## Absorption and emission of radiation in the region of an avoided level crossing

# M. J. O'Callaghan and A. Gallagher\*

Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309

#### T. Holstein<sup>†</sup>

## Physics Department, University of California at Los Angeles, Los Angeles, California 90024 (Received 17 January 1985)

The spectrum for absorption and emission of radiation by colliding atoms or a diatomic molecule is calculated for spectral regions dominated by an avoided level crossing. Example processes are absorption during an atom-atom collision with separation to either crossing atomic state, total absorption to both crossing states, and spontaneous emission during a collision with either state initially populated. Absorption and emission by bound diatomic molecules (including photodissociation) is described by the theory, and as an example it is applied to the  $Cs_2 A - X$  band. Spectra due to singlevelocity and impact-parameter collisions, as well as thermal and impact-parameter averages, are given. The shapes of the resulting spectra are parametrized by the interaction strength (or excitation transfer probability) between the crossing levels and the slopes of the ground- and excited-state potentials (assumed constant) in the region of the level crossing. The theory is applied to two observations of such regions that have been reported. We conclude that measurements of spectra in the region of level crossing is a very powerful diagnostic of the potentials and transfer probability in the level-crossing region, which is responsible for most inelastic atom-atom energy-transfer processes.

## I. INTRODUCTION

Theories are available that describe the pressure broadening of atomic lines (also called "radiative collisions") under essentially all conditions, but these reduce to simple, widely applicable forms in only two limits: The impact theory describes the line core and the quasistatic theory the far wings of the line.<sup>1,2</sup> The shape of the line core is primarily related to the long-range collisional interactions and normally is described in terms of perturbed atoms. The far wings are related to the close-range adiabatic molecular potentials and can also be described as continuum molecular spectra or spectroscopy of the collision complex.

The quasistatic theory for the far-wing intensity is closely related to the classical Franck-Condon principle and is applicable only to adiabatic molecular states which are not significantly coupled to other states by the nuclear motion. Inelastic (electronic-state-changing) atom-atom collisions deal with a situation where there are nonadiabatic couplings between these adiabatic states. When these nonadiabatic couplings occur across a relatively narrow range of internuclear separation R, they are generally described in terms of level crossings or avoided level crossings. This model is based on the Landau-Zener theory in which the diabatic states cross at  $R_c$ , but due to the coupling between them the adiabatic states undergo an avoided crossing in this region.<sup>3</sup> The Born-Oppenheimer violating terms, due to the non-negligible nuclear velocity, cause a breakdown of the adiabatic approximation and thus transitions between adiabatic states in the regions of avoided level crossings. These terms also invalidate the quasistatic theory in the spectral regions associated with

these level crossings. The Landau-Zener description of the transition probability in this crossing region is one of the most widely used theories in atom-atom collision processes. We use this simple model for the potentials and interactions here as the basis of a calculation of the spectrum associated with this level-crossing region.

Since these avoided level crossings are responsible for energy transfer in most inelastic atom-atom collisions, and for predissociation and other processes in diatomic molecules, this is a very interesting region to diagnose spectroscopically. It is the purpose of this paper to provide a general theory for the spectrum absorbed or emitted in the wavelength regions corresponding to these avoided level crossings. This theory is intended to provide a general basis for analyzing spectra in such regions and to note the exceptional diagnostic power contained in such a spectrum.

We are limiting the present calculation to linearly changing potentials and a constant interaction in the region of the level crossing, in the same manner that the Landau-Zener approximation handles such crossings. The Landau-Zener theory also considers the nuclear motion as a constant-velocity straight-line path, just as in the original "classical path" approximation to line-shape theory, and we also use this approximation here. It is our belief that these are a rather good approximation if they are handled in the following manner. The quasistatic spectrum  $I(\omega)^{QS}$  of the radiatively coupled diabatic state, which would have applied in the absence of the perturbing (crossing) state, is multiplied by a factor  $\overline{L}(\omega)$  calculated here, which contains the effect of the crossing. Since the crossing is highly localized in R and frequency  $\omega$ , the effect of the crossing can thus be accurately represented.

The quasistatic spectrum itself accurately reflects the effects of the actual motion and potential shapes outside the crossing region and of the diabatic states everywhere except in the region of a classical satellite.<sup>1</sup> In this sense the theory here presented is a very general theory, which can be applied to many situations without the need for detailed computer calculations.

With the above  $L(\omega)$  approach the approximation of straight-line, constant-velocity motion in the crossing region is valid if the nuclear kinetic energy is large compared to the changes in potential in the crossing region (i.e.,  $kT \gg V_{12}$ , where  $V_{12}$  is the interaction between the crossing levels). The quasistatic spectrum itself contains the exponential distribution factor representing curvilinear paths and the effect of the changes in potential upon the nuclear motion outside the crossing region. Thus, this calculation has applicability to bound-free, free-free, and bound-bound diatomic spectra as long as most of the states of nuclear motion do not have turning points in the neighborhood of  $R_c$ . This includes atom-atom collisions, molecular photodissociation, and molecular band shapes.

Some spectrum calculations that include nonadiabatic effects have been carried out for specific diatomic cases,<sup>4</sup> but these involve a full solution of the coupled-state Schrödinger equation for the nuclear wave functions, Franck-Condon integrations of these computer solutions, and sums over angular momentum. Thus general insights are not easily obtained from these, nor are they generally concerned with isolated level crossings. It is our intent here to show the general features for isolated crossings for many cases of interaction strength ( $V_{12}$ ) and potential slopes, so that the entire class of such experiments can be analyzed from these calculations.

As examples of the use of the theory presented here we will apply it to two measurements of spectra which show evidence of an avoided crossing.<sup>5,6</sup> We will not apply it to a Xe<sub>2</sub> case that has been reported recently,<sup>7</sup> due to uncertainty regarding the associated potentials and transition moments. Other examples doubtless exist, and it is our belief that many other cases could and should be observed, as this is a very powerful method for diagnosing the crossing region.

In Fig. 1 we give an example of an avoided level crossing and two bands which it influences. These hypothetical Na-Kr potentials are modeled after those calculated by Pascale and Vandeplanque,<sup>8</sup> but with slight changes to better illustrate the issues of interest here. The  $5P\Sigma$  and  $6S\Sigma$  adiabatic potentials in Fig. 1 undergo an avoided crossing at  $R_c$ , and we have indicated by dashed lines the diabatic-state potentials in this region. Also shown in the figure are the radiative transitions corresponding to strong dipole moments from the  $6S\Sigma$  diabatic state and the  $5P\Sigma$ diabatic state, the former being in the visible and the latter being in the uv region. The quasistatic spectrum, due to each of these transitions between a pair of diabatic states, has a single-valued relation  $\omega(R) = [V_i(R)]$  $-V_i(R)$   $\hbar^{-1}$  between the optical frequency ( $\omega$ ) and the internuclear separation (R), where  $V_i(R)$  refers to the upper, and  $V_i(R)$  to the lower, molecular diabatic state. The absorption or emission spectrum in the wings is given by the well-known quasistatic-theory result,<sup>9</sup> for emission



FIG. 1. Hypothetical Na-Kr adiabatic potentials represented by solid lines, diabatic potentials by dashed lines, and strongly allowed radiative transitions by vertical lines.

intensity  $I(\omega)$ ,

$$I(\omega)_{ij}^{OS} = \frac{4\pi R^2}{|d\omega/dR|} \left[ \frac{\omega}{\omega_0} \right] \left[ \frac{g_i}{g_{A(i)}} \right] \Gamma(R)$$
$$\times \exp\left[ \frac{-V_i(R)}{kT} \right] n_{A(i)} n_B , \qquad (1a)$$

and for the absorption coefficient  $k(\omega)$ ,

$$k(\omega)_{ij}^{\text{QS}} = \frac{4\pi R^2}{|d\omega/dR|} \left[ \frac{\lambda^2}{8\pi c} \right] \left[ \frac{g_i}{g_{A(i)}} \right] \Gamma(R)$$
$$\times \exp\left[ \frac{-V_j(R)}{kT} \right] n_{A(j)} n_B . \tag{1b}$$

Here  $n_{A(i)}$  is the density of atoms A in state *i* that connects to the diabatic state *i*, and  $n_B$  is the density of species B.  $\Gamma(R)$  is the spontaneous emission rate between the diabatic states *i* and *j*, and  $g_i$  is the statistical weight. (This expression also applies to stable diatomic molecules with appropriate relations between  $n_{AB(i)}$  and  $n_{A(i)}n_B$ .) Equations (1) are applicable when the relative population of nuclear motion states is characterized by a temperature. The avoided crossing at  $R_c$  changes this diabatic quasistatic spectra in the frequency region near  $\omega(R_c)$ .

In this Na-Kr example, one could excite in or detect emission from any of the bands that connect to the  $6S\Sigma$ or  $5P\Sigma$  states. For example, following uv absorption (during a collision) from the  $X\Sigma$  ground state to the coupled  $6S\Sigma$  and  $5P\Sigma$  states in the crossing region one could observe fluorescence from the 5P (or 6S) atomic state. Conversely, if the 5P (or 6S) atomic state were optically excited one would observe this same uv spectrum in emission, modified slightly by the different  $(k/k_0)$  factors and different V(R) in the exponential factor of Eqs. (1).

In Fig. 2 we qualitatively show an expanded view of the relevant Na-Kr difference potentials from Fig. 1, and the associated spectra. The spectra represented by dashed lines are the quasistatic spectra corresponding to the strongly allowed  $5P\Sigma - 3S\Sigma$  and  $6S\Sigma - 3P\Sigma$  diabatic-state transitions. As described previously, we represent the actual spectrum as being the product  $I(\omega)^{QS}L(\omega)$ , where  $L(\omega)$  contains the effects due to the avoided crossing. Qualitative shapes expected for spectra have been drawn as solid lines on the left side of Fig. 2, where four spectra, labeled *i-j*, are shown. In an emission experiment, the first state (6S or 5P) is the initially populated atomic state (at large R), and the second state (3P or 3S) is the final state after emission of a photon. The wavelength region of the observed emission band determines this final state. In an absorption experiment, 3S or 3P is the initially populated atomic level and 6S or 5P is populated after absorption of the wavelength shown in the figure. In this case the final state (6S or 5P) is detected by its fluorescence of an atomic line.

The essential features of these spectra are the appearance of satellites due to the adiabatic potential extrema and a step in intensity due to a small probability for "hopping" from one adiabatic state to another (corresponding to a small probability for remaining in a given diabatic state). For the spectra shown in Fig. 2 this intensity step is about a factor of 10, corresponding to a 10% hopping probability. The spectrum for total absorption from the 3S state is just the sum of the 6S-3S and 5P-3S spectra and similarly for total absorption from the  $3P\Sigma$  state.

The results of this paper are thus presented as spectra that describe absorption from a lower adiabatic state followed by separation to either or both of the crossing states. As already noted, the same  $L(\omega)$  multipliers also



FIG. 2. Na-Kr difference potentials (right side) and the resulting spectra (left side). The dashed line on the left is the diabatic-state spectrum and the solid lines qualitatively indicate the spectra for absorption or emission between the states indicated.

yield the spectrum for spontaneous emission during a collision, after either of these atomic states is initially populated. Within these possibilities one obtains a different crossing-region spectrum if one absorbs further in the wing than the crossing frequency and observes emission at the crossing frequency. This corresponds to absorption at  $R < R_c$  followed by a single traversal of the crossing region. Photodissociation of a bound molecule is also described by this "single-crossing" spectrum. On the other hand, absorption at  $\omega$  near  $\omega(R_c)$  with separation to an atomic state involves two transversals of  $R_c$ . We add the spectra from these two crossings incoherently in the current theory due to the phase cancellations that normally occur in impact parameter (b) and velocity ( $v_N$ ) averaging.

## **II. THEORY**

It is well known<sup>10,11</sup> that if the nuclear motion is taken to be a constant-velocity, straight-line (classical) path during a collision the Franck-Condon integral for the spectrum, taken over WKB nuclear states, reduces to  $\int dt \phi_{\alpha'}^*(t)\mu\phi_{\alpha}(t)e^{i\omega t}$  for a transition of frequency  $\omega$  between well-isolated electronic states  $\alpha$  and  $\alpha'$ . The farwing emission intensity is determined by a single collision during the time of interest and can then be expressed as an average over the spectrum due to complete, isolated collisions that occur at t = 0:

$$I(\omega) = \frac{2\omega^4}{3\pi c^3} \left| \int_{-\infty}^{\infty} dt \langle \phi_{\alpha}(t) | \mu | \phi_{\alpha'}(t) \rangle e^{i\omega t} \right|_{av}^2, \quad (2)$$

where the average is over impact parameter and velocity, weighted by the probability of occurrence per unit time. Here

$$\phi_{\alpha}(t) = \chi_{\alpha}(R, r_1, r_2, \dots, r_n)$$

$$\times \exp\left[-i\hbar^{-1}\int_{-\infty}^{t} U_{\alpha}(t')dt'\right]$$

is the diatomic electronic wave function with the nuclear coordinate given by  $R = (b^2 + v_N^2 t^2)^{1/2}$ , with impact parameter b and internuclear velocity  $v_N$ ;  $\chi_a(R, r_1, r_2, \ldots, r_n)$  is the electronic-state wave function for fixed R; and the av subscript refers to an average over collisions. This only applies to isolated states, which we identify as the diabatic states in the present case. The quasistatic spectrum [Eqs. (1)] for isolated states is obtained by evaluating Eq. (2) with the stationary phase approximation, then velocity and impact-parameter averaging, although the exponential distribution factor is lost by taking straight-line collision paths.<sup>1,2,9</sup> Or alternatively, Eqs. (1) with the exponential factor can be obtained directly from the Franck-Condon integrals with WKB wave functions,<sup>9</sup> as done originally by Jablonski.<sup>11</sup>

This time-domain picture of the classical path is shown diagrammatically in the top half of Fig. 3 for the Na-Kr collision example. We will now label the molecular states  $\phi_{\alpha}$  as  $\phi_0$  and  $\phi_{0'}$  for lower states of the radiative transitions and  $\phi_1$  and  $\phi_2$  for the diabatic crossing states.  $\phi_2$  has a transition dipole moment  $\mu_{20}$  and  $\mu_{20'}$  to states 0 and 0' and  $\phi_1$  has transition dipole moments  $\mu_{10}$  and  $\mu_{10'}$ .



FIG. 3. Potentials  $V_i(R)$  and occupation probabilities  $|a_i|^2$  during the course of a straight-line, classical-path Na-Kr atomic collision, as indicated at the top of the figure.

When the nonadiabatic coupling of states 1 and 2 is considered, the emission spectrum to state 0 associated with the crossing region is given by

$$I(\omega) = \frac{2\omega^4}{3\pi c^3} \left| \int_{-\infty}^{\infty} dt \langle \phi_0(t) | \mu | \psi(t) \rangle e^{i\omega t} \right|_{av}^2, \quad (3)$$

where

$$\psi(t) \cong B_1(t)\chi_1(R_c, r_1, r_2, \dots, r_n) + B_2(t)\chi_2(R_c, r_1, r_2, \dots, r_n)$$
(4)

is now the superposition of  $\chi_1(t)$  and  $\chi_2(t)$  that results from a collision of initially separated atoms that approach in one of these diabatic states. (The radiating atom A is initially in the atomic state 2 or 1 and a portion  $g_{mol}/g_{atomic}$  of the collisions follows the particular diabatic state of interest.) We assume the lower states are isolated at  $R = R_c$ , so that  $\phi_0(t)$  and  $\phi_0(t)$  adequately describes them. In Eq. (4) we have approximated the spatial part of the diabatic wave functions by their values at  $R = R_c$ ; this is equivalent to choosing  $\mu_{20}$ ,  $\mu_{20}$ ,  $\mu_{10}$ , and  $\mu_{10'}$ , as well as the interaction strength  $V_{12}$ , to be constants. The transition dipole moments are defined by

$$\langle \chi_i(R_c, r_1 r_2, \ldots, r_n) | \mu | \chi_j(R_c, r_1, r_2, \ldots, r_n) \rangle = \mu_{ij} .$$
(5)

With these matrix elements, substituting Eq. (4) and the form of  $\phi(t)$  given below Eq. (2) into Eq. (3) yields for the transition to state 0

$$I_{i0}(\omega) = \frac{2\omega^4}{3\pi c^3} \left| \int_{-\infty}^{\infty} dt \left[ \mu_{20} B_2(t) + \mu_{10} B_1(t) \right] \times \exp \left[ i \hbar^{-1} \int_{-\infty}^t U_0(t') dt' \right] e^{i\omega t} \Big|_{av}^2.$$
(6)

The subscripts on  $I(\omega)$  indicate that this is the spectrum due to a transition from initially populated state *i* to state 0, and  $B_1(t)$  and  $B_2(t)$  must be evaluated for this initial condition.

The probability amplitudes for the adiabatic states are indicated diagrammatically as  $|a_1|^2$  and  $|a_2|^2$  in Fig. 3. As noted previously, the full emission spectrum for collision with state 2 initially populated comes from both of the  $R_c$ -region crossings, shown in Fig. 3, and we add the spectra incoherently. Thus, for the example of state 2 initially populated, as shown in Fig. 3, we calculate the spectrum due to a single  $R_c$ -region transversal with a population  $|a_2|^2 = 1$  initially in state 2 at  $R \gg R_c$ . We then add a single-crossing spectrum due to  $|a_1|^2 = P$  initially at  $R \ll R_c$  and then add the single-crossing spectrum due to  $|a_2|^2 = 1 - P$  initially at  $R \ll R_c$ . By time reversal, this same composite spectrum describes absorption from state 0 with separation to state 2. Of course, an equivalent calculation applies for separation to state 1. Since a great deal of insight is gained from single-crossing solutions, and they also apply directly to photodissociation of stable molecules or absorption at  $R < R_c$  followed by emission at  $R \sim R_c$ , we will show many single-crossing spectra as well as these full "two-crossing" spectra.

An expanded view of states 1 and 2 in the crossing region is indicated in Fig. 4. Here we choose notation  $U_i(R)$  to indicate the diabatic-state potentials,  $V_i(R)$  for the adiabatic-state potentials, and  $V_{12}$  for the interaction between diabatic states 1 and 2 ( $\chi_1$  and  $\chi_2$ );  $F_i = dU_i(R_c)/dR_c$  are the slopes of the diabatic potentials in the crossing region. The Hamiltonian matrix elements in this approximation are given by

$$\langle \chi_0 | H | \chi_0 \rangle = U_0 = E_0 + F_0(R - R_c) ,$$

$$\langle \chi_1 | H | \chi_1 \rangle = U_1 = E_c + F_1(R - R_c) ,$$

$$\langle \chi_2 | H | \chi_2 \rangle = U_2 = E_c + F_2(R - R_c) ,$$

$$\langle \chi_1 | H | \chi_2 \rangle = V_{12} = V_{21} .$$

$$(7)$$

We will now calculate the spectrum due to a single crossing of  $R = R_c$  at  $t = t_1$  in Fig. 4. In the limit of a weak radiation field, being considered here, the following state-1-and-2 coupled equations then result from time-dependent perturbation theory in the crossing region:

$$i\hbar B_{1} = [F_{1}v(t-t_{1})+E_{c}]B_{1}+V_{12}B_{2} ,$$

$$i\hbar B_{2} = [F_{2}v(t-t_{1})+E_{c}]B_{2}+V_{12}B_{1} .$$
(8)

In Eqs. (8) we have made the substitution  $R = R_c + v(t-t_1)$  where  $v = v_N(1-b^2/R_c^2)^{1/2}$  (see Fig. 3). Note that this corresponds to passing through  $R_c$  from small R to large R as in the second crossing of Fig. 3. We can remove the  $E_c$  terms corresponding to the center of the



FIG. 4. Expanded view of the potentials in a crossing region.

crossing region from Eqs. (8) by including this in new  $B_{i0}(t)$  coefficients. We can also simplify Eq. (6) by including the time dependence of  $\phi_0(t)$  in these  $B_{i0}(t)$ . Thus we define

$$\boldsymbol{B}_{i0}(t) = \boldsymbol{B}_{i}(t) \exp\left[i\omega_{c}t + i\hbar^{-1}\int_{-\infty}^{t}U_{0}(t')dt'\right], \qquad (9)$$

where  $\omega_c = (E_c - E_0)/\hbar$ . We then obtain from Eqs. (8)

$$i\hbar \dot{B}_{10} = F_{10}v(t-t_1)B_{10} + V_{12}B_{20} ,$$

$$i\hbar \dot{B}_{20} = F_{20}v(t-t_1)B_{20} + V_{12}B_{10} ,$$
(10)

where  $F_{i0} = F_i - F_0$ . With these substitutions, Eq. (6) becomes

$$I(\omega) = \frac{2\omega^4}{3\pi c^3} \left| \int_{-\infty}^{\infty} dt [\mu_{20} B_{20}(t) + \mu_{10} B_{10}(t)] e^{i(\omega - \omega_c)t} \right|_{av}^2,$$
(11)

where the time limits  $\pm \infty$  correspond to the *R* well outside the crossing region. The solutions  $B_{i0}(t)$  from Eqs. (10) in Eq. (11) yield the spectrum. By this substitution we have shown that only the slope differences  $F_{20}$  and  $F_{10}$  influence the spectrum, as expected since this is just as in the ordinary theory for isolated states where only potential differences are relevant.<sup>1,2</sup> Consequently, we will classify the various spectra in terms of these slope differences, and for easy conceptualization we will use diagrams

of the potential differences,  $U_2 - U_0 = E_c - E_0 + F_{20}(R - R_c)$  and  $U_1 - U_0 = E_c - E_0 + F_{10}(R - R_c)$ .

Integration of Eqs. (10) from  $t = -\infty$  to  $\infty$  yields<sup>3</sup> the well-known Landau-Zener expression for the probability P of hopping to a different adiabatic state in traversing the crossing:

$$P = \exp(-2\pi\gamma), \quad \gamma = V_{12}^2 (\hbar v \mid F_{20} - F_{10} \mid)^{-1}. \quad (12)$$

To obtain the single-crossing spectrum we could evaluate Eqs. (10) for the  $B_{i0}(t)$  that result from one state (2 or 1) initially populated at  $t = -\infty$ . These  $B_{i0}(t)$  would then be used in Eq. (11), which Fourier analyzes them to obtain  $I(\omega)$ . These  $I(\omega)$  then have to be averaged over impact parameters and collision velocities to obtain a thermally averaged spectrum. The amplitudes  $B_i(t)$  are rapidly oscillating functions, as is the exp[ $i(\omega - \omega_c)t$ ] factor in Eq. (11). Thus Eqs. (10) and (11) must be evaluated with considerable care to obtain accurate solutions. A far easier procedure can be followed, which saves a factor of  $> 10^2$  in computer time, by recognizing that the integral in Eq. (11) represents the Fourier transform of the timedependent amplitudes  $B_{i0}(t)$ . Thus it is much more direct to transform Eqs. (10) into coupled differential equations for the Fourier-transform coefficients  $c_{i0}(\omega)$  of the  $B_{i0}(t)$ , and then the spectrum is given by the squared value of these coefficients. In particular, we define

$$c_{i0}(\omega) = \int_{-\infty}^{\infty} B_{i0}(t) e^{i(\omega - \omega_c)t} dt .$$
<sup>(13)</sup>

Then Eq. (11) becomes

$$I(\omega) = \frac{2\omega^4}{3\pi c^3} |\mu_{20}c_{20}(\omega) + \mu_{10}c_{10}(\omega)|_{av}^2.$$
(14)

Multiplying the coupled equations (10) by  $\exp[i(\omega - \omega_c)t]$ and integrating over time then yields coupled equations for the  $c_{i0}(\omega)$ :

$$i\frac{\partial c_{10}}{\partial \beta} = \gamma \frac{|F_{20} - F_{10}|}{F_{10}} (-\beta c_{10} + c_{20}),$$
  

$$i\frac{\partial c_{20}}{\partial \beta} = \gamma \frac{|F_{20} - F_{10}|}{F_{20}} (c_{10} - \beta c_{20}),$$
(15)

where

$$\beta = \hbar(\omega - \omega_c)/V_{12}$$

In obtaining Eqs. (15) an integration by parts is taken and the product function at the integral limits  $t \rightarrow \pm \infty$  is dropped, since it oscillates rapidly about zero. For  $\beta$  in the region of interest the  $c_{i0}(\beta)$  solutions of Eqs. (15) do not oscillate rapidly and Eq. (14) requires simply adding them and taking their absolute value. Thus, reliable solutions were obtained easily with a Runge-Kutta algorithm and a laboratory minicomputer.

The slope differences appearing in Eqs. (15) may be written in terms of an average slope  $\langle F_0 \rangle$ , a slope difference  $\Delta F_0$ , and a ratio  $s_0$ . Allowing for the j=0 or 0' lower level, we define

$$s_{j} = \langle F_{j} \rangle / \Delta F_{j}, \quad \langle F_{j} \rangle = (F_{2j} + F_{1j})/2,$$

$$\Delta F_{j} = (F_{2j} - F_{1j})/2.$$
(16)

Without loss of generality, we will label the states such that  $F_{20}$  is always greater than  $F_{10}$ . Equations (15) then become

$$i\frac{\partial c_{10}}{\partial \beta} = \frac{2\gamma}{s_0 - 1} (-\beta c_{10} + c_{20}) ,$$
  

$$i\frac{\partial c_{20}}{\partial \beta} = \frac{2\gamma}{s_0 + 1} (c_{10} - \beta c_{20}) .$$
(17)

There are now two classes of solutions. In the first case  $F_{20} > 0 > F_{10}$  or  $|s_0| < 1$ , and the adiabatic-state difference potentials have an extremum in the level-crossing region [Fig. 5(a)]. In this case, one expects and calculates a satellite in the spectrum. In the second case,  $|s_0| > 1$ , which is equivalent to  $F_{20} > F_{10} > 0$  or  $F_{10} < F_{20} < 0$  [Figs. 5(b) and 5(c)]. In this case the adiabatic difference potentials do not have an extremum in the crossing region, and we do not expect or obtain a satellite in the spectrum.

We are describing experiments in which an atom initially in state *i* undergoes a radiative transition to state *j* during a collision, and we will specialize to the case  $\mu_{20'}=1$ ,  $\mu_{10'}=0$  and  $\mu_{20}=0$ ,  $\mu_{10}=1$  as illustrated in Fig. 3. As noted in Eqs. (11) and (14), the emission spectra for these transitions are labeled  $I_{ij}(\omega)$ . For the conditions described below Eqs. (1) the absorption spectrum  $k_{ij}(\omega)$  is related to  $I_{ij}(\omega)$  by the Einstein A/B relation,<sup>9</sup> as in Eqs. (1), so we will only describe  $I_{ij}(\omega)$  below. This  $I_{ij}(\omega)$  spectrum also describes the intensity distribution in molecular bound-bound and bound-free bands when *i* and *j* are identified with the molecular states at  $R > R_c$ .

When state 1 is initially populated, the spectrum associated with a transition to state 0 is given by Eq. (14) with  $\mu_{10}=1, \mu_{20}=0$  [i.e.,  $I_{10}(\omega) \propto |c_{10}(\omega)|_{av}^2$ ]. Here  $c_{10}(\omega)$  is obtained by solving Eqs. (17) for an initial condition corresponding to unit population in state 1 and none in state 2 at the appropriate asymptotic  $\omega$  corresponding to large *R*. This corresponds to  $B_{10}(t_i)=1$  and  $B_{20}(t_i)=0$  in Eqs. (10), where the initial time  $t_i$  is a large negative number. On evaluating Eq. (13) in this asymptotic region using the stationary phase approximation and the asymptotic solution  $B_{i0}(t)=\exp[-iF_{10}v(t-t_1)^2/2\hbar]$  from Eqs. (10), the initial conditions for Eqs. (17) become

$$c_{20}(\beta \to -\infty) = 0,$$
  

$$c_{10}(\beta \to +\infty) = (h^{-1}dV_{10}/dt)^{-1/2}$$
  

$$= [h^{-1}F_{10}v_N(1-b^2/R_c^2)^{1/2}]^{-1/2}.$$

FIG. 5. Qualitative shapes of difference potentials for different slope ratios: (a) |s| < 1, (b) s > 1, and (c) s < 1. Solid lines are adiabatic curves, dashed lines are diabatic curves.

[Note that this  $|c_{10}(\beta \rightarrow +\infty)|^2$  is the  $|d\omega/dt|^{-1}$  factor of the normal quasistatic line-shape theory.<sup>9</sup>] In the other asymptotic limit (post crossing) we should obtain  $|c_{10}(\beta \rightarrow -\infty)|^2 = e^{-2\pi\gamma} |c_{10}(\beta \rightarrow +\infty)|^2$ .  $c_{10}(\omega_S)$  also contains a phase factor, but this has no effect on the spectrum, and for convenience we set it equal to 1. For this same initial condition the spectrum associated with a transition to state 0' is given by Eq. (14) with 0 replaced by 0' and  $\mu_{10'}=0$ ,  $\mu_{20'}=1$  [i.e.,  $I_{10'}(\omega) \propto |c_{20'}(\omega)|^2$ ]. Here  $c_{20'}(\omega)$  is obtained by solving Eqs. (17) modified by  $0\rightarrow 0'$ , subject to the appropriate boundary conditions. Similarly,  $I_{20}(\omega)$  and  $I_{20'}(\omega)$  are found by solving Eqs. (17) for the case of state 2 being initially populated at large R and inserting these  $c_{ii}(\omega)$  into Eq. (14).

If we had used the actual diabatic potentials  $U_i(R)$ , rather than the linear approximations, and actual collision orbits rather than the straight-line constant-velocity approximation, the spectrum  $I(\omega)_{ij}$  calculated with Eq. (6) or (14) would yield  $\sum_i I_{ij}(\omega) = I_{\alpha j}^{QS}(\omega)$  at  $\omega$  far from  $\omega_c$ (large  $|\beta|$ ). Here  $\alpha$  refers to the diabatic state that is radiatively connected to the lower-state j. With our simplifying approximations we instead obtain the  $T = \infty$  value of  $I_{\alpha j}^{QS}(\omega_c)$  at large  $|\beta|$  [see Eqs. (1)]. The difference, due to the variation in  $R^2 \exp[-V(R)/kT]$ , is a slowly varying, smooth function of  $\omega$ , so we correct our solution to the actual quasistatic spectrum by taking

$$I_{ii}(\omega) = \overline{L}_{ii}(\omega) I_{\alpha i}^{\text{QS}}(\omega)$$
(18a)

for emission and

$$k_{ij}(\omega) = \overline{L}_{ij}(\omega) k_{\alpha j}^{QS}(\omega)$$
(18b)

for absorption, where we have indicated by  $\overline{L}(\omega)$  the impact parameter and velocity averaging

$$\overline{L}_{ij}(\omega) = \frac{|F_{\alpha j}|}{hR_c^2} \int_0^\infty db \ b \\ \times \int_0^\infty dv_N f(v_N) v_N |c_{\alpha j}(\omega, v_N, b, i)|^2 .$$
(19)

Here we have explicitly noted the dependence of the  $c_{\alpha j}(\omega)$  on the initially populated state (*i*) and on *b* and *v*, and the constant in front of the integral normalizes  $\sum_{i} L_{ij}(\omega)$  to 1 far from the crossing.

As shown in a comparison below, we have found that there is little difference between  $\overline{L}_{ij}(\omega)$  obtained from the full b and  $v_N$  average in Eq. (19) and that obtained from only the  $v_N$  averaging for a fixed, appropriately chosen b. As it was much easier to carry out only the  $v_N$  average, we generally present such  $v_N$ -averaged  $\overline{L}_{ij}(\omega)$  below. These are also normalized by  $\sum_i \overline{L}_{ij}(\omega)=1$  far from the crossing. In the discussions below, we also frequently present the integrand of Eq. (19) without b or  $v_N$  averaging, in order to compare these single b,v solutions to the averaged spectrum. These single b,v solutions will be labeled  $L_{ij}(\omega)$ ; they are normalized to correspond to unit population in the initial state. In one instance the result of b and  $v_N$  averaging is compared to these.

The averaging, as in Eq. (19) or velocity averaged only with b = 0, results in a spectrum that depends on tem-

perature T, reduced mass  $\mu$ , and the potentials only through  $s_{\alpha}$  and  $P_S = e^{-2\pi\gamma_S}$ , where

$$\gamma_{S} = V_{12}^{2} / (\hbar | F_{20} - F_{10} | \tilde{v}) = \frac{V_{12}^{2}}{\hbar | F_{20} - F_{10} |} \left( \frac{\mu}{kT} \right)^{1/2}.$$
(20)

Here  $\tilde{v}$  is the most probable collision speed at temperature T. This  $P_S$  is the probability of making a transition from one adiabatic state to the other for a b = 0 collision at the most probable collision speed for a single crossing of  $R_c$ . This  $P_S$  will be used to label the v-averaged and (v,b)-averaged spectra, as well as two- $R_c$ -crossing spectra, although the averaged transition probability is different from  $P_S$ . Thus all combinations of  $\mu$ , T and potentials that produce the same  $P_S$  are represented by the spectra given below. The relation between  $P_S$  and the averaged transition probability will be given with these spectra.

The approximation of splitting the spectrum into  $\overline{L}$  and quasistatic parts [Eqs. (18) and (19)] is done so that these  $\overline{L}_{ij}(\omega)$  solutions can be used with all possible forms of  $U_i(R)$  potentials and all  $V_{12}$  values. As  $\omega \rightarrow \omega_c(\beta \rightarrow 0)$ , the primary region of interest, the accuracy of this approximation improves, and at large  $|\beta|$  it is also as good as the quasistatic theory, which is generally quite accurate. However, it is not formally correct, as we are replacing the average of a product with the product of two averages.

The  $f(v_N)$  in Eq. (19) is the Maxwellian distribution of collision speeds at the gas temperature. That this is appropriate at  $R_c$ , where the potential difference  $\Delta U_i = U_i(R) - U_i(\infty)$  may exceed kT, follows<sup>9</sup> from the canonical distributions of nuclear motion in a potential  $U_i(R)$  that is necessary for the validity of Eqs. (1), i.e.,

$$d^{3}P d^{3}R \exp[-E(P,R)/kT] = d^{3}R \exp[-V(R)/kT]d^{3}P \exp(-P^{2}/2\mu kT)$$

The condition for validity of this distribution will now be discussed.

The Maxwellian distribution of velocities in the crossing region is, of course, accurate for all  $|U_i(R_c)|$  $-U_i(\infty) | \ll kT$ , where  $U_i$  is the diabatic-state potential of the initially populated state [Fig. 6(a)]. It is also valid for collisions that enter or exit along a repulsive  $U_i(R)$ potential, even if  $U_i(R) - U_i(\infty) \gg kT$  [Figs. 6(b) and 6(c)], as discussed in the preceding paragraph using the canonical distribution of internuclear motion in  $U_i(R)$ . It is valid for strongly (more than kT) attractive initial-state interactions only if the bound states are thermally populated relative to free-collision states and if the vibrational spacings at  $R_c$  are less than kT. These criteria for attractive excited states are often not satisfied in fluorescence experiments, since the bound excited states are often less than thermally populated. This underpopulation of bound excited states is particularly severe if, as is likely, the crossing under study here causes rapid predissociation of these bound states. In this case fluorescence in the crossing region is almost entirely due to free-collision states that approach from  $R = \infty$  with an  $\sim kT$  wide range of energies and arrive at  $R_c$  with a similar spread of energies



FIG. 6. Illustration of various cases for absorption and emission between attractive and repulsive states.

and a mean energy of  $\sim U_i(\infty) - U_i(R_c) + kT$ . Absorption and separation to this attractive state *i* similarly involves only the free-collision states. This case is shown diagrammatically in Fig. 6(d).

We will assume that trajectories for  $b > R_c$  make a negligible contribution to the spectrum in the frequency range of interest, so we need only integrate over b from 0 to  $R_c$  in Eq. (19). We have carried out these averages first over  $v_N$ , which removes all of the oscillations in  $I(\omega)$ . The impact-parameter average is then relatively easy.

The linearization of R(t) to  $R - R_c = v_N t (1 - b^2/R_c^2)^{1/2}$  becomes a very poor approximation for the  $b \rightarrow R_c$  (grazing-incidence) case, as does the assumption that the two crossings add incoherently. As  $b \rightarrow R_c$  the Landau parameter  $\gamma$  becomes very small, the collision becomes nearly adiabatic, and a relatively narrow satellite in the initial adiabatic state V(R) occurs (for |s| < 1). However, after velocity averaging, the peak height of this narrow satellite in  $L_{ij}(\omega)$  grows as  $(1 - b^2/R_c^2)^{-\alpha}$ , where  $\alpha < \frac{1}{2}$ . Thus, when the  $\int db b$  of Eq. (19) is taken at fixed  $\omega$ , a finite spectrum is obtained at all frequencies. In practice, convergence at all frequencies was easily obtained, as described in Sec. III.

## **III. RESULTS**

In the present paper we have evaluated the spectra only for the most common situation, where the diabatic crossing states have strong transition moments to different lower levels. This means that in Eq. (14) for  $I(\omega)$  only one of the  $\mu_{ij}$  is nonzero. As discussed previously, we therefore consider two lower states, labeled 0 and 0', such that  $\mu_{20}=0$ ,  $\mu_{10}=1$  and  $\mu_{20'}=1$ ,  $\mu_{10'}=0$  (see Fig. 1 as an example where  $6S\Sigma = 2$ ,  $5P\Sigma = 1$ ,  $3P\Sigma$  or  $3P\Pi = 0'$ ,  $3S\Sigma = 0$ ). As described previously, we will present our results as a line-shape function  $\overline{L}_{ij}(\omega)$  such that the complete spectrum is given by  $I_{ij}(\omega) = \overline{L}_{ij}(\omega) I_{\alpha j}^{QS}(\omega)$ , where  $I_{\alpha j}^{\rm QS}(\omega)$  is the  $\alpha \rightarrow j$  quasistatic spectrum of the dipoleallowed diabatic state  $\alpha$ . This  $I_{ij}(\omega)$  is the spectrum which corresponds to a system initially in diabatic state i(=1 or 2) making a radiative transition to state j (=0 or 1)0'). The absorption coefficient for the inverse  $j \rightarrow i$  transition is given by  $k_{ij}(\omega) = T_{ij}(\omega)I_{ij}(\omega)$ , where  $T_{ij}(\omega)$  $=(B_{j\alpha}/A_{\alpha j})\exp[-\hbar(\omega-\omega_0)/kT]$  is a thermodynamic factor relating absorption and emission of a thermal vapor, and  $A_{\alpha j}$  and  $B_{\alpha j}$  are Einstein A and B coefficients. This same factor relates absorption and emission coefficients in the quasistatic theory.<sup>9</sup> The total absorption by an atom initially in state *j* is given by

$$k_{j}(\omega) = k_{1j}(\omega) + k_{2j}(\omega) = [\overline{L}_{1j}(\omega) + \overline{L}_{2j}(\omega)]k_{aj}^{QS}(\omega)$$
$$= A_{j}(\omega)k_{aj}^{QS}(\omega) ,$$

where we have defined the total absorption multiplier as

$$A_j(\omega) = \sum_i \bar{L}_{ij}(\omega) .$$
<sup>(21)</sup>

As noted below Eq. (19), the various  $\overline{L}_{ij}(\omega)$  will be labeled by their values for  $s_j$  and  $P_S$  [see Eqs. (16) and (20)] and plotted as  $\overline{L}_{ij}(\beta)$ , where  $\beta$  is related to  $\omega$  by Eqs. (15). Spectra for single-velocity and impact-parameter collisions, thermal averages, and thermal-plus-impactparameter averages for both single and double crossings are presented for a variety of  $s_j$  and  $P_S$  values. The single-crossing spectra will be for passing through  $R_c$ from small to large R. As discussed previously, the temperature corresponding to a value of  $P_S$  depends on the slopes and  $V_{12}$ , as given by Eq. (20). Since the associated temperature depends on the particular atom-atom system to be considered, the thermally averaged  $\overline{L}_{ii}(\omega)$  will be labeled only by  $P_S$ . In general, only  $L_{20}(\omega)$  and  $L_{20'}(\omega)$ will be presented, since, as will be discussed,  $L_{10}(\omega)$  and  $L_{10'}(\omega)$  may be easily obtained from them. Given a set of adiabatic potentials and a temperature, it is easy to calculate the values for  $s_i$  and  $P_S$ , for which a corresponding  $L_{ij}(\omega)$  may be found in our results. Conversely, given an experimental spectrum (either emission or absorption), information about the adiabatic potentials may be inferred by comparison with the  $L_{ii}(\omega)$  presented here. Examples will be given in Sec. IV, where we apply our theory to some published measurements.

Figure 7 shows all of the  $L_{ij}(\beta)$  for the  $s_0=0$ ,  $s_0 = 0.75$ ,  $P_S = 0.1$  single-crossing case (without any b or  $v_N$  averaging). These spectra would not be observed in a normal atom-atom collision experiment, since they correspond to a fixed b and  $v_N$  and to absorption at  $R < R_c$ followed by emission at  $R \sim R_c$ . In addition, the quasistatic spectrum results from averaging over b and v a single b,  $v_N$  spectrum for the diabatic-state oscillator. Something very similar to the single  $b, v_N$  spectrum might be observed in molecular photodissociation, but it is shown here primarily to offer insight into the types of spectra obtained before averaging. Also, in Fig. 7 we have shown



FIG. 7. Illustration of the line-shape multiplier  $L_{ij}(\beta)$  for a single b and  $v_N$  and the spectrum  $I_{ij}(\beta) = L_{i0}(\beta)I_{aj}^{QS}(\beta)$ , where the dashed lines are  $I_{aj}^{QS}(\beta)$ . The upper two figures relate to the  $i \rightarrow 0$  band, with  $s_0 = 0$ , as indicated in the potential diagram to the right. The lower figures are the  $i \rightarrow 0'$  band, with  $s_{0'} = -0.75$ , as indicated.

$$\begin{split} &I_{ij}(\beta) = L_{ij}(\beta) I_{\alpha j}^{\rm QS}(\beta) \text{ with the } I_{\alpha j}^{\rm QS}(\beta) \text{ having the qualitative features to be expected for the Na-Kr example shown in Fig. 1. Note that <math>\beta = \hbar(\omega - \omega_c)/V_{12}$$
 with  $\hbar\omega_c = E_c - U_0(R_c)$  for the  $L_{i0}$  spectra and  $\hbar\omega_c = E_c - U_0'(R_c)$  for the  $L_{i0'}$  spectra, where  $E_c = U_1(R_c) = U_2(R_c)$ . Thus these 0 and 0' spectra are in different wavelength regions. The fluorescent spectra which would result from starting in diabatic state 2 correspond to the  $L_{2j}(\beta)$  and those for starting in state 1 are the  $L_{1j}(\beta) - L_{2j}(-\beta) = P$ . For cases where  $|s_j| > 1$ ,  $L_{1j}(\beta) + L_{2j}(\beta) = 1$ .

In Fig. 8 the *b*-and- $v_N$ -averaged spectrum, the  $v_N$ -averaged spectrum for b = 0, and the single  $b, v_N$  spec-



FIG. 8. Illustration of the effects of velocity and impactparameter averaging on the line-shape multiplier  $L_{20}(\beta)$  for s=0. Single  $b, v_N$  (----),  $P_S=0.05$ ;  $v_N$  averaged (----),  $P_S=0.1$ .

trum are intercompared for the  $s_j=0$ , single-crossing case. Here, in order to obtain the same averaged hopping probability, we have chosen  $P_S=0.1$  for the *b*-and- $v_N$ averaged case and  $P_S=0.05$  for the latter two cases, i.e., the *b* averaging lowers the average hopping probability from 0.1 at b=0 to 0.05. As expected, all of the oscillations in the single  $b, v_N$  spectrum smooth out after averaging, except for a very weak undulation to the left of the satellite. This undulation also occurs for traditional satellites between isolated states, which are due to an extremum in the difference potential.<sup>12-14</sup> It is due to residual interference between contributions to  $I(\omega)$  that come from  $R > R_c$  and  $R < R_c$  for the same  $\omega$ . The large oscillations in the single  $b, v_N$  spectrum are due to the same cause.

It is noteworthy that a major satellite occurs in Fig. 8 near  $\beta = -1$ , the position where the initially populated adiabatic-state potential difference  $V_2(R) - V_0(R)$  has extremum, while no satellite or bump occurs near  $\beta = +1$ , although  $V_1(R) - V_0(R)$  has an extremum at this frequency. This can be understood by recognizing that the amplitude transferred to this "final" adiabatic state comes from the "initial" state during the transversal of the crossing. Thus, the final-state amplitude does not oscillate at the instantaneous frequency  $V_1(R)/\hbar$ , and as a result it does not produce a satellite at  $\beta = +1$ . As will be seen below, this absence of a second satellite in a single crossing occurs for all P and  $s_i$  values.

In Fig. 9 we show the variation of a  $v_N$ -averaged b = 0, single-crossing  $\overline{L}_{20'}(\beta)$  with  $s_j$  for  $P_S = 0.1$ . The resulting changes include a stretching or shrinking along the  $\beta$  axis as well as the change in shape as  $s_i$  passes through  $\pm 1$ . For  $|s_i| < 1$  we have the satellite feature as noted previously (Fig. 5 discussion) and none when  $|s_i| > 1$ . Another property is that for  $|s_i| < 1$  the solutions (with or by without  $v_N$  and averaging) are related b  $L_{ij}(\beta, s_j) = L_{ij}(\beta, -s_j)$ and for  $|s_{i}| > 1$ by  $L_{ij}(\beta, s_i) = L_{ij}(-\beta, -s_j)$ . Within each of the three re-



FIG. 9. Variation of  $\overline{L}_{20'}(\beta)$  with s, for the  $v_N$ -averaged  $P_S = 0.1$  case.

gions  $s_j < -1$ ,  $-1 < s_j < 1$ ,  $s_j < 1$  the solutions for different  $s_j$  are related by  $L_{ij}(\beta',s'_j) = L_{ij}(\beta,s_j)$  where  $\beta' = \beta[|1-(s'_j)^2|/|1-s^2_j|]^{1/2}$ . As  $s_j$  varies from 0 towards  $\pm 1$  the energy at which either of the adiabatic potentials is parallel to the lower level moves towards  $U_i(R_c)$  (refer to Figs. 4 and 5) and thus the satellite moves towards  $\beta=0$ .

In Fig. 10 the variation of  $\overline{L}_{20'}(\beta)$  with  $P_S$  is shown for b = 0 and  $s_j = 0$ . Note that as the collision becomes progressively more adiabatic  $(P_S \rightarrow 0)$  the satellite becomes more pronounced and moves towards  $\beta = -1$ . Before  $v_N$  averaging the asymptotic values of  $L_{20'}(\beta)$  are equal to the relative probabilities of being in state 2 before and after the crossing, i.e., the ratio equals  $P_S$ . However, as will be discussed shortly, this is not the case after  $v_N$  averaging.

In Fig. 11 we show an array of single-crossing  $L_{2i}(\beta)$ 



FIG. 10. Variation of the thermally averaged  $\overline{L}_{20'}(\beta)$  with  $P_S$  for s = 0.



FIG. 11. Single  $b_{v_N}$  (rapidly oscillating) and  $v_N$ -averaged (smooth)  $L_{ij}(\beta)$  for a range of  $P_S$  values. s = -2 for the top row and s = 0 for the bottom row.

and  $\overline{L}_{2i}(\beta)$  for  $P_S = 0.9, 0.5, 0.1, \text{ and } 0.01$  and  $s_i = -2$ and 0. Again, only single b,  $v_N$  and  $v_N$ -averaged spectra are shown. The averaged and unaveraged  $L_{1i}(\beta)$ , for  $s_{0'}=s_0$ , may be obtained from these  $L_{2j}(\beta)$  by  $L_{10}(\beta) = L_{20'}(-\beta), \quad L_{10'} = L_{20}(-\beta) \text{ for } |s_j| < 1 \text{ and}$  $L_{10}(\beta) = L_{20'}(\beta), \ L_{10'}(\beta) = L_{20}(\beta) \text{ for } |s_j| > 1.$  Also note that for the single  $b, v_N$  spectra  $L_{20'}(\beta) - L_{20}(\beta) = P$ for  $|s_j| < 1$  and  $L_{20'}(\beta) + L_{20}(\beta) = 1$  for  $|s_j| > 1$ . As shown diagrammatically in Fig. 5, these  $s_i = -2$  spectra in the top row of Fig. 11 correspond to potential slopes  $F_{10}$  and  $F_{20}$  such that the adiabatic potentials V(R) have no extrema. Thus, as discussed previously, the corresponding  $L_{2i}(\beta)$  show no satellites. The  $s_i = 0$  case of equal and opposite slopes  $(F_{10} = -F_{20})$ , shown in the bottom row of Fig. 11, is characteristic of all cases in which  $F_{10}$  and  $F_{20}$  have opposite signs, and the V(R) therefore have extremas. For this range of slope ratios  $(|s_i| < 1)$  a satellite always occurs. In fact, all  $s_i$  cases with  $|s_i| < 1$ can be generated from these s = 0 spectra, as discussed previously and demonstrated in the Appendix, by simply changing the horizontal ( $\beta$ ) axis, i.e., as  $|s_i| \rightarrow 0$ , the satellite becomes more sharply peaked near  $\beta = -1$ . Similarly, all  $s_i > -1$  cases can be obtained from the  $s_i = -2$ case shown in Fig. 11 by altering the horizontal scale, again as described in the Appendix. The  $s_i > 1$  cases are obtained simply by replacing  $\beta$  by  $-\beta$  in the  $s_i < -1$ cases. Thus all single-crossing slope ratios  $(s_i)$  and many transition probability cases ( $P_S = 0.01, 0.1, 0.5, 0.9$ ) can be obtained from the spectra shown in Fig. 11.

The asymptotic intensities of the single  $v_N$ , b=0,  $|s_j| < 1$  spectra in Fig. 11 are in the ratio  $L_{20'}(\infty)/L_{20'}(-\infty) = P_S$ , since these  $L_{20'}(\beta)$  are proportional to the population in diabatic state 2 and  $P_S$  is the hopping probability. This simple relationship no longer holds for the  $v_N$ -averaged or b-and- $v_N$ -averaged spectra  $\overline{L}_{20}(\beta)$ . This occurs because in the asymptotic limits the intensity  $|c_{20}(\beta)|^2$  is proportional to the population  $|B_{20}(\beta)|^2$  in state 2 times a factor  $(dR/dt)^{-1}$ , which is

proportional to  $v_N^{-1}(1-b^2/R_c^2)^{-1/2}$ . Thus the averaged single-crossing hopping probability  $\overline{P}$  is given by

$$P = \langle P(v_N, b) \rangle_{av}$$
  
=  $\frac{2}{\overline{v}_N R_c^2} \int_0^{R_c} db \ b \ \int_0^\infty dv_N v_N f(v_N) P(v_N, b) \ , \quad (22)$ 

where  $\overline{v}_N$  is the average collision velocity and  $P(v_N,b) = \exp\{-2\pi V_{12}^2/[\hbar|F_{20}-F_{10}|v_N(1-b^2/R_c^2)^{1/2}]\}$  from Eqs. (12) with  $v = dR/dt = v_N(1-b^2/R_c^2)^{1/2}$ . In contrast, the ratio of averaged intensities for the crossing is given by

$$\frac{\bar{L}_{20'}(\infty)}{\bar{L}_{20'}(-\infty)} = \frac{h}{|F_{20'}|} \left\langle \frac{P(v_N, b)}{v_N (1 - b^2 / R_c^2)^{1/2}} \right\rangle_{\rm av}$$
(23)

which weights small  $v_N$  and increasing *b*. The quantity in large angle brackets is the  $\beta \rightarrow \infty$  limit of  $|c_{\alpha j}|^2$  in Eq. (19), and we have made use of the fact that



FIG. 12. Averaged hopping probability  $\overline{P}$  for both  $v_N$  averaging only (solid line) and b and  $v_N$  averaging (dashed line) plotted as functions of  $P_S$ .

 $\overline{L}_{20'}(-\infty)=1$  due to normalization. Because of the weighting, the asymptotic values of the single  $v_N$  and  $v_N$ -averaged spectra in Figs. 10 and 11 are not exactly the same; this can be seen most clearly in the  $P_S=0.1$  example in the bottom row of Fig. 11.

The result of numerically evaluating Eq. (22) for  $\overline{P}$ , with b and  $v_N$  averaging and with only  $v_N$  averaging for b = 0, is compared to  $P_S$  in Fig. 12. (Recall that  $P_S$  is the hopping probability for a single b = v,  $v_N = \tilde{v}_N$  collision.) The ratio of the asymptotic emission intensity after a sinthat prior crossing, gle crossing to to the  $L_{20'}(\infty)/\overline{L}_{20'}(-\infty)$ , will be denoted by the symbol  $\mathscr{L}$ . The value of  $\mathscr{L}$ , for b and  $v_N$  averaging and  $v_N$  averaging only with b = 0, has been computed from Eq. (19) using asymptotic expressions for the  $|c_{\alpha j}|^2$ . The results are given in Fig. 13, where the averaged values are compared to the b = 0,  $v = \tilde{v}_N$  ratio.

In both the fluorescence and absorption experiments the two-crossing spectra should actually be used in the case of free atomic collisions to include the effect of absorbing (or emitting) at both  $R_c$  crossings. So far the  $L_{ij}$  that have been presented have been for increasing-R crossings only. The  $L_{ij}$  for decreasing-R crossings are obtained from the increasing-R by interchanging state labels  $1 \leftrightarrow 2$  and  $0 \leftrightarrow 0'$  in the i,j subscripts. Since ultimately we are interested in *b*-and- $v_N$ -averaged spectra we add the spectra from the two crossings incoherently; this is justified due to the cancellations of all rapid oscillations that occur with *b* and  $v_N$  averaging.

Referring to Fig. 3 it is apparent that the two-crossing, single  $b, v_N$  spectrum may now be written as  $L_{20'}^{2x}(\beta) = [L_{10}(\beta) + PL_{20'}(\beta) + (1-P)L_{10}(\beta)]/2$  with corresponding expressions for the other  $L_{ij}^{2x}$ . Here the factor of  $\frac{1}{2}$  is included for normalization. As in Eq. (19) the averaged spectrum can now be written as



FIG. 13.  $\mathscr{L}$  for both  $v_N$  averaging only (solid line) and b and  $v_N$  averaging (dashed line) plotted as functions of  $P_S$ .

$$\overline{L}_{20'}^{2x} = \frac{1}{hR_c^2} \int_0^\infty db \ b \ \int_0^\infty dv_N f(v_N) v_N$$

$$\times [ |F_{10}| |c_{10}|^2 + P |F_{20'}| |c_{20'}|^2 + (1-P) |F_{10}| |c_{10}|^2]/2,$$
(24)

where appropriate initial conditions and slopes are used in evaluating the  $|c_{\alpha j}|^2$ . Again there are corresponding expressions for the other  $L_{ij}^{2x}$ . In order to make use of the



FIG. 14. Single  $b_{v_N}$  (rapidly oscillating) and  $v_N$ -averaged (smooth) two-crossing line-shape multipliers  $L_{ij}^{2x}(\beta)$  for a range of  $P_S$  values. s = -2 in the top row and s = 0 in the bottom row.

single-crossing spectra we will use the following approximation to Eq. (24) for the two-crossing spectrum:

$$\bar{L}_{20'}^{2x}(\beta) = [\bar{L}_{10}(\beta) + \mathscr{L}\bar{L}_{20'}(\beta) + (1 - \mathscr{L})\bar{L}_{10'}(\beta)]/2, 
\bar{L}_{20}^{2x}(\beta) = [\bar{L}_{10'}(\beta) + \mathscr{L}\bar{L}_{20}(\beta) + (1 - \mathscr{L})\bar{L}_{10}(\beta)]/2.$$
(25)

Equation (25) is used for b = 0,  $v_N$  averaging, and for band  $v_N$  averaging, as long as all the  $\overline{L}_{ij}(\beta)$  and  $\mathscr{L}$  are averaged in the same way. The ratio  $\mathscr{L}$ , rather than  $\overline{P}$ , is used in Eq. (25) so that the emission intensity from diabatic state  $\phi_2$  after passing through the first crossing is equal to the emission intensity just before entering the second crossing, i.e., the population of the state is unaltered between crossings. The principle source of error in making the approximation of Eq. (24) is in treating the velocity distribution at the second crossing as being thermal, when in fact it is somewhat different due to the velocity selectivity of the hopping probability.

From the relations among the  $L_{ij}$  described above we can obtain the  $L_{1j}^{2x}$  as  $L_{10}^{2x}(\beta) = L_{20'}^{2x}(-\beta)$ ,  $L_{10'}^{2x}(\beta)$  $= L_{20}^{2x}(-\beta)$  for  $|s_j| < 1$  and  $L_{10}^{2x}(\beta) = L_{20'}^{2x}(\beta)$ ,  $L_{10'}^{2x}(\beta)$  $= L_{20}^{2x}(\beta)$  for  $|s_j| > 1$  for unaveraged or averaged  $L_{ij}^{2x}(\beta)$ . Of course, these relations between the spectra only hold for  $s_0 = s_{0'}$ . The previous comments regarding  $s_j$  variations also apply to these two-crossing spectra; all cases are contained in the spectra shown in Fig. 14, with appropriate changes in the  $\beta$  scale as described in the Appendix. Note that these thermally averaged two-crossing spectra do exhibit a weak maximum near  $\beta = -1$ , which was absent in the single-crossing case. This is due to approaching the second crossing with some population in the initially unpopulated state.

In Figs. 15 and 16 we show thermally averaged totalabsorption multiplier  $A_j(\beta) = \overline{L}_{1j}^{2x}(\beta) + \overline{L}_{2j}^{2x}(\beta)$  (for total absorption to states 1 and 2) since that is observed in some experiments. Examples of such experiments are the following. (1) Measurement of light attenuation (a twocrossing case). (2) Observation of total fluorescence from both states 1 and 2, or a state 3 to which these both radiate (a two-crossing case). (3) If state 2 is bound by many kT, absorption to 2 generally predissociates to state 1 be-



FIG. 15. Thermally averaged total-absorption spectra  $A_0(\beta)$  for  $P_S = 0.9$ ,  $P_S = 0.5$ ,  $P_S = 0.1$ ,  $P_S = 0.01$  and  $s_0 = 0$ .



FIG. 16. Thermally averaged total-absorption spectra for  $P_s = 0.01$  and s = 0.0, s = 0.5, s = 0.9.

fore radiation, so that fluorescence from state 1 represents essentially all of the absorption (a two-crossing case). (4) Photoabsorption from a bound molecule leads to dissociation, by absorbing directly to a repulsive state 1 or indirectly to bound states in state 2 that predissociate to state 1 (a single-crossing case). It is worth noting that in a molecular photodissociation experiment, spectra similar to the single  $b, v_N$  cases may be obtained by absorbing from a (optical-pumping-labeled, Ref. 15) single v'', J'' state.

For  $|s_j| > 1$  the two-crossing absorption spectrum is flat, i.e.,  $A_j(\beta) = 1$ . This is due to symmetry properties of the  $L_{ij}(\beta)$ , which are given in the Appendix.

# IV. COMPARISON TO EXPERIMENTS

We will discuss two published measurements of the spectra in the region of level crossings.<sup>5,6</sup> There are probably other observations that could be fitted into this picture, but these two are sufficient to demonstrate how to apply the present theory and as examples of its applicability.

(1) The green-wavelength absorption of Cs in the presence of a He buffer is dominated by absorption from the (primarily repulsive)  $6S\Sigma$  ground state to the  $5D\Sigma$  and  $7S\Sigma$  states of CsHe. The difference potentials, obtained by slightly modifying those calculated by Pascale<sup>16</sup> as suggested by the experimental spectrum, are shown on the right side of Fig. 17, and the "absorption" spectrum measured by Ferray et al. is shown on the left side. In this experiment the 852-nm fluorescence from the 6P state was actually detected while a laser was tuned in the (500-700)-nm region. This 852-nm fluorescence should be proportional to the total absorption to bound and free states of the 7S $\Sigma$  and 5D $\Sigma$  states, since the absorption to  $7S\Sigma$  yields primarily bound states. These should predissociate to 5D before radiation, and the 852-nm (6P-6S) fluorescence then follows the  $5D \rightarrow 6P$  decay.

The  $5D\Sigma$  state has a relatively strong transition moment to the  $6S\Sigma$  (ground) state, so we label these states 1 and 0, respectively, and take  $\alpha = 1$  in Eqs. (18). That the  $7S\Sigma$ - $6S\Sigma$  transition moment is small can be seen from



FIG. 17. Cs-He difference potentials (right side) and the measured (Ref. 5) total-absorption spectrum (left side). The adiabatic potential differences  $V_i - V_j$  are solid lines and the diabatic potential differences  $U_i - U_j$  are dashed lines.

the rapid decrease of intensity on the red wing of the 7S-6S (537-nm transition) in the data of Ref. 5, and this is verified by theory.<sup>14</sup> The quasistatic absorption spectrum  $k(\omega)_{10}^{OS}$  of the diabatic-state 1-to-0 transition, obtained from the difference potential  $U_1(R) - U_0(R)$  drawn in Fig. 17 as a dashed line, is shown as a solid line in the top figure of Fig. 18. When the Sando-and-Wormhoudt<sup>12</sup> satellite shape is used for the diabatic-state satellite at 5560 Å the dotted line in Fig. 18, which we label  $k(\omega)_{10}^{OS'}$ , is obtained. The value of  $s_0$  (-0.28) is obtained from the slopes  $F_{10}$  and  $F_{20}$  of the diabatic states in the crossing region, as shown in Fig. 17. For a temperature of 630 K with  $V_{12}$  and the adiabatic and diabatic potentials shown in Fig. 17, we calculate  $P_S \cong 0.23$ . From Fig. 13 it is seen that  $P_S = 0.23$  corresponds to  $\mathscr{L} \cong 0.1$  (after both b and



FIG. 18. Illustration of steps followed to calculate the Cs-He total-absorption spectrum (upper figure), and comparison of the calculated spectrum (dashed line) to the measured spectrum (solid line) in the lower figure.

 $v_N$  averaging). For a fixed value of  $\mathscr{L}$  (but different  $P_S$ ) Fig. 8 illustrates that the principle difference in the shapes of the spectra for  $v_N$  averaging versus b and  $v_N$  averaging is that the peak moves  $\sim 10\%$  closer to  $\beta = 0$  in the latter case. We therefore use the  $v_N$ -averaged  $P_S = 0.1$  $(\mathscr{L} \cong 0.1)$  curve of Fig. 15 to construct the totalabsorption line-shape multiplier  $A_0$ , but we expand the  $\beta$ scale by 10% in order to make it correspond to the totally averaged  $P_S = 0.23$  case. Since the  $L_{ij}(\beta)$  of Fig. 15 are for  $s_0=0$ , the  $\beta$  scale must also be multiplied by the factor  $[1-(0.28)^2]^{1/2}$  to make them correspond to  $s_0 = -0.28$ . The resulting  $A_0$  multiplier is shown as a dashed line on the top of Fig. 18, where we have used  $\beta = \hbar(\omega - \omega_c) / V_{12}$  and  $\hbar \omega_c = V_{20}(R_c) = V_{10}(R_c)$ . The lower half of Fig. 18 shows the experimental spectrum as a solid line and  $k_{10}^{OS'}(\omega)A_0(\omega)$  as a dashed line, arbitrarily normalized to the experimental spectrum since we are not concerned here with the actual value of  $\mu_{10}$ . As can be seen, the heights and positions of the satellites on either side of the minimum and the depth of the minimum are well represented by the calculated spectrum. This example clearly demonstrates how the transfer probability parameter  $P_S$  is accurately discernable from such data, since it determines the depth of the minimum and the shape of the satellites. The role of the slope ratio  $s_i$  is less clear without detailed fitting, which we have not done here.

The 5560-A wavelength of the diabatic-state satellite is very close to the 5600-A peak of  $A_0(\omega)$  in Fig. 18. As a result, the adiabatic difference potential reaches the same value at three different R, and the resulting three stationary-phase contributions to the intensity are coherently superimposed. Thus we do not expect our calculation to be accurate in this wavelength region. However, the size of the  $k_{10}^{OS}(\omega)$  and thus the predicted spectrum in the 5600-Å region is largely controlled by the steepness of  $V_{6s}$ , through the  $\exp[-V_0(R)/kT]$  factor in Eqs. (1) times  $\exp[-h(\nu-\nu_0)/kT]$ , as applies to absorption. The fact that the calculated spectrum is somewhat too small in the 5600-Å region is an indication that  $V_{6s}$ should probably be less steep in this  $R \cong (6-7)$ -Å region.

The  $V_{12}$  we used to obtain this good agreement between measured and calculated spectra is about a factor of 4.6 larger than the value calculated by Pascale,<sup>16</sup> and, in addition, we have shifted the difference potentials of Ref. 16 by  $-350 \text{ cm}^{-1}$ . We believe this is excellent accuracy for the calculation of potentials and mixing between highly excited states, and we would also like to draw attention to the great value of these calculated potentials in providing guidance for these interpretations.

(2) The  $A^{1}\Sigma_{u}$  state of the alkali dimers mixes with the  ${}^{3}\Pi_{u}$  state due to spin-orbit interaction, and these two states undergo an avoided crossing, as shown in Fig. 19. The *A*-*X* band of these alkali dimers should thus include the effect of this avoided crossing. Although this *A*-*X* band is a bound-bound spectrum the averaged intensity distribution (except in this crossing region) is very well<sup>17</sup> represented by the quasistatic spectrum  $I(\omega)_{A-X}^{OS}$ . As already noted, the present calculations also apply without significant modification to this avoided crossing because the vibration spacing at  $R_{c}$  is much less than kT. The effect of this avoided crossing on the Cs<sub>2</sub> *A*-*X* band has



FIG. 19. Cs<sub>2</sub> potentials (lower figure) and the associated absorption spectrum (upper figure). The measured absorption spectrum is the rapidly oscillating line; the A-X band  $I_{A-X}^{QS}(\omega)$  is the solid line, continued past 1.13  $\mu$ m as a short-dashed line; and the calculated spectrum  $A_0(\omega)I_{A-X}^{QS}(\omega)$  is the long-short-dashed line.

been reported by Benedict et al.,<sup>6</sup> who noted that the hole they observed in the absorption spectrum at 1.16  $\mu$ m was due to this avoided crossing. In Fig. 19 we show their Cs<sub>2</sub> absorption spectrum and the relevant Cs<sub>2</sub> potentials from Ref. 6. In the top half of Fig. 19 we reproduce the measured  $k(\omega)$  and calculated  $k(\omega)_{A-X}^{QS}$  from Ref. 6, and the latter times the  $A_0(\omega)$  we calculate for  $\mathcal{L}=0.01$  and  $V_{12} = 150 \text{ cm}^{-1}$ , where these parameters are chosen to fit the measured depth and width of the hole in the A-Xband. As in the previous Cs-He example, the quasistatic (diabatic-state) spectrum has a classical satellite just beyond the crossing wavelength, this time at 1.22  $\mu$ m. This again complicates the interpretation, since the quasistatic spectrum must be modified in this satellite region, and multiple coherences occur. Nonetheless, it is still clear from Fig. 19 that the present theory explains most features of the observed spectra rather well, including the extra satellite humps on either side of the minimum.

### **V. CONCLUSIONS**

Bound-bound molecular spectra are the most exact and powerful tool known for determining atom-atom interactions, which are normally referred to as diatomic molecular potentials. Almost all current knowledge of diatomics comes from such spectra. When a repulsive state is of interest, as is often the case in atom-atom energy-transfer collisions, free-free and bound-free continuum spectra are generally the most definitive method of obtaining the potentials. This approach is particularly accurate for transitions from a bound state that is already known (e.g., photodissociation), but it can also yield a unique and reasonably accurate set of potentials without this prior knowledge.<sup>9</sup> Velocity-selected differential scattering is another accurate, but difficult, method for studying repulsive states.

Here we have shown that, in addition to directly yielding the potentials of isolated states, molecular continuum spectra can also yield potentials in the region of level crossings. One can thus obtain the level-crossing parameters for inelastic atom-atom collisions (or molecular spectra) that result from isolated level crossings. We have shown the patterns of spectral behavior to be expected for a variety of level-crossing parameters and types of experiments. Based on these spectra in Sec. III the inversion procedure from data to  $V_{12}$  and potential slopes appears fairly straightforward and possibly unique.

The  $R_c$  value cannot be directly inferred from the crossing-region spectrum, but the entire quasistatic spectrum combined with ground-state potentials or molecular size can yield a fairly good estimate for this, as well as the dipole moments  $\mu_{10}$  and  $\mu_{20}$ .

In Sec. IV we have shown two examples of comparisons to spectra. The present theory fits these quite well, but we have not attempted here a detailed inversion to get accurate  $V_{12}$  and the potential slopes from the data. These examples clearly indicate the power and feasibility of this approach to the study of level crossings.

### ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant No. PHY-82-00805 through the University of Colorado. We wish to thank Dr. J. P. Visticot for valuable comments.

### APPENDIX: RELATIONSHIPS BETWEEN THE $L_{ii}(\beta)$

The initial conditions for the  $c_{ij}(\beta)$ , in the frequencyspace differential equations [Eqs. (17)], are determined by the initial conditions in the time domain. For example, if the initial condition at  $t = -\infty$  is  $B_1 = 0$ ,  $B_2 = 1$  in Eqs. (8) [the case shown diagrammatically in Fig. 5(a)], then for  $|s_0| < 1$  we must have  $c_{10}(\beta \rightarrow \infty) = 0$  since state 1 is unoccupied at large positive  $\beta$  [see Fig. 5(a)]. As discussed in the text, we set  $c_{10}(\beta) = 0$ ,  $c_{20}(\beta) = e^{-\pi\gamma} [F_{20}h^{-1}v_N(1-b^2/R_c^2)^{1/2}]^{-1/2}$  at some large positive  $\beta$  and integrate the equations (17) from positive to negative values of  $\beta$ . From similar arguments, the initial conditions on the  $c_{ij}(\omega)$  may be found for  $|s_0| > 1$ and either state initially (in time) occupied.

In order to demonstrate the properties of the  $|c_{i0}(\omega)|^2$  it is useful to rewrite Eqs. (17) directly in terms of these amplitudes with the  $d\omega/dt$  factors, mentioned in conjunction with Eq. (13), having been factored out. The appropriate substitutions for  $|s_0| < 1$  are

$$c_{10} = \left[\frac{hG_{10}}{\Delta F_0 v_N (1-b^2/R_c^2)^{1/2}(s_0-1)}\right]^{1/2} e^{i\theta},$$
  

$$c_{20} = \left[\frac{hG_{20}}{\Delta F_0 v_N (1-b^2/R_c^2)^{1/2}(s_0+1)}\right]^{1/2} e^{i\phi}, \quad (A1)$$
  

$$\xi = \theta - \phi,$$

where  $G_{10}$ ,  $G_{20}$ ,  $\theta$ , and  $\phi$  are real functions of  $\beta$  and  $G_{10}, G_{20} \ge 0$ .  $\Delta F_0$  is defined in Eqs. (16). When these substitutions are used, Eqs. (17) become

$$\frac{\partial G_{10}}{\partial \beta} = 4\gamma \left[ \frac{G_{10}G_{20}}{1-s_0^2} \right]^{1/2} \sin \xi ,$$

$$\frac{\partial G_{20}}{\partial \beta} = 4\gamma \left[ \frac{G_{10}G_{20}}{1-s_0^2} \right]^{1/2} \sin \xi ,$$

$$\frac{\partial \xi}{\partial \beta} = -\frac{4\gamma\beta}{1-s_0^2} + \frac{2\gamma \cos \xi}{(1-s_0^2)^{1/2}} \times \left[ \left[ \frac{G_{10}}{G_{20}} \right]^{1/2} + \left[ \frac{G_{20}}{G_{10}} \right]^{1/2} \right] .$$
(A2)

In order to have  $G_{10}, G_{20}$  be positive for  $|s_0| > 1$ , appropriate sign changes must be made in Eqs. (A1) which lead to equations different from (A2). Only equations corresponding to  $|s_0| < 1$  will be presented here though results for  $|s_0| > 1$  will be stated. The normalized unaveraged line-shape functions discussed in the text are related by

$$L_{10}(\omega) = G_{10}(\omega), \ L_{10'}(\omega) = G_{20'}(\omega),$$
 (A3a)

where the  $G_{ij}(\omega)$  result from Eqs. (A2) for state 1 initially populated, and

$$L_{20'}(\omega) = G_{20'}(\omega), \ L_{20}(\omega) = G_{10}(\omega),$$
 (A3b)

where the  $G_{ij}(\omega)$  result from Eqs. (A2) for state 2 initially populated.

The first two of Eqs. (A2) require  $G_{10} - G_{20} = \text{const}$  since their derivatives are identical. For  $|s_0| > 1$ , it is

- \*Also at Quantum Physics Division, National Bureau of Standards, Boulder, CO 80309.
- <sup>†</sup>Deceased.
- <sup>1</sup>N. Allard and J. Kielkopf, Rev. Mod. Phys. 54, 1103 (1982).
- <sup>2</sup>S. Y. Chen and M. Takeo, Rev. Mod. Phys. **29**, 20 (1957).
- <sup>3</sup>L. Landau, Phys. Z. Sowjetunion 1, 46 (1932); C. Zener, Proc. R. Soc. London, Ser. A 137, 696 (1932); E. Stueckelberg, Helv. Phys. Acta 5, 539 (1932); M. S. Child, *Molecular Collision Theory* (Academic, London, 1974).
- <sup>4</sup>P. Julienne, M. Krauss, and W. Stephens, Chem. Phys. Lett. 38, 374 (1976).
- <sup>5</sup>M. Ferray, J. P. Visticot, J. Lozingot, and B. Sayer, J. Phys. B 13, 2571 (1980).
- <sup>6</sup>R. Benedict, D. Drummond, and L. Schlie, J. Chem. Phys. 66, 4600 (1977).
- <sup>7</sup>N. Bowering, T. Raymond, and J. Keto, Phys. Rev. Lett. **52**, 1880 (1984).

found that  $G_{10}+G_{20}=\text{const.}$  Using initial conditions as described in the text for the  $c_{ij}(\omega)$  imposes the conditions  $|G_{10}-G_{20}|=P$  and  $G_{10}+G_{20}=1$  where P is the hopping probability defined by Eqs. (12). When  $s_0=s_{0'}$ , these relations together with Eqs. (A3) yield  $|L_{10}-L_{10'}|=P$ ,  $|L_{20}-L_{20'}|=P$  for  $|s_0|<1$  and  $L_{10}+L_{10'}=1$ ,  $L_{20}+L_{20'}=1$  for  $|s_0|>1$  as is evident from Fig. 11 for the  $L_{2j}$ . When averaging over  $v_N$  is considered P is replaced by  $\mathscr{L}$ .

If the substitutions  $G_{10} \rightarrow G_{20}$ ,  $G_{20} \rightarrow G_{10}$ ,  $\beta \rightarrow -\beta$ ,  $\xi \rightarrow \xi + \pi$  are made in Eqs. (A2), these equations are left unchanged. This fact, taken together with the initial conditions, means that  $L_{20}(\beta) = L_{10'}(-\beta)$  and  $L_{20'}(\beta)$  $= L_{10}(-\beta)$  for the case  $s_0 = s_{0'}$ ,  $|s_0| < 1$ . These relations show how the  $L_{1j}(\beta)$  are obtained from the  $L_{2j}(\beta)$ of Fig. 11. For  $|s_0| > 1$ , it is found that  $L_{20}(\beta)$  $= L_{10'}(\beta)$  and  $L_{20'}(\beta) = L_{10}(\beta)$ .

Another important property is the behavior of Eqs. (A2) under the change  $s_0 \rightarrow -s_0$ . If  $|s_0| < 1$ , then no change occurs so that  $L_{ij}(s_j,\beta) = L_{ij}(-s_j,\beta)$ , but if  $|s_0| > 1$ , we find  $L_{ij}(s_j,\beta) = L_{ij}(-s_j,-\beta)$ . This relation makes it possible to generate the s = 2 solutions from those shown for s = -2 in Fig. 11.

If the substitution  $\beta' = \beta/(1-s_0^2)^{1/2}$  is made in Eqs. (A2), the following is obtained:

$$\frac{\partial G_{10}}{\partial \beta'} = 4\gamma (G_{10}G_{20})^{1/2} \sin \xi ,$$

$$\frac{\partial G_{20}}{\partial \beta'} = 4\gamma (G_{10}G_{20})^{1/2} \sin \xi ,$$

$$\frac{\partial \xi}{\partial \beta'} = -4\gamma \beta' + 2\gamma \cos \xi \left[ \left[ \frac{G_{10}}{G_{20}} \right]^{1/2} + \left[ \frac{G_{20}}{G_{10}} \right]^{1/2} \right] .$$
(A4)

Note that  $s_0$  does not appear in these equations. This means that within a given regime of  $s_0 > 1$ ,  $|s_0| < 1$ , or  $s_0 < -1$  a solution for some value of  $s_0$  may be obtained from that for some other value of  $s_0$  by appropriately rescaling the  $\beta$  axis,  $L_{ij}(s_0,\beta) = L_{ij}(s'_0,\beta')$  where  $\beta(1-s_0^2)^{-1/2} = \beta'(1-s_0'^2)^{-1/2}$ .

- <sup>8</sup>J. Pascale and J. Vandeplanque, J. Chem. Phys. **60**, 2278 (1974).
- <sup>9</sup>D. Drummond and A. Gallagher, J. Chem. Phys. **60**, 3426 (1974). See Ref. 1 therein.
- <sup>10</sup>S. Bloom and H. Margenau, Phys. Rev. 90, 791 (1953).
- <sup>11</sup>A. Jablonski, Phys. Rev. 68, 78 (1945).
- <sup>12</sup>K. M. Sando and J. C. Wormhoudt, Phys. Rev. A 7, 1889 (1973).
- <sup>13</sup>J. Szudy and W. Baylis, J. Quant. Spectrosc. Radiat. Transfer 15, 641 (1975).
- <sup>14</sup>C. Carrington and A. Gallagher, Phys. Rev. A 10, 1464 (1974).
- <sup>15</sup>M. Kaminsky, R. Hawkins, F. Kowalski, and A. Schawlow, Phys. Rev. Lett. 37, 683 (1976).
- <sup>16</sup>J. Pascale, Phys. Rev. A 26, 2709 (1982); 28, 632 (1983).
- <sup>17</sup>L. Lam, A. Gallagher, and M. Hessel, J. Chem. Phys. 66, 3550 (1977).