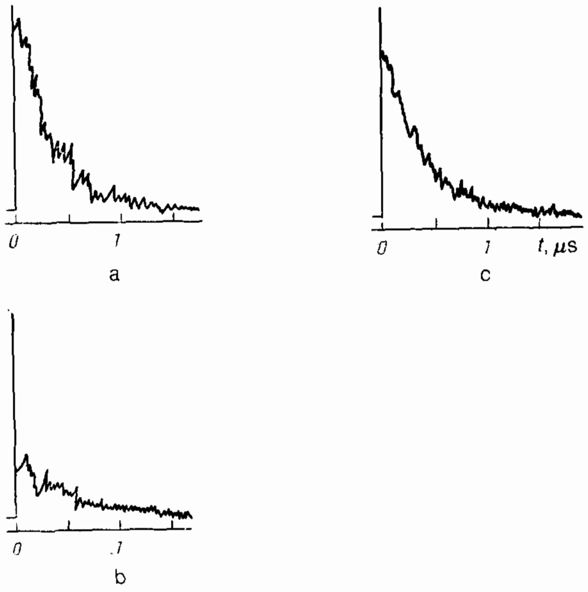

FIG. 5. Fluorescence attenuation in excitation of the rotational states $J = 1$ (a), $J = 1–2$ (b) (here we have in mind excitation in the minimum between the appropriate lines of the spectrum) and $J = 2$ (c). $T_{rot} = 3$ K; $\tau_{pulse} = 3$ ns; $\Delta\nu = 0.5$ cm^{-1} (Ref. 61).

ly excited rotational state J.[2] The rotational constants for the zero vibrational level in S_0 and S_1 are[25b,77] $A = B = 0.2$ cm^{-1} and $C = 0.1$ cm^{-1}. In rotational cooling in a supersonic stream to $T_{rot} < 10$ K and excitation by laser radiation with a full spectral width of $\Delta\nu = 0.3–0.003$ cm^{-1} in the interval ± 7 cm^{-1} from the beginning of band $0_0^0 S_1$-S_0, one observes fluorescence from the states $J = 0–15$, which corresponds to the P and R transitions, as well as the Q band[28a,28b,61] (Fig. 6). *Each transition has its own characteristic attenuation kinetics.* For example, the excitation of the P(1) line yields a slow monoexponential attenuation with chaotic quantum beats[22,28a,30] (Fig. 7). In excitation of the P(2) and R(0) lines, etc., there appears a fast component as in Figs. 3 and 5 (Refs. 22, 24, 27, 28, 32, 37, 38, 47, 48). It is clear in Figs. 5, 6, and 8 that the ratio of the amplitudes of the fast and slow components changes greatly depending on J, and also (as was first observed in Refs. 24, 26, and 42) when there is a shift in the frequency of excitation from the maximum of the rovibronic line to the minimum between neighboring lines. In Ref. 40 changes in φ were detected along the rotational contour. These changes were associated with the slow component.

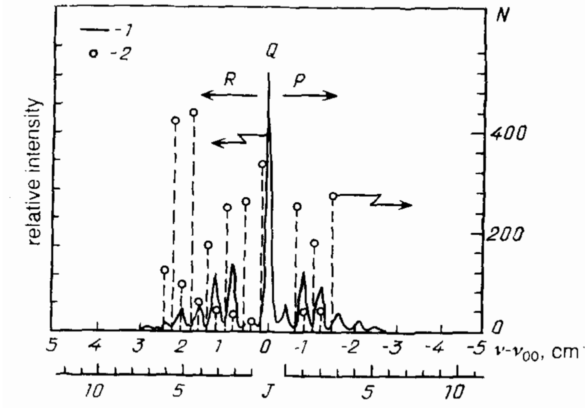

FIG. 6. Spectrum of fluorescence excitation (1) and the value of $N = C_{fast}/C_{slow}$ (2) (resolution $\Delta\nu = 0.1$ cm^{-1}) (Ref. 61).

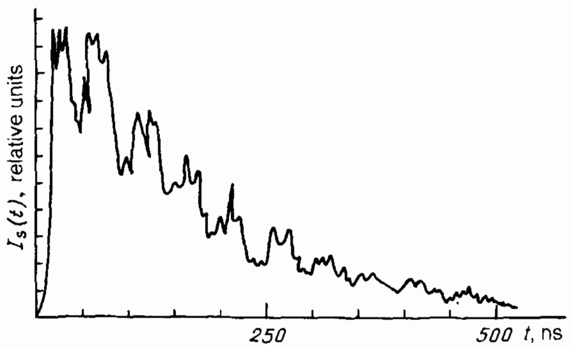

FIG. 7. Fluorescence attenuation excited at the maximum of the rovibronic component $P(1)$ at $\Delta\nu_{coh} = 130$ and 300 MHz (Refs. 22, 24, 26, 60).

Direct observation of the fast component in excitation with τ_{pulse} from 60 to 2 ps yielded[32,38,39,48,78] $\tau_{fast} = 120$ ps. In these experiments the coherent width of the laser pulse $\Delta\nu_{coh} \equiv \hbar\Delta\omega_{coh} = \hbar/\tau_{pulse}$ ($\hbar = 1/2\pi \quad c = 5.3$ cm^{-1} ps) changed from 0.1 to 3 cm^{-1} (the incoherent width was of the same order or less), and, consequently, excited a different number of rotational sublevels. One can also conclude from the insensitivity of τ_{fast} to rotational cooling[39] that τ_{fast} does not depend on J, and this is supported by direct observation.[48] Also independent of J arc $\varphi_{fast} = 6\cdot 10^{-4}$ (Refs. 49 and 78) and $\tau_{slow} = 400$ ns (Refs. 24, 28b, 30, 37, 38, 41a, 52, 61, and 78) (see Fig. 8); however, φ_{slow} and N exhibit a strong dependence[4,40,41,44,49] on J. For $J = 5–22$, it was found

$$\varphi_{slow} = 0{,}124\,(2J + 1)^{-1} \tag{6.1}$$

(Fig. 9) and

$$N = \alpha\,(2J + 1) \tag{6.2}$$

(see Fig. 8; for $J < 5$ this tendency is retained;[50] in Ref. 28c

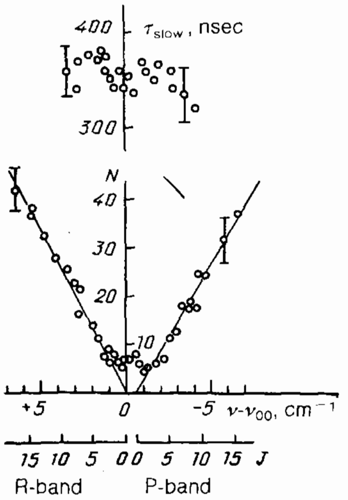

FIG. 8. Change in $N = C_{fast}/C_{slow}$ and τ_{slow} along the rotational contour.[26-28] Straight lines are Eq. (6.2).

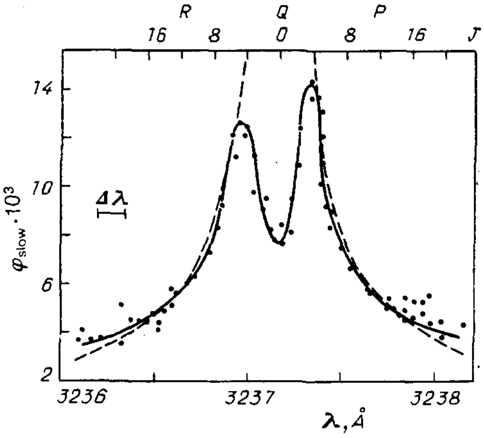

FIG. 9. ●-absolute quantum yield of fluorescence $T_{\text{rot}} \sim 30$ K, spectral resolution $\Delta\lambda = 0.11$ Å. Above are the values of J for the P and R branches. The solid line is provided for ease of visual perception, the dashed line is empirical Eq. (6.1) (Ref. 49).

the contribution was found to be $\sim J^2$). The parameter N is determined either from the second ratio[49,61] (Eq. (4.16)) and then from the data presented above $\alpha = 16$, or from the first ratio, which yields $\alpha = 0.3$–1.3 for picosecond excitation[28b,38,48] and $\alpha = 0.15$–0.3 for nanosecond excitation[24,37,52] (see the discussion at the end of section 6.4). The smooth dependence of Eq. (6.2) is for excitation at the maxima of the rovibronic lines, while at the minima between neighboring lines (curve in Fig. 5b) N increases severalfold[24,42,61] (even by a factor of ten); φ_{slow} also falls.[50]

6.2. Superhigh resolution spectra

When $\Delta\nu$ is decreased to 200 kHz ($6.7\cdot 10^6$ cm^{-1}) the rovibronic components of the excitation spectrum break up into lines with residual Doppler broadening of 50–1 MHz ($(1.7$–$0.034)\cdot 10^{-3}$ cm^{-1} (Refs. 23, 25, 26, and 60). They correspond to the molecular states Φ_n formed as a result of singlet-triplet mixing of zero states Φ_s and Φ_l. Especially detailed studies have been made of spectral regions adjoining singlet states with $J = 0$ (Fig. 10) and 1, and $K = 0$. The corresponding transitions, P(1) and R(0) are separated by a wide gap of 25 GHz, and contain narrow "clusters" of lines, that is, groups of 12 lines with a relative intensity of more than 1% (and many weak lines) which fill narrow intervals of width $\delta_J = 3.7$ and 2.2 GHz. Thus, the number of triplet states in each group is $N_T = 11$, and their density is $\rho_l = N_T/\delta_J = 90$ and 150, which is in agreement with the value[1,38] 100 states/cm^{-1} calculated from the Haarhoff formula[79] (finer estimates which consider the electronic and nuclear spins yield noticeable divergences of calculated and observed values[25b] of ρ_l). An important observation is that N_T does not depend on J, at least until[26] $J = 4$; however, it is incorrect to see a contradiction here with Eq. (6.2), since $N_T \neq N$ (see item 2 in the next subsection).

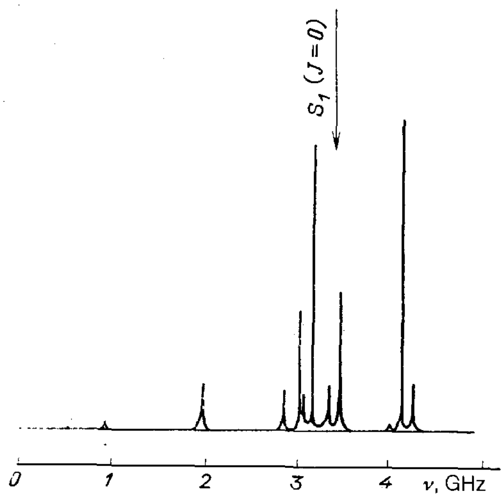

FIG. 10. Fluorescence excitation spectrum measured in the region of the rovibronic component $P(1)$ with a resolution of 10 MHz, $T_{\text{rot}} = 3$ K, $\tau_{\text{pulse}} = 40$ ns (Refs. 23, 25, 26). The beginning of reckoning of ν was selected arbitrarily. Twelve lines are visible which correspond to precise molecular states with energies E_n, which arise as a result of the interaction of one light singlet state (its position is indicated with an arrow) with 11 dark triplet states; the intensities of the lines are proportional to the squares of the amplitudes a_{sn}^2.

The lifetimes $\tau_{\text{obs}(n)} = 200$–$560$ ns and intensities of these lines have also been measured[25] and this information was used to establish the intensity of absorption. Using the reverse problem method[80a] the parameters of the zero Hamiltonian were determined, that is, the position of the zero levels E_s and E_l, their rates of decay (Eq. (3.1)) $2\gamma_s = 5$ MHz and $2\gamma_l = 0.6$–5 MHz, and matrix elements $S_1 - T_1$ of the interaction $v_{sl} = 70$–460 MHz (0.0023–0.015 cm^{-1}). The small value of v_{sl} can be explained by the weak overlap of vibrational wave functions due to the small mixing and deformation of potential surfaces S_1 and T_1 relative to one another.[80b] The radiation time of attenuation was calculated using the total absorption[26,81] $S_1 \leftarrow S_0$: $\tau_{\text{rad}(s)} = 210$–$450$ ns ($2\gamma_{\text{rad}(s)} \equiv 1/2\pi\tau_{\text{rad}(s)} = 0.35$–$0.76$ MHz). The main relaxation process contributing to γ_s and γ_l is radiationless transition[46] into S_0; as can be seen from the figures presented, $\gamma_{\text{rad}(s)} \sim \gamma_{\text{RT}(s)} \sim \gamma_{\text{RT}(l)}$.

6.3. The mechanism of strong $S_1 - T_1$ coupling in the intermediate case

It follows from experimental data that $\gamma_s \sim \gamma_l \sim 10^{-5}$ cm^{-1} $\ll \rho_l^{-1} \approx 10^{-2}$ cm^{-1}; thus, the case of slight broadening, case I is realized (see sections 2 and 3), in which it is necessary to differentiate the limits of strong and weak coupling (see Fig. 2). The data in Ref. 25 show that the two strongest triplet states have $v_{sl} = 0.015$ cm^{-1} $\gtrsim \rho_l^{-1}$, while for the remaining states $v_{sl} \ll \rho_l^{-1}$. Thus, strictly speaking, there is no limit of strong or weak coupling, and numerical methods should be used,[10b,73,82,83] and one should also consider broadening of the zero levels.[84] The recovery of the attenuation kinetics from spectra of molecular states yields diverse behavior, including irregular beats[23,31] and a fast component.[26,31,43] An example of this reconstruction of decay with excitation in the Q band is shown in Fig. 11 (the corresponding spectrum of molecular states is not accurately known, thus, a simple model was used which is based on known spectra of the type presented in Fig. 10).

Before the discovery of spectra of molecular states, according to Ref. 1, data on pyrazine and other molecules were discussed, as a rule, on the basis of the mechanism of strong coupling from section 4 (see, however, section 6.5), and here we conduct an analogous analysis. Justification for this is that at $J > 1$ one observes a fast component with the characteristics presented in section 6.1, and for $J > 4$, one can expect an increase in the density of the vibrational-rotational

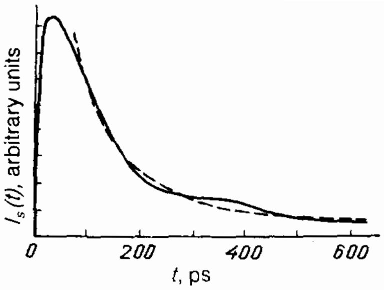

FIG. 11. A calculated fluorescence attenuation curve for excitation in the Q band with incoherent population of singlet states with different J, each of which interacts with its own "bundle" of triplet states, forming a molecular spectrum of the type presented in Fig. 10. The dashed line is the exponent with $\tau_{\text{fast}} = 100$ ps (Refs. 26, 43).

states $\rho_l \sim 2J + 1$ due to violation of the rules for selecting K for the $S_1 - T_1$ coupling in a weakly asymmetrical gyroscope (in pyrazine[38,52] $A - B \approx 0.015$ cm^{-1}) and the consequent onset of a strong coupling limit. We note the following correlations between theory and experiment.

1) From Eq. (4.8) from known φ_{fast} and τ_{fast} we find $\tau_{\text{rad}(s)} = 200$ ns in agreement with the value calculated from absorption.

2) Taking into account that $k_s \approx 1/\tau_{\text{fast}}$ does not depend on J, from Eq. (4.1) we find $N \sim \rho_l \sim 2J + 1$ in agreement with Eq. (6.1). In turn, k_s does not depend on N (and consequently, on J), because in Eq. (2.9) v_{sl} is a purely electronic matrix element of spin-orbital interaction V_{so} distributed among N vibrational-rotational states of the triplet, and from the preservation of normalization $v_{sl} = V_{\text{so}}/N^{1/2}$.

The parameter in Eq. (4.1) is linked with N_T through the expression

$$N = \frac{\pi\hbar N_T}{\delta_J \tau_{\text{fast}}}. \qquad (6.3)$$

Then, substituting experimental data (if δ_J is expressed in Hz, then $\hbar = 1/2\pi$), we obtain $N = (1\text{–}2)N_T$. Since N_T and τ_{fast} do not depend on J, the observed dependence Eq. (6.2) may be linked with a decrease in δ_J; however, the nature of the narrowing of clusters of triplet states is unclear.

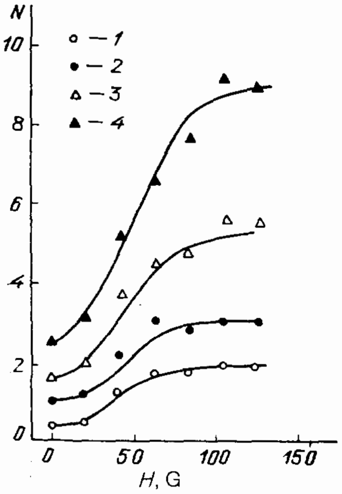

FIG. 12. Dependence of $N = C_{\text{fast}} \times C_{\text{slow}}$ on the magnetic field for various rovibronic levels.

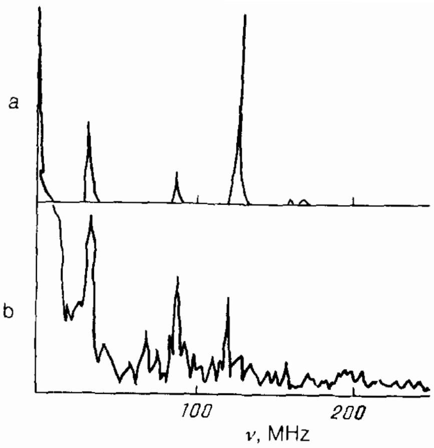

FIG. 13. Fourier transforms of fluorescence intensity $I_s(t)$ from the initially prepared state S_1 ($J = 0$).

The difference between N and N_T means that *in addition to the strongest triplet states there are other states which also participate in the distribution of oscillator strength and the initial population of the light state.*

3) From $\gamma_s \sim \gamma_l$ and $N \gg 1$ it follows that Eqs. (4.2) and (4.10) are satisfied; the latter explains why τ_{slow} does not depend[52] on J. In Ref. 50 it is assumed, as follows from Ref. 71, that $\tau_{\text{slow}} \sim N$ and increases with J, but this would be so in the case which is the converse of Eq. (4.2).

4) In deuteration ρ_l should increase and v_{sl}^2 which is proportional to the Franck–Condon factor should decrease due to a decrease in vibrational frequencies. This is confirmed by an experiment[31] which observed a decrease in τ_{fast} by a factor of 1.5, the reverse effect of deuteration,[66,67] and an increase in N by a factor of 4 in pyrazine-d$_4$. Calculation according to Eqs. (2.9) and (4.1) yields a decrease in v_{sl}^2 by a factor of 2.7, which agrees with the calculation of ρ_l in Ref. 31. An average value of 167 MHz is obtained for v_{sl} in accordance with the data in section 6.2.

5) An external magnetic field weakens the selection rule for V_{so}, increasing by a factor of 3 (according to the number of spin sublevels) the density of triplet states interacting with a singlet state. This leads to an increase in N by a factor of 3 in fields up to 150 G (Refs. 30, 52, 60) (Fig. 12); τ_{fast} and τ_{slow} do not change for the same reason as in items 2 and 3.

6) The Fourier spectra of observed irregular quantum beats of the slow component[22,26,29,30] have peaks at frequencies which coincide with the distances between lines in high resolution spectra (Fig. 13). This is confirmed by the fact that the beats are linked with coherent excitation of molecular states, and are evidence for the strong coupling limit, since in weak coupling only periodic quantum beats are possible (section 5.2).

7) Deviations from exponentiality and quantum beats of fluorescence depolarization are linked with dephasing of coherently excited molecular states.[52,54,55]

8) If beats and the fast component are due to coherent excitation of many molecular states Φ_n, then these effects should disappear when an individual state is excited (see section 4.5). This is confirmed by experiment (see Fig. 14).

9) The dependence of quantum yield on pressure $\varphi(p)$ in the gas phase is not subject to the Stern–Volmer law. This

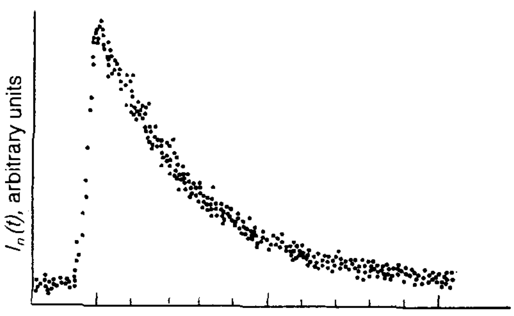

FIG. 14. Typical picture of monoexponential fluorescence attenuation from isolated molecular states Φ_n excited by a narrowband laser with $\Delta\nu_{\rm coh} = 25$ MHz and $\theta_{\rm pulse} = 40$ ns in the region of transition $P(1)$ (Refs. 25a, 26, and 60). The spectrum of these states is shown in Fig. 10. The function presented here, $I_n(t)$, corresponds to the strongest line in Fig. 10 with $\tau_{{\rm obs}(n)} = 280$ ns. Comparison with Fig. 7 shows that beats disappear when $\Delta\nu_{\rm coh}$ become less than the distances between E_n levels.

follows from Eqs. (4.8), (4.10), and (4.14), where it is necessary that $\tau^{-1}_{{\rm VR}(l)} = k_p p$ ($\tau_{{\rm VR}(s)} = 0$ for the zero vibrational level in S_1). Actually $\varphi_{\rm fast}$ does not depend on p, since dephasing is faster than vibrational relaxation at $p \leqslant 100$ Torr, and for $\varphi_{\rm slow}(p) \equiv \varphi(p) - \varphi_{\rm fast}$ one obtains the expression $\varphi_{\rm slow}(0)/\varphi_{\rm slow}(p) = 1 + Ap$, where $A = \tau_{{\rm RT}(l)} k_p$ (this reduces to the Stern–Volmer law for $\varphi_{\rm fast} = 0$). Experiment confirms[1] this dependence and yields $A = 10.5$ Torr^{-1}. The values of $\tau_{\rm slow}$ given in section 6.1 are for $p = 0$, thus, one can set $\tau_{{\rm RT}(l)} = \tau_{\rm slow}(p = 0) = 400$ ns, and then $k_p = 2.6 \cdot 10^7$ s$^{-1}\cdot$Torr^{-1}, which is a factor of 2 greater than the gas kinetic value.[1] It is likely that this figure should be even higher, since to quench fluorescence a molecule needs to lose a very small amount of energy (of the order of δ_J) in order to leave the zone of strongly interacting triplet states.

At $p > 20$ Torr, $\varphi_{\rm slow}$ is small and only a fast component is observed.[1,4,78] We stress that at $p > 100$ Torr there is a transition from the intermediate state to the statistical limit, since $2\gamma_l \approx k_p p/2\pi > 400$ MHz, which exceeds the average distance between levels (see section 6.2). Thus, *the fast component observed in picosecond excitation at the high pressure limit is typical statistical decay, and not dephasing.* In nanosecond excitation the kinetics of decay are modified according to Eqs. (1.3) and (1.9).

10) The observed quantum yield is small,[49,50] which agrees with Eqs. (4.8) and (4.15).

11) Calculations using the model of an asymmetrical top[61] showed that in the intervals between strong absorption lines at small values of J there is weak absorption in transitions with large J, and this explains (in view of Eq. (6.1)) the increase in N observed in Refs. 24, 42, 50, and 61.

6.4. The nature of the fast component

Of fundamental importance is the issue of the modification of fast decay when $\tau_{\rm pulse}$ increases to $\gtrsim \tau_{\rm fast}$. In many papers, beginning with Ref. 1, it was assumed that even in nanosecond excitation the fast component in Eq. (4.12) was due to dephasing, and its decay was modified according to Eqs. (1.3) and (1.9) which, when the exciting pulse has an exponential form, yield[61] $I_{\rm fast}(t) = \zeta\tau^{-1}_{{\rm rad}(s)} \exp(-\zeta t/\tau_{\rm fast})$, where $\zeta = \tau_{\rm fast}/\tau_{\rm pulse}$ (a change in amplitude and rate of attenuation with an unchanged quantum yield, Eq. (1.7)). However, these formulas are applicable only in the statistical limit, when the balance equation (1.2) is valid; in the case of dephasing they do not work (see section 3). Indeed, *the increase in $\tau_{\rm pulse}$ to values $\gtrsim \tau_{\rm fast}$ should lead to the* disappearance of dephasing. Actually, since $\Delta\omega_{\rm coh}$ becomes smaller than the widths of the band of N interacting states (of the order of k_s or δ_J), the initial excitation affects only some of them, and instead of dephasing, quantum beats appear; when $\Delta\omega_{\rm coh}$ becomes smaller than the distances between levels, there remains one slow component in a pure form (see item 8 in section 6.3). In Ref. 47 when $\tau_{\rm pulse}$ is increased from 21 to 70 ps, the fast component becomes strongly nonexponential (although the results of this paper were partially revised in Ref. 48), and in nanosecond excitation[1] it simply reproduces the shape of the exciting pulse. Thus, one should conclude[49,60] that *the fast component of decay observed in nanosecond excitation is not associated with dephasing and is not a purely molecular property;* it depends on the properties of the exciting radiation and may be due not only to dephasing, but also to other processes. We already saw in item 9 in section 6.3 that at the high pressure limit it is not associated with dephasing even in picosecond excitation (but is a molecular property); other examples will be given in the next section.

Taking this conclusion into account, we must reexamine the results of the comparison of theory and experiment made above. There is no doubt that independently of the nature of the fast component (and even of its very presence) *the slow component is always a purely molecular property,* since Eq. (1.5) is satisfied, and its parameters, $C_{\rm slow}$, $\tau_{\rm slow}$, and $\varphi_{\rm slow}$ are linked with the molecular parameters of the equations in section 4. In particular, $C_{\rm slow} \sim \varphi_{\rm slow} \sim 1/N$ and N are given by Eq. (4.1). Thus, all the concepts presented above which involve the dependences of these parameters on rotation, pressure, the magnetic field, and deuteration, remain in force, and k_s in item 2 of section 6.3 should be understood as a formally defined parameter of Eq. (2.9) not linked with $\tau_{\rm fast}$. On the other hand, the parameters of the fast component in nanosecond excitation lose the sense which was assigned to them in section 4, and now are simply unknown constants which depend on the means of excitation and detection.[50] Then Eq. (4.16) defines from Eq. (4.1) not N, but a new parameter $N' = \zeta' N$, where ζ' depends on the conditions of excitation (and is not equal to ζ). It is important, however, that the parameters of the fast component do not depend on rotation, pressure, and the magnetic field. Thus, for example, on the basis of the measured dependence of N' on J, one can state that empirical equation (6.1) holds true for N. In this equation α depends on the conditions of excitation. This explains the large scatter of α values in various experiments.

In summary, we again stress that the ratio $C_{\rm fast}/C_{\rm slow}$ is not the number of strongly coupled states, and its dependence on rotation and other factors is reflected by the behavior of the slow component, if these factors have no effect on the fast component.[60] Thus, at first glance the question arises of "lost states."[59] This question is posed with respect to the fact that there are many fewer states in very high resolution spectra than is predicted by the ratio $C_{\rm fast}/C_{\rm slow}$. However, it is posed again with regard to the fact that $N > N_T$ (see item 2 in section 6.3).

6.5. Other mechanisms of fast decay

The suggestion was made that the fast component is associated with nonresonant (Rayleigh or Raman) scattering of light.[24] The main argument for this is the fact that N increases in excitation in the intervals between the rovibronic lines, where in a symmetrical top there should be no luminescence at all since the appropriate conditions are not present. Experiments in Refs. 50 and 61 confirmed the existence of this effect, but it was explained in the framework of the theory of strong coupling (see item 11 in section 6.3). Nonetheless, it still makes sense to consider the hypothesis of nonresonant light scattering, which does not contradict the undoubted, proven direct recording of the existence of an intramolecular process of dephasing for several rovibronic levels (see section 6.1). Each level should be dominated by its own mechanism of fast decay.

The theory of nonresonant light scattering was developed in Refs. 26, 42, 45, and 46. The main idea reduces to the following. If the exciting laser is tuned in resonance with a homogeneously broadened molecular transition $\Phi_0 \to \Phi_s$ and Eq. (1.5) is satisfied, then the radiation slowly attenuates according to Eq. (1.6) with a small quantum efficiency. As one moves further from resonance, nonresonant light scattering appears with a small length $\sim \tau_{\text{pulse}}$. Its amplitude falls as the detuning increases, but the "effectiveness" (that is, the specially defined quantum yield) increases, and the kinetics of luminescence as a whole may be regarded as biexponential. Numerical calculations[84–86] show that at large detuning levels and $\Delta\omega_{\text{coh}}$ values, the amplitude of nonresonant light scattering is large enough to isolate the fast component from the background of the slow component.

The mechanism of vibrational crossing was also proposed.[49,50,59] In essence, the mechanism is as follows. In excitation of an isolated molecular state Φ_n luminescence attenuates exponentially. However, at $J \gg 1$ each rovibronic line in the parallel band $\Delta K = 0$ is inhomogeneously broadened due to transitions with different values of K, which have small energy gaps ($\sim 10^{-4} K^2 \cdot \text{cm}^{-1}$; in Refs. 25b and 29 the P(2) band and several others were expanded into K components). Thus, the observed kinetics is due to the imposition of typical statistical decays with different characteristic times $\tau_{\text{obs}(n)} \sim \tau_l$ from Eq. (4.10) (Ref. 51). It is further proposed that the main role in the quenching of triplet states is played by a "parallel" (proportional to K) Coriolis interaction which leads to transitions between vibrational sublevels T_1 (that is, the first term in Eq. (4.10) is nonzero for isolated molecules as well). Then[87,88] $\tau_l^{-1} = a + bK^2$ and asymmetry arises between states with $K = 0$ and $K \neq 0$, especially if $a \ll b$. In a model of vibrational crossing the fast component is linked with the decay of states with $K \neq 0$, and the slow component with states with $K = 0$ (see also Ref. 37). The exception is states with $J = 0$ and 1, which are excited by lines $P(1)$ and $R(0)$, since here, due to the rules of selection, only $K = 0$ is prepared[2)] and the fast component should be absent. This is what is observed.

Calculations in Ref. 87 show that at the statistical limit the effect of Coriolis interaction on intercombinational crossing is small; however, experimental data were obtained on the effect of Coriolis interaction on the redistribution of vibrational energy in S_1 and the internal crossing $S_1 \rightsquigarrow S_0$. For example, in benzene in the region of "channel 3" (E_{vib} in $S_1 \gtrsim 3000 \text{ cm}^{-1}$) lines with $K \neq 0$ disappear from rovibronic excitation spectra.[89] The temperature redistribution of intensity in the fluorescence spectrum of anthracene is also associated with Coriolis interaction.[90a] The effect of Coriolis interaction on vibrational redistribution in S_1 was detected in Ref. 90b. In Refs. 26, 44 it was shown that the distribution of intensity in the observed rovibronic excitation spectra of pyrazine could be explained by the contribution of Coriolis interaction between S_0 and S_1, thus $a \sim b$. Other examples are given in Ref. 50. The study of rotational effects in radiationless transition[91] T_1 S_0 and of the phosphorescence spectra of pyrazine in direct excitation[92] $S_0 \to T_1$ has not yet indicated the effect of Coriolis interaction near the potential minimum T_1; however, such an effect near the minimum of S_1 is certainly possible, and it was observed in pyramidine.[93] A critical point in this theory is the condition $a \ll b$, since there appears to be no physical basis for it ("parallel" and "perpendicular" Coriolis interaction, generally speaking, are of the same order), and at $a \sim b$ it is impossible to explain the large value of the ratio $\tau_{\text{slow}}/\tau_{\text{fast}} \approx 3000$. In very high resolution spectra[25b] the intensities of lines with $K \neq 0$ is larger than in lines with $K = 0$, which contradicts the hypothesis about the dominance of parallel Coriolis interaction. It is possible, however, that Coriolis interaction is responsible for the observed decrease in quantum efficiency as J increases.[25c]

7. BEATS AND BIEXPONENTIAL ATTENUATION IN ANTHRACENE

Another interesting area of application of the theory is molecules whose fluorescence attenuates nonexponentially, although the gap $\Delta E_{S_1T_1}$ is large and the effect of the triplet state T_1 can appear only with additional broadening of the vibrational sublevels S_1 when the balance equation (1.2) is applicable. In these molecules the reason for nonexponential decay is selective interaction between vibrational sublevels of the singlet state[35,36] S_1 (Fig. 15).

The first and most studied representative of this class is anthracene ($\Delta E_{S_1T_1} \approx 13000 \text{ cm}^{-1}$), in which Zewail *et al.*[35] detected quantum beats and biexponential fluorescence attenuation in rapid excitation of the S_1 sublevels which corre-

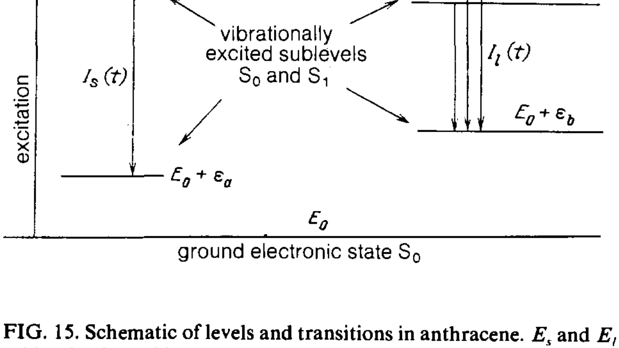

FIG. 15. Schematic of levels and transitions in anthracene. E_s and E_l are sublevels of S_1 which correspond to vibrational energy E_{vib}; $E_0 + \varepsilon_a$ and $E_0 + \varepsilon_b$ are vibrational sublevels of the ground state; $I_s(t)$ and $\Sigma I_l(t)$ are the intensity of fluorescence in type a and type b bands, respectively; v_{sl} is anharmonic interaction.

spond to one or two quanta of optically active vibrations in the interval $E_{\rm coh} \leqslant 2000$ cm^{-1}. Special studies have shown that these effects are not associated with the effect of the triplet state (for example, the frequencies and amplitudes of the quantum beats do not depend on the magnetic field), and are due to anharmonic interaction of the given light level E_s with N dark levels E_l, which belong to the same electronic state S_1.

The division of states into light and dark in absorption in this case is due to the fact that normal vibrations have different Franck–Condon factors. In radiation all states become light, but for the same reason the corresponding transitions lie in different spectral intervals, since they are completed in accordance with the Franck–Condon principle in different sublevels of the ground state. Thus, there are type *a* bands (transitions from the initially prepared state Φ_s) and type *b* bands (transitions from states Φ_l).

Figure 16 shows the fluorescence attenuation curves for anthracene in type *a* bands in excitation of various initial states. At a small value of $E_{\rm coh}$ there are no dark states Φ_l, which would effectively interact with Φ_s (that is, $N=0$), and thus the initial state decays according to an exponential law (curve 1). As $E_{\rm coh}$ increases one or several such states appear ($N \geqslant 1$) and the intensity begins to oscillate (curve 2). At large $E_{\rm coh}$ the number of interacting states is large ($N \gg 1$) and the decay becomes biexponential (curve 3) (the characteristics of biexponential curve 3 are $\tau_{\rm fast} = 22$ ps, $\tau_{\rm slow} = 6.4$ ns, $C_{\rm fast}/C_{\rm slow} = 17$; in the figure this ratio is less because curve 3 is the convolution of the true attenuation curve and of the response function of a detecting system with a time constant of 80 ps).[35b]

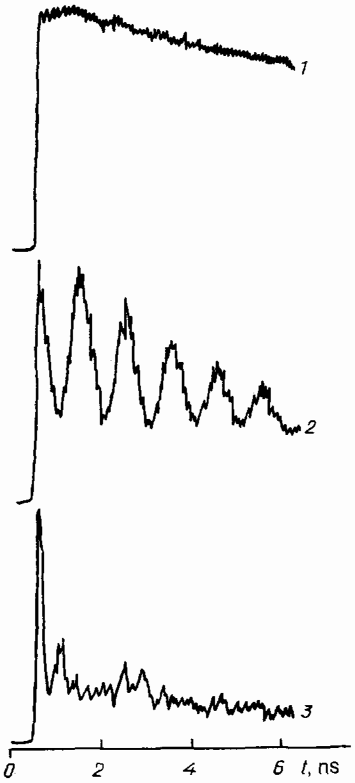

FIG. 16. Fluorescence attenuation of anthracene in type *a* bands ($\varepsilon_a = 390$ cm^{-1}).

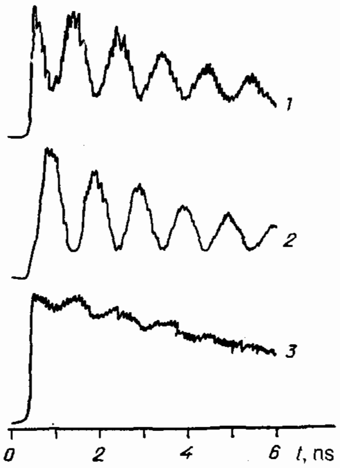

FIG. 17. Fluorescence attenuation from a state with $E_{\rm vib} = 1420$ cm^{-1}.

The interpretation of these results is completely obvious. At small values of $E_{\rm coh}$ the limits of weak coupling occur. Since Φ_s and Φ_l belong to one electronic state, their half-widths are approximately identical, and in the case $N=1$ the intensity oscillates according to Eqs. (5.9) and (5.10). At $N>1$ the oscillations have a quasi-periodic character and may establish the defined correlations between frequencies and between phases of the corresponding Fourier components, which have been verified experimentally.[35] The values of v_{sl} estimated from observed periods of oscillations, lie at 0.01–0.1 cm^{-1}. At $N \gg 1$, there is a transition to the strong coupling limit due to a decrease in the distances between levels E_l, and a fast component appears due to dephasing.

As indicated in section 5.5, in the case $N=1$ the beats in intensity in type *a* and type *b* bands should be in antiphase. This is demonstrated by curves 1 and 2 in Fig. 17. More detailed analysis of curves *1–3* (in particular, a consideration of high-frequency oscillations, which are visible in the figure) shows that actually the interaction of four or five levels appears here.[35b]

Based on the results of experiments one can compose the following picture of the processes of redistribution of vibrational energy in the first excited singlet state of anthracene. Levels with $E_{\rm vib} \leqslant 1200$ cm^{-1} are isolated and in their lifetime they do not experience any changes. At $E_{\rm vib} = 1300$–1500 cm^{-1} each level interacts with a small number ($N = 2$–10) of other levels, which leads to reversible energy exchange between them with characteristic frequencies ~1-10 GHz.

When $E_{\rm vib} \simeq 1800$ cm^{-1} the number of interacting levels is large and the process becomes irreversible, preserving, however, features of quantum behavior in the fast stage (dephasing in times ~20 ps). Finally, when $E_{\rm vib} \gg 1800$ cm^{-1}, the slow component disappears, and the fast component is converted into a typical statistical decay with the same characteristic time, 20 ps, that is, a transition to a completely irreversible kinetic process of intramolecular vibrational relaxation occurs. This is caused by the coalescence of levels (case II in section 2) analogous to what occurs when the width of levels increases as pressure increases in the gas phase (see item 9 in section 6.3).

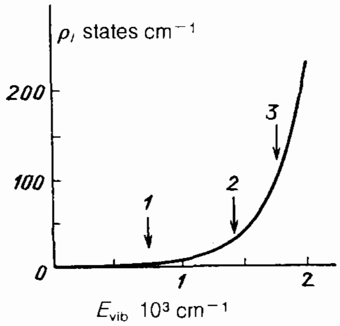

FIG. 18. Density of vibrational states of anthracene, found by direct calculation of the number of states.[35b]

Changes in the character of intramolecular dynamics as E_{vib} increases may be linked with an increase in the density of vibrational states. It is clear from Fig. 18 that at $\rho_l < 10$ states/cm^{-1} there is no relaxation; reversible energy exchange begins in the interval $\rho_l = 25$–40, and vibrational relaxation at $\rho_l \approx 120$ states/cm^{-1}.

The results of these experiments demonstrated the high selectivity of anharmonic interactions. For example, at $E_{vib} = 1380$ cm^{-1} there are three strongly coupled vibrational states in the 8.4 GHz interval, while the total number of states in this interval at $\rho_l = 25$ states/cm^{-1} is a minimum of a factor of 2 higher.

In conclusion we recall the very interesting observations of the effect of rotation on the described effects and the polarization studies in anthracene and other molecules[35,36] (we note that rotation has no effect on intercombinational crossing $S_1 - T_1$, and this has been proven experimentally in the case of naphthalene[94]).

8. CONCLUSION

The experimental discovery of the intermediate case of large molecules, including the limits of strong and weak coupling, which was predicted by theory, is a significant event in molecular spectroscopy, since it introduces radical changes into our concepts of the nature of molecular fluorescence and radiationless transitions. Indeed, traditional understanding of these processes in isolated particles was based on the assumption that in the process of excitation we prepare a luminescent state which then decays either only radiatively (atoms and small molecules) or both with and without radiation (large molecules) at rates equal to the sum of the rates of these processes (statistical limit). The basis for the statistical limit in large molecules was that, due to the rapid increase in the density of states with vibrational energy, the levels quickly lose their individuality, coalescing into a so-called quasi-continuum[34] in which it is impossible for coherence and rotation effects to appear.

Indeed, it turns out that intramolecular interactions (for example, spin-orbital interaction between states S_1 and T_1 in pyrazine and anharmonic interaction of vibrational sublevels of S_1 in anthracene) have a high selectivity: due to the defined prohibitions each light state effectively interacts only with a small part of the isoenergetic dark states. Consequently, a relatively rare spectrum of active states is formed, which makes it possible to observe phenomena associated with the intermediate case.

In the intermediate case at the limit of strong singlet-triplet coupling, the mixed state is initially prepared (if one removes fast dephasing) and thus there is no radiationless transition $S_1 \rightsquigarrow T_1$ in pyrazine in the typical sense, although the quantum yield of fluorescence is small, and the quantum yield of the formation of triplets is close to unity[1] (it is of course possible to consider dephasing as a radiationless transition $S_1 \rightsquigarrow T_1$, but even then this is not a radiationless transition in the typical sense, since dephasing depends on the excitation conditions, and its rate does not add to the rate of radiation attenuation). With the addition of a buffer gas, relaxation begins in the ground vibrational state T_1 and the slow component of fluorescence, which is associated with the decay of mixed states, disappears; simultaneously there is a transition from the intermediate case to the statistical limit, since the collision widths become greater than the distances between levels, and the initially prepared state becomes a pure state S_1. Thus, in dense vapors only the fast component remains, and its decay is defined by the typical radiationless transition $S_1 \rightsquigarrow T_1$. An analogous transition from the intermediate case to the statistical limit for intramolecular vibrational relaxation in S_1 is observed in anthracene as the vibrational energy increases.

A clear manifestation of the individuality of states is rotational effects. It was known theoretically and experimentally that at the statistical limit the effect of rotation on the velocity of intercombinational crossing is negligible; in the intermediate case, as was shown by experiment, the kinetics of fluorescence depend on the rotational state. For example, in a given vibrational state of pyrazine, one observes in different rotational sublevels mono- and biexponential attenuation with changing quantum yields and durations as well as quantum beats. There will be no great surprise if it is found that in this system all possible mechanisms of fluorescence attenuation are realized. However, the very origin of the dependence of quantum yield and the number of strongly coupled states on vibrational quantum numbers remains unexplained in its entirety. An important problem is the establishment in each case of the mechanism of fast decay and the investigation of the contribution of Coriolis interaction to the attenuation of the slow component of fluorescence.

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[1)] When using other definitions, it is necessary to introduce the corresponding changes into Eqs. (4.7) and (4.12).

[2)] Usually the rotation numbers in S_1 and S_0 are denoted by J', K' and J'', K'', and the transitions $S_1(J') \leftrightarrow S_0(J'')$ by $P(J'')$ when $J' = J'' - 1$ and $R(J'')$ when $J' = J'' + 1$. For parallel bands the selection rule $K' = K''$ holds true, thus the lines $P(1)$ and $R(0)$ are distinct in the sense that they contain only one K component ($K' = K'' = 0$), while all remaining lines in the P and R bands are superpositions of incoherent transitions with the participation of various K components, and the Q band is the superposition of transitions with different $J'(=J'')$.

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