Transitions in a three-term system: Raman scattering and stimulated conformation transformations in molecules

S. I. Vetchinkin, V. L. Bakhrakh, and I. M. Umanskiĭ

Institute of Chemical Physics, Academy of Sciences of the USSR

(Submitted 15 December 1980; resubmitted 26 May 1981)
Zh. Eksp. Teor. Fiz. **81**, 1182–1194 (October 1981)

The amplitude is found for a transition of a general form *A–C–B* in a system of three molecular terms for the case in which there is no direct interaction between the initial and final states *A* and *B* and the motion may be treated as quasiclassical (i.e., in the WKB approximation). The three-term model accounts for transitions in atomic-molecular collisions and radiative processes in molecular systems that are allowed in the second order in the interaction. A quasiclassical theory of Raman scattering is developed, which makes it possible to determine the form of an excited electronic term in a diatomic molecule from the resonance-scattering spectrum. It is shown that a new laser process—a light-scattering-induced conformation transition—is possible for a certain class of molecules.

PACS numbers: 33.20.Fb, 36.20.Ey

The Landau-Zener problem[1] concerning transitions between two intersecting molecular terms is well known. If there is no direct interaction between the terms A and B, e.g., if the transition is symmetry-forbidden, the transition can go only through a third term C. The corresponding problem for three or more terms has not been solved, except in special cases.[2,3] We shall consider transitions of the general form $A-B-C$ in a system of three molecular terms in which there is no direct interaction between the initial and final states A and B under the assumption that the motion on each of the terms may be treated as quasiclassical (i.e., in the WKB approximation).

The three-term model explains transitions between terms of different multiplicity ($^1\Sigma-^3\Sigma$) when these terms are crossed in an atomic collision by a term having a large spin-orbit interaction ($^3\Pi$), transitions between molecular states of the same parity ($g-g$) as a result of mixing of these states with a state of opposite parity (u) incident to the application of a uniform electric field, and other processes that are forbidden to the first order in the intramolecular interaction or in the strength of the external field. This model is of special interest for the theory of radiative transitions in molecular systems. The concept of quasienergy states in an external field that varies periodically in time[4] makes it possible to treat radiative processes by analogy with transitions in a conservative system. A generalization of the Landau-Zener theory for radiative collisions with transitions between two crossing quasienergy terms is given in Refs. 5–7. We shall consider a system of three quasienergy terms; this model makes it possible to establish an analogy between the more complicated radiative processes in molecules and nonadiabatic transitions in collisions between atoms and molecules. The radiative processes that are satisfactorily described in the three-term approximation include resonance Raman scattering, intercombination transitions in molecular vibronic spectra, quenching of a metastable state in radiative collisions, and some other phenomena. In this paper we give a quasiclassical interpretation of Raman scattering. It is also shown that a new laser process is possible for certain molecules: a conformation transition induced by light scattering.

The amplitude for the transition $A-B$ in a system of weakly coupled terms $A-C-B$ when there is no direct interaction between the initial and final terms ($V_{AB}=0$) is determined by the matrix element

$$I_{ACB}=\langle\psi_A|V_{AC}G_E{}^C V_{CB}|\psi_B\rangle \tag{1}$$

in the second order of perturbation theory. Here ψ_A and ψ_B are the wave functions for the motion of the nuclei on the terms A and B, respectively, G_E^C is the Green's function for the term, C, V_{AC} and V_{CB} are the interaction matrix elements averaged over the electron coordinates, and E is the energy of motion on the term C (i.e., $E=E_A=E_B=E_C$ in a closed molecular system, and $E=E_A\pm\hbar\omega$, $E_B\pm\hbar\omega$ for radiative processes). We shall consider the dependence of I_{ABC} on the energy E and on the forms and relative positions of the terms A, B, and C under such conditions that the motion on each of the terms is quasiclassical (the transition itself, generally speaking, may be quantum process).

Figures 1 and 2 show transition schemes for three intersecting terms for the above-barrier and below-barrier cases. In calculating I_{ACB} we may properly use the quasiclassical expressions for ψ_A and ψ_B and G_E^C provided the turning points x_A, x_B, and a_C are far from the points x_{AC} and x_{CB} where the terms cross, so that the corresponding phases $S(x_A, x_{AC})$, $S(x_B, x_{BC})$, $S(a_C, x_{CA})$, and $S(a_C, x_{CB})$ are large; here

$$S(x_A, x_{AC})=\int_{x_A}^{x_{AC}} p_A dx$$

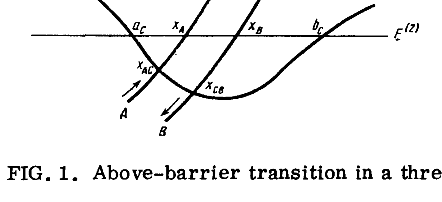

FIG. 1. Above-barrier transition in a three-term system.

0038-5646/81/100629-07$02.40

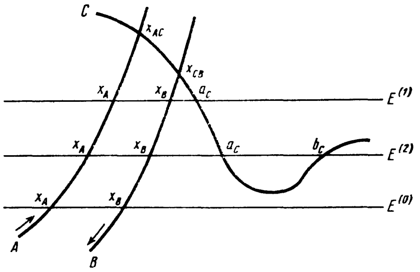

FIG. 2. Subbarrier transition in a three-term system.

is the cut-off action and

$$p_A=[2(E-U_A(x))]^{1/2}$$

is the momentum for the motion on the term A (here and below $\hbar=\mu=1$). We also assume that the points x_{AC} and x_{BC} where the terms cross are far enough apart; this makes it possible to distinguish two transition mechanisms: the Landau-Zener mechanism, and the Frank-Condon mechanism. When the width γ_C of the term C is large and the momentum p_C of the motion on that term is small, the complicated stepwise Landau-Zener process $A-C-B$ naturally reduces to two independent transitions $A-C$ and $C-B$; we shall be interested in the case in which γ_C is small and the phase of the motion on the term C is conserved.

THE QUASICLASSICAL GREEN'S FUNCTION

The form of the Green's function G_E in the quasiclassical region is of interest in itself. We shall use the well-known expression for G_E in terms of linearly independent solutions χ^+ and χ^- of the homogeneous equation:

$$G_E(x_1,x_2)=2\chi^+(x_<)\chi^-(x_>)/\Delta,\quad \Delta=\chi^-(x)\frac{d}{dx}\chi^+(x)-\chi^+(x)\frac{d}{dx}\chi^-(x), \tag{2}$$

where Δ is the Wronskian, and $x_<$ ($x_>$) is the smaller (larger) of x_1 and x_2. Here and below we shall be considering a Green's function $G_E=G_E^-$ with asymptotic waves coming in from infinity. Then the solution χ^+ corresponds to a particle moving in the positive direction from $x=-\infty$, and χ^-, to a particle moving in the negative direction from $x=+\infty$. In the quasiclassical region, the Green's function $G_E(x_1,x_2)$ is a linear combination of four independent solutions:

$$G_E(x_1,x_2)=g_E(x_1,x_2)+A\cos S(x_1,x_2)+B\exp[+iS(x_1)+iS(x_2)]+C\exp[-iS(x_1)-iS(x_2)], \tag{3}$$

where

$$g_E(x_1,x_2)=\frac{-i}{[p(x_1)p(x_2)]^{1/2}}\exp[-iS(x_<,x_>)] \tag{4}$$

is the Green's function for the case in which there are no turning points, and the additional terms representing standing and traveling waves take account of reflections from the boundaries of the classically allowed region. A, B, and C are constants as long as the values of the variables x_1 and x_2 are far from turning points, and they change discontinuously when either of the variables passes through a turning point. There must be exponentially large terms in the physical solution; hence $A=C=0$ when

$$\operatorname{Im}[S(x_1)+S(x_2)]>0$$

and $A=B=0$ when

$$\operatorname{Im}[S(x_1)+S(x_2)]<0,$$

provided at least one of the arguments x_1 and x_2 lies in a classically inaccessible region. In the general case, the coefficients A, B, and C must be so chosen as to ensure the correct behavior of the solutions $\chi^\pm(z)$ in passing around the turning points in the space of the complex variables z_1 and z_2 in accordance with well-known rules[8] and formula (2).

LANDAU-ZENER AND FRANCK-CONDON TRANSITIONS

The function

$$\psi_A(x_1)V_{AC}(x_1)G_E^C(x_1,x_2)V_{CB}(x_2)\psi_B(x_2)$$

in the matrix element (1) has a saddle point on the $\{x_1,x_2\}$ plane at the point (x_{AC},x_{CB}) where the potential curve $U_A(x)$ crosses the curve $U_C(x)$ and $U_B(x)$ crosses $U_C(x)$, and as the argument point recedes from the saddle point the function either falls or oscillates rapidly except in the region $x_1\approx x_2$, in which the normal derivatives of the Green's function $g_E(x_1,x_2)$ are discontinuous. Thus, the matrix element breaks up into a sum of integrals

$$I_{ACB}=I_{ACB}^{LZ}+I_{ACB}^{FC}, \tag{5}$$

where I_{ABC}^{LZ} is the contribution from the region containing the saddle point (x_{AC},x_{CB}) and I_{ACB}^{FC} is the contribution from the source region $x_1=x_2$. The integral I_{ACB}^{LZ} can be calculated by the method of steepest descents for a multidimensional space[9] and, in view of the general expression (2) for the Green's function, is given by

$$I_{ACB}^{LZ}=\left(\frac{V_{AC}}{(|p\Delta U'|)^{1/2}}\right)_{AC}\left(\frac{V_{CB}}{(|p\Delta U'|)^{1/2}}\right)_{CB}\Phi_{ACB} \tag{6}$$

provided the saddle point (x_{AC},x_{CB}) is isolated. The subscript AC (or CB) indicates that the corresponding bracketed quantity is to be taken at the crossing point of the corresponding terms, i.e., where $U_A(x)$ crosses $U_C(x)$ [or $U_C(x)$ crosses $U_B(x)$];

$$(\Delta U')_{AC}=\frac{d}{dx}(U_A-U_C)_{x_{AC}}$$

is the difference between the slopes of the terms at their crossing point; and Φ_{ACB} is a phase factor to be determined. In calculating the integral I_{ACB}^{FC} we shall assume that the momentum p_C is so large that the nonanalytic part of the Green's function $g_E(x_1,x_2)$ will vary more rapidly on receding from the axis $x_1=x_2$ than all the other factors. Then

$$g_E(x_1,x_2)=-i\exp[-ip(x)|x_1-x_2|]/p(x) \tag{7}$$

and as a result we have

$$I_{ACB}^{FC}=\left\langle\psi_A\middle|V_{AC}\frac{1}{E-U_C}V_{CB}\middle|\psi_B\right\rangle. \tag{8}$$

If there are turning points on the term C, the Green's function G_E^C will contain additional terms that are not present in g_E, but these terms are analytic on $x_1=x_2$ and their contribution will therefore be fully included in I^{LZ}_{ACB}.

It is easy to see that the two terms I^{LZ}_{ACB} and I^{FC}_{ACB} in the total amplitude (5) represent different transition mechanisms. The matrix element I^{LZ}_{ACB} represents successive transitions $A-C$ and $C-B$ localized at the points x_{AC} and x_{CB}, respectively, in each of which momentum is conserved, and which take place with a phase advance corresponding to the motion from x_{AC} to x_{CB} on the intermediate term C. Thus, the real part of I^{LZ}_{ACB} represents the contribution from two successive Landau-Zener transitions. The imaginary part of the elastic scattering amplitude ($A=B$) determines the probability for decay to the term C in accordance with the optical theorem. The imaginary part of the amplitude for the inelastic process ($A \neq B$) takes account of the interference of the currents from A and B to the term C.

The second term, I^{FC}_{ACB}, in the complete amplitude takes account of the contribution from the Franck-Condon transitions $A-C$ and $C-B$ as calculated for stationary nuclei and subsequently integrated over the entire path of the atoms, which are regarded as moving slowly enough for the adiabatic approximation to be valid.

It is important that the conditions for the quasiclassical (WKB) approximation have been used only in calculating the integrals (by the method of steepest descents), while the quantum formulation of the physical problem as a whole has been retained. That is why it was possible to distinguish and compare two transition mechanisms at the same time: the quasiclassical Landau-Zener mechanism, and the Franck-Condon quantum mechanism. We note that it is possible to distinguish the two different transition mechanisms when the quasiclassical phase of the motion on term C is large: $|S(x_{AC}, x_{CB})| \gg 1$. When the saddle points x_{AC} and x_{CB} approach each other the Landau-Zener and Franck-Condon transitions can no longer be distinguished. As the parameter E falls below the points where the terms cross,

$$E<U_C(x_{AC}),\ U_C(x_{CB}),$$

the amplitude I^{LZ}_{ACB} for the Landau-Zener transition falls off exponentially while the amplitude for the Franck-Condon transition, generally speaking, decreases according to a power law:

$$I^{FC}_{ACB} \sim \frac{V^2}{E-U_C}\langle\psi_A|\psi_B\rangle.$$

In the classically accessible region

$$E>U_C(x_{AC}),\ U_C(x_{CB})$$

the Landau-Zener transition, as a rule, will dominate the Franck-Condon transition.

THE QUASICLASSICAL PHASES

Off the line $x_1 = x_2$ the Green's function $G_E(x_1, x_2)$ factors in accordance with Eq. (2), and therefore the integral I^{LZ}_{ACB} reduces to a one-dimensional one, so that

$$I^{LZ}_{ACB}=\frac{2}{\Delta}\int \psi_A^{*} V_{AC}\chi^{+}\,dz \int \chi^{-} V_{CB}\psi_B dz \qquad (9)$$

when $x_{AC} < x_{CB}$. When the energy is high enough, i.e. when

$$E>U_C(x_{AC}),\ U_C(x_{CB})$$

the functions ψ_A, ψ_B, and $\chi^{\pm}$ oscillate rapidly near the crossing points x_{AC} and x_{CB} of the terms and all the necessary integrals can be calculated by the method of steepest descents. As a result, we obtain the following expression for the phase factor provided there are no turning points on the term C:

$$\Phi_{ACB}=\exp\left[iS(x_B, x_{BC}, x_{CA}, x_A)-i\pi/2\right], \qquad (10)$$

where

$$S(x_B, x_{BC}, x_{CA}, x_A)=\int_{x_{AC}}^{x_A} p_A dx+\int_{x_{BC}}^{x_{AC}} p_C dx+\int_{x_B}^{x_{BC}} p_B dx \qquad (11)$$

is the cut-off classical action calculated from the turning point x_A on the term A to the turning point x_B on the term B via the intermediate term C. It is not difficult to see an analogy between the resulting solution (10) and the well-known[1,8] problem of potential scattering if we regard $S(x_B, x_{BC}, x_{CA}; x_A)$ as the phase of the motion in the effective potential produced by the segments of the terms $A-C-B$. The difference is that this "effective potential" is, generally speaking, not single values (see Fig. 1) and the phase advance in the integration over the path $x_A-x_{AC}-x_{CB}-x_B$ is not monotonic.

The model involving motion on the terms $A-C-B$ differs substantially from the potential scattering problem when there are turning points on the term C. In this case the solutions $\chi^{\pm}$ contain reflected waves, in accordance with Eq. (3). The resulting phase factor Φ_{ACB} takes account of the interference of these waves, and for values of E exceeding the potential energy at the points where the terms cross, it is given by

$$\Phi_{ACB}=2\cos\left[S(x_A, x_{AC}, a_C)+\pi/4\right]\exp\left[iS(x_B, x_{BC}, a_C)-i\pi/4\right] \qquad (12)$$

if there is one turning point a_C (Fig. 1, $E^{(1)}$), and by

$$\Phi_{ACB}=\frac{2}{\cos S(a_C, b_C)}\cos\left[S(x_A, x_{AC}, a_C)+\pi/4\right]\cos\left[S(x_B, x_{BC}, b_C)-\pi/4\right] \qquad (13)$$

if there are two turning points $a_C < b_C$ on the term C (Fig. 1, $E^{(2)}$). Here

$$S(x_A, x_{AC}, a_C)=\int_{x_A}^{x_{AC}} p_A dx+\int_{x_{AC}}^{a_C} p_C dx \qquad (14)$$

is the cut-off action running from x_A to x_{AC} on the term A and from x_{AC} to a_C on the term C. The number of different phases S in each of the solutions (10), (12), and (13) is equal to the number of independent contours joining the turning points x_A and x_B in the set of intersecting terms. The presence of imaginary parts in expressions (10) and (12) is due to the possibility that the system may decay on term C. When the motion on term C is finite [the case of Eq. (13)] the function Φ_{ACB} is real (for real values of E) and contains the resonance factor $[\cos S(a_C, b_C)]^{-1}$, which shows that long-lived bound states are formed on term C in the process.

At low energies, when

$$E<U_C(x_{AC}),\ U_C'(x_{CB}) \text{ and } p(x)=-i(2|E-U(x)|)^{1/2},$$

the action S is imaginary and the functions $\chi^{\pm}$ contain large and small components in the subbarrier region. When $x_B < x_C$, a product of the form $\psi_B\chi^-$ has no extrema on the real axis x. We continue the solution ψ_B analytically into the classically inaccessible region in such a manner that the product $\psi_B\chi^-$ will break up into terms having extrema at x_{CB}, just as in Sec. 51 of Ref. 1. Then all the integrals in Eq. (9) may be calculated by the method of steepest descents. As a result, we have

$$\Phi_{ACB}=\exp\,[iS(x_B,\ x_{BC},\ x_{CA},\ x_A)] \tag{15}$$

if there are no turning points (Fig. 2, $E^{(0)}$) and

$$\Phi_{ACB}=\exp\,[iS(x_B,\ x_{BC},\ x_{CA},\ x_A)]\{1-{}^1/_2\exp\,[i2S(a_C,\ x_{CB},\ x_B)]\} \tag{16}$$

if there is one turning point a_C on term C (Fig. 2, $E^{(1)}$); if there are two turning points a_C and b_C on term C we have

$$\Phi_{ACB}=\exp\,[iS(x_B,\ x_{BC},\ x_{CA},\ x_A)]\{1+{}^1/_2\operatorname{tg}S(a_C,\ b_C)\exp[i2S(b_C,\ x_{CB},\ x_B)]\} \tag{17}$$

if both turning points are outside the barrier region, i.e., if $a_C,\ b_C > x_A, x_B$ (Fig. 2, $E^{(2)}$), or

$$\Phi_{ACB}=\frac{1}{2\cos S(a_C,\ b_C)}\exp[iS(a_C,\ x_{CA},\ x_A)+iS(x_B,\ x_{BC},\ b_C)], \tag{18}$$

if $x_A < a_C$ and $b_C < x_B$ so that the term C separates the classically inaccessible region into separate regions (Fig. 3).

The characteristic factor

$$\exp\,[iS(x_B,\ x_{BC},\ x_{CA},\ x_A)]$$

in Eqs. (15)–(17) is the amplitude for penetrating the barrier formed by segments of the terms A, B, and C. The complex factor

$$\{1-{}^1/_2\exp\,[i2S(a_C,\ x_{CB},\ x_B)]\}$$

in (16) takes account of the possibility that the system may decay on term C when the particle penetrates into the classically allowed region and goes off to infinity after passing through the additional barrier B–C (Fig. 2) with the penetration factor

$$\exp\,[i2S(a_C,\ x_{CB},\ x_B)].$$

When

$$|S(a_C,\ x_{CB},\ x_B)|\gg 1$$

this correction is not important in (16), but the situation is different in the case of resonances, as in (17). The additional term in (17) is due to the effect of the long-lived bound states that arise when the motion on the term C turns out to be finite (Fig. 2, $E^{(2)}$). Then the phase relations depend substantially on the positions of the turning points on the terms A, B, and C. When the term C separates the entire forbidden region between the terms A and B into two distinct regions A–C and C–B (Fig. 3) the phase factor (18) represents successive transitions through the independent barriers A–C and C–B, which are enhanced by resonance when E approaches the energy of a quasistationary state localized in the intermediate C well.

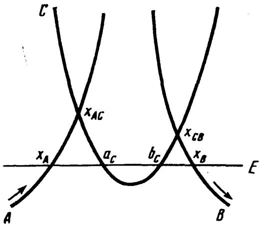

FIG. 3. Transition through two barriers.

The results (9)–(18) show how the transition amplitude depends on the kinetic energy and on the positions and shapes of the potential curves. The three-term model is of special interest in connection with radiative processes since the position of the quasienergy term is related to the frequency of the electromagnetic radiation and may be different under different experimental conditions.

RAMAN SCATTERING (RS)

The RS cross section is given by the well-known Kramers-Heisenberg formula

$$\sigma=\Big|\sum_C\{I_{ACB}(E_A+\omega)+I_{ACB}(E_B-\omega)\}\Big|^2\frac{\omega\omega'^3}{c^4}\,do', \tag{19}$$

in which A and B are the initial and final electronic-vibrational states of the molecule, the sum is taken over all electronic states C, $I_{ACB}(E)$ is a component of the scattering tensor in the notation of Eq. (1), and V_{AC} and V_{CB} are the dipole-moment matrix elements for the electronic transition; the remaining notation is standard.[10,11] It follows from Eq. (19) that after the conservation of energy in the elementary interaction event has been taken into account the scattering of light by the molecule can be treated as a nonadiabatic transition with the nuclei moving on the quasienergy terms $A=U_A(x)+\omega$, $B=U_B(x)+\omega'$, and $C=U_C(x)$.

In RS spectroscopy one usually investigates vibrational transitions in which the electronic state does not change. In this case the quasienergy terms $A=U_A(x)+\omega$ and $B=U_B(x)+\omega'$ are congruent and are shifted with respect to each other by the quantity $\omega-\omega'$, which is equal to the energy of the vibrational-rotational transition (see Fig. 4). The positions of the points where the quasienergy terms A and B cross the term C depend on the difference between the exciting frequency ω and the frequency ω_{FC} of the vertical transition A–C. For low or high frequencies ($\omega \ll \omega_{FC}$ or $\omega \gg \omega_{FC}$) the terms A,

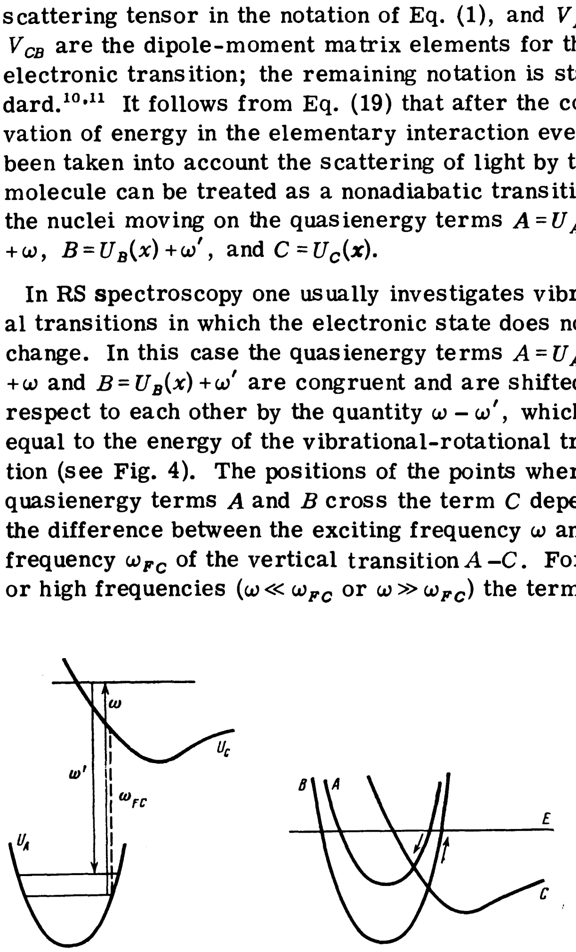

FIG. 4. Raman scattering as a transition in a system of three quasienergy terms.

B, and C either do not cross or cross in the classically inaccessible region. In the region of the electronic absorption band $\omega_{FC}-\delta\omega \lesssim \omega \lesssim \omega_{FC}+\delta\omega$ and a quasiclassical A–C–B transition is possible. The condition $|S(x_{AC}, x_{CB})| \gg 1$ is satisfied, at least for the overtones, and when the frequency difference $|\omega-\omega_{FC}|$ is large enough it is also satisfied for the fundamental tone. Then, as we saw above, one can distinguish two transition mechanisms: the Franck-Condon and Landau-Zener mechanisms.

According to Eq. (8), we have

$$\sum_{C}\{I^{FC}_{ACB}(E_A+\omega)+I^{FC}_{ACB}(E_B-\omega)\}=\langle A|\alpha(\omega)|B\rangle,$$

for the sum over all electronic states of the Franck-Condon contributions; here $\alpha(\omega)$ is the polarizability of the molecule with the nuclei held stationary. This result leads to the widely known[11] Placzek theory. Thus, the Franck-Condon mechanism accounts for RS far from the electronic-vibrational absorption band.

Stepwise nonadiabatic Landau-Zener transitions become important in the vicinity of the electronic-vibrational absorption band. Equations (9)–(18) establish the dependence of the intensity of the scattered light on the exciting frequency ω and the position and form of the excited electronic term. As ω varies, $I^{LZ}_{ACB}(\omega)$ either oscillates weakly, as in (12) and (16), or has resonances

$$[\cos S(a_c, b_c)]^{-1}\sim 1/(E-E_k),$$

as in (13), (17), and (18), depending on how pronounced the vibrational structure E_k is in the absorption band. I^{LZ}_{ACB} falls exponentially as ω recedes from the absorption band.

The Landau-Zener mechanism accounts for well-known features of resonance RS spectra.[12,13]

OVERTON INTENSITIES IN RESONANT RAMAN SCATTERING (RRS) SPECTRA

According to Eqs. (9)–(18), the ratio of the intensity of the n-th order line to that of the fundamental tone for a fixed excitation frequency ω is

$$\frac{J_n}{J_1}=\left|\frac{V_{CB_n}(p\Delta U')_{CB_1}}{V_{CB_1}(p\Delta U')_{CB_n}}\right|\varphi_n \tag{20}$$

under ordinary conditions in which $\omega \gg \omega_0$, where ω_0 is the frequency of the normal vibration. The quantity $(p\Delta U'/V)_{CB_n}$ is calculated at the point where the excited electronic term C crosses the quasienergy term $B_n = U_A(x)+\omega_n$ [$\omega_n \approx \omega - n\omega_0$ is the frequency of the $(n-1)$-th overtone] and, as a rule, varies slowly with the overtone-number n. In the region of the electronic-vibrational absorption band, the phase factor $\varphi_n = |\Phi_{ACB_n}/\Phi_{ACB_1}|^2$ either oscillates in accordance with (13) or, in the case of a structureless band (12), assumes the constant value $\varphi_n = 1$. Turning away from oscillations, therefore, we may assert that the production of a slowly falling sequence of overtones is characteristic of the Landau-Zener mechanism. The most thorough experimental studies of RRS spectra have been carried through for the I_2 molecule. The spectrum of molecular I_2 frozen in an argon matrix[14] has been determined for seven different emission modes of an argon laser. The electronic terms of I_2 are diagramed in Fig. 5, and the wavelengths of the laser light are also given there. The longest and most intense sequence of overtones (n = 1–25) was observed for λ = 5309 Å, i.e., for a frequency $\omega \approx \omega_{FC}$ very close to that of the vertical transition from the ${}^1\Sigma_g^+$ ground state to the excited ${}^3\Pi_{0u}^+$ triplet term. As the difference between the frequencies ω and ω_{FC} increases, the relative intensity of the lines falls and the RRS spectrum degenerates into an ordinary RS spectrum in the wings of the absorption band (at λ = 6471 Å and λ = 4579 Å).

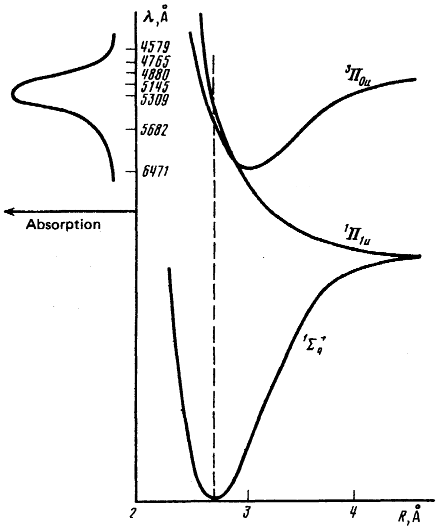

FIG. 5. Electronic terms of the I_2 molecule.

The relative intensities of overtones as determined experimentally[14] and calculated with formula (20) are compared in Fig. 6. The spread of local fields in the matrix covers over the vibrational structure of the electronic absorption spectrum, and this makes it possible to average out the oscillating factors in formulas (12) and (13). The singlet term was not taken into account since its contribution to the scattering is small (~20%, Ref. 14). The segment of the ${}^3\Pi_{0u}^+$ term in

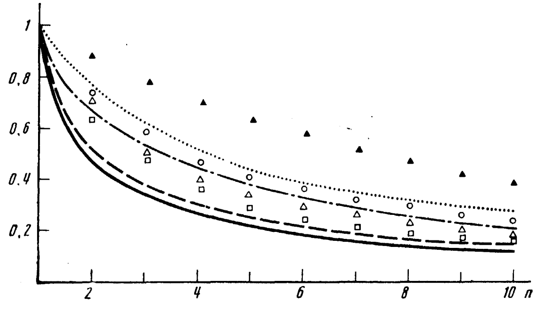

FIG. 6. Experimental points[14] and theoretical curves for the relative intensities of the overtones in the Raman scattering spectrum of the I_2 molecule for several values of the wavelength of the exciting light: 5309 Å—▲, dotted curve; 5145 Å—○, dash-dot curve; 5682 Å—△, dashed curve; 4880 Å—□, full curve.

the neighborhood of the equilibrium interatomic distance was approximated in the calculations by a parabola [with the slope $U_C'(x) = 0.64(x-7)$ in units in which $\hbar = \mu = \omega_0 = 1$]. The results correctly reproduce the intensity distribution of the overtones as well as the dependence of the overtone intensities on the frequency of the exciting light. Thus, the theory makes it possible to determine the forms of excited electronic terms of diatomic molecules from data on intensities in RRS spectra.

The difference between theory and experiment for I_2 is most marked for $\lambda = 5309$ Å; this should be expected, since the conditions for the applicability of the quasiclassical (WKB) approximation for the fundamental tone and the lower overtones are violated near the Franck-Condon frequency. Quantum models of RRS are discussed in Ref. 15.

LIGHT-SCATTERING-INDUCED CONFORMATION TRANSITIONS

Among the phenomena characteristic of polyatomic molecules, conformation transformations, i.e., transitions between different equilibrium positions within a single (ground-state) adiabatic term, are of considerable interest. The classical example is the cyclohexane molecule C_6H_{12}, which has two stable configurations ("chair" and "boat"); there are also the numerous class of cis-trans isomers, a few nitrogen-containing molecules, and others. In many chemical compounds, conformation transitions are accompanied by changes in the physical properties or biological activity of the molecules. For example, if isomer A has center of inversion while isomer B has no center of symmetry, the dipole moment of the molecule increase from $D=0$ to $D \sim 1$ Db in the transition from A to B. We shall treat a change in the conformation of a molecule within the limitations of a one-dimensional model as a transition between diabatic terms A and B incident to motion on the reaction coordinate x (Fig. 7). In the symmetric case, the probability for a spontaneous transition is

$$W_{AB} = (\omega_0/2\pi) \exp[i2S(x_B, x_{BA}, x_A)], \tag{21}$$

where ω_0 is the frequency of the vibrations about an isolated equilibrium position. The molecule will retain its initial conformation for a long time provided the barrier U_{AB} between the equilibrium positions is broad and high. Exciting the molecule increases the rate of isomeric transformations, but this is accompanied by heating of the material and possibly by chemical reactions in it. We shall show that electromagnetic radiation can induce conformation transformations of molecules as a result of scattering processes.

A periodic external force whose frequency ω is close to the electronic absorption frequency ω_{AC} will considerably increase the probability for the $A-B$ transition provided the $A-C-B$ process with an electronic term C that has no barrier can be involved. Or course, if the $A-B$ transition is to take place an energy $E_A - E_B$ equal to the difference between the energies of the initial and final states of the molecule must be transferred to the surroundings or a photon of frequency $\omega' = \omega + E_A - E_B$ must be re-emitted. The radiative transition $A-B$ is a special case of Raman scattering.

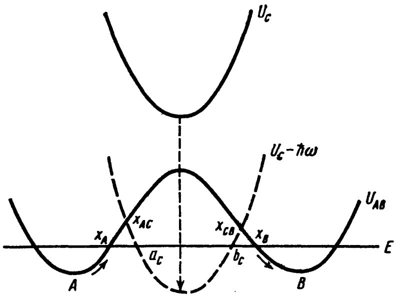

FIG. 7. A stimulated conformation transition.

The probability per unit time W_{ACB} for a stimulated conformation transition is

$$W_{ACB} = c\varepsilon^2\sigma/8\pi\omega, \tag{22}$$

where σ is given by Eq. (19) and ε is the electric field strength of the light wave. W_{ACB} will obviously be maximal for $\omega \approx \omega_{AC}$ when the term U_C crosses the quasienergy terms $U_A + \omega$ and $U_B + \omega'$ in the region of the barrier formed by the adiabatic potential U_{AB} (Fig. 7) and effectively reduces the barrier. On comparing W_{ACB} with the probability W_{AB} for a spontaneous conformation transition in a symmetric well for reasonable values of the parameters ($V_{AC} \sim V_{CB} \sim 1$ Db, $\omega \sim 10^5$ cm^{-1}, $\omega_0 \sim 10^3$ cm^{-1}, $\varepsilon \sim 10^4$ W/cm, and $\omega \approx \omega_{AC}$) we find $W_{ACB} \sim 10^9 W_{AB}$ for the case in which the term C slopes gently. The value $R \sim 5(\hbar/\mu\omega_0)^{1/2}$ was used for the distance between the equilibrium positions in calculating W_{AB}; in the absence of an effective barrier, the stimulated transition probability W_{ACB} does not depend on R.

The molecular conversion process $A-B$ can be detected spectroscopically by the appearance of new frequencies $\omega' = \omega + E_A - E_B + n\omega_B$ characteristic of the isomer B in the spectrum of the scattered light. The cross section for a stimulated conformation transition in the region of the absorption band agrees in order of magnitude with the cross sections $\sigma \sim 10^{-21} - 10^{-24}$ cm^2 ordinarily obtained for resonance Raman scattering.[12]

High incident-light intensities I are required to produce a concentration of converted molecules high enough to be detected by physicochemical means. For $I \sim 10^6$ W/cm^2 ($\varepsilon \sim 10^6$ V/cm) the induced transition probability is $W_{ACB} \sim 10^{-4} - 10^{-7}$ sec^{-1}, and this makes it possible to produce fairly high concentrations (~1%) of converted molecules in times of the order of $10^2 - 10^5$ sec.

The probability $W_{ACB}(\omega)$ for a conformation transition induced by the field $\varepsilon_\omega \cos\omega t$ and the probability $W_{BCA}(\omega')$ for the reverse transition induced by the field $\varepsilon_{\omega'} \cos\omega' t$ with $\omega' = \omega + E_A - E_B$ are related by the formula

$$\varepsilon_{\omega'}^2 \omega^3 W_{ACB}(\omega) = \varepsilon_\omega^2 \omega'^3 W_{BCA}(\omega'), \tag{23}$$

in accordance with the principle of detailed balancing. In a field of fixed frequency ω the cross sections for the direct and inverse processes $A-B$ and $B-A$ are the same only when $E_A = E_B$, as in the case of a symmetric well. In the asymmetric case $E_A \neq E_B$ we have $W_{ACB}(\omega)$

$\neq W_{BCA}(\omega)$, and the difference between the cross sections for the direct and inverse processes $A-B$ and $B-A$ can be seen most clearly in the frequency region in which the phase factor Φ_{ACB} varies substantially. When $\omega \approx \omega_{AC}$ ($\omega \approx \omega_{BC}$) the transition $A-B$ ($B-A$) is dominant. Thus, by varying the frequency of the incident radiation one can in principle effect a directed change in the geometry of the molecule, and it is also important that this process is reversible.

This optical method for effecting directed changes (and the reverse changes) in the dielectric or other physicochemical properties of matter that depend on the distribution of the molecules over their possible conformations will doubtless find interesting applications.

[1] D. D. Landau, and E. M. Lifshitz, Kvantovaya mekhanika (Quantum mechanics), Nauka, Moscow, 1974 (Engl. Transl., Pergamon Press, 1977).

[2] Yu. N. Demkov and V. I. Osherov, Zh. Eksp. Teor. Fiz. **53**, 1159 (1967) [Sov. Phys. JETP **26**, 916 (1968)].

[3] V. I. Osherov, V. G. Ushakov, and A. I. Voronin, J. Phys. B**13**, 1507 (1980).

[4] Ya. B. Zel'dovich, Usp. Fiz. Nauk **110**, 1507 (1973) [Sov. Phys. Usp. **16**, 427 (1973)].

[5] L. I. Gudzenko and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. **62**, 1686 (1972) [Sov. Phys. JETP **35**, 877 (1972)].

[6] R. Z. Vitlina, A. V. Chaplik, and M. V. Éntin, Zh. Eksp. Teor. Fiz. **67**, 1667 (1974) [Sov. Phys. JETP **40**, 829 (1974)].

[7] S. I. Vetchinkin, V. L. Bakhrakh, and I. M. Umanskiĭ, Opt. Spektrosk. **44**, 857 (1978) [Opt. Spectrosc. **44**, 507 (1978)].

[8] J. Heading, Introduction to phase integral methods, Methuen (Barnes & Noble), 1962.

[9] M. V. Fedoryuk, Metod perevala (The method of steepest descents), Nauka, Moscow, 1977.

[10] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, Relyativistskaya kvantovaya teoriya (Relativistic quantum theory), Part I, Nauka, Moscow, 1968 [Pergamon, 1971].

[11] G. Placzek, The Rayleigh and Raman Scattering, U.S. AEC Report, UCRL-Trans-526(L) (1962).

[12] P. P. Shorygin, Usp. Fiz. Nauk **109**, 293 (1973) [Sov. Phys. Usp. **16**, 99 (1973)]; Usp. Khim. **47**, 1697 (1978).

[13] D. L. Rousseau and P. F. Williams, J. Chem. Phys. **64**, 3519 (1976).

[14] J. M. Grzybowski and L. J. Andrews, J. Raman Spectrosc. **4**, 99 (1975).

[15] S. I. Vetchinkin, I. M. Umanskiĭ, V. L. Bakhrakh, and A. D. Stepukhovich, Opt. Spektrosk. **48**, 49 (1980) [Opt. Spectrosc. **48**, 26 (1980)].

Translated by E. Brunner