

Optical spectroscopy of Landau-Zener transitions

A. Z. Devdariani and Yu. N. Sebyakin

State University, Leningrad

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The problem of the influence of the interaction of quasimolecular states on the profile of the wing of a spectral line is solved subject to assumptions typical of the Landau-Zener model. The expressions obtained include averaging over the impact parameters and over the Maxwellian distribution of the colliding atoms. Quasicrossing of terms (levels) leads to the appearance of either two maxima (satellites) or a maximum and a minimum in the wing; separation between them depends on the nonadiabaticity parameter. This circumstance makes it possible to use the experimental data on the satellites in the wing of a spectral line in determination of the matrix element of the interaction between states and also the cross section of the corresponding inelastic transition. The expressions obtained are used to describe the absorption experiments and inelastic transitions in K-He and Cs-He quasimolecules.

1. INTRODUCTION

The interaction between quasimolecular states results in nonadiabatic transitions in collisions of atoms and molecules, which can be frequently described by the Landau-Zener equation.^{1,2} The main difficulty in calculation of the transition probability and reaction cross section is in this case associated with calculation of the matrix element of the interaction between the states. Therefore, the inverse problem is frequently solved: the experimental differential cross section of the process is used to find, with the aid of the Landau-Zener model, the nonadiabaticity parameter (Massey) parameter, which includes also the matrix element of the interaction. This approach represents essentially the content of the "collision spectroscopy" (discussed in the review given in Ref. 3) in the part which uses the Landau-Zener model.

The states participating in the investigated process very often have a quasisteady width associated with the possibility of emission of photons or electrons. The question therefore arises whether the interaction of states in the course of a collision affects the form of the electron or photon spectrum and if so, how? An analysis shows that the interaction of terms does indeed give rise to singularities in the spectrum^{4,5} and the singularities associated with the crossing of terms are in typical cases so characteristic that they provide a new way for determination of the parameters of the nonadiabatic interaction of states based on a study of quasimolecular spectra (which should give the answer to the question formulated above).

We shall derive analytic expressions describing the singularities in a spectrum which is formed in the region of the Landau-Zener interaction between quasimolecular states. With the aim of application to optical spectra, which are usually investigated using a gas cell, these expressions are averaged over the impact parameters and over the Maxwellian distribution of the velocities of the colliding atoms, which distinguishes the treatment given below from those reported in Refs. 6 and 7. The proposed theory generalizes the results of the ordinary quasistatic theory of broadening of spectral lines⁸ to the case of interacting states.

Allowing for the stages of approach and separation of atoms in the process of formation of a spectrum and for the averaging procedures described above makes the expres-

sions for these spectra so simple (in the case of absorption) that a simple procedure can be used to determine the nonadiabaticity parameter from the data on singularities in optical spectra. This circumstance is associated with the fact that the form of the spectrum and the probability of a nonadiabatic transition in the case when the Landau-Zener model is valid depend on the same parameter. The results obtained are applied, by way of illustration, to Cs-He and K-He quasimolecules.

2. FORMULATION OF THE PROBLEM AND MAIN RESULTS

The problem of finding the emission (or absorption) spectrum of a system of two interacting quasimolecular terms is considered in its general form in Refs. 5 and 6. In a classical description of the motion of colliding atoms on the assumption that their velocities have a Maxwellian distribution the frequency profile of a wing of a spectral emission line is given by the following expression⁸ (in the atomic system of units):

$$I(\omega) = \frac{4\omega^3}{3c^3(kT)^2} \left(\frac{8kT}{\pi\mu} \right)^{1/2} \int_0^{\rho_{\max}} \rho d\rho \int_0^{\infty} Q(E) E^{1/2} dE \times \left\langle \left\langle \left| \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \psi(t) | \mathbf{d} | \psi_0(t) \rangle \right|^2 \right\rangle \right\rangle, \quad (1)$$

where \mathbf{d} is the dipole moment of a quasimolecule; $\psi(t)$ and $\psi_0(t)$ are the wave functions of the initial and final states of a quasimolecule; the symbol $\langle \langle \dots \rangle \rangle$ denotes summation over the directions of polarization and escape of an emitted photon; $Q(E)$ is the Maxwellian distribution function of the relative energies of a collision; μ is the reduced mass of the colliding atoms; T is the absolute temperature; π is the impact parameter. The interatomic distance $R(v, \rho, t)$ is assumed to be parametrically dependent on time and v is the relative velocity of the colliding atoms.

When two states interact, the wave function $\psi(t)$ can be represented in the form

$$\psi(t) = a_1(t) \exp\left(-i \int^t \mathcal{U}_1 dt'\right) |\varphi_1\rangle + a_2(t) \exp\left(-i \int^t \mathcal{U}_2 dt'\right) |\varphi_2\rangle, \quad (2)$$

where $|\varphi_{1,2}\rangle$ are the electron wave functions of the investigated states, $\mathcal{U}_{1,2}(t)$ and $a_{1,2}(t)$ are the diabatic energies and amplitudes of the states dependent parametrically on time. The wave function $\psi_0(t)$ can be represented in an analogous form:

$$\psi_0(t) = \exp\left(-i \int \mathcal{U}_0 dt'\right) |\varphi_0\rangle. \quad (3)$$

This situation is illustrated in Fig. 1.

Substitution of Eqs. (2) and (3) into Eq. (1) gives

$$I_{em}(\omega) = \frac{8\pi\omega^3}{3c^3(kT)^2} \left(\frac{8kT}{\pi\mu}\right)^{1/2} \int_0^{\rho_{max}} \rho d\rho \int_0^{\infty} Q(E) E^{\hbar} dE \\ \times \left\langle \left\langle \left| \int_{-\infty}^{\infty} dt \exp(i\omega t) \left[a_1 \exp\left(-i \int (\mathcal{U}_1 - \mathcal{U}_0) dt'\right) \langle \varphi_1 | \mathbf{d} | \varphi_0 \rangle \right. \right. \right. \\ \left. \left. \left. + a_2 \exp\left(-i \int (\mathcal{U}_2 - \mathcal{U}_0) dt'\right) \langle \varphi_2 | \mathbf{d} | \varphi_0 \rangle \right] \right|^2 \right\rangle \right\rangle. \quad (4)$$

Assuming next that the nonadiabatic interaction of the states is described by the Landau-Zener model,^{1,2} we shall postulate that the diabatic energies $\mathcal{U}_{0,1,2}$ depend linearly on time in the region where the terms cross and the matrix element of the interaction V_{12} is constant. It is known that in this case the amplitudes $a_{1,2}(t)$ can be calculated in a closed form² in terms of the functions of a parabolic cylinder. The time integral in Eq. (4) reduces to one of the tabulated integrals (Ref. 9). Subsequent integration with respect to ρ is carried out analytically by introducing a new variable $E^* = E[1 - \rho^2/R_0^2 - U_{1,2}(R_0)/E]$ and integrating the result by parts.¹⁰ The final expression for the profile $I_{em}(\omega)$ is

$$I_{em}^{(1)}(\omega) = 2\pi^{1/2} R_0^2 \exp\left(-\frac{U_1(R_0)}{kT}\right) \\ \times \int_0^{\infty} \frac{dx \exp(-x)}{x^{1/2}} W(\Omega, s, 1, 2, x), \quad (5)$$

$$W(\Omega, s, 1, 2, x) = \exp\left(-\frac{3\pi}{2} \frac{\xi}{x^{1/2}}\right) \\ \times \left\{ \frac{\Gamma_1}{|F_{10}|} \left| D_{-i\xi/x^{1/2}} \left(\exp\left(i \frac{3\pi}{4}\right) \right. \right. \right. \\ \left. \left. \left. \times \frac{\xi^{1/2}}{x^{1/4}} \Omega \right) \right|^2 + \frac{\Gamma_2}{|F_{20}|} \left| \frac{\xi^{1/2}}{x^{1/4}} D_{-i\xi/x^{1/2}-1} \right|^2 \right. \\ \left. + 2s \left(\frac{\Gamma_1 \Gamma_2 \xi^{1/2}}{|F_{10} F_{20}| x^{1/4}} \right)^{1/2} \operatorname{Re} \left(\exp\left(-i \frac{3\pi}{4}\right) \right. \right. \right. \\ \left. \left. \left. \times D_{-i\xi/x^{1/2}} \bar{D}_{-i\xi/x^{1/2}-1} \right) \right\}, \quad (6)$$

where R_0 is the coordinate of the point of intersection of the terms: $F_{i0} = F_i - F_0$ ($i = 1$ or 2) is the difference between the forces at this point; $\Gamma_{1,2} = \frac{4}{3} \omega^3 d_{1,2}^2 / c^3$ are the widths of the diabatic state; $D_\nu(z)$ is a parabolic cylinder function⁹;

$$\Omega = -\frac{|F_{10} - F_{20}|}{|F_{10} F_{20}|^{1/2}} \frac{\omega - \omega_0}{V_{12}}. \quad (7)$$

$$\xi = \frac{V_{12}^2}{|F_{10} - F_{20}| (2kT/\mu)^{1/2}}. \quad (8)$$

The parameter Ω is a dimensionless frequency (frequency in units of the splitting of the difference adiabatic terms at the point of term crossing). The quantity ω_0 repre-

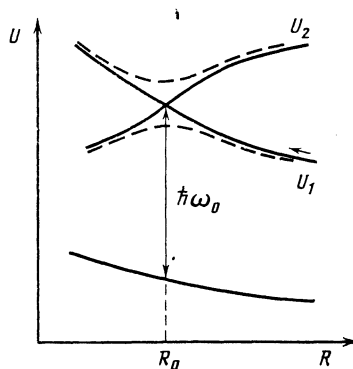


FIG. 1. Characteristic pattern of terms in the case of formation of absorption and emission spectra in region of pseudocrossing of terms. The continuous curves represent the diabatic terms and the dashed curves represent the adiabatic terms.

sents the energy of an emitted photon at the point of crossing of the R_0 terms (Fig. 1). The values $\Omega = \pm 2$ correspond to extrema (at F_{10} and F_{20} with opposite signs) of the adiabatic terms. The quantity ξ represents the Massey parameter of a given nonadiabatic process.

Equations (5) and (6) apply to the case when the initial term is either repulsive or attractive subject to the condition $U_1(R_0) < kT$ (i.e., we can ignore the orbiting effects). The index 1 in Eq. (5) for $I_{em}^{(1)}(\omega)$ reflects the fact that these expressions correspond to the initial condition when the diabatic state 1 is occupied in the limit $R \rightarrow \infty$. The corresponding expressions for $I_{em}^{(2)}(\omega)$ are obtained from Eqs. (5) and (6) by reversing the sign of the quantities Ω and s and transposing the indices $1 \rightleftharpoons 2$.

The probability of a single nonadiabatic transition in the case under discussion when $v_T = (2kT/\mu)^{1/2}$ is $P = \exp(-2\pi\xi)$.

The quantity s in Eq. (6) is described by

$$s = \frac{\langle \langle \varphi_1 | \mathbf{d} | \varphi_0 \rangle \langle \varphi_0 | \mathbf{d} | \varphi_2 \rangle \rangle}{\left[\langle \langle \varphi_1 | \mathbf{d} | \varphi_0 \rangle \rangle \langle \langle \varphi_0 | \mathbf{d} | \varphi_2 \rangle \rangle \right]^{1/2}}. \quad (9)$$

Let us consider in greater detail the meaning of the parameter s . In the derivation of Eqs. (5) and (6) it is assumed that the states 1 and 2 have the same quasimolecular symmetry (pseudocrossing of terms is possible only between such states). In this case we have $s = \pm 1$ and the sign of s is governed by the signs of the radial matrix elements encountered in calculation of $\langle \varphi_{1,2} | \mathbf{d} | \varphi_0 \rangle$ and depends on the specific quasimolecular system and states being investigated.

As pointed out above, the states 0, 1, and 2 correspond to specific values of the modulus of the projection of the total electron momentum of the quasimolecule along the interatomic axis, i.e., these states may be degenerate only with respect to the sign of such projection. This circumstance does not affect the final result for the $I_{em}^{(j)}(\omega)$ profile since the interaction V_{12} is independent of the sign of the projection of the total electron momentum.

Equations (5) and (6) are valid in the case of single passage through the pseudocrossing region. Optical spectra of quasimolecules are investigated as a rule in a gas cell, which corresponds to a situation when the nonadiabatic interaction region is crossed twice in the course of a collision (on approach and separation of the colliding atoms). In the case of such double passage through the pseudocrossing re-

gion in the absence of other crossings, the expressions for $I_{em}^{(1)}(\Omega)$ become (\sim above a symbol denotes double passage through the term pseudocrossing region)

$$I_{em}^{(1)}(\Omega) = 2\pi^{1/2} R_0^2 \exp\left(-\frac{U_1(R_0)}{kT}\right) \int_0^\infty \frac{dx \exp(-x)}{x^{1/2}} \times \left\{ W(\Omega, s, 1, 2, x) + \left[1 - \exp\left(-\frac{2\pi\xi}{x^{1/2}}\right) \right] W(\Omega, s, 2, 1, x) + \exp\left(-\frac{2\pi\xi}{x^{1/2}}\right) W(-\Omega, -s, 1, 2, x) \right\}, \quad (10)$$

$$I_{em}^{(2)}(\Omega) = I_{em}^{(1)}(-\Omega, -s, 2 \leftrightarrow 1). \quad (11)$$

The expressions for $I^{(i)}(\Omega)$ and $I^{(i)}(\omega)$, where $i = 1$ and 2 , can be rewritten in a clearer form if we note that the quantities $4\pi R_0^2 (\Gamma_i / |F_{j0}|) \exp(-U_i(R_0)/kT)$ are identical with the usual spectral line profiles predicted by quasi-static theories of the broadening⁸ in the case of the diabatic terms 1 and 2 in the vicinity of the point of their crossing (without allowance for the interaction). We therefore represent the quantities $I^{(i)}(\Omega)$ [Eqs. (5) and (6)] as follows:

$$I_{em}^{(i)}(\Omega) = 1/2 \left[\sum_j L_{ij}(\Omega) I_j^{qs} + L_i^{int}(\Omega) (I_1^{qs} I_2^{qs})^{1/2} \right], \quad (12)$$

$$I_j^{qs} = 4\pi R_{jc}^2 \frac{\Gamma_j(R_{jc})}{|d\Delta U_{j0}/dR|_{R_{jc}}} \exp(-U_{in}(R_{jc})/kT), \quad (13)$$

$\Delta U_{j0} = U_j - U_0$, $R_{jc}(\omega)$ is the "Condon" point found from the condition $\Delta U_{j0}(R_{jc}) = \hbar(\omega - \omega_0)$; $U_{in}(R)$ is the potential of the initial state [$U_j(R)$ for emission and $U_0(R)$ for absorption], whereas the functions $L_{ij}(\Omega)$ and $L_i^{int}(\Omega)$ are described by

$$L_{11}(\Omega) = \frac{1}{\pi^{1/2}} \int_0^\infty \frac{dx}{x^{1/2}} \exp\left(-x - \frac{3\pi}{2} \frac{\xi}{x^{1/2}}\right) \times \left| D_{-i\xi/x^{1/2}} \left(\exp\left(i \frac{3\pi}{4} \frac{\xi^{1/2}\Omega}{x^{1/4}}\right) \right) \right|^2, \quad (14)$$

$$L_{12}(\Omega) = \frac{1}{\pi^{1/2}} \int_0^\infty \frac{dx}{x^{1/2}} \exp\left(-x - \frac{3\pi}{2} \frac{\xi}{x^{1/2}}\right) \times \left| \frac{\xi^{1/2}}{x^{1/4}} D_{-i\xi/x^{1/2}-1} \left(\exp\left(i \frac{3\pi}{4} \frac{\xi^{1/2}\Omega}{x^{1/4}}\right) \right) \right|^2 = L_{11}(\Omega) - f(\xi), \quad (15a)$$

$$f(\xi) = \frac{1}{\pi^{1/2}} \int_0^\infty \frac{dx}{x^{1/2}} \exp\left(-x - \frac{2\pi\xi}{x^{1/2}}\right), \quad (15b)$$

$$\frac{1}{s} L_1^{int}(\Omega) = \frac{2\xi^{1/2}}{\pi^{1/2}} \int_0^\infty \frac{dx}{x^{1/2}} \exp\left(-x - \frac{3\pi}{2} \frac{\xi}{x^{1/2}}\right) \times \text{Re} \left\{ \exp\left(-\frac{3\pi}{4} i\right) D_{-i\xi/x^{1/2}} \left(\exp\left(i \frac{3\pi}{4} \frac{\xi^{1/2}\Omega}{x^{1/4}}\right) \right) \overline{D_{-i\xi/x^{1/2}-1} \left(\exp\left(i \frac{3\pi}{4} \frac{\xi^{1/2}\Omega}{x^{1/4}}\right) \right)} \right\}, \quad (16)$$

and the remaining $L_{ij}(\Omega)$ functions obey the relationships

$$L_{22}(\Omega) = L_{11}(-\Omega), \quad L_{21}(\Omega) = L_{12}(-\Omega), \quad L_2^{int}(\Omega) = -L_1^{int}(-\Omega). \quad (17)$$

It should be noted that the form of the spectrum ob-

tained in the case of two interacting states when the width of one of them vanishes ($\Gamma_2 = 0$) is related to I_1^{qs} also in Ref. 7. The difference between the expression (12) and that obtained in Ref. 7 lies not only in the greater generality and an allowance for interference, but also in the fact that the coefficients L_{i1} are obtained in Ref. 7 by numerical integration of the Fourier-transformed system of equations for the Landau-Zener model followed by averaging over the velocities assuming that the impact parameter is zero. In the case of L_{ij} which occur in Eq. (12), this integration of the system of equations and the subsequent double averaging reduces to integration of a known special function. In the final analysis this circumstance provides an opportunity for deriving convenient analytic expressions for the spectral profile in different limiting cases (see Sec. 3).

It follows from Eqs. (14)–(17) that only two out of the six functions in Eq. (12) are independent. This can be selected to be $L_{11}(\Omega)$ and $L_1^{int}(\Omega)$, which are discussed in Sec. 3. It should be noted that writing down Eqs. (5) and (6) for $I_{em}^{(i)}(\Omega)$ in the form of Eq. (12) makes it possible to widen the range of validity of the expressions obtained if I_j^{qs} is calculated at the Condon point R_{jc} [Eq. (13)] and not at the point R_0 , as should be done in accordance with Eqs. (5) and (6). In this case Eq. (12) represents "matching" of the $I_{em}^{(i)}(\Omega)$ profile in the vicinity of the crossing point to the profiles I_j^{qs} far from this region where the behavior of the potentials $U_j(R)$ and $U_0(R)$ and of the widths $\Gamma_j(R)$ may be quite arbitrary.

Following the above procedure used to obtain Eqs. (5) and (6) and to go over to Eqs. (12) and (13), we find that expressions for double passage given by Eqs. (10) and (11) transform similarly:

$$I_{em}^{(i)}(\Omega) = 1/2 \left\{ (I_1^{qs} + I_2^{qs}) \sum_j (L_{ij}(\Omega) - \tilde{L}_{ij}(\Omega)) + \sum_j (L_{ij}(\Omega) + \tilde{L}_{ij}(-\Omega)) I_j^{qs} + (2L_i^{int}(\Omega) - \tilde{L}_i^{int}(\Omega) - \tilde{L}_i^{int}(-\Omega)) (I_1^{qs} I_2^{qs})^{1/2} \right\}, \quad (18)$$

where

$$\tilde{L}_{11}(\Omega) = \frac{1}{\pi^{1/2}} \int_0^\infty \frac{dx}{x^{1/2}} \exp\left(-x - \frac{7\pi}{2} \frac{\xi}{x^{1/2}}\right) \times \left| D_{-i\xi/x^{1/2}} \left(\exp\left(i \frac{3\pi}{4} \frac{\xi^{1/2}\Omega}{x^{1/4}}\right) \right) \right|^2, \quad (19)$$

$$\tilde{L}_{12}(\Omega) = \tilde{L}_{11}(\Omega) - \frac{1}{\pi^{1/2}} \int_0^\infty \frac{dx}{x^{1/2}} \exp\left(-x - \frac{4\pi\xi}{x^{1/2}}\right) = \tilde{L}_{11}(\Omega) - f(2\xi), \quad (20)$$

$$\frac{1}{s} \tilde{L}_1^{int}(\Omega) = \frac{2\xi^{1/2}}{\pi^{1/2}} \int_0^\infty \frac{dx}{x^{1/2}} \exp\left(-x - \frac{7\pi}{2} \frac{\xi}{x^{1/2}}\right) \times \text{Re} \left(\exp\left(-i \frac{3\pi}{4}\right) D_{-i\xi/x^{1/2}} \overline{D_{-i\xi/x^{1/2}-1}} \right). \quad (21)$$

The remaining \tilde{L}_{ij} functions are related by expressions similar to Eq. (15). Only two \tilde{L}_{ij} functions are independent (for example, \tilde{L}_{11} and \tilde{L}_1^{int}).

The above expressions are valid in the case of emission

spectral line profiles. The profile of an absorption spectral line is described by a simpler expression:

$$I_{ab}(\Omega) = I_{em}^{(1)}(\Omega) + I_{em}(\Omega) \\ = [(L_{11}(\Omega) + L_{11}(-\Omega) - f(\xi)) (I_1^{qs} + I_2^{qs}) \\ + (L_1^{int}(\Omega) - L_1^{int}(-\Omega)) (I_1^{qs} I_2^{qs})^{1/2}]. \quad (22)$$

It therefore follows that the absorption profile $I_{ab}(\omega)$ obtained for the case of the Landau-Zener crossing of terms can be expressed in terms of the quasistatic absorption profiles I_j^{qs} for the diabatic potential curves and in terms of two universal functions $L_{11}(\Omega)$ and $L_1^{int}(\Omega)$ such that the combination $L_{11}(\Omega) + L_{11}(-\Omega)$ is an even function of Ω , whereas $L_1^{int}(\Omega) - L_1^{int}(-\Omega)$ is an odd function. The presence of an interference term [$\sim (I_1^{qs} I_2^{qs})^{1/2}$] leads (in those cases when it differs from zero) to an additional increase in $I_{ab}(\omega)$ in one of the ranges of Ω ($\Omega \geq 0$) and a reduction in the other range ($\Omega \leq 0$). The last circumstance is related to the singularities of the behavior of the adiabatic state widths in the case of quasicrossing of two terms.⁴ For example, for $\Gamma_{1,2} \neq 0$ and $s = 1$ the width of one of the adiabatic states increases in the vicinity of the crossing point to $\frac{1}{2}(\Gamma_1^{1/2} + \Gamma_2^{1/2})^2$, whereas the width of the other decreases to $\frac{1}{2}(\Gamma_1^{1/2} - \Gamma_2^{1/2})^2$. It is this redistribution of the widths of the adiabatic states which is reflected by the function $L_1^{int}(\Omega) - L_1^{int}(-\Omega)$ which is odd relative to Ω .

3. PROPERTIES OF THE FUNCTIONS $L_{11}(\Omega)$ and $L_1^{int}(\Omega)$

Let us consider the properties of the functions $L_{11}(\Omega)$ and $L_1^{int}(\omega)$ describing singularities in the absorption spectrum associated with the Landau-Zener interaction between two states. If asymptotic expressions for the parabolic cylinder functions in the case when the argument of the function is large⁹ are substituted into Eqs. (14) and (16) for $|\Omega| \gg 1$, we find that

$$L_{11}(\Omega) = \begin{cases} 1 + O(1/\Omega^2), & \Omega \rightarrow \infty, \\ f(\xi) + O(1/\Omega^2), & \Omega \rightarrow -\infty, \end{cases} \quad (23)$$

$$\tilde{L}_{11}(\Omega) = \begin{cases} f(\xi) + O(1/\Omega^2), & \Omega \rightarrow \infty, \\ f(2\xi) + O(1/\Omega^2), & \Omega \rightarrow -\infty, \end{cases} \quad (24)$$

$$L_1^{int}(\Omega), \tilde{L}_1^{int}(\Omega) \sim O(1/\Omega), \quad |\Omega| \rightarrow \infty. \quad (25)$$

The corresponding asymptotic expressions for the remaining L_{ij} and \tilde{L}_{ij} functions are obtained from Eqs. (15), (17), and (20).

It follows from Eqs. (25), (25), and (22) that, in particular, far from the nonadiabatic interaction region ($|\Omega| \gg 1$), we have

$$I_{ab}(\omega) \approx I_1^{qs}(\omega) + I_2^{qs}(\omega), \quad (26)$$

which is identical with the result obtained employing the usual quasistatic theory⁸ to describe the absorption by two noninteracting states.

In the limit $\xi \gg 1$ the functions $L_{11}(\Omega)$ and $L_1^{int}(\omega)$ can be described by simple analytic expressions. These expressions can be obtained using asymptotic equations for the parabolic cylinder functions occurring in Eqs. (14) and (16), which are obtained by the method of comparison with a standard when $\xi \gg 1$:

$$D_{-i\eta} \left(\exp \left(i \frac{3\pi}{4} \right) \eta^{1/2} \Omega \right) \underset{\eta \gg 1}{\approx} \exp \left(\frac{3\pi}{4} \eta + i \frac{\eta}{2} + i \frac{\pi}{4} \right) \eta^{-\frac{i\eta}{2}} \\ \times \left\{ \pi^{1/2} \left(\frac{\Omega + 2}{\Omega - 2} \right)^{1/4} (3/4 \eta h(\Omega))^{1/6} \text{Ai} \left[- (3/4 \eta h)^{1/3} \right] - \right. \\ \left. - i \left(\frac{\pi}{6} \right)^{1/2} \left(\frac{1/2 \eta h}{\Omega + 2} \right)^{1/2} \left[J_{2/3} \left(\frac{\eta h}{2} \right) - J_{-2/3} \left(\frac{\eta h}{2} \right) \right] \right\}, \quad (27)$$

where $\text{Ai}(z)$ is the Airy function and

$$h(\Omega) = \int_0^{\Omega} dx (x^2 - 4)^{1/2}.$$

The asymptotic form of the function $\eta^{1/2} \exp(i3\pi/4) \times D_{-i\eta-1}(\exp(i3\pi/4)\eta^{1/2}\Omega)$ is obtained from Eq. (27) by reversing the sign in front of the second term within braces. An analysis of the second term in the braces of Eq. (27) shows that its contribution is negligible compared with the contribution of the first term in the region $\Omega \approx 2$, where a satellite forms in the $\xi \gg 1$ limit under consideration. We need to allow for the contribution of this term only in the range $\Omega \geq 2$, where asymptotic expressions for the Bessel function $j_{\pm 3/2}(\eta h/2)$ can be used. Substituting Eq. (27) into Eqs. (11)–(16) we find that the functions $L_{11}(\Omega)$ and $L_1^{int}(\Omega)$ become

$$L_{11}(\Omega) = 3\pi^{1/2} \left(\frac{\Omega + 2}{|\Omega - 2|} \right)^{1/2} z_c^{1/2} \mathcal{L}(z_c) + \frac{1}{2} \begin{cases} \left(\frac{\Omega - 2}{\Omega + 2} \right)^{1/2}, & \Omega > 2, \\ \frac{1}{3^{1/2}} \left(\frac{2 - \Omega}{2 + \Omega} \right)^{1/2} \exp(12^{1/2} z_c), & \Omega < 2, \end{cases} \quad (28)$$

$$\frac{1}{s} L_1^{int}(\Omega) = 6\pi^{1/2} \left(\frac{\Omega + 2}{|\Omega - 2|} \right)^{1/2} z_c^{1/2} \mathcal{L}(z_c) - \begin{cases} \left(\frac{\Omega - 2}{\Omega + 2} \right)^{1/2}, & \Omega > 2, \\ \frac{1}{3^{1/2}} \left(\frac{2 - \Omega}{2 + \Omega} \right)^{1/2} \exp(12^{1/2} z_c), & \Omega < 2, \end{cases} \quad (29)$$

where $z_c = (\frac{3}{4}\xi h(\Omega))^{2/3}$ and $\mathcal{L}(z)$ is a function tabulated in Ref. 11 and defined by

$$\mathcal{L}(z) = \int_0^{\infty} \frac{dy}{y^2} e^{-1/y^3} \text{Ai}(-zy), \quad (30)$$

which appears in the description of a satellite of a spectral line associated with an extremum of the difference potential.¹¹ This is not accidental, because in the case $\xi > 1$, atoms move in adiabatic potentials and the probability of a transition between these is exponentially low. In the case under

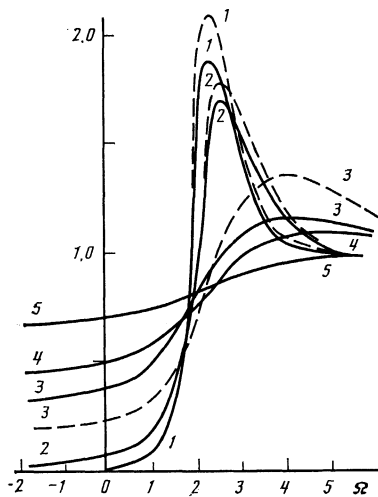


FIG. 2. The function $L_{11}(\Omega)$ plotted for different values of the parameter ξ . The continuous curves are the results of a numerical calculation based on Eq. (14), and the dashed curves are calculated from Eq. (28). 1) $\xi = 1.0$; 2) $\xi = 0.5$; 3) $\xi = 0.1$; 4) $\xi = 0.06$; 5) $\xi = 0.02$.

discussion when $F_{10}F_{20} < 0$ each of the difference adiabatic terms has an extremum, which accounts for the appearance of the function $\mathcal{L}(z)$ in Eqs. (28) and (29). The deviation from the dependence of z_c on Ω compared with Ref. 11 is due to the fact that the adiabatic terms in the region of a Landau-Zener crossing depend hyperbolically on R and not quadratically, as in Ref. 11. It should be noted that in Eqs. (28) and (29) an allowance is made also for the change in the widths of the adiabatic states in the vicinity of the point of term crossing.

In general, the values of the functions L_{11} and L_1^{int} and others can be found by numerical integration employing Eqs. (14), (16), (19), and (21). Figures 2 and 3 gives the results of such calculations for the functions $L_{11}(\Omega)$ and $L_1^{int}(\Omega)$ carried out for different values of the parameter ξ . These figures include also the results of calculations based

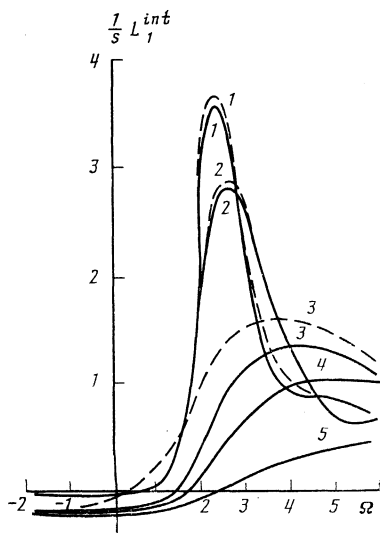


FIG. 3. The function $(1/s)L_1^{int}(\Omega)$ plotted for different values of the parameter ξ . The continuous curves represent numerical calculations based on Eq. (16), whereas the dashed curves are calculated from Eq. (29). 1) $\xi = 1.0$; 2) $\xi = 0.5$; 3) $\xi = 0.1$; 4) $\xi = 0.06$; 5) $\xi = 0.02$.

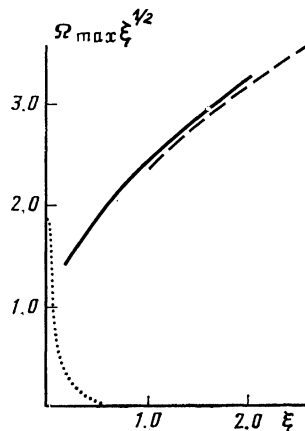


FIG. 4. Dependence of $\Omega_{max}\xi^{1/2}$ on ξ . The continuous curve represents the results of a numerical calculation and the dashed curve is calculated from Eq. (31). The dotted curve is the function $\pi^{1/2}f(\xi)$.

on Eqs. (28) and (29). Such a comparison shows that calculations carried out using the approximate expressions (28) and (29) agree well with the results of a rigorous calculation even for $\xi \gtrsim 0.1$. It follows from these plots that an increase in ξ which occurs for $\Omega \gtrsim 2$ makes the maximum more prominent. The function $f(\xi)$ is plotted in Fig. 4.

Using Eqs. (28) and (29) and the numerical values of the function $\mathcal{L}(z)$ (Ref. 11), we can readily obtain analytic expressions for the position of the maximum of the functions $L_{11}(\Omega)$ and $L_1^{int}(\Omega)$ when $\xi \gtrsim 1$. Since the maxima of these functions are close to $\Omega = 2$, the second terms in Eqs. (28) and (29) can be ignored and we can assume $z_c = \xi^{2/3}(\Omega - 2)$. Then,

$$\Omega_{max} \approx 2 + 0.33/\xi^{1/3}, \quad (31)$$

$$L_{11}(\Omega_{max}) \approx \frac{1}{2s} L_1^{int}(\Omega_{max}) \approx 1.87\xi^{1/3}. \quad (32)$$

It follows from Eqs. (31) and (32) that for $\xi \gtrsim 1$, we have $\Omega \approx 2.2L_{11} \approx L_1^{int}/s$, so that according to Eq. (22) we now find

$$I_{ab}(\Omega \approx \pm 2) \approx 1.87\xi^{1/3} [(I_1^{QS})^{1/2} \pm s(I_2^{QS})^{1/2}]^2,$$

which describes the behavior of the widths of the adiabatic states discussed at the end of Sec. 2.

4. SPECTROSCOPY OF LANDAU-ZENER CROSSINGS; K-He QUASIMOLECULE

Our analytic expressions and the results of the numerical calculations make it possible to describe a spectral line profile at frequencies corresponding to pseudocrossing of two quasimolecular terms (levels) or to obtain from an experimental spectrum some information on the nature of the nonadiabatic interaction of states in the pseudocrossing region. The parameter which represents this interaction is $-\xi$.

On the whole, when the spectrum is formed in the vicinity of the Landau-Zener crossing of terms we can have two characteristic situations. The first corresponds to the case when $I_1^{QS} \approx I_2^{QS}$ and both these quantities depend weakly [compared with $L_{11}(\Omega)$ and $L_1^{int}(\Omega)$] on Ω . Under the conditions indicated above, the presence of an interference term

in Eq. (22) within one of the wings of an absorption line [corresponding to the positive value of the interference term in Eq. (22)] gives rise to a maximum (satellite), whereas in the other wing there is a dip (representing a fall practically to zero at $I_1^{QS} = I_2^{QS}$ for $\xi \gg 1$). The second case is realized for $I_1^{QS} \ll I_2^{QS}$ (or vice versa). In this limit the contribution of the interference term can be ignored so that the absorption spectrum exhibits two maxima (satellites) corresponding to maxima of the function $L_{11}(\Omega) + L_{11}(-\Omega)$. This limit is typical of a situation in which a radiative transition to one of the diabatic states is forbidden (i.e., the corresponding value of Γ is zero).

Determination of the parameter ξ from the experimental data on the $I_{ab}(\omega)$ profile is generally based on selecting the variable parameter ξ which gives the best agreement between the experimental profile and the theoretical curve described by Eq. (22). If the quantities $I_{1,2}^{QS}$ depend weakly on Ω compared with $L_{11}(\Omega)$ and $L_{11}^{int}(\Omega)$, in the vicinity of the frequency ω_0 , a rapid estimate of the parameter ξ can be obtained using a simpler procedure. In this case the experimentally determined separation $\delta\omega_{max}$ between the maxima of $I_{ab}(\omega)$ (or between the maximum and minimum) is related to the dimensionless frequency Ω_{max} at which the functions $L_{11}(\Omega)$ and $L_{11}^{int}(\Omega)$ reach an extremum (for a given ξ):

$$\Omega_{max} = \frac{|F_{10} - F_{20}|}{|F_{10}F_{20}|^{1/2}} \frac{\delta\omega_{max}}{V_{12}} = \frac{1}{2\xi^{1/2}} \left(\frac{|F_{10} - F_{20}|}{|F_{10}F_{20}|} \right)^{1/2} \frac{\delta\omega_{max}}{v_T^{1/2}}. \quad (33)$$

Figure 4 shows a trace of the dependence of $\Omega_{max} \xi^{1/2}$ on ξ [the values of $\Omega_{max}(\xi)$ are found by numerical calculation (Figs. 2 and 3) and for $\xi > 1$ they are calculated from Eq. (31)].

The forces F_{10} and F_{20} can either be found in the usual way from the experimental spectrum (using the monotonic part),¹² or can be estimated theoretically. The latter task is much simpler than calculation of the matrix element of the interaction V_{12} . Next, we can use the graph in Fig. 5 to find the value of ξ at which the function $\Omega_{max} \xi^{1/2}$ is equal to the quantity $(\delta\omega_{max}/2)(|F_{10} - F_{20}|/v_T|F_{10}F_{20}|)^{1/2}$ deduced

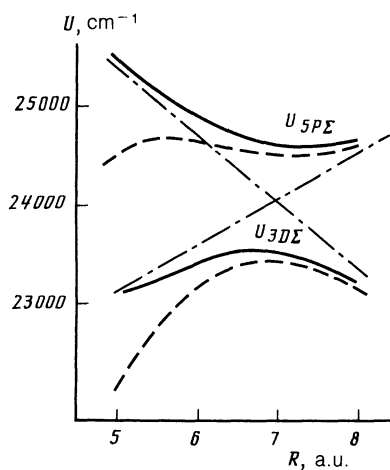


FIG. 5. Quasimolecular terms of the $5P\Sigma$ and $3D\Sigma$ states of the K-He system calculated by the pseudopotential method (continuous curves). The dashed curves represent the difference terms $U_{5P\Sigma} - C_{4S\Sigma}$ and $U_{3D\Sigma} - U_{4S\Sigma}$. The chain curves are the diabatic potentials.

from the experimental data, and then ξ obtained from Eq. (8) is used to calculate V_{12} .

Let us illustrate this method of determining the nonadiabaticity parameter ξ by considering a specific example involving a study of the absorption spectrum of a K + He mixture at wavelengths in the range $4080 \text{ \AA} \leq \lambda \leq 4640 \text{ \AA}$. The experiments were reported in Ref. 13 and, in particular, two satellites with maxima at $\lambda_1 = 4093 \text{ \AA}$ and $\lambda_2 = 4360 \text{ \AA}$ were observed in the absorption spectrum. These satellites are associated with pseudocrossing of terms (at $R_0 \approx 7a_0$) correlated with the $5P\Sigma$ and $3D\Sigma$ states of the K-He quasimolecule (in this case the absorption occurs from the $4S\Sigma$ ground state). Figure 5 gives the results of a calculation of the terms of the $5P\Sigma$ and $3D\Sigma$ states of the K-He molecule in the range of the internuclear distances of interest to us. The calculation was carried out using the pseudopotential method (see Refs. 14 and 15) allowing for the $4p, 5s, 3d, 5p, 4d, 6s, 4f,$ and $6p$ configurations of the K atom. It follows from the calculated results that the terms of the $5P\Sigma$ and $3D\Sigma$ states have a minimum ($R = 7.3a_0$) and a maximum ($R = 6.7a_0$), respectively, and these may be interpreted as forming through crossing of the corresponding diabatic terms (chain curves in Fig. 5). We shall now determine which value of V_{12} should be deduced from the experimental results. According to Ref. 13, at $T = 525 \text{ K}$, the positions of the satellites in the absorption coefficient are such that $\Omega_{max} \xi^{1/2} = 3.5$. According to Eq. (31) this corresponds to the values $\xi \approx 2.6$ and $V_{12} \approx 686 \text{ cm}^{-1}$. The latter agrees well with the results of calculations plotted in Fig. 5 ($V_{12} \approx 514 \text{ cm}^{-1}$).

5. SINGULARITIES OF THE ABSORPTION COEFFICIENT AND THE INELASTIC TRANSITION CROSS SECTION, Cs-He QUASIMOLECULE

The above method for determining the nonadiabaticity parameter ξ makes it possible to employ the characteristic singularities (satellites) in the wing of a profile of a spectral line to determine the rate constant and cross section of the corresponding nonadiabatic process, because in the Landau-Zener model these quantities also depend basically on the parameter ξ . We illustrate it by considering the Cs-He system for which the absorption spectrum was recorded experimentally in the range $5000 \text{ \AA} \leq \lambda \leq 7000 \text{ \AA}$ in work reported in Ref. 16. This range of wavelengths corresponds to transitions from the $6S\Sigma$ quasimolecular ground state to the $7S\Sigma$ and $5D\Sigma$ states. The absorption spectrum has two satellites ($\lambda_1 \approx 5600 \text{ \AA}$ and $\lambda_2 \approx 5880 \text{ \AA}$) the appearance of which is attributed in Ref. 16 to the presence of extrema of the difference potentials of the $7S\Sigma, 5D\Sigma,$ and $6S\Sigma$ states. However, the formation of extrema can be described using the concept of pseudocrossing of diabatic terms, which are correlated with the $7S\Sigma$ and $5D\Sigma$ states. If the forces $F_{10,20}$ are estimated using the potentials in Ref. 7, we find that at the experimental temperature $T = 630 \text{ K}$ $\Omega_{max} \xi^{1/2} \approx 2$, which on the basis of the plot in Fig. 5 gives $\xi \approx 0.53$ and $V_{12} \approx 350 \text{ cm}^{-1}$. A comparison with the numerical solution (discussed above) made in Ref. 7 therefore gave the value 220 cm^{-1} .

Analytic expressions for the rate constant $K_{ij}(T)$ of a Landau-Zener process when the terms have different relative positions in the initial and final states and the points of their quasicrossing are obtained in Ref. 17. In particular, in the case of the situation in the Cs-He system a nonadiabatic

transition from the $7S\Sigma$ to the $5D\Sigma$ state makes the expression for $K_{if}(T)$

$$K_{if}(T) = \bar{\sigma}_{if} \bar{v} = \bar{v} \pi R_0^2 \left\{ -\frac{4U_i(R_0)}{kT} \mathcal{F}(\xi^*) + \exp\left(-\frac{U_i(R_0)}{kT}\right) \langle P_-(\xi^*, T^*) \rangle \right\}, \quad (34)$$

where $\bar{v} = (8kT/\pi\mu)^{1/2}$; $U_i(R_0)$ is the potential energy at the point R_0 of crossing of the terms, measured from the energy of the original quasimolecular term when $R \rightarrow \infty$; $\mathcal{F}(\xi^*)$ is a function tabulated by Moiseiwitsch¹⁸; the function $\langle P_- \rangle$ is the average probability calculated in Ref. 17, and the parameters ξ^* and T^* are related as follows to ξ :

$$T^* = 1/(2\pi\xi)^2, \quad \xi^* = 2\pi\xi / \left(-\frac{U_i(R_0)}{kT}\right)^{1/2}. \quad (35)$$

The quantity $U_i(R_0)$ for the $7S\Sigma - 5D\Sigma$ transition is calculated in Ref. 19, which gives 200 cm^{-1} , whereas the experimental data on the absorption profile^{16,20} give $U_i(R_0) \approx 500 \text{ cm}^{-1}$. The coordinate is $R_0 \approx 6.6a_0$ (Ref. 19). Using the above value of $\xi = 0.53$, we find from Eq. (35) that $T^* \approx 0.09$ and $\xi^* \approx 5.0-3.0$ for $U_i(R_0) = 200-500 \text{ cm}^{-1}$. For these values of the parameters T^* and ξ^* we can use Eq. (34) [and employ the values of the functions $\mathcal{F}(\xi^*)$ and $\langle P_-(\xi^*, T^*) \rangle$ tabulated in Refs. 17 and 18] to obtain the following expressions describing the cross section of the $7S\Sigma-5D\Sigma$ nonadiabatic transition:

$$\bar{\sigma}_{7S-5D} \approx 4.2 - 8.4 \text{ \AA}^2 \text{ when } U_i(R_0) = 200 - 500 \text{ cm}^{-1} \quad (36)$$

The quantity obtained is in agreement with the experimental value $\bar{\sigma}_{7S-5D} \approx 5 \text{ \AA}^2$ (Ref. 21), which confirms independently the correctness of the proposed method for finding the interaction between terms.

6. CONCLUSIONS

An analytic investigation of the spectrum formed in the case of the Landau-Zener quasicrossing of terms has made it possible to determine the characteristic features in the profiles of the spectral line wings which appear in this case. It is shown that in the wing of an absorption line there are either two maxima (satellites) or one maximum and a dip (minimum). The formation of two satellites which accompanies

the crossing of terms makes it possible to employ the experimental data on the positions of such satellites to determine quite simply the Massey parameter of the corresponding nonadiabatic transition (i.e., precisely the quantity which is most difficult to determine by other experiments and calculations) and to estimate the cross section of the corresponding process. The results obtained in this way for the Cs-He system are in good agreement with the experimental data on the $7S\Sigma-5D\Sigma$ transition cross section.

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