

in infinite systems. Although there is as yet no effective method of calculating the reflection matrix, one can hope that it will remain a smooth function of the energy and can be specified with the aid of a small number of parameters.

In conclusion, the authors are grateful to A. P. Kovtun for providing the results of the calculations of the electron structure of the SF<sub>6</sub> molecule. The authors thank V. P. Sachenko and A. P. Kovtun for a discussion of the manuscript.

- <sup>1</sup>The energy is measured in this paper in Rydbergs, and the remaining quantities are given in the atomic system of units.  
<sup>2</sup>We use here real spherical functions, the so-called cubic harmonics. <sup>[1]</sup>Therefore  $m$  does not have the meaning of the magnetic quantum number, and merely numbers harmonics with a definite value of orbital angular momentum ( $m = 1, 2, \dots, 2l + 1$ ). The symbol  $L$  denotes the pair of numbers ( $l, m$ ). Bearing in mind that all the calculations are carried out in this paper in a definite irreducible representation of the point group of the system, corresponding to the chosen  $L$  on the central atom, we shall hereafter frequently omit the index  $L$ , or replace it by the symbol of the irreducible representation.

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## Effects of the Landau-Zener type in the optical spectra of molecules

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We investigate the influence of nonadiabatic coupling of electron-vibrational terms of molecular systems on their optical properties. It is shown that Landau-Zener effects in the vicinity of the quasicrossing of the terms lead to a substantial restructuring of the energy spectrum, to beats in the absorption line intensities, and to asymmetry in the absorption and emission spectra. Typical objects in which the predicted singularities can be observed are indicated. The case of laser-induced quasicrossing of terms is considered separately.

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When a theory is developed for the theory of electron-vibrational optical spectra of molecular systems it is important to take into account the fact that the excited term to which the transition is realized is as a rule not isolated and has regions of approach (quasicrossing) with the ground-state or some other excited terms in configuration space of the molecule. A special role can be played here by quantum states that result from the

nonadiabatic coupling of the terms in the quasicrossing region. The coupling of the term can be due to electron-vibrational interaction, to spin-orbit coupling, or to mixing of these states by external laser radiation (induced quasicrossing).

If the matrix element of the coupling of the terms is comparable in magnitude with the characteristic distance between the vibrational conditions, then a sub-

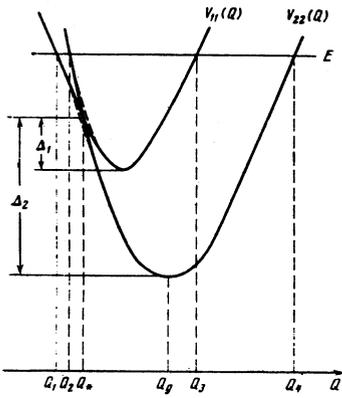


FIG. 1. Crossing interacting diabatic terms of a molecular system (the dashed curves show the adiabatic terms for the case of extremely strong coupling).

stantial restructuring of the energy spectrum of the excited state and of its wave function takes place in the vicinity of the quasicrossing region, and this should lead to some distinct manifestations.

The problem of the approaching terms was investigated extensively in connection with the problem of inelastic atomic collisions (the Landau-Zener theory<sup>[1-3]</sup>). The purpose of the present work was to construct a theory of broad optical-absorption bands, which takes into account effects of the Landau-Zener type in the region where the terms approach each other. It will be shown that allowance for the interaction of the terms in the quasicrossing region leads to an irregular fine structure of the band in the frequency region where the terms approach each other, and to appearance of quantum beats in the absorption line intensity. In the case of laser-induced quasicrossing, the parameters that characterize the produced singularities depend on the frequency and on the intensity of the external laser radiation, and this leads to an important possibility of controlling the shape of the absorption line, which is important for practical applications.

1. We consider the spectrum of a single-configuration molecular system that intersecting "diabatic" terms  $V_{11}(Q)$  and  $V_{22}(Q)$  in the respective electronic states 1 and 2 (see Fig. 1). We seek the wave function of the molecule in the form

$$\Psi(\mathbf{r}, Q) = \Phi_1(Q) \varphi_1(\mathbf{r}, Q) + \Phi_2(Q) \varphi_2(\mathbf{r}, Q), \quad (1)$$

where  $\varphi_{1,2}(\mathbf{r}, Q)$  are the electron wave functions corresponding to the equilibrium configuration  $Q_e$  of the molecule. The wave functions  $\Phi_{1,2}(Q)$  satisfy the system of equations

$$\frac{\hbar^2}{2m} \frac{d^2 \Phi_i}{dQ^2} + (E - V_{ii}(Q)) \Phi_i = V_{ij}(Q) \Phi_j; \quad (2)$$

$m$  is the reduced mass of the nuclei;  $i, j = 1, 2; i \neq j$ ;  $V_{ij}(Q)$  are the term-coupling matrix elements made up of the functions  $\varphi_{i,j}(\mathbf{r}, Q)$ .

Assume that the intersection point of the diabatic terms  $Q_*(V_{11}(Q_*) = V_{22}(Q_*))$  has a higher energy position than the first few vibrational levels in the potential wells  $V_{ii}(Q)$ , and that the interaction  $V_{ij}(Q)$  is not large enough to alter radically the pattern of the initial terms in all of configuration space, i.e.,

$$|V_{ij}(Q)| \ll \min(\Delta_1, \Delta_2, |\Delta_2 - \Delta_1|),$$

where  $\Delta_i$  is the energy interval between the bottom of

the  $i$ -th term and the crossing point. In this case the interaction of the terms  $V_{ij}(Q)$  is of importance only near  $Q_*$ , and far from this point the solutions of the system (2) takes the form of WKB waves corresponding to motion in independent potentials  $V_{11}(Q)$  and  $V_{22}(Q)$ :

$$\Phi_i(Q) = \frac{A_i^+}{(p_i(Q))^{1/2}} \exp\left\{ \frac{i}{\hbar} \int_{Q_i}^Q dQ' p_i(Q') - i \frac{\pi}{4} \right\} + \frac{A_i^-}{(p_i(Q))^{1/2}} \exp\left\{ -\frac{i}{\hbar} \int_{Q_i}^Q dQ' p_i(Q') + i \frac{\pi}{4} \right\}, \quad (3)$$

$$p_i(Q) = [2m(E - V_{ii}(Q))]^{1/2}, \quad (4)$$

$Q_i$  are the classical turning points (see Fig. 1).

The amplitudes  $A_i^\pm$  are interconnected by the  $S$ -matrix of the inelastic two-channel scattering on the region of the nonadiabatic coupling of the terms:

$$\begin{pmatrix} A_1^+ \\ A_2^+ \end{pmatrix} = S \begin{pmatrix} A_1^- \\ A_2^- \end{pmatrix}. \quad (5)$$

The unitary  $2 \times 2$   $S$ -matrix can be represented in the form

$$S = e^{2i\theta} \begin{pmatrix} M & N \\ -N^* & M^* \end{pmatrix}, \quad M = P + (1-P)e^{2i\varphi}, \quad (6)$$

$$N = 2[P(1-P)]^{1/2} \sin 0e^{2i\varphi},$$

where  $P(E)$ ,  $\theta(E)$ ,  $\varphi(E)$ ,  $\varphi_1(E)$  are real function of the energy;

$$0 \leq P(E) \leq 1.$$

If the energy of the relative motion of the nuclei exceeds sufficiently  $V_{ii}(Q_*)$  (a criterion will be given later on), then the scattering by the crossing terms can be represented as the result of two successive independent passages through the nonadiabaticity region. In this case  $P(E)$  is the probability that the system will remain on the initial term after passage through the nonadiabaticity region, and  $1 - P(E)$  is the probability that it will go to another term. The removal of the system to another term after passing twice through the nonadiabaticity region can occur in two ways: it can remain on the initial term after the first passage through the crossing point and go over to the second in the course of the second passage, or conversely go over during the first passage and remain on that term in the second passage. The parameter  $\theta(E)$  in the off-diagonal element of the  $S$  matrix reflects the interference of these alternatives.

The wave functions  $\Phi_{1,2}(Q)$  corresponding to the bound states should take the following form in the regions adjacent to the turning points  $Q_{3,4}$  (see Fig. 1):

$$\Phi_{i,2}(Q) \sim \left[ \frac{1}{p_{i,2}(Q)} \right]^{1/2} \sin \left( \frac{1}{\hbar} \int_{Q_i}^{Q_{3,4}} dQ' p_{i,2}(Q') + \frac{\pi}{4} \right). \quad (7)$$

Equating (7) to (3), we obtain with the aid of (5) a system of two linear homogeneous equations

$$A_1^- e^{-i(\alpha_1 + \varphi)} + [MA_1^- + NA_2^-] e^{i(\alpha_1 + \varphi)} = 0, \quad (8)$$

$$A_2^- e^{-i(\alpha_2 + \varphi)} + [-N^* A_1^- + M^* A_2^-] e^{i(\alpha_2 + \varphi)} = 0,$$

$$\alpha_{i,2}(E) = \frac{1}{\hbar} \int_{Q_{i,2}}^Q dQ p_{i,2}(Q). \quad (9)$$

Equating the determinant of the system (8) to zero,

we obtain an equation for the energy spectrum of the molecular system:

$$\begin{aligned} \cos(\chi_1 + \chi_2 + 2\varphi) + |M| \cos(\chi_1 - \chi_2 + \arg M) &= 0, \\ |M| &= [1 - 4P(1-P)\sin^2\theta]^{1/2}, \\ \arg M &= \arctg \left[ \frac{(1-P)\sin 2\theta}{P + (1-P)\cos 2\theta} \right]. \end{aligned} \quad (10)$$

In the case of weak coupling of the terms  $P \rightarrow 1$  the  $S$ -matrix (6) goes over into the unit matrix and Eq. (10) degenerates to

$$\cos \chi_1 \cos \chi_2 = 0,$$

meaning quantization in two individual diabatic wells. In the case of strong coupling we have  $P \ll 1$  and (10) takes the form

$$\cos(\chi_1 + \varphi + \theta) \cos(\chi_2 + \varphi - \theta) = 0,$$

which corresponds to quantization in individual adiabatic wells.

In the case of coupling of intermediate strength  $0 < P < 1$  the positions of the individual levels are determined by the transcendental equation (10), and has a complicated and irregular dependence on the level number because of interference effects in the scattering on the nonadiabaticity region. This distinguishes strongly the effects introduced by the quasicrossing of the term from the results of ordinary anharmonicity.

Normalizing in the usual manner<sup>[4]</sup> the wave function  $\Psi_n(\mathbf{r}, Q)$  that is quasiclassical in  $Q$  and corresponds to the  $n$ -th energy level, we get

$$\frac{|A_{1n}|^2}{\omega_1(E_n)} + \frac{|A_{2n}|^2}{\omega_2(E_n)} = \frac{m}{2\pi}, \quad (11)$$

where  $2\pi/\omega_{1,2}(E_n)$  are the periods of the classical motion in wells 1 and 2 respectively at the energy  $E_n$ . With the aid of (11) and (8) we obtain

$$\begin{aligned} |A_{1n}|^2 &= |A_{1n}^-|^2 = \frac{m\omega_1(E_n)}{2\pi} \\ &\times \left[ 1 + \frac{\omega_1(E_n)}{\omega_2(E_n)} \frac{1 + |M_n|^2 + 2|M_n|\cos(2\chi_{1n} + 2\varphi_n + \arg M_n)}{1 - |M_n|^2} \right]^{-1}, \\ |A_{2n}|^2 &= |A_{2n}^-|^2 = \frac{m\omega_2(E_n)}{2\pi} \\ &\times \left[ 1 + \frac{\omega_2(E_n)}{\omega_1(E_n)} \frac{1 + |M_n|^2 + 2|M_n|\cos(2\chi_{2n} + 2\varphi_n - \arg M_n)}{1 - |M_n|^2} \right]^{-1}. \end{aligned} \quad (12)$$

We consider the absorption coefficient  $K(\Omega)$  of light frequency  $\Omega$  by such a system in the case of low temperatures ( $\hbar T \ll \hbar \omega_0$ , where  $\omega_0$  is the frequency of the fundamental tone), when only the ground state of term 2 is populated. Then  $K(\Omega)$  takes the form

$$K(\Omega) = \frac{(2\pi)^2 N_0 \Omega}{\hbar c} |d_{12}|^2 \sum_n |L_{0n}|^2 \delta(\Omega_{n0} - \Omega), \quad (13)$$

where  $N_0$  is the number of molecules per unit volume,  $n$  numbers the energy levels  $E_n$ ,

$$L_{0n} = \int dQ \Phi_{1n}^*(Q) \Phi_{20}(Q)$$

is the Franck-Condon factor,  $\Phi_{20}(Q)$  is the oscillator wave function of the ground state of the molecule,  $\hbar Q_{n0} = E_n - E_0$  ( $E_0$  is the energy of the ground state of the

molecule),  $c$  is the speed of light, and  $d_{12}$  is the dipole matrix element.

The function  $\Phi_{20}(Q)$  is given by

$$\begin{aligned} \Phi_{20}(Q) &= \pi^{-1/4} \sigma^{-1/2} \exp[-(Q-Q_0)^2/2\sigma^2], \\ \sigma &= \hbar/m\omega_0. \end{aligned} \quad (14)$$

Since the wave function  $\Phi_{in}(Q)$  is quasiclassical, the Franck-Condon factor  $L_{0n}$  can be calculated by the saddle-point method. The result is

$$|L_{0n}|^2 = \frac{2\hbar\pi^{1/2}}{f_{1\sigma}} \exp\left\{-\left(\frac{E_n - V_{11}(Q_0)}{f_{1\sigma}}\right)^2\right\} |A_{1n}|^2, \quad (15)$$

where  $\bar{f}_1$  is the slope of the term 1 at  $Q = Q_0$ . With the aid of (13), (15), and (12) we obtain the final expression for the absorption coefficient:

$$\begin{aligned} K(\Omega) &= \frac{4\pi^2 N_0 |d_{12}|^2 m \Omega}{c f_{1\sigma}} \omega_1(E_0 + \hbar \Omega) \\ &\times \exp\left\{-\left[\frac{\hbar \Omega + E_0 - V_{11}(Q_0)}{f_{1\sigma}}\right]^2\right\} \sum_n \chi_n \delta(\Omega_{n0} - \Omega) = K_0(\Omega) \sum_n \chi_n \delta(\Omega_{n0} - \Omega), \\ \chi_n^{-1} &= 1 + \frac{\omega_1(E_n)}{\omega_2(E_n)} \frac{1 + |M_n|^2 + 2|M_n|\cos(2\chi_{1n} + 2\varphi_n + \arg M_n)}{1 - |M_n|^2}. \end{aligned} \quad (16)$$

Here  $K_0(\Omega)$  is the envelope of the absorption band for the non-interacting terms.

In the case of negligibly weak term coupling formula (16) goes over into the known expression for broad molecular absorption bands.<sup>[5]</sup> In the case of a coupling of intermediate strength, the interference terms in the scattering by the quasicrossing region manifest themselves not only in the irregular arrangement of the absorption lines, but, according to (16), lead also to beats in the intensities of these lines. The singularities of the absorption coefficients are determined by the matrix elements of the two-channel inelastic-scattering  $S$ -matrix, which can be calculated by well-developed numerical procedures.<sup>[6,7]</sup> If, however, the level of the energy satisfies the condition

$$\left| \frac{(2m)^{1/2} [E_n - V_{ii}(Q_0)]^{1/2} (f_2 - f_1)}{\hbar f_2 f_1} \right| \gg 1 \quad (17)$$

( $-f_i$  is the slope of the  $i$ -th term at the crossing point), we can obtain an asymptotic expression that accounts for the spectrum and for the intensities of the individual lines.

To solve the system (2) near  $Q_*$  we retain only the terms that are linear in  $x = Q - Q_*$  in the expansion of the potentials  $V_{ii}(Q)$  in the region of the quasicrossing point (the linear-term approximation). Changing over in the system (2) to the momentum representation

$$u_i(p) = \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{+\infty} dp \exp\left(-\frac{ipx}{\hbar}\right) \Phi_i(x), \quad (18)$$

we obtain

$$\begin{aligned} \left(\frac{p^2}{2m} - E\right) u_1 - i\hbar f_1 \frac{du_1}{dp} &= V u_2, \quad \left(\frac{p^2}{2m} - E\right) u_2 - i\hbar f_2 \frac{du_2}{dp} = V u_1; \\ V &= -V_{12}(Q_*), \quad E = E - V_{11}(Q_*) = E - V_{22}(Q_*). \end{aligned} \quad (19)$$

We put for concreteness  $f_{1,2} > 0$  and  $f_2 > f_1$ . Let

$$t = \frac{2\alpha p}{F\hbar}, \quad \alpha = \frac{2mV}{\hbar^2}, \quad a^2 = \frac{F\Delta F}{8\alpha^3}, \quad b^2 = \frac{\varepsilon\Delta F}{2\alpha F}, \quad (20)$$

$$F = \frac{2m}{\hbar^2}(f_1 f_2)^{1/2}, \quad \Delta F = \frac{2m}{\hbar^2}(f_2 - f_1), \quad \varepsilon = \frac{2mE}{\hbar^2}.$$

We seek  $u_i(p)$  in the form

$$u_{1,2}(p) = \left(\frac{1}{f_{1,2}m}\right)^{1/2} A_{1,2}(p) \exp\left\{\frac{i}{\hbar f_{1,2}}\left(Ep - \frac{p^2}{2m}\right)\right\}, \quad (21)$$

$$A_{1,2}(p) = B_{1,2}(t) \exp\{\pm i^{1/2} i^{1/2} (a^2 t^2 - b^2 t)\}. \quad (22)$$

The wave function  $\Phi_i(x)$  are given, according to (18), by

$$\Phi_i(x) = \left(\frac{1}{2\pi\hbar m f_i}\right)^{1/2} \int_{-\infty}^{+\infty} dp A_i(p) \exp\left\{\frac{i}{\hbar}\left[px + \frac{1}{f_i}\left(Ep - \frac{p^2}{2m}\right)\right]\right\}. \quad (23)$$

As  $x \rightarrow -\infty$  the functions  $\Phi_i(x)$  decreases exponentially, owing to our choice of the integration contour in (18). If  $x \rightarrow +\infty$ , then the integral (23) has saddle points  $p_i(x) = \pm[2m(E + f_i x)]^{1/2}$  and we have the following asymptotic expressions for  $\Phi_i(x)$ :

$$\begin{aligned} \Phi_i(x) \xrightarrow{x \rightarrow +\infty} & \frac{A_i(+\infty)}{[p_i(Q)]^{1/2}} \exp\left[\frac{i}{\hbar} \int_{Q_i}^Q dQ' p_i(Q') - \frac{i\pi}{4}\right] \\ & + \frac{A_i(-\infty)}{[p_i(Q)]^{1/2}} \exp\left[-\frac{i}{\hbar} \int_{Q_i}^Q dQ' p_i(Q') + \frac{i\pi}{4}\right], \quad (24) \\ A_i(\pm\infty) & = \lim_{p \rightarrow \pm\infty} A_i(p). \end{aligned}$$

Comparing (24) with (3), we get

$$A_i^* = A_i(\pm\infty). \quad (25)$$

The substitutions (21) and (22) reduce the system (19) to

$$\begin{aligned} \frac{d^2 B_2}{dt^2} + \left[\frac{1}{4} + \frac{1}{4}(a^2 t^2 - b^2)^2 - ia^2 t\right] B_2 &= 0, \\ B_1 &= -\left[2i \frac{dB_2}{dt} + (a^2 t^2 - b^2) B_2\right]. \quad (26) \end{aligned}$$

Equations (26), as is well known, have no analytic solutions in the entire range of variation of  $t$ . We confine ourselves therefore to an investigation of the absorption coefficient  $K(\Omega)$  in the frequency region satisfying the condition (17) ( $E_n = E_0 + \hbar\Omega$ ), which means a large difference between the actions along the paths  $Q_1 Q_*$  and  $Q_2 Q_*$ . (See Fig. 1) for the motion in the potential wells  $V_{11}(Q)$  and  $V_{22}(Q)$ , respectively. The case  $E_0 + \hbar\Omega - V_{11}(Q_*)$ , shown in Fig. 1, is of greatest interest because the singularities that arise in the shape of the absorption band are quite substantial. In the case of the inverse inequality, the quasicrossing point near which the transition from term to term takes place is in the region below the barrier, and for frequencies satisfying the condition (17) the corrections to the spectrum and absorption coefficient turn out to be exponentially small.

The condition (17) makes it possible to use the WKB method for the solution of Eqs. (26). We obtain

$$\begin{aligned} B_2(t) \approx & C_2 \left[\frac{t-b/a}{t+b/a}\right]^{i\gamma} \exp\left[\frac{i}{2}\left(\frac{a^2 t^2}{3} - b^2 t\right)\right] \\ & - \frac{C_1}{2a^2} \left[\frac{t-b/a}{t+b/a}\right]^{-i\gamma} \frac{1}{t^2 - (b/a)^2} \exp\left[-\frac{i}{2}\left(\frac{a^2 t^2}{3} - b^2 t\right)\right]; \quad (27) \end{aligned}$$

$\gamma = 1/8ab$ ;  $C_{1,2}$  are constants independent of  $t$ .

In the derivation of (27) we assumed for simplicity, besides (17), that  $b^4 \gg 1$ , i.e.,

$$\frac{1}{4} \left[ \frac{E_0 + \hbar\Omega - V_{11}(Q_*)}{V_{12}(Q_*)} \right]^2 \frac{(f_2 - f_1)^2}{f_1 f_2} \gg 1. \quad (28)$$

Depending on the system parameters, the minimal frequency, starting with which the foregoing asymptotic estimates are valid, is determined either by (17) or by (28). The WKB approximation for Eq. (26) is violated near the points  $t = \pm b/a$  ( $p = \pm(2mE)^{1/2}$ ). Joining together the asymptotic forms (27) with the exact solutions of (26) in the vicinity of these points, it is easy to obtain the parameters of the S matrix (6) (see the Appendix):

$$\begin{aligned} \varphi &= 0, \quad \varphi_1 = \pi/2, \\ \theta &= -\frac{2}{3} \frac{b^4}{a} - 2\gamma \ln \frac{2b}{a} + \arg \Gamma(i\gamma) + \gamma \ln 4\gamma + \frac{\pi}{4} \\ p &= e^{-2\pi\gamma}, \end{aligned} \quad (29)$$

where

$$2\pi\gamma = \frac{\pi V^2}{\hbar(f_2 - f_1)} \left(\frac{2m}{E}\right)^{1/2}$$

is the Landau-Zener parameter.

The condition (17) leads to  $\theta \gg 1$  in the region of applicability of formulas (29). If  $2\pi\gamma \ll 1$ , then the corrections calculated for the spectrum with the aid of (10) coincide with the result of the ordinary perturbation theory concerning the term interaction. In the case of large values of the Landau-Zener parameter, Eq. (10) jointly with (29) gives, in the region of applicability of (29), the correct position of the adiabatic levels as well as the nonadiabatic corrections for these levels. At energies satisfying the intermediate coupling condition ( $2\pi\gamma \sim 1$ ), the above-mentioned interference singularities appear in the positions and intensities of the absorption lines (the results of the numerical calculations will be given below).

2. We proceed to the case of laser-induced quasicrossing. Consider the absorption of weak light on going from the ground term 0 to a system of two excited terms 1 and 2 coupled by a strong electromagnetic field  $\mathcal{E}$  of frequency  $\Omega_0$  (see Fig. 2). We consider the part of the band corresponding to absorption by the term 2. Assume that the proper crossing of the terms 1 and 2 is energywise remote from the spectral region of interest to us.

The wave functions  $\Phi_i(Q, t)$  ( $i = 1, 2$ ) of the excited state satisfy the system of equations

$$\begin{aligned} i\hbar \frac{\partial \Phi_{1,2}}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \Phi_{1,2}}{\partial Q^2} - W_{11,22}(Q, t) \Phi_{1,2} - W_{12,21}(Q, t) \Phi_{2,1}, \\ W_{ij}(Q, t) = V_{ij}(Q) + d_{ij} \mathcal{E} \cos \Omega_0 t, \quad i, j = 1, 2. \quad (30) \end{aligned}$$

We consider for simplicity the case when the molecule has no dipole moments in the excited states 1 and 2 ( $d_{11} = d_{22} = 0$ ), but  $d_{12} \neq 0$ . We seek the solution of the system (30) in the form

$$\Phi_{1,2}(Q, t) = e^{-iE_0 t / \hbar} \sum_{l=-\infty}^{+\infty} e^{-i\Omega_0 l t} \Phi_{1,2}^{(l)}(Q). \quad (31)$$

Substituting (31) in (30), we obtain an infinite system of

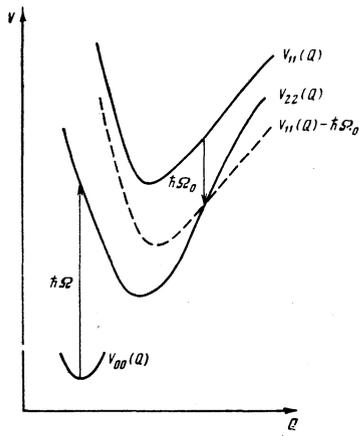


FIG. 2. Quasicrossing induced by a laser (the dashed curve shows the photon replica of term 1).

coupled equations:

$$\frac{\hbar^2}{2m} \frac{d^2 \Phi_{1,2}^{(s)}}{dQ^2} + (E + s\hbar\Omega_0 - V_{11,22}(Q)) \Phi_{1,2}^{(s)} = V_{12,21}(Q) \Phi_{2,1}^{(s)} + 1/2 d_{12,21} (\Phi_{2,1}^{(s+1)} + \Phi_{2,1}^{(s-1)}). \quad (32)$$

By suitable choice of the frequency  $\Omega_0$  (see Fig. 2) we arrange to have, in the region of the classical turning points corresponding to the spectral region of interest to us, a root of the equation

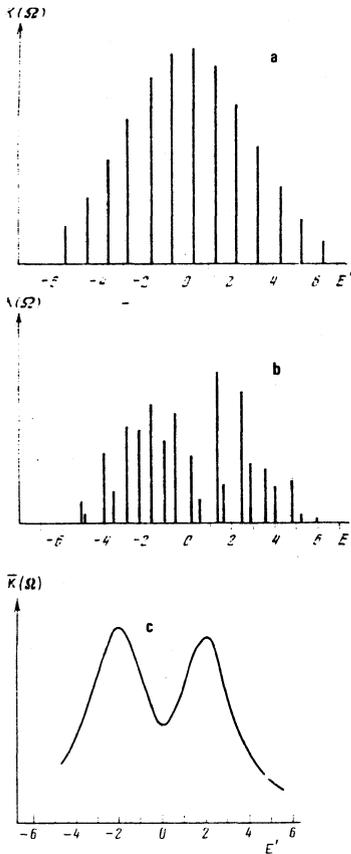


FIG. 3. Result of numerical calculation of the absorption spectrum in the case  $\kappa_{1,2}(E) = \pi(E - E_{01,2})/\hbar\omega_{1,2}$ ,  $\hbar\omega_1/\hbar\omega_2 = 0,7$ ,  $f_1\sigma_0/\hbar\omega_1 = 3(\sigma_0 = (\hbar/m\omega_0)^{1/2})$ ;  $E' = [\hbar\Omega + E_0 - V_{11}(Q_g)]/\hbar\omega_1$ . (a) Case of negligibly small coupling of the terms 1 and 2; (b) case of intermediate coupling:  $V_{12}(Q_*)/\hbar\omega_1 = 1$ ,  $(V_{11}(Q_g) - V_{11}(Q_*))/\hbar\omega_1 = 20$ ,  $f_1\sigma_1/\hbar\omega_1 = 1$ ,  $f_2\sigma_1/\hbar\omega_1 = 3(\sigma_1 = (\hbar/m\omega_1)^{1/2})$ ; (c) absorption spectrum averaged over an energy interval  $\sim 2\hbar\omega_1$ .

$$V_{11}(Q) - V_{22}(Q) = \pm \hbar\Omega_0, \quad (33)$$

corresponding to the upper sign (for the potential-curve arrangement corresponding to Fig. 2). Since the proper crossing of the terms 1 and 2 is far away, that root of (33) which corresponds to the lower sign (antiresonant coupling) lies in the classically forbidden region for the spectral region of the quasi-energy  $E$  of interest to us. This leads to an exponentially small coupling between the quasi-energy harmonics  $\Phi_1^{(1)}$ ,  $\Phi_2^{(2)}$  and  $\Phi_2^{(0)}$ ,  $\Phi_1^{(-1)}$ , so that we can uncouple the system (32):

$$\begin{aligned} \frac{\hbar^2}{2m} \frac{d^2 \Phi_1^{(1)}}{dQ^2} + (E + \hbar\Omega_0 - V_{11}(Q)) \Phi_1^{(1)} &= \frac{1}{2} d_{12} \mathcal{E} \Phi_2^{(0)}, \\ \frac{\hbar^2}{2m} \frac{d^2 \Phi_2^{(0)}}{dQ^2} + (E - V_{22}(Q)) \Phi_2^{(0)} &= \frac{1}{2} d_{21} \mathcal{E} \Phi_1^{(1)}. \end{aligned} \quad (34)$$

Equations (34) are perfectly analogous to the system (2) considered above. Consequently the absorption coefficient  $K(\Omega)$  of the probing light, on going to the term 1 in the presence of strong mixing laser radiation, is also determined by a formula similar to (16). It is necessary to put in the asymptotic expressions (29)

$$V = 1/2 |d_{12}| \mathcal{E};$$

$Q_*(\Omega_0)$  is that root of Eq. (33) which corresponds to the upper sign;

$$\begin{aligned} \gamma &= \frac{m^{3/2} |d_{12} \mathcal{E}|^2}{4\hbar (f_2 - f_1) [2(E_0 + \hbar\Omega - V_{11}(Q_*))]^{3/2}}; \\ a^2 &= \frac{(f_1 f_2)^{1/2} (f_2 - f_1) \hbar^2}{8 |d_{12} \mathcal{E}|^2}; \\ b^2 &= \frac{(f_2 - f_1) (E_0 + \hbar\Omega - V_{11}(Q_*))}{(f_1 f_2)^{1/2} |d_{12} \mathcal{E}|}. \end{aligned}$$

Naturally, the slopes of the terms depend on the frequency of the laser radiation in terms of the parameter  $Q_*(\Omega_0)$ .

3. We proceed to a discussion of the results and to an estimate of the possible experimental situation. Figure 3b shows the absorption band obtained by numerical means for the case when the unperturbed spectrum of the diabatic terms  $V_{11}(Q)$ ,  $V_{22}(Q)$  can be regarded as locally equidistant in the vicinity  $Q_*$ , i.e.,

$$\kappa_1(E) = \pi \left( \frac{E - E_{01}}{\hbar\omega_1} \right), \quad \kappa_2(E) = \pi \left( \frac{E - E_{02}}{\hbar\omega_2} \right). \quad (35)$$

The interaction  $V_{12}$  ensures the intermediate character of the coupling within the entire band. Figure 3b confirms the conclusion that the lines have an irregular arrangement and that beats of their intensity are produced. For comparison, Fig. 3a shows the unperturbed absorption spectrum obtained in the case of negligibly weak coupling ( $V_{12} = 0$ ). The interference effects in the scattering on the nonadiabaticity region lead not only to beats in the intensity of the neighboring lines, but to a large scale redistribution of the intensity inside the band. This is evidenced by Fig. 3c, which shows the absorption coefficient averaged over an energy interval  $\sim 2\hbar\omega_1$ .

The two-term model of Fig. 1 is usually resorted to for an explanation of the electron vibrational bands in

molecules, local centers of crystals, and other objects. In the case of negligibly weak coupling of the terms it explains the Gaussian character of the broad bands and the corrections that must be introduced in them to account for anharmonicity and other effects.

In many cases, however, experiment reveals much more complicated optical-spectrum structures with irregular alternation of the maxima, which cannot be explained in the simple model of two non-interacting terms (see, e.g., [8]). One of the possible causes of such complicated structures, in our opinion, may be the effect, investigated in the present article, of non-adiabatic coupling of the terms.

The distinguishing features of this effect, which make it possible to differentiate it from other causes of complex optical spectra (for example, simple superposition of different electron-vibrational bands), may be the following: a) the splitting-off of an irregular fine structure in a limited section of the broad absorption band (including one without structure); b) the strong asymmetry of the absorption bands in luminescence (no interference singularities should be observed in luminescence spectra since the luminescence proceeds as a rule from the ground vibrational level of the excited term, which lies lower in energy than the crossing point). We note that the complicated absorption bands may also stem from the nonadiabatic coupling of two excited terms. It is easy to verify that the aforementioned attributes of the effect are present also in this case.

By way of example, we consider the optical spectra of the molecule of the benzophenone in which, as is well known, [9] it is possible to separate the carbonyl group responsible for the long-wave part of the electron-vibrational bands. The corresponding absorption and emission spectra are shown in Figs. 4a and 4b. Figure 4c shows the arrangement of the ground vibrational

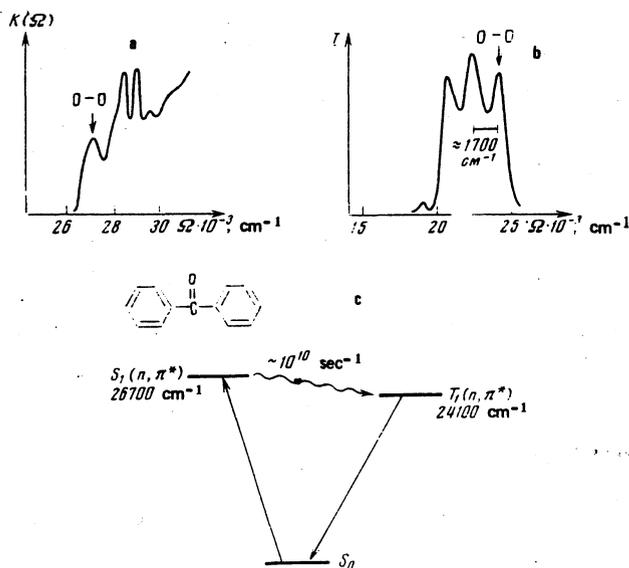


FIG. 4. (a) Absorption spectrum of benzophenone<sup>[10]</sup> mixed with ethanol and ether at 77 K; (b) emission spectrum of benzophenone<sup>[11]</sup> at 77 K,  $I$  is the relative intensity; (c) energy level scheme of the carbonyl group of the benzophenone molecule.<sup>[9]</sup>

levels of the lowest and of the first two excited terms of the carbonyl group of benzophenone.

The emission spectrum (Fig. 4b) has a clearly pronounced vibrational structure with a progression frequency  $1700 \text{ cm}^{-1}$  corresponding to the C=O bond. On the contrary, the absorption spectrum reveals clearly an irregularity both in the arrangement and in the intensities of the individual lines (see Fig. 4a).

It is noted in the literature that the terms  $S_1(n, \pi^*)$  and  $T_1(n, \pi^*)$  have a large spin-orbit coupling that manifests itself in the large rate of the intercombination  $S_1 \rightarrow T_1$  transition and in the complete absence of fluorescence.<sup>[9]</sup>

Thus, the appreciable asymmetry of the emission and absorption bands and the irregular structure of the absorption bands are in good agreement with the foregoing distinguishing attributes of the effect investigated in the present article, and can be interpreted as consequences of a nonadiabatic coupling of the terms  $T_1(n, \pi^*)$ .

A detailed quantitative comparison of theory with experiment is made difficult by the absence of reliable information on the arrangement and shapes of the adiabatic potentials of the excited states, to which the singularities of the absorption spectrum are most sensitive because of the interference character of the effect.

Term crossing, as is well known, plays a decisive role in the predissociation phenomenon.<sup>[4]</sup> A corresponding typical term arrangement is shown in Fig. 5. At an energy above the predissociation threshold ( $E > E_{\text{thr}}$ ) the spectrum of the electron-vibrational system is continuous, a fact that manifests itself in the diffuse character of the absorption spectrum. The spectrum is discrete below the predissociation spectrum, and in the case of intermediate term coupling it should be subject to the singularities described above.

Of definite interest from the experimental point of view is the case of laser-induced quasicrossing, considered in Sec. 2. Let two excited states be dipole-mixed with oscillator strength  $\sim 1$  and let the distance between terms be  $0.5\text{--}1 \text{ eV}$ ; then  $d_{12} \sim 5 \text{ D}$ . Owing to the anharmonicity of the excited states, the distance between levels may be smaller than the ground-state vibrational quantum and the quantity  $|d_{12}| \varepsilon$  becomes com-

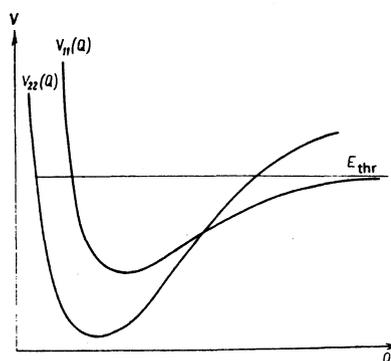


FIG. 5. Molecular-term arrangement typical of predissociation.

parable with it in fields  $\sim 10^5$  V/cm. This value of the field still does not lead to breakdown in sufficiently rarefied molecular gases.<sup>[12]</sup> By varying the frequency of the laser radiation, we can displace the section with the absorption singularities within a broad band. By controlling the radiation intensity (i.e., the coupling of the terms), we can control the irregular part of the band.

## APPENDIX

To satisfy the boundary conditions of the system (26) as  $t \rightarrow \infty$ , it is necessary to put  $C_1 = A_1(-\infty)$ ,  $C_2 = A_2(-\infty)$  in the asymptotic expression (27), which is valid in this region. Near  $t = -b/a$ , expression (27) takes the form

$$B_2(\tau) = C_2(-2b/a)^{i\gamma} \exp(ib^2/3a) \tau^{-i\gamma} \exp(-iab\tau^2/2) - \frac{C_1}{2a^2} \left(-\frac{2b}{a}\right)^{-i\gamma-1} \exp\left(-\frac{ib^2}{3a}\right) \tau^{i\gamma-1} \exp\left(\frac{iab\tau^2}{2}\right), \quad \tau = t + \frac{b}{a}. \quad (\text{A.1})$$

The choice of the cut and of the branch of the power-law function is shown in Fig. 6. On the other hand, near this point the equation for  $B_2(t)$  takes the form

$$\frac{d^2 B_2}{dt^2} + \left[ \frac{1}{4} + a^2 t^2 \tau^2 + iab \right] B_2 = 0. \quad (\text{A.2})$$

The substitution  $z = (2ab)^{1/2} \tau e^{-ia/4}$  reduces (A.2) to the parabolic-cylinder equation:

$$\frac{d^2 B_2}{dz^2} + \left[ (i\gamma-1) + \frac{1}{2} - \frac{z^2}{4} \right] B_2 = 0, \quad (\text{A.3})$$

which has a general solution of the form

$$B_2(z) = \alpha D_{i\gamma-1}(z) + \beta D_{-i\gamma}(-iz). \quad (\text{A.4})$$

Using the well-known asymptotic expressions for the parabolic-cylinder functions<sup>[12]</sup> we can readily obtain the transition matrix of the fundamental WKB system of the waves when  $\tau$  ranges from  $-\infty$  to  $+\infty$ :

$$\begin{pmatrix} -\tau^{-i\gamma} \exp(-iab\tau^2/2) \\ \tau^{i\gamma-1} \exp(iab\tau^2/2) \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 2\gamma e^{2\pi i} [1 - e^{-2\pi i}]^{1/2} e^{-i\theta} \\ 1/2 \gamma^{-1} e^{-2\pi i} [1 - e^{-2\pi i}]^{1/2} e^{i\theta} & e^{-2\pi i} \end{pmatrix} \times \begin{pmatrix} \tau^{-i\gamma} \exp(-iab\tau^2/2) \\ \tau^{i\gamma-1} \exp(iab\tau^2/2) \end{pmatrix} \quad (\text{A.5})$$

In the region of the point  $t = +b/a$  expression (27) is of the form

$$B_2(\tau_i) = C_2 \left(\frac{2b}{a}\right)^{-i\gamma} \exp\left(-\frac{ib^2}{3a}\right) \tau_i^{i\gamma} \exp\left(\frac{iab\tau_i^2}{2}\right) - \frac{C_1}{2a^2} \left(\frac{2b}{a}\right)^{i\gamma-1} \exp\left(\frac{ib^2}{3a}\right) \tau_i^{-i\gamma-1} \exp\left(-\frac{iab\tau_i^2}{2}\right), \quad \tau_i = t - \frac{b}{a}. \quad (\text{A.6})$$

Comparing (A.6) and (A.1) we obtain the matrix of the transition through the region  $-b/a < t < b/a$ :

$$\begin{pmatrix} \tau^{-i\gamma} \exp(-iab\tau^2/2) \\ \tau^{i\gamma-1} \exp(iab\tau^2/2) \end{pmatrix} \rightarrow \begin{pmatrix} e^{\pi i} (2b/a)^{-2i\gamma} \exp(-2ib^2/3a) & 0 \\ 0 & -e^{-\pi i} (2b/a)^{2i\gamma} \exp(2ib^2/3a) \end{pmatrix} \times \begin{pmatrix} \tau_i^{i\gamma} \exp(iab\tau_i^2/2) \\ \tau_i^{-i\gamma-1} \exp(-iab\tau_i^2/2) \end{pmatrix}. \quad (\text{A.7})$$

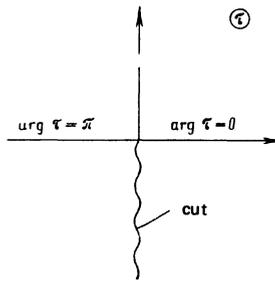


FIG. 6.

In the region of the point  $t = +b/a$  Eq. (26) is reduced by the substitution mentioned above to the form

$$\frac{d^2 B_2}{dz_i^2} + \left[ i\gamma + \frac{1}{2} - \frac{z_i^2}{4} \right] B_2 = 0. \quad (\text{A.8})$$

The matrix of the transition through the region  $t \approx b/a$  is of the form

$$\begin{pmatrix} \tau_i^{i\gamma} \exp(iab\tau_i^2/2) \\ \tau_i^{-i\gamma-1} \exp(-iab\tau_i^2/2) \end{pmatrix} \rightarrow \begin{pmatrix} e^{-2\pi i} & 2\gamma e^{-\pi i} [1 - e^{-2\pi i}]^{1/2} e^{i\theta} \\ 1/2 \gamma^{-1} e^{\pi i} [1 - e^{-2\pi i}]^{1/2} e^{-i\theta} & 1 \end{pmatrix} \times \begin{pmatrix} \tau_i^{i\gamma} \exp(iab\tau_i^2/2) \\ \tau_i^{-i\gamma-1} \exp(-iab\tau_i^2/2) \end{pmatrix}. \quad (\text{A.9})$$

Multiplying now the transformations (A.5), (A.7), and (A.9), and substituting formula (A.1), we easily find that the S matrix takes the form (6) with the parameters (29).

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