

Resonance Raman scattering by a predissociative state

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The resonance scattering of light by a predissociative state is described in the model of four intersecting terms $A-(1,2)-B$, with strong coupling between terms 1 and 2. A closed representation of Green's function is constructed for the model in which the intermediate electron terms 1 and 2 are strongly bound. The transition amplitude $I_{A(1,2)B}$ is found in the quasiclassical approximation. Resonant scattering of light by the predissociated ${}^3\Pi_{0u}$ state of interhalogen molecules is considered in detail.

With all the obvious differences between chemical reactions and radiative transitions in molecules, there is an undoubted analogy between the elementary mechanisms in these processes. In both cases, we have to deal with the motion of nuclei on certain potential surfaces, and with transitions when these surfaces intersect. In chemical reactions, the nuclei move due to molecular terms whereas, in radiative processes, they move due to terms (quasiterms) of the molecule dressed with the photon "coat" $U(x) + N\hbar\omega$, where $U(x)$ is the molecular term, x represents the position of the nuclei, and ω is the photon frequency. The quasienergy picture¹ enables us to look upon radiative processes in molecules as, in many ways, similar to nonadiabatic transitions in atomic and molecular collisions.

In collisions, the molecular term picture is uniquely determined by the nature of the colliding bodies insofar as their interaction is concerned. In radiative processes, the situation is more varied. The relative positions of the quasiterms and their interactions in crossing regions depend on the frequency and intensity of the light wave, which can be readily varied under experimental conditions.

The usual electronic-vibrational transition scheme for the absorption or emission of light by a molecule in the quasienergy representation has the same appearance as the two-term model in the theory of slow atomic collisions (Landau-Zener problem²). In the absence of a direct coupling between the initial (A) and final (B) states, e.g., as a consequence of symmetry selection rules, the transition can proceed through a further term C . Transitions in a system of three (or more) crossing terms $A-C-B$ are complex nonadiabatic transitions and describe forbidden transitions in slow atomic collisions and two-photon processes in molecules.³⁻⁵ A more complex situation arises in the case of multichannel reactions, where we have to deal with transitions in a system of four or more crossing terms. In radiative processes, the four-term model describes the scattering of light in the absorption band of two strongly coupled electronic states, for example, scattering on a predissociated term. The four-term model takes into account two features of the multichannel problem, namely, interference between optically active electronic states (reaction channels) and distortion of the shape of these terms, right up to a change in the nature of adiabatic-diabatic terms under the influence of coupling.

We shall consider the theory of complex nonadiabatic transitions $A-(1,2)-B$ with strong coupling between electronic states 1 and 2, and its applications in the spectroscopy of resonance Raman scattering (RRS) by diatomic molecules. We shall obtain a quasiclassical expression for the transition amplitude in the four-term system

$$I_{A(1,2)B} = \langle A | V \mathcal{G} V | B \rangle \quad (1)$$

in second-order perturbation theory in the weak coupling between the terms $A-(1,2)$ and $(1,2)-B$ in the presence of strong coupling between the intermediate terms 1 and 2, where $|A\rangle, |B\rangle$ are the electron-nuclear wave functions, \mathcal{G} is the Green's function for the model of two strongly-coupled electron terms 1 and 2, and V is the radiative coupling operator.

The expression we shall obtain is the solution of the direct and inverse problem of the theory of two-photon spectra in the presence of a strong electron-nuclear coupling. The resonant scattering of light on the predissociated state of molecules of the form Br_2 , IBr , and other interhalogens is discussed in detail.

TWO-CHANNEL GREEN FUNCTIONS

The analytic properties of multichannel Green's functions in the theory of nonadiabatic coupling are of independent interest. We shall assume that nonadiabatic interactions can be as strong as desired but, essentially, they are localized in a limited region of space (Landau-Zener model).

In the adiabatic approximation, \mathcal{G} is the convolution of electronic and nuclear Green's functions, so that

$$\mathcal{G}(x, r; x', r') = \sum_n g_{nn}(x, x') |n\rangle \langle n|, \quad (2)$$

where $g_{nn}(x, x')$ is the Green's function for the nuclear motion in the adiabatic potential $U_{nn}(x)$, $|n\rangle$ is the electron wave function for fixed nuclei, and x, r are the nuclear and electronic coordinates, respectively. This sum is evaluated over the complete spectrum of adiabatic electronic states n . When the dynamics of the electron-nuclear coupling is taken into account, we have

$$\mathcal{G}(x, r; x', r') = \sum_{n,m} G_{nm}(x, x') |n\rangle \langle m|. \quad (3)$$

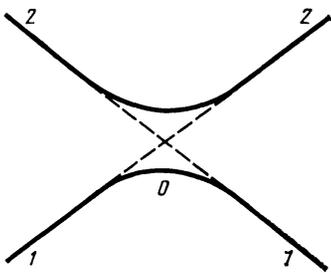


FIG. 1. Diabatic 2-1, 1-2, and adiabatic 1-1, 2-2 terms.

The off-diagonal terms $m \neq n$ characterize nonadiabatic transitions. Motion in the reaction coordinate is assumed one-dimensional, and we consider $\mathcal{G}(x, r; x', r')$ for the two-term model $n, m = 1, 2$ of a general form on the assumption that the source, the observer, and the turning point are sufficiently distant from the nonadiabatic region $x \sim 0$.

Figure 1 shows the crossing terms and defines the branch labels. Outside the region of interaction, the function \mathcal{G} is conveniently written in the form

$$\mathcal{G} = \sum_n \mathcal{G}_n, \quad (4)$$

where

$$[E - H(x, r)] \mathcal{G}_n(x, r; x', r') = \delta(x - x') |n\rangle \langle n|. \quad (5)$$

The component \mathcal{G}_n of the solution can be interpreted as the influence function of a point source located on the term n . In the region $x' < x, x' < 0$ one of the solutions of (5) can then be written in the form

$$\mathcal{G}_{10}(x, r; x', r') = \frac{1}{\Delta_{10}} \Psi_{10}^{out}(x', r') \Psi_{10}^{in}(x, r), \quad (6)$$

where

$$\Psi_{10}^{out}(x', r') = f_{10}(x') |1\rangle \quad (7)$$

is a unit wave departing from the interaction region along the 1-0 branch (plus a reflected wave in the case of a closed 1-0 channel). The linearly independent solution of the multichannel equation, given by

$$\Psi_{10}^{in}(x, r) = [f_1^+(x) + R_{11}^{+-} f_1^-(x)] \langle 1| + R_{12}^{+-} f_{20}(x) \langle 2| \quad (8)$$

for $x < 0$ and by

$$\Psi_{10}^{in}(x, r) = R_{11}^{++} f_{01}(x) \langle 1| + R_{12}^{++} f_{02}(x) \langle 2| \quad (9)$$

for $x > 0$, describes the propagation of a unit wave incident on the interaction region along the 1-0 channel, and the subsequent branching for the solution that is regular on segments of the 0-1, 0-2, and 2-0 terms. The functions are solutions of the single-channel Schroedinger equation with the corresponding asymptotic behavior: f_n^+ and f_n^- are unit waves propagating over the term n in the positive and negative directions, respectively, and f_{01}, f_{02}, f_{20} are solutions that are regular on the corresponding branches of the 0- n and n -0 terms, normalized to the unit component of the wave departing from $x = 0$. Next,

$$\Delta_{10} = \frac{1}{2} \left[f_{10} \frac{d}{dx} (f_1^+ + R_{11}^{+-} f_1^-) - (f_1^+ + R_{11}^{+-} f_1^-) \frac{d}{dx} f_{10} \right] \quad (10)$$

is the Wronskian of the nuclear solutions, where $\Delta_{10} = i$ for an open channel (for which $f_{10} = f_1^-$). The transition coefficients form the unitary matrix (R_1^+) . If we suppose that this matrix is known, we can continue the solution of (6) beyond the region of interaction ($x > 0$).

The point-source influence functions $\mathcal{G}_{01}, \mathcal{G}_{02}$, and \mathcal{G}_{20} for channels 0-1, 0-2, and 2-0 will be determined by analogy. The conditions of unitarity and symmetry for all the transition matrices (R_n^\pm) have the form

$$\begin{aligned} R_{nm}^{--} / \Delta_{0n} &= R_{mn}^{++} / \Delta_{m0}, \\ R_{nm}^{-+} / \Delta_{0n} &= R_{mn}^{-+} / \Delta_{0m}, \\ R_{nm}^{+-} / \Delta_{n0} &= R_{mn}^{+-} / \Delta_{m0}. \end{aligned} \quad (11)$$

These relationships ensure that the fluxes incident at $x = 0$ and leaving $x = 0$ are equal for an arbitrary position x' of the source, and that the situation is symmetric under time reversal. This also means that there are no additional particle sources within the interaction region.

The representation of the auxiliary solutions $\mathcal{G}_{01}, \mathcal{G}_{02}$, and \mathcal{G}_{20} in terms of the elements of the matrices (R_n^\pm) was found by considering the physically intuitive picture of flux branching in the region of $x \sim 0$. It is obvious that, for $xx' < 0$, the positions of the source and observer are not equivalent, i.e.,

$$\mathcal{G}_{0n}(x, r; x', r') \neq \mathcal{G}_{0n}(x', r'; x, r),$$

as in the case of a ray crossing the separation boundary between two media.

It is readily seen that the linear combination of all the auxiliary solutions

$$\mathcal{G}(x, r; x', r') = [\mathcal{G}_{01}(x, r; x', r') + \mathcal{G}_{02}(x, r; x', r')] \Theta(x') + [\mathcal{G}_{10}(x, r; x', r') + \mathcal{G}_{20}(x, r; x', r')] \Theta(-x'), \quad (12)$$

where $\Theta(y) = 1$ and $\Theta(-y) = 0$ for $y > 0$, has the correct asymptotic behavior, is symmetric under the interchange of x and x' , and constitutes a two-channel Green's function.

The nuclear components of the multichannel Green's function are symmetric under the simultaneous interchange of the nuclear coordinates and electronic indices

$$\mathcal{G}_{nm}(x, x') = \mathcal{G}_{mn}(x', x), \quad (13)$$

and constitute bilinear combinations of adiabatic (diabatic) solutions f_n^\pm outside the nonadiabatic region, with coefficients that change when the argument x or x' passes through the quasicrossing point $x = 0$.

The relationships given by (3)-(13) define the multichannel Green's functions in the one-dimensional model of atomic collisions in terms of single-channel solutions. The single-channel solutions describe different ways of crossing the strong interaction region along diabatic and adiabatic trajectories.

GREEN'S FUNCTIONS IN THE QUASICLASSICAL REGION

The above expressions enable us to use familiar quantum-mechanical models as the single-channel solutions.

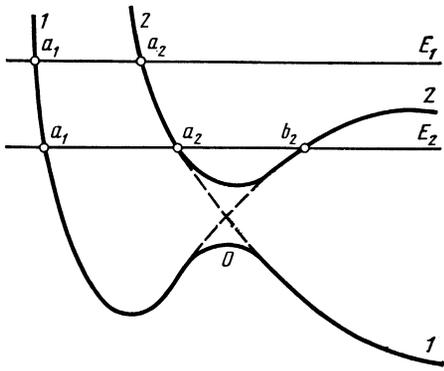


FIG. 2. Predissociation (E_2) and interference (E_1) during molecular-term crossing.

From now on, we shall confine our attention to the simple quasiclassical situation.

The matrix (R_n^\pm) is determined in the quasiclassical situation in accordance with the usual rules for crossing the nonadiabatic region,⁶ and its form depends on the relationship of the crossing region and turning points. Figure 2 illustrates typical crossing of terms with different slopes. High energies

$$V > U_{11}(\infty), \quad U_{22}(\infty)$$

correspond to the scattering problem, and lower energies to predissociation and resonances.

When one of the channels is closed and the energy E lies above the crossing point of diabatic terms, the nuclear components G_{mn} have the following form for $x, x' < 0$ ($\hbar = \mu = 1$)

$$G_{nn}(x, x') = \frac{|\alpha|^2}{\Delta} g_{nn} e^{-iS_{12}} \cos S_{22} + \frac{1}{\Delta} e^{-2\delta} g_{nm} e^{-iS_{22}} \cos S_{12}, \quad (14)$$

$$G_{mn}(x, x') = \frac{i|\alpha|}{2\Delta} e^{-\delta} f_{m0}(x) f_{n0}(x'), \quad (15)$$

where S_{nm} is the classical action given by

$$S_{nm}(\lambda, \mu) = \int_{\lambda}^{\mu} p_{nm} dx, \quad p_{nm} = [2(E - U_{nm})]^{1/2}$$

for diabatic terms U_{nm} and by

$$S_{nn}(\lambda, \mu) = \int_{\lambda}^{\mu} \left[p_{nn} + \left(\frac{\pi}{2} - (-1)^n \varphi \right) \delta(x) \right] dx$$

$$\varphi = \frac{\pi}{4} - \arg \Gamma \left(i \frac{\delta}{\pi} \right) + \frac{\delta}{\pi} \left[\ln \left(\frac{\delta}{\pi} \right) - 1 \right],$$

for adiabatic terms U_{nn} . In these expressions, φ is the quantum phase equal to $\pi/2$ in the adiabatic limit and $3\pi/4$ in the diabatic limit.⁷ Moreover,

$$|\alpha|^2 = 1 - e^{-2\delta}, \quad (16)$$

$$\Delta = e^{-iS_{12}} \cos S_{22} + i e^{-2\delta} \sin(S_{12} - S_{22});$$

and the nonadiabaticity factor is given by

$$\delta = \frac{1}{2i} \int_{z_0^*}^{z_0} (p_{11} - p_{22}) dz, \quad (17)$$

where z_0, z_0^* are the crossing points of adiabatic terms in complex space,

$$f_{m0} = \frac{2}{p_{mm}^{1/2}} \cos \left[S_{mm}(a_m, x) - \frac{\pi}{4} \right], \quad (18)$$

and g_{nm} are the quasiclassical single-channel Green's functions found in Ref. 5 and given by

$$g_{n1} = \frac{-2i}{[p_{n1}(x) p_{n1}(x')]^{1/2}} \cos \left[S_{n1}(a_n, x_{<}) - \frac{\pi}{4} \right] \times \exp \left\{ i S_{n1}(a_n, x_{>}) - i \frac{\pi}{4} \right\} \quad (19)$$

for infinite motion along the 1-1, 2-1 terms and by

$$g_{n2} = \frac{-2}{[p_{n2}(x) p_{n2}(x')]^{1/2}} \frac{1}{\cos S_{12}} \cos \left[S_{n2}(a_n, x_{<}) - \frac{\pi}{4} \right] \times \cos \left[S_{n2}(x_{>}, b_2) - \frac{\pi}{4} \right] \quad (20)$$

for finite motion along 1-2, 2-2 terms. For brevity, we have used $S_{nm} = S_{nm}(a_n, b_m)$ to denote the action in the case of motion due to the term U_{nm} between the turning points a_n and b_m .

Thus, the nuclear components of the multichannel Green's function constitute a linear combination of diabatic and adiabatic Green's functions (14) plus the mixed product of the solutions (15), which include backward inelastic scattering.

The zeros of the Wronskian Δ determine the position and lifetime of the predissociated states. Variation of δ affects the shift ΔE_v and the broadening Γ_v of the level E_v , until there is a change in the nature of the resonance (diabatic or adiabatic). In the limiting case, when $\delta \ll 1$, we find that

$$\Delta = (-1)^{v+1} \frac{2\pi}{\omega_{12}} e^{-iS_{12}} [E - (E_v + \Delta E_v - i\Gamma_v)],$$

$$\Delta E_v = \delta \frac{\omega_{12}}{2\pi} \sin 2S_{22}, \quad (21)$$

$$\Gamma_v = 2\delta \frac{\omega_{12}}{2\pi} \cos^2 S_{22}, \quad \frac{2\pi}{\omega_{12}} = \int_{a_1}^{b_2} \frac{dx}{p_{12}},$$

where E_v is determined by the Bohr quantization condition $S_{12}(a_1, b_2) = \pi(v + \frac{1}{2})$ for motion along the diabatic term 1-2. The $\delta = 0$ Green function is equal to the sum of diabatic solutions:

$$\mathcal{G} = \mathcal{G}_{12} + \mathcal{G}_{21}.$$

In the opposite limit, when $\delta \gg 1$, we obtain

$$\Delta = (-1)^{v+1} \frac{2\pi}{\omega_{22}} e^{-iS_{12}} [E - (E_v + \Delta E_v - i\Gamma_v)],$$

$$\Delta E_v = \frac{\omega_{22}}{2\pi} e^{-2\delta} \sin 2S_{12}, \quad (22)$$

$$\Gamma_v = 2 \frac{\omega_{22}}{2\pi} e^{-2\delta} \cos^2 S_{12}, \quad \frac{2\pi}{\omega_{22}} = \int_{a_2}^{b_2} \frac{dx}{p_{22}}.$$

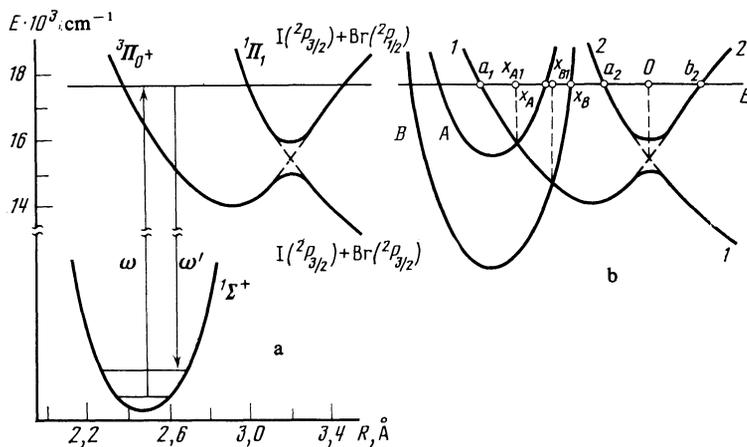


FIG. 3. RRS in a system of terms with strong nonadiabatic bonding (IBr molecule): a—molecular-term representation, b—quasiterm representation.

The quantity E_v is determined by the Bohr quantization condition $S_{22}(a_2, b_2) = \pi(v + \frac{1}{2})$ for motion along the adiabatic term 2-2. The Green's function for $\delta = \infty$ is equal to the sum of adiabatic solutions:

$$\mathcal{G} = \mathcal{G}_{11} + \mathcal{G}_{22}.$$

Near the pole, the resonance term of the Green's function is the product of the wave functions of quasistationary states. For $x, x' < 0$, the Green's function has the form

$$\begin{aligned} \mathcal{G} &= |n\rangle \langle n| g_{n1}(x, x') + [E - (E_v + \Delta E_v - i\Gamma_v)]^{-1} \\ &\times \left\{ |m\rangle \varphi_v^{m2}(x) + |n\rangle (-1)^v \frac{\Delta E_v - i\Gamma_v}{(2\Gamma_v)^{1/2}} f_{m0}(x) \right\} \\ &\times \left\{ \varphi_v^{m2}(x') \langle m| + (-1)^v \frac{\Delta E_v - i\Gamma_v}{(2\Gamma_v)^{1/2}} f_{m0}(x') \langle n| \right\}, \quad (23) \end{aligned}$$

which is valid to within terms $\sim \Gamma$, where $\varphi_v^{m2}(x)$ is the nuclear wave function for the binding term U_{m2} ; $m = 1$, $n = 2$ in the diabatic limit ($\delta \ll 1$) and $m = 2$, $n = 1$ in the adiabatic limit ($\delta \gg 1$).

RRS IN THE HIGHLY NONADIABATIC REGION

Figure 3 shows the Raman scattering scheme in the region of the transition to the predissociated state: (a) in the molecular-term representation and (b) in the quasiterm representation. The term scheme is typical for halogen and interhalogen molecules.

The above expression for the two-channel Green's function enables us to find the transition amplitude $I_{A(1,2)B}$ (1) in an analytic form. The principal contribution to the integral (1) is provided by the regions of crossing of quasiterms A and B with term 1. Assuming that all the term-crossing points are distant from one another, we can evaluate (1) by the method of steepest descents. For the case shown in Fig. 3, we have

$$\begin{aligned} I_{A(1,2)B} &= I_{A(1-1)B} \frac{1 - e^{-2\delta}}{\Delta} e^{-iS_{12}} \cos S_{22} \\ &+ I_{A(1-2)B} \frac{e^{-2\delta}}{\Delta} e^{-iS_{22}} \cos S_{12}, \quad (24) \end{aligned}$$

$$I_{A(1-1)B} = \langle A | V \mathcal{G}_{11} V | B \rangle, \quad I_{A(1-2)B} = \langle A | V \mathcal{G}_{12} V | B \rangle.$$

The adiabatic 1-1 and diabatic 1-2 scattering amplitudes are as follows:

$$\begin{aligned} I_{A(1-1)B} &= \left(\frac{V_{A1}}{(p\Delta U')^{1/2}} \right)_{A1} \left(\frac{V_{1B}}{(p\Delta U')^{1/2}} \right)_{1B} \\ &\times \cos \left[S(a_1, x_{A1}, x_A) - \frac{\pi}{4} \right] \exp \left[iS(a_1, x_{B1}, x_B) - i \frac{\pi}{4} \right], \quad (25) \end{aligned}$$

$$\begin{aligned} I_{A(1-2)B} &= \left(\frac{V_{A1}}{(p\Delta U')^{1/2}} \right)_{A1} \left(\frac{V_{1B}}{(p\Delta U')^{1/2}} \right)_{1B} \frac{1}{\cos S_{12}} \\ &\times \cos \left[S(a_1, x_{A1}, x_A) - \frac{\pi}{4} \right] \cos \left[S(x_B, x_{1B}, b_2) - \frac{\pi}{4} \right], \quad (26) \end{aligned}$$

which was shown previously in Refs. 3 and 4. In these expressions, V_{A1} and V_{1B} are the matrix elements of the radiative transitions, and $(\Delta U')_{A1}$ and $(\Delta U')_{1B}$ are the differences between term slopes, calculated at the crossing point.

The intramolecular interaction gives rise to interference between the diabatic and adiabatic scattering amplitudes. When the excitation frequency ω is close to the quasicrossing point (the difference is of the order of the splitting of terms 1 and 2), the interaction parameter is large: ($2\delta \gtrsim 1$). In the adiabatic limit $2\delta \gg 1$, and the main role is played by scattering by the repulsive adiabatic term 1-1, so that $I_{A(1,2)B} \approx I_{A(1-1)B}$ and the scattering amplitude has no poles and varies smoothly with exciting frequency.

For excitation frequencies that are distant from the quasicrossing region, the interaction parameter is small and, in the diabatic limit ($2\delta \ll 1$), the amplitude $I_{A(1,2)B}$ becomes identical with the scattering amplitude for the 1-2 diabatic term. Near resonance with the quasistationary state, the principal contribution to the amplitude $I_{A(1,2)B}$ is provided by the pole term. The contribution of this term, given by (23), is equal to the estimate based on the Fano method:⁸

$$\begin{aligned} |I_{A(1,2)B}^{\text{Fano}}|^2 &= \left| \int dE \frac{\Gamma_v/\pi}{E - (E_0 + \omega) + i\sigma} \frac{\langle n | \varphi \rangle \langle \varphi | 0 \rangle}{(E - E_v - \Delta E_v)^2 + \Gamma_v^2} \right|_{\sigma \rightarrow 0}^2 \\ &= \frac{|\langle n | \varphi \rangle \langle \varphi | 0 \rangle|^2}{(E_0 + \omega - E_v - \Delta E_v)^2 + \Gamma_v^2}. \quad (27) \end{aligned}$$

Figure 4 shows the RRS spectrum of the IBr molecule and its dependence on the exciting frequency ω , calculated from (24)–(26). The molecular terms and the matrix ele-

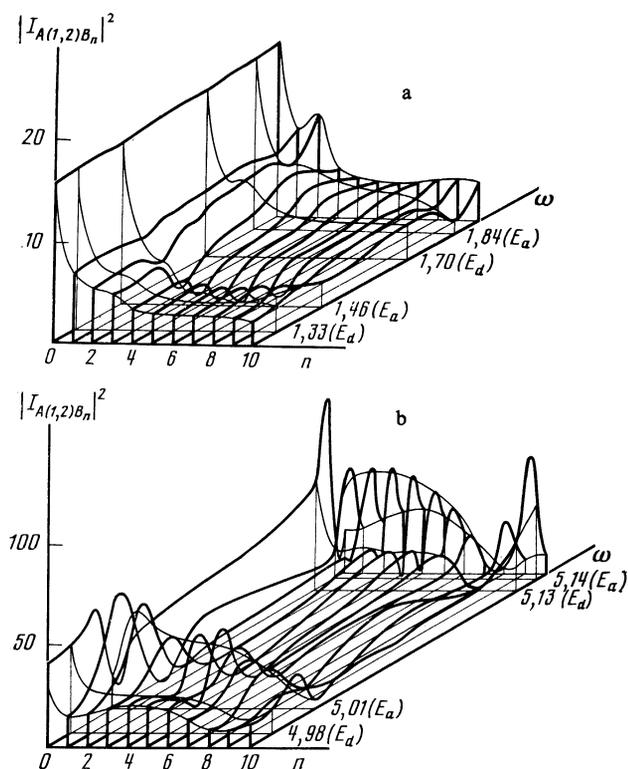


FIG. 4. Vibrational structure of the RRS spectrum of the IBr molecule as a function of the frequency of exciting radiation: in the region of quasicrossing (a) and well away from the quasicrossing region (b).

ment of their interaction ($V_{12} = 205 \text{ cm}^{-1}$) were taken from Refs. 9–11. Figure 4a corresponds to excitation frequencies lying near the quasicrossing region, for which $\delta \sim 1.3$ –1. Figure 4b corresponds to frequencies that are distant from the quasicrossing region, for which $\delta \approx 0.6$ (we are using the system of units in which $\hbar = \mu = \omega_0 = 1$, where ω_0 is the frequency of vibrations in the ground electronic state). A sharp rise in intensity (cf. Fig. 4b) occurs for resonances with the quasistationary states ($\omega \approx E_d$). The quantities E_d and E_a are the roots of the equation $\text{Re } \Delta = 0$ and characterize the position of stationary levels in the diabatic and adiabatic limits, respectively (measured from the term quasicrossing point). The section along the ω axis gives the excitation profile for an individual overtone. The considerable asymmetry of the excitation profile is explained by interference between the resonance part of scattering (27) and the nonresonance part which, in this case, is small. As can be

seen from Figs. 4a and 4b, the excitation profile varies from the highly irregular form, characteristic for discrete RRS (Fig. 4b), to the smooth form, typical for scattering on the non-binding term (Fig. 4a) for which the exciting frequency approaches the quasicrossing region.

Nonadiabaticity manifests itself also in the distribution of the overtones at fixed exciting frequency ω (envelope along the n axis). As the exciting frequency approaches the nonadiabatic region, the intensity distribution rapidly changes its character in the same way as in the transition from scattering on a bound state to scattering on a non-binding term.

The effect of nonadiabaticity on the intensity and width of distant overtones ($n = 28, 37$) in the spectrum of the IBr molecule was calculated in Ref. 12. Such distant states were chosen because they had the largest overlap integrals with the intermediate states $^3\Pi$ and $^1\Pi$. Our results show that interference between the diabatic and adiabatic channels manifests itself in the relative intensity variations along the entire series of overtones, right down to the lowest-order overtones, and is considerable when the exciting frequency approaches the frequency of the transition to the quasicrossing region. Experimentally, it is simpler to investigate this effect than to establish changes in the excitation spectrum of a high-order line.

Thus, studies of RRS spectra of molecules in the ground electronic state can be used to determine the position, shape, and nonadiabatic parameters of excited electronic terms.

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