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Collision induced transitions between $^2\Pi$ and $^2\Sigma$ states of diatomic molecules: Quantum theory and collisional propensity rules

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We develop the exact quantum description, free of any dynamical approximations, of rotationally inelastic collision induced transitions between $^2\Pi$ and $^2\Sigma$ electronic states of a diatomic molecule. An explicit connection is made between the matrix elements of the electrostatic coupling, described in an asymptotically exact *diabatic* basis, and the results of an *ab initio* calculation of the appropriate atom-molecule *adiabatic* electronic wave functions of A' and A'' symmetry. Analysis of the quantum close-coupled equations demonstrates that the use of Franck-Condon approximations in the description of $E \rightarrow E$ energy transfer is unjustified and, furthermore, that in collisions involving homonuclear diatomic molecules the s/a permutation-inversion symmetry of the molecular wave functions will be rigorously conserved. The extension of the infinite-order sudden approximation to electronically inelastic $^2\Pi \rightarrow ^2\Sigma$ processes allows us to predict two new collisional propensity rules: (a) When $\Delta J = 0$ the cross sections will become vanishingly small for transitions which conserve the e/f symmetry index of the molecular wave function. (b) In a high- J Hund's case (b) limit transitions from either the F_1 or F_2 $^2\Pi$ -state manifolds will populate only one of the Σ -state spin-doublet levels, consistent with a physical model in which the electronic spin S is a spectator so that the relative orientation of N and S is preserved during the collision.

I. INTRODUCTION

There has been considerable attention¹⁻⁸ devoted in recent years to developing the theoretical description of inelastic collisions involving open-shell diatomic molecules, where the relative motion of the collision partners can couple not only with the rotational motion of the molecule but also with the molecular electronic spin and/or orbital angular momenta. Most of this work has been limited to transitions between rotational and fine or hyperfine-structure levels of a *single* electronic state. However, the growing body of experimental studies⁹⁻²² devoted to the study of collision induced transitions between *different* electronic states now provides the incentive for the development of an exact theoretical description of these processes. Particularly relevant are the recent investigations by Katayama, Miller, and Bondybey of transitions between the $A^2\Pi$ and $X^2\Sigma^+$ states of CN,¹² CO⁺,^{13,14} and N₂⁺,^{15,16} and by Setser, Rosenwaks, and co-workers of transitions between the $A^3\Sigma_u^+$, $B^3\Pi_g$, and $W^3\Delta_u$ states of N₂.^{20,21}

Inspired by early experimental work^{9,10} on CN by Broida and collaborators, Gelbart and Freed²³ developed a simple mechanism for $E \rightarrow E$ energy transfer which made use of the known²⁴ non-Born-Oppenheimer mixing between various vibrotation levels of the $X^2\Sigma^+$ and $A^2\Pi$ states of CN. We have extended²⁵ this type of model and applied²⁶ it specifically to collision induced transitions between the low-lying $^1\Sigma^+$ and $^1\Sigma^-$ states of the alkaline earth oxides, where there had been suggestions²⁷⁻³⁰ that spin-orbit and/or orbit-rotation perturbations³¹ played an important role. It is now clear, however, that rapid $E \rightarrow E$ transfer occurs even in the absence of non-Born-Oppenheimer perturbations, as estab-

lished by the experimental work on N₂⁺^{15,16} and N₂,¹⁷⁻²² where the permutation-inversion symmetry of the molecular Hamiltonian²¹ prohibits any mixing between gerade and ungerade molecular electronic states.

In order to understand fully these electronically inelastic molecular collisions it is first necessary to develop a framework for the exact quantum description of the dynamics, which is free of the assumptions and approximations which characterized the earlier theoretical work mentioned above. In particular it will be important to separate the mixing between different electronic states caused by the electrostatic interaction with the collision partner, which will persist even between molecular states of different inversion symmetry, and the mixing induced by non-Born-Oppenheimer perturbations in the isolated molecule.

Our description of the wave function of the atom + molecule system will involve an expansion in an electronically *diabatic* basis, involving the $^2\Sigma$ and $^2\Pi$ wave functions of the isolated molecule. We shall demonstrate how one can obtain the necessary electrostatic coupling matrix elements, in this *diabatic* basis, from the electronically *adiabatic* energies and wave functions which would be the result of an *ab initio* calculation on the atom + molecule system. In this analysis we shall make use of an important series of papers by Rebenrost and Lester,^{12,33} which dealt with the related problem of the collision of an atom in a 2P electronic state with a closed-shell molecule.

The molecular Hamiltonian and wave functions of the isolated open-shell diatomic molecule are reviewed in Sec. II. This is followed in Sec. III by the complete discussion of the electrostatic coupling between the molecular states induced by approach of the collision partner. Then in Sec. IV we introduce the fully quantum description of the collision dynamics. In Sec. V we show how the resulting close-coupled equations can be decoupled in the infinite-order sud-

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TABLE I. Assignment of quantum numbers, indices, and labels to rotational levels of a diatomic molecule in ${}^2\Pi$ and ${}^2\Sigma$ electronic states.

Total angular momentum ^b	Π states ^a				
	ϵ^c	e/f	I^d	gerade s/a	ungerade s/a
$J+1$	+1	e	—	a	s
	—1	f	+	s	a
J	+1	e	+	s	a
	—1	f	—	a	s
Σ^+ states					
N^e	ϵ	e/f	I^d	gerade s/a	ungerade s/a
$J+1$	$J+1/2$	+1	e	—	a
	$J+3/2$	—1	f	+	s
J	$J-1/2$	+1	e	+	s
	$J+1/2$	—1	f	—	a
Σ^- states					
N^e	ϵ	e/f	I^d	gerade s/a	ungerade s/a
$J+1$	$J+1/2$	+1	e	—	a
	$J+3/2$	—1	f	+	s
J	$J-1/2$	+1	e	+	s
	$J+1/2$	—1	f	—	a

^a We assume a pure case (a) representation for the Π state. The assignment of the labels is identical for the $\Omega = 1/2$ and $\Omega = 3/2$ states. See Ref. 45 for a further clarification of the symmetry properties of the two Λ -doublet levels and the assignment of labels in the case (b) limit.

^b Without loss of generality we assume $(J - 1/2)$ is even.

^c See Eq. (1).

^d Total parity, see Ref. 40.

^e Value of the nuclear rotational angular momentum, the case (b) label.

den^{34–38} limit. Within the sudden limit we will obtain a number of useful new scaling relations (Sec. VI). Subsequently, in Sec. VII we use this formal work to demonstrate that the molecular s/a permutation-inversion symmetry will be rigorously conserved in collisions involving homonuclear open-shell diatomic molecules (such as N_2^+), and also to analyze critically the validity of Franck–Condon approximations for electronically inelastic collisions. Finally, we derive in Sec. VIII certain collisional propensity rules, similar to those we have derived previously^{5–7} for transitions entirely within a given electronic state. A brief conclusion follows. For those readers interested only in the implications of the collisional propensity rules, sudden factorization, and scaling relations on collision induced interelectronic transitions, we emphasize that the discussion in Secs. VI and VIII is independent of the exact quantal description of the intermolecular potential and scattering dynamics developed in Secs. II–V.

In the present article we shall explicitly ignore the additional degree of complexity imposed by the presence of non-Born–Oppenheimer mixing between the two electronic states of the isolated molecule in question. Consequently, the qualitative conclusions as derived here will apply only to systems where this mixing is either symmetry forbidden [as, for example, in N_2^+] or small [as, for example, between the $A\,{}^2\Pi(v' = 8)$ and $X\,{}^2\Sigma^+(v'' = 12)$ manifolds of CN^{24}]. The explicit treatment of collision induced transitions in the presence of strong non-Born–Oppenheimer mixing will be deferred to a later publication.

II. MOLECULAR ELECTRONIC STATES

The vibration-rotation-electronic wave functions of the isolated diatomic molecule will be described in a Hund's case (a) basis,^{31,39} namely,

$$|JM\Omega\epsilon\Lambda v\rangle = 2^{-1/2} [|JM\Omega\rangle | \Lambda\Sigma \rangle + \epsilon | JM, -\Omega \rangle | -\Lambda, -\Sigma \rangle] | v \rangle. \quad (1)$$

Here J denotes the total angular momentum with projection along space- and molecule-fixed axes of M and Ω , respectively; $| \Lambda\Sigma \rangle$ denotes the electronic wave function with projections Λ and Σ , respectively, of the electronic orbital and spin angular momenta along the molecular axis; and $| v \rangle$ denotes the vibrational wave function with quantum number v . For a ${}^2\Sigma$ state $\Lambda = 0$, $\Sigma = 1/2$, and $\Omega = 1/2$; for a ${}^2\Pi_{3/2}$ state $\Lambda = 1$, $\Sigma = 1/2$, and $\Omega = 3/2$; and for a ${}^2\Pi_{1/2}$ state $\Lambda = 1$, $\Sigma = -1/2$, and $\Omega = 1/2$. The symmetry index ϵ can take on the values ± 1 and the total parity of the molecular wave function is given by $\epsilon(-1)^{J-1/2+s}$,^{40,41} where $s = 1$ for Σ^- states and zero otherwise. For Π and Σ^+ states the $\epsilon = +1$ levels are labeled e and the $\epsilon = -1$ levels, labeled f .^{41,42} This assignment is reversed for Σ^- states. The assignment of ϵ , e/f , and parity to the molecular eigenstates is clarified in Table I.

The coordinate representation of the rotational wave functions in Eq. (1) is³⁹

$$|JM\Omega\rangle = [(2J+1)/4\pi]^{1/2} D_{M\Omega}^J(\alpha\beta, \gamma=0), \quad (2)$$

where $D_{M\Omega}^J$ is a rotation matrix element⁴³ with Euler angles which specify the orientation of the molecule with respect to a space-fixed coordinate system. We use active rotations⁴⁰ as defined by Brink and Satchler.⁴³ In a diatomic molecule the choice of the third Euler angle γ is arbitrary but must be made consistently for both the rotational and electronic parts of the wave function.³⁹ We have chosen $\gamma = 0$ here and have normalized accordingly, so that for $\beta = \pi/2$ the molecule frame x axis lies along the negative space frame z axis.

In this case (a) basis the matrix elements of the total Hamiltonian (electronic, spin-rotational, spin-orbit) can be defined²⁴ in terms of the following quantities:

TABLE II. The molecular Hamiltonian matrix in a case (a) basis consisting of ${}^2\Sigma$ and ${}^2\Pi$ vibration-rotation-electronic states.

i	H_{ij} ^a		
	$j = 1$	2	3
1	$x(x - \epsilon)B_\Sigma + T_\Sigma$	$\beta(1 - \epsilon x) + \alpha$	$-\beta(x^2 - 1)^{1/2}$
2	$\beta(1 - \epsilon x) + \alpha$	$x^2 B_\Pi + T_\Pi - \frac{1}{2}A_\Pi$	$-B_\Pi(x^2 - 1)^{1/2}$
3	$-\beta(x^2 - 1)^{1/2}$	$-B_\Pi(x^2 - 1)^{1/2}$	$(x^2 - 2)B_\Pi + T_\Pi + \frac{1}{2}A_\Pi$

^aReference 24. The definition of the states is $1 \equiv |JM_{\frac{1}{2}}\epsilon^2\Sigma v\rangle$, $2 \equiv |JM_{\frac{1}{2}}\epsilon^2\Pi v\rangle$ and $3 \equiv |JM_{\frac{3}{2}}\epsilon^2\Pi v\rangle$. The quantity $x \equiv J + 1/2$. For notational simplicity we have suppressed the dependence on the vibrational quantum numbers of the vibronic term values, rotational constants, spin-orbit constant, and the two non-Born–Oppenheimer matrix elements defined in Eq. (3). Note that the molecular Hamiltonian is diagonal in J , M , and ϵ .

$T_\Sigma(v)$, $T_\Pi(v) \equiv$ vibronic terms of the Σ and Π states, respectively;

$B_\Sigma(v)$, $B_\Pi(v) \equiv$ rotational constants of the Σ and Π states, respectively;

$A_\Pi \equiv$ spin-orbit constant in the Π state;

as well as the two non-Born–Oppenheimer matrix elements. The first of these is the orbit-rotation term²⁴

$$B(v', v) \equiv \langle v' | \langle \Lambda = 1, \Sigma | B(r) L_+ | \Lambda = 0, \Sigma \rangle | v \rangle, \quad (3)$$

where $B(r) \equiv \hbar^2/2\mu r^2$ (r designates the vibrational coordinate and μ the reduced mass of the diatomic molecule), and L_+ is the raising operator associated with the electronic orbital angular momentum. The integration in Eq. (3) extends over the vibrational and electronic degrees of freedom. The second non-Born–Oppenheimer matrix element is the spin-orbit term²⁴ $\alpha(v', v)$, which is defined identically to Eq. (3) except that $B(r)$ is replaced by the spin-orbit coupling constant $A(r)/2$. The complete molecular Hamiltonian matrix is given in Table II. We have not included the spin-rotation and Λ -doubling parameters,²⁴ since these lead to energy shifts which are negligible on the scale of a typical collision experiment.

In general the α and β off-diagonal coupling terms are small²⁴ and thus result in significant mixing between the Born–Oppenheimer Π and Σ states only where the rotational ladders of two different vibrational levels v' and v become degenerate.^{24,25} Usually this is confined to a narrow range of values of J (for various v' , v pairs), which corresponds to the location of maximum perturbation in the rotational progressions in observed spectra.

At large J , the off-diagonal mixing between the two Hund's case (a) Π states ($\Omega = 1/2$ and $\Omega = 3/2$) becomes increasingly large relative to the spin-orbit splitting.⁴⁴ This induces a mixing between the two case (a) wave functions in this intermediate coupling region. Eventually, a case (b) description⁴⁵ of the ${}^2\Pi$ state becomes appropriate, as will be discussed in more detail in Sec. VII B.

The vibronic wave functions of a homonuclear diatomic molecule are either symmetric (s) or antisymmetric (a) with respect to permutation of the identical nuclei.³¹ For *gerade* electronic states the even parity levels are s and the odd parity levels, a .⁴⁴ This association is reversed for *ungerade* states. The assignment of the s/a labels is clarified in Table I. Since the molecular Hamiltonian is totally symmetric, for a homonuclear diatomic molecule the α and β non-Born–Op-

penheimer coupling terms vanish between states of different permutation-inversion symmetry (as, for example, the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states of N_2^+).

III. ATOM–MOLECULE ELECTROSTATIC POTENTIAL

Since the cylindrical symmetry of the molecule is lifted by the approach of a collision partner, even if spherically symmetric, except of course for collinear geometries, electrostatic coupling will occur between Π and Σ electronic states which are characterized by different cylindrical symmetry. We are speaking here within an electronically *diabatic* description; the connection will be drawn later with the electronically *adiabatic* description that would be used in an *ab initio* calculation of the energies and wave functions of the atom + molecule system.

In order to describe this mixing it is first necessary to specify that the electronic wave functions will be described in a molecular frame (xyz) with z axis oriented along the molecular figure axis. The orientation of the molecular frame with respect to a space-fixed coordinate system is described by the Euler angles in Eq. (2). However, the collision is most conveniently described^{2,3,5,6,8} by making reference to the body frame (XYZ), where the Z axis lies along the vector displacement of the atom with respect to the center of mass of the molecule which we denote by R . The orientation of the molecular frame with respect to the body frame will be defined by the Euler angles $0, \theta, 0$.⁴⁶ Without loss of generality we have set the first and third Euler angles in the molecule-body transformation equal to zero. This choice implies that the y axes coincide in both frames, and, furthermore, that the xz planes coincide when $\theta = \pi/2$ (i.e., when the molecular figure axis is perpendicular to R).

In an earlier paper⁴⁶ we have analyzed in detail the electrostatic mixing between the electronic states of a Π -state molecule induced by the approach of a closed-shell perturber. For convenience we will partition the electronic wave function into spin and orbital terms

$$|\Lambda\Sigma\rangle = |\Lambda\rangle|\Sigma\rangle. \quad (4)$$

This partitioning is strictly speaking valid only for one- and two-electron wave functions. However, for more than two electrons, Slater determinants can be used to show that the results derived below are completely general.⁴⁶ The electrostatic coupling matrix elements between two diabatic states with arbitrary projections of the electronic orbital angular

momentum along the molecular figure axis are functions of R , r , and θ . These can be formally expanded as⁴⁶

$$\langle \Lambda' | V_{el} | \Lambda \rangle = \sum_{l=|\Lambda-\Lambda'|}^{\infty} d_{\Lambda-\Lambda',0}^l(\theta) V_{l,\Lambda'-\Lambda}(R, r). \quad (5)$$

Here $d_{mm'}^l$ is a reduced rotation matrix element,⁴⁶ $V_{lm}(R, r)$ can be related to an integral over the electronic coordinates, and r designates the vibrational coordinate. The $V_{lm}(R, r)$ satisfy the symmetry relation⁴⁶

$$V_{lm}(R, r) = V_{l,-m}(R, r). \quad (6)$$

In order to explore the connection between the electrostatic matrix elements given formally by Eq. (5) and the results of an *ab initio* calculation of the corresponding atom-molecule potential surfaces, it will be convenient to work with the definite symmetry Π -state electronic wave functions⁴⁶

$$|\Pi\eta\rangle = 2^{-1/2} [|\Lambda=1\rangle + \eta|\Lambda=-1\rangle], \quad (7)$$

where $\eta = \pm 1$. The $\eta = 1$ wave function is *antisymmetric* with respect to reflection in the molecule frame xz plane and the $\eta = -1$ wave function, *symmetric*. Thus the Σ^+ and $\Pi(\eta = -1)$ wave functions have A' symmetry in the reduced C_s symmetry group of the three atom system, while the $\Pi(\eta = 1)$ wave function has A'' symmetry.⁴⁷

Within the diabatic basis consisting of the Σ^+ , $\Pi(\eta = 1)$ and $\Pi(\eta = -1)$ wave functions the nonzero electrostatic matrix elements are given by specifying the appropriate values of Λ and Λ' in Eq. (5). We find

$$\langle \Sigma^+ | V_{el} | \Sigma^+ \rangle \equiv V_{\Sigma}(R, \theta, r) = \sum_{l=0}^{\infty} V_l^{\Sigma}(R, r) d_{00}^l(\theta), \quad (8)$$

$$\begin{aligned} \langle \Sigma^+ | V_{el} | \Pi(\eta = -1) \rangle \\ = -\langle \Pi(\eta = -1) | V_{el} | \Sigma^+ \rangle \equiv V_1(R, \theta, r) \\ = 2^{1/2} \sum_{l=1}^{\infty} V_l^1(R, r) d_{10}^l(\theta), \end{aligned} \quad (9)$$

and

$$\begin{aligned} \langle \Pi(\eta') | V_{el} | \Pi(\eta) \rangle &= \delta_{\eta\eta'} [V_{\Pi}(R, \theta, r) + \eta V_2(R, \theta, r)] \\ &= \delta_{\eta\eta'} \left[\sum_{l=0}^{\infty} V_l^{\Pi}(R, r) d_{00}^l(\theta) \right. \\ &\quad \left. + \eta \sum_{l=2}^{\infty} V_l^2(R, r) d_{20}^l(\theta) \right]. \end{aligned} \quad (10)$$

The quantities V_{Σ} , V_{Π} , V_1 , and V_2 designate the four independent diabatic potentials, which are each functions of R , r , and θ . The coefficients in the expansion of the angular dependence of each of these potentials, given in general by Eq. (5), are designated V_l^{Σ} , V_l^{Π} , V_l^1 , and V_l^2 . Each of the expansion coefficients are functions of the two radial coordinates R and r . As expected the single A'' wave function is not coupled with either of the A' wave functions. Furthermore, since $d_{10}^1(\theta=0) = 0 = d_{10}^1(\theta=\pi)$,⁴⁸ in collinear geometries the matrix of the electrostatic potential is purely diagonal; the Σ^+ and $\Pi(\eta = -1)$ wave functions correspond to different representations in $C_{\infty v}$ symmetry. It is worthwhile to observe that the diagonal Π state matrix elements for $\eta = 1$ and $\eta = -1$ differ in the relative phase of the $V_l^{\Pi}(R, r)$ and $V_l^2(R, r)$ contributions.

In the quantum treatment of the atom-molecule collision,

to be developed below, we shall expand the total wave function in terms of *adiabatic* vibronic states of the molecule, which are independent of the relative atom-molecule orientation angle θ . To proceed with this development it will be necessary to know the dependence on R , θ , and r of the V_{Σ} , V_{Π} , V_1 , and V_2 terms defined in Eqs. (9) and (10), or, alternatively, the dependence on R and r of the V_l^{Σ} , V_l^{Π} , V_l^1 , and V_l^2 terms in Eqs. (6) and (8)–(10). The situation is considerably more complicated than that encountered earlier in the treatment of inelastic collisions involving either a pure $^2\Sigma^+$ electronic state,^{5,8} where it is necessary to describe only the V_{Σ} potential, or a pure $^2\Pi$ state,^{1–3,6,46} where it is necessary to describe only the V_{Π} and V_2 potentials. In these cases there is no mixing between the $^2\Sigma^+$ and $^2\Pi$ states, and the required potentials can be obtained from *ab initio* calculations of the $\langle \Sigma^+ | V_{el} | \Sigma^+ \rangle$ or $\langle \Pi(\eta) | V_{el} | \Pi(\eta) \rangle$ electrostatic matrix elements (which are purely diagonal and correspond to the electronically *adiabatic* A' and, in the case of the $^2\Pi$ state, A'' potential energy surfaces) at various values of R , θ , and r . The *ab initio* points can then be fit to the formally correct expansion in l [Eq. (5)] by integration over θ to yield the V_l terms.^{48,49} In this context note that Eqs. (8) and (10) are identical⁴⁶ to the earlier developments^{1–3,5,6,8} in terms of regular and associated Legendre polynomials, because of the equivalence between those functions and the $d_{m0}^l(\theta)$ reduced rotation matrix elements.

Unfortunately, in the present case of mixing between $^2\Sigma^+$ and $^2\Pi$ states, it is not possible to extract the required *four* independent diabatic potentials [V_{Σ} , V_{Π} , V_1 , and V_2] from the *three* adiabatic potential surfaces, corresponding to the two A' and one A'' wave functions, which would result from an *ab initio* calculation. Inspired by the work of Rebentrost and Lester,³² we have developed a solution to this dilemma, as follows.

At each value of R , θ and r , the two electronically *adiabatic* wave functions of A' symmetry can be written as linear combinations of the Σ^+ and $\Pi(\eta = -1)$ *diabatic* wave functions, namely

$$\psi_1 = \cos \chi |\Sigma^+\rangle + \sin \chi |\Pi(\eta = -1)\rangle, \quad (11)$$

$$\psi_2 = -\sin \chi |\Sigma^+\rangle + \cos \chi |\Pi(\eta = -1)\rangle. \quad (12)$$

The expansion coefficients are all trigonometric functions of an adiabatic mixing angle χ , which can be obtained by resolution of the 2×2 Hamiltonian matrix defined by Eqs. (8)–(10). We have

$$\chi = \frac{1}{2} \tan^{-1} \left[\frac{2V_1}{V_{\Sigma} - (V_{\Pi} - V_2)} \right], \quad (13)$$

where we have suppressed the dependence on R , θ , and r . Since V_1 vanishes for $\theta = 0$ and $\theta = \pi$, χ equals zero for collinear geometries. It is also possible to derive the following relations between the *adiabatic* energies E_1 and E_2 corresponding to the wave functions ψ_1 and ψ_2 , which would be the direct result of an *ab initio* calculation:

$$\frac{1}{2}(E_1 - E_2) \sin 2\chi = V_1, \quad (14)$$

$$(E_1 - E_2) \cos 2\chi = V_{\Sigma} - V_{\Pi} + V_2, \quad (15)$$

and

$$E_1 + E_2 = V_{\Sigma} + V_{\Pi} - V_2. \quad (16)$$

The electronically adiabatic wave function of A'' symmetry, which we designate ψ_3 , is equal to the diabatic $\Pi(\eta = 1)$ wave function, with energy as a function of R , r , and θ given by Eq. (10), namely

$$E_3 = V_{\Pi} + V_2. \quad (17)$$

The discussion contained in the preceding paragraph is similar to the discussion of Rebentrost and Lester,³² except for the inclusion of the V_2 potential [Eq. (11)], which was explicitly ignored by Rebentrost and Lester.⁵⁰ As will be shown in Appendix A, in the particular case of collisions involving a homonuclear diatomic molecule the added symmetry associated with the permutation of the two identical nuclei implies that only *even* l terms will enter into the expansions for V_{Σ} , V_{Π} , and V_2 [Eqs. (8) and (10)]; and, in the expansion for V_1 [Eq. (9)] only *even* l terms will enter if the Σ and Π states have the *same* inversion symmetry, but only *odd* l terms will enter if the Σ and Π states have *opposite* inversion symmetry. From the symmetry properties⁴⁶ of the reduced rotation matrix elements this implies that $V(R, \theta, r) = V(R, \pi - \theta, r)$ for each of the diabatic matrix elements in Eqs. (8)–(10), *except* for Σ and Π states of opposite inversion symmetry, in which case the V_1 term satisfies the symmetry relation $V_1(R, \theta, r) = -V_1(R, \pi - \theta, r)$.

At each R , θ , and r the four unknown diabatic matrix elements are uniquely defined by the four linear equations (14)–(17). These can be solved to yield

$$V_{\Sigma} = E_1 \cos^2 \chi + E_2 \sin^2 \chi, \quad (18)$$

$$V_{\Pi} = \frac{1}{2}(E_1 \sin^2 \chi + E_2 \cos^2 \chi + E_3), \quad (19)$$

$$V_1 = \frac{1}{2}(E_1 - E_2) \sin 2\chi, \quad (20)$$

and

$$V_2 = \frac{1}{2}(-E_1 \sin^2 \chi - E_2 \cos^2 \chi + E_3). \quad (21)$$

Thus with the knowledge of the three adiabatic potential surfaces and the adiabatic mixing angle χ , it is possible to obtain the required diabatic potentials. The dependence of χ on R , θ , and r can, in principle, be obtained, following Rebentrost and Lester,³² by realizing from Eqs. (11) and (12) that, for R and r fixed,

$$\langle \psi_2 | \partial / \partial \theta | \psi_1 \rangle = -\langle \psi_1 | \partial / \partial \theta | \psi_2 \rangle = \partial \chi / \partial \theta. \quad (22)$$

This matrix element can be calculated either directly, or by finite differences in terms of the overlap between $\psi_2(\theta)$ and $\psi_1(\theta + \delta\theta)$ as follows:

$$\langle \psi_2 | \partial / \partial \theta | \psi_1 \rangle \simeq \langle \psi_2(\theta) | \psi_1(\theta + \delta\theta) \rangle / \delta\theta. \quad (23)$$

By expansion of $\chi(\theta)$ in an orthogonal basis it is possible to obtain χ from the knowledge of its derivative, as follows: $\partial \chi / \partial \theta$ will vanish at $\theta = 0$ and $\theta = \pi$, since $\chi(\theta)$ is periodic in this polar angle. Since $\chi(\theta)$ itself vanishes at $\theta = 0$ and $\theta = \pi$, an appropriate orthogonal basis is formed by the associated Legendre polynomials of order 2, which behave asymptotically as⁵¹

$$\lim P_l^2(\cos \theta) \sim \sin^2 \theta \simeq \theta^2 \quad (\text{for } \theta \text{ small}). \quad (24)$$

We then write, using the equivalence between $P_l^2(\theta)$ and $d_{20}^l(\theta)$,⁴³

$$\chi(\theta) = \sum_{l=2} C_l d_{20}^l(\theta). \quad (25)$$

Note that the expansion coefficients are functions of R and r .

As will be shown in Appendix B the first nonzero C_l coefficient is given by

$$C_2 = (5/4)6^{-1/2} \int_0^\pi (3 \cos \theta - \cos^3 \theta) (\partial \chi / \partial \theta) d\theta, \quad (26)$$

and the remainder ($l > 2$) can be generated by the two-term recursion relation

$$\begin{aligned} & \frac{(l+2)[(l+1)^2 - 4]^{1/2}}{(2l+3)} C_{l+1} - \frac{(l-1)(l^2 - 4)^{1/2}}{(2l-1)} C_{l-1} \\ &= -\frac{(2l+1)}{2} \int_0^\pi d_{20}^l(\theta) (\partial \chi / \partial \theta) \sin^2 \theta d\theta, \end{aligned} \quad (27)$$

with $l = 2, 3, \dots$. If the derivative of the adiabatic mixing angle has been determined at discrete values of θ in an *ab initio* calculation, then the integrals in Eqs. (26) and (27) can be evaluated numerically. This allows us to determine the expansion coefficients in Eq. (25), at least for low l , and hence obtain an approximation to $\chi(\theta)$ itself. From this, and the adiabatic electronic energies, one can obtain from Eqs. (18)–(21) the required electrostatic matrix elements in the diabatic basis at a finite grid of values of R , r , and θ .

IV. QUANTUM CLOSE-COUPLED FORMULATION OF THE COLLISION DYNAMICS

The total Hamiltonian for the atom + molecule system can be written as

$$\begin{aligned} H(\mathbf{r}, \mathbf{R}) = & -\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left(R^2 \frac{d}{dR} \right) \\ & + \frac{L_{\text{op}}^2}{2\mu R^2} + H_{\text{mol}}(\mathbf{r}) + V_{\text{el}}(R, r), \end{aligned} \quad (28)$$

where the first two terms correspond, respectively, to the relative and orbital kinetic energy of the atom–molecule pair; the third term is the diatomic molecule Hamiltonian, which we shall assume remains identical to the Hamiltonian of the isolated molecule, given in Table I; and the last term corresponds to the electrostatic coupling, which vanishes at sufficiently large R . The total atom–molecule wave function is usually expanded^{2–6,8,52,53} in terms of eigenfunctions of the total angular momentum \mathcal{J} , which are defined by

$$\begin{aligned} |JL\Omega\epsilon\Lambda\nu \mathcal{J} \mathcal{M}\rangle = & \sum_{M_L} (JMLM_L | \mathcal{J} \mathcal{M}) \\ & \times |LM_L\rangle |JM\Omega\epsilon\Lambda\nu\rangle, \end{aligned} \quad (29)$$

where $(\dots | \dots)$ is a Clebsch–Gordan coefficient, \mathcal{M} is the space-frame projection of \mathcal{J} , and L is the orbital angular momentum of the atom–molecule pair with space-frame projection M_L .

If one writes the total wave function as a linear combination of terms of the form (29), then, in the usual manner, the expansion coefficients can be shown to satisfy a set of “close-coupled” (CC) equations.^{2,3,5,6,8,52,53} The two nuclear kinetic energy terms in the Hamiltonian are diagonal in the total- \mathcal{J} basis, since L is a good quantum number for those operators. The matrix elements of the molecular Hamiltonian summarized in Table II are diagonal in L , J , and ϵ .

The desired matrix elements of the electrostatic poten-

tial in the $|JL\Omega\epsilon\Lambda v \mathcal{J}\mathcal{M}\rangle$ basis can, from Eq. (1), be written⁴⁶ as a linear combination of terms of the form

$$\sum_{\substack{MM' \\ M_L M_L'}} (JMLM_L | \mathcal{J}\mathcal{M}) (J'M'L'M_L' | \mathcal{J}'\mathcal{M}') \langle L'M_L' | \times \langle J'M'\Omega' | \langle v' | \langle \Lambda', \Sigma' | V_{el} | \Lambda, \Sigma \rangle | v \rangle | JM\Omega \rangle | LM_L \rangle. \quad (30)$$

Since the electrostatic potential is spin-independent, the innermost matrix element in Eq. (30) vanishes unless $\Sigma' = \Sigma$. Also, since it will be difficult enough to carry out the necessary *ab initio* calculations at one value of the molecular bond length r , we shall make a Franck–Condon approximation

$$\langle v' | \langle \Lambda' | V_{el} | \Lambda \rangle | v \rangle \simeq \langle v' | v \rangle \langle \Lambda' | V_{el}(R, r_0, \theta) | \Lambda \rangle, \quad (31)$$

where r_0 is the average bond length at which the potential has been determined. We can then introduce the formal expansion in Eq. (5) and carry out the integration over \hat{r} , and \hat{R} to obtain, using Eqs. (25) and (26) of Ref. 46,

$$\delta_{\mathcal{J}\mathcal{J}'} \delta_{\mathcal{M}\mathcal{M}'} \delta_{\Sigma\Sigma'} (-1)^{\mathcal{J}+J'+\Omega-\Lambda-\Lambda'} \times [(2L+1)(2L'+1)(2J+1)(2J'+1)]^{1/2} \langle v' | v \rangle \quad (32) \\ \times \sum_T \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J' & l & J \\ -\Omega' & \Lambda' - \Lambda & \Omega \end{pmatrix} \\ \times \begin{Bmatrix} J' & L' & \mathcal{J}' \\ L & J & l \end{Bmatrix} V_l^{\Lambda' - \Lambda}(R, r_0),$$

where $\{\dots\}$ and $\{\dots\}$ are, respectively, Wigner $3j$ and $6j$ symbols.⁴³

With Eq. (32) one can write the desired electrostatic matrix elements in the $|JL\Omega\epsilon\Lambda v \mathcal{J}\mathcal{M}\rangle$ basis in the following general form:

$$V_{JL\Omega\epsilon\Lambda v, J'L'\Omega'\epsilon'\Lambda'v'}(R) = (-1)^{\mathcal{J}+J'+\Omega-\Lambda-\Lambda'} \times [(2L+1)(2L'+1)(2J+1)(2J'+1)]^{1/2} \\ \times \langle v' | v \rangle \sum_T \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J' & L' & \mathcal{J}' \\ L & J & l \end{Bmatrix} \\ \times \frac{1}{2} [1 - \epsilon\epsilon' (-1)^{J'+J'+l}] V_l(J'\Omega'\epsilon'\Lambda', J\Omega\epsilon\Lambda; R). \quad (33)$$

Here the V_l coefficients are defined by

$$V_l(J'\frac{1}{2}\epsilon'\Sigma, J\frac{1}{2}\epsilon\Sigma; R) = \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} V_l^\Sigma(R), \quad (34) \\ V_l(J'\Omega'\epsilon'\Pi, J\Omega\epsilon\Pi; R) \\ = \delta_{\Omega\Omega'} \begin{pmatrix} J' & l & J \\ -\Omega & 0 & \Omega \end{pmatrix} V_l^\Pi(R) \\ + \epsilon(1 - \delta_{\Omega\Omega'}) \begin{pmatrix} J' & l & J \\ -\Omega' & 2 & -\Omega \end{pmatrix} V_l^\Pi(R), \quad (35)$$

$$V_l(J'\frac{1}{2}\epsilon'\Sigma, J\frac{1}{2}\epsilon\Pi; R) = V_l(J'\frac{1}{2}\epsilon'\Pi; J\frac{1}{2}\epsilon\Sigma; R) \\ = \epsilon \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix} V_l^\Pi(R), \quad (36)$$

$$V_l(J'\frac{1}{2}\epsilon'\Pi, J\frac{1}{2}\epsilon\Sigma; R) = \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & \frac{1}{2} \end{pmatrix} V_l^\Pi(R), \quad (37)$$

and

$$V_l(J'\frac{1}{2}\epsilon'\Sigma, J\frac{3}{2}\epsilon\Pi; R) = \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & -1 & \frac{3}{2} \end{pmatrix} V_l^\Pi(R). \quad (38)$$

If the Franck–Condon approximation is *not* made, then the matrix elements of the electrostatic potential averaged over the vibrational and electronic coordinates [Eq. (31)] will be explicitly indexed in the vibrational quantum numbers, namely,

$$\langle v' | \langle \Lambda' | V_{el} | \Lambda \rangle | v \rangle = V_{\Lambda'\Lambda}(v', v; R, \theta). \quad (39)$$

These vibrationally indexed potential matrix elements can now be expanded exactly as before [Eq. (5)], and matrix elements can be formed in the $|JL\Omega\epsilon\Lambda v \mathcal{J}\mathcal{M}\rangle$ basis. The resulting expressions are identical to those given in Eq. (33) except that the initial and final vibrational indices appear instead *within* the V_l terms, so that, for example, the Σ – Π coupling matrix element [Eq. (36)] becomes

$$V_l(J'\frac{1}{2}\epsilon'\Sigma v', J\frac{1}{2}\epsilon\Pi v; R) \\ = \epsilon \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix} V_l^\Pi(v', v; R), \quad (40)$$

where the $V_l^\Pi(v', v; R)$ coefficients refer to the expansion of the vibrationally indexed diabatic matrix elements [Eq. (39)] with $\Lambda' = 0$ and $\Lambda = 1$. Entirely equivalent vibrationally indexed expressions replace Eqs. (34)–(38).

The CC equations are propagated into the asymptotic region, where the S matrix can be obtained by standard procedures.^{5,6,8,52,53} The S - and T -matrix elements are indexed in the $J, L, \Omega, \epsilon, v$, and \mathcal{J} quantum numbers and indices for both the initial and final states. The degeneracy averaged integral cross sections are given by

$$\sigma_{J\gamma \rightarrow J'\gamma'} = \frac{\pi}{(2J+1)k_{J\gamma}^2} \sum_{L\mathcal{L}'} (2\mathcal{J}+1) |T_{JL\gamma, J'L'\gamma'}^{\mathcal{J}}|^2, \quad (41)$$

where the indices $\Omega, \epsilon, \Lambda, v$ are denoted collectively by γ , and $k_{J\gamma}^2$ is the wave vector in the initial channel.

In practice one must include enough diabatic $|JM\Omega\epsilon\Lambda v\rangle$ states to ensure convergence of the calculated S -matrix elements. If a particular subset of these states are nearly isoenergetic, then the off-diagonal elements of the molecular Hamiltonian (Table II) will be large, compared with the difference between the diagonal elements, so that substantial off-diagonal coupling will occur, even at $R = \infty$. In this case before solving the CC equations we construct the total- \mathcal{J} basis functions out of the diagonalized (deperturbed) molecular wave functions, namely,

$$|JL\epsilon F_i \mathcal{J}\mathcal{M}\rangle = \sum_{MM_L} (JMLM_L | \mathcal{J}\mathcal{M}) |LM_L\rangle |JMF_i\epsilon\rangle. \quad (42)$$

For a given J, M , and ϵ , F_i with $i = 1-3$ designates the particular linear combination of the $^2\Sigma$, $^2\Pi_{1/2}$, and $^2\Pi_{3/2}$ wave functions which diagonalizes the molecular Hamiltonian. If $D(J)$ designates the diagonalizing transformation, then, formally

$$|JMF, \epsilon\rangle = D_{11}|JM\frac{1}{2}\epsilon\Sigma v_\Sigma\rangle + D_{12}|JM\frac{1}{2}\epsilon\Pi v_\Pi\rangle + D_{13}|JM\frac{3}{2}\epsilon\Pi v_\Pi\rangle. \quad (43)$$

We observe that these transformed functions still define a *diabatic* basis, since we have assumed that the magnitude of the spin-orbit and orbit-rotation terms in the molecular Hamiltonian is independent of the presence of the collision partner. The desired matrix elements of the electrostatic potential can be obtained from a linear transformation of the potential matrix in the $|JL\Omega\epsilon\Lambda v\rangle$ basis, that is,

$$V_{J'L'\epsilon'F', J\epsilon F}^{\mathcal{J}} = \sum_{\substack{\Pi\Pi' \\ \Lambda\Lambda' \\ vv'}} D(J)_{F', J'\Lambda'v'} V_{J'L'\Omega'\epsilon'v', J\Omega\epsilon v}^{\mathcal{J}} [D(J)]_{F, J\Lambda v}^T. \quad (44)$$

V. INFINITE-ORDER SUDDEN APPROXIMATION

If the orbital angular momentum operator in Eq. (28) is taken to be a constant $L_{\text{op}}^2 = L^2$ and the molecular Hamiltonian set equal to some effective constant energy, then the CC equations can be solved within the infinite-order sudden (IOS) approximation.³⁴⁻³⁸ In this approximation the orientation angle θ is taken to be frozen during the time of the collision. This frozen-angle scattering results in an angle-dependent sudden S function. We shall initially assume that the averaging over the vibrational wave functions of the initial and final states can be done *after* computation of the sudden S function at a range of values of the molecular bond length. This we denote as a “vibrationally frozen” sudden approximation. Imposition of the Franck-Condon approximation then leads to S -matrix elements in the total- \mathcal{J} basis [Eq. (29)] which are isomorphic with the matrix elements of the electrostatic potential [Eqs. (33)–(38)].

In the case of scattering of a molecule in a pure Σ electronic state, the sudden (fixed-orientation) S function is obtained by solution of a one-channel problem.^{5,6,8,35-38} In the present situation, because the mixing due to the electrostatic coupling persists even though the atom-molecule orbital and rotational motion has been completely decoupled, we require *four* sudden S functions, equivalent to the four diabatic potentials defined by Eqs. (8)–(10), which we denote $S_\Sigma(\theta, r_0)$, $S_\Pi(\theta, r_0)$, $S_1(\theta, r_0)$, and $S_2(\theta, r_0)$. (Here we have explicitly restricted ourselves to an average value of r , in the Franck-Condon sense.)

For $E \rightarrow E$ transfer between the $^2\Sigma^+$ and $^2\Pi$ electronic states of a diatomic molecule these *four* S functions are obtained as follows⁴⁷: The V_Σ , V_Π , V_1 , and V_2 potentials define two separate diabatic fixed-angle scattering problems—a one-dimensional problem with potential $V_\Pi + V_2$, corresponding to scattering on the A'' adiabatic surface; and a two-dimensional problem with diagonal potentials V_Σ and $(V_\Pi - V_2)$ and off-diagonal potential V_1 , corresponding to scattering on the two A' surfaces. Within a *diabatic* framework it is unjustified to diagonalize this 2×2 problem before calculating the S matrix, unless one is willing to include off-diagonal terms in d/dR and d^2/dR^2 . The θ -dependent S -matrix element arising from solution of the 1×1 problem is

equal to $S_\Pi + S_2$; the two diagonal S -matrix elements arising from solution of the 2×2 problem are equal to S_Σ and $(S_\Pi - S_2)$; and the one off-diagonal S -matrix element from the 2×2 problem is equal to S_1 . The S_Π and S_2 S functions can be obtained directly by taking the sum and difference of the appropriate diagonal S matrix elements. Finally, the θ dependence of S_Σ , S_Π , S_1 , and S_2 can be fit to expansions in $d_{m0}^l(\theta)$ exactly as the V_Σ , V_Π , V_1 , and V_2 potentials [Eqs. (8)–(10)].

By imposing the Franck-Condon approximation as described earlier in this section we are implicitly assuming that the vibrational motion of the molecule is *slow* compared to the time scale of the collision, which may not be justified. If the potential is known over a range of values of r , then it is possible to carry out a *vibrationally adiabatic* IOS calculation, in which the vibrational motion is assumed to be *fast* compared to the time scale of the collision. This type of approximation has been used by several groups⁵⁴⁻⁶⁰ in the treatment of rovibrationally inelastic collisions of molecules in $^1\Sigma^+$ electronic states. The dimensionality of the IOS 1×1 and 2×2 fixed-angle scattering problems now becomes multiplied by the number of different Σ and Π vibrational levels that are included. Inclusion of n_Σ Σ -state vibrational levels and n_Π Π -state vibrational levels results in an $(n_\Sigma + n_\Pi) \times (n_\Sigma + n_\Pi)$ and an $n_\Pi \times n_\Pi$ fixed angle scattering problem. The potential matrix now involves the vibrationally indexed potential defined by Eq. (39). The relevant Σ - Σ and Σ - Π S functions are also vibrationally indexed [$S_\Sigma(v', v; \theta)$, $S_1(v', v; \theta)$] and are given directly by the appropriate S -matrix elements from the $(n_\Sigma + n_\Pi) \times (n_\Sigma + n_\Pi)$ scattering problem; while the $S_\Pi(v', v; \theta)$ and $S_2(v', v; \theta)$ S functions are equal to one-half the sum and difference, respectively, of the appropriate Π -labeled S -matrix elements from the solution of the $(n_\Sigma + n_\Pi) \times (n_\Sigma + n_\Pi)$ and $n_\Pi \times n_\Pi$ scattering problems. These various S functions can then be fit to expansions in $d_{m0}^l(\theta)$, exactly as the diabatic potentials, to generate S -matrix elements in the $|JL\Omega\epsilon\Lambda v\rangle$ basis which are isomorphic with those given by, for example, Eq. (39).

The \mathcal{J} -labeled T -matrix elements introduced in Eq. (41) are related to the corresponding S -matrix elements by

$$T_{JL\gamma, J'L'\gamma'}^{\mathcal{J}} = \delta_{JJ'}\delta_{LL'}\delta_{\gamma\gamma'} - S_{JL\gamma, J'L'\gamma'}^{\mathcal{J}}. \quad (45)$$

Regardless of whether the IOS approximation is carried out within the Franck-Condon or vibrationally adiabatic limits, the dependence of the S -matrix elements on the angular momentum quantum numbers is *identical*. Following the development leading to Eqs. (33)–(38) we find that the IOS approximation to the total- \mathcal{J} S -matrix elements is

$$S_{JL\Omega\epsilon\Lambda v, J'L'\Omega'\epsilon'\Lambda'v'}^{\mathcal{J}} = i^{L'+L-2L} (-1)^{J'+J+\mathcal{J}-\Omega} \times [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \times \sum_{\gamma} \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J' & L' & \mathcal{J} \\ L & J & l \end{Bmatrix} \times \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{J'+J+l}] S_l(J'\Omega'\epsilon'\Lambda'v', J\Omega\epsilon\Lambda v). \quad (46)$$

An overall phase factor corresponding to the “correct phase” convention of Khare *et al.*⁶¹ has been incorporated

into Eq. (46). The S_l coefficients in Eq. (46) are defined, in analogy with Eqs. (34)–(38), by

$$S_l(J' \frac{1}{2} \epsilon' \Sigma v', J \frac{1}{2} \epsilon \Sigma v) = \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} S_l^{\Sigma}, \quad (47)$$

$$S_l(J' \Omega' \epsilon' \Pi v', J \Omega \epsilon \Pi v) = \delta_{\Omega' \Omega} \begin{pmatrix} J' & l & J \\ -\Omega & 0 & \Omega \end{pmatrix} S_l^{\Pi} + \epsilon(1 - \delta_{\Omega' \Omega}) \begin{pmatrix} J' & l & J \\ -\Omega' & 2 & -\Omega \end{pmatrix} S_l^{\Sigma}, \quad (48)$$

$$S_l(J' \frac{1}{2} \epsilon' \Sigma v', J \frac{1}{2} \epsilon \Pi v) = S_l(J' \frac{1}{2} \epsilon' \Pi v', J \frac{1}{2} \epsilon \Sigma v) = \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix} S_l^{\Pi}, \quad (49)$$

$$S_l(J' \frac{3}{2} \epsilon' \Pi v', J \frac{1}{2} \epsilon \Sigma v) = \begin{pmatrix} J' & l & J \\ -\frac{3}{2} & 1 & \frac{1}{2} \end{pmatrix} S_l^{\Pi}, \quad (50)$$

and

$$S_l(J' \frac{1}{2} \epsilon' \Sigma v', J \frac{3}{2} \epsilon \Pi v) = \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & -1 & \frac{3}{2} \end{pmatrix} S_l^{\Pi}. \quad (51)$$

For notational convenience the explicit dependence on the vibrational quantum numbers, discussed above in both the Franck–Condon and vibrationally adiabatic limits, has been suppressed on the right-hand side of Eqs. (47)–(51). The S_l coefficients on the right-hand side of Eqs. (47)–(51) are the coefficients in the expansion of the angle dependence of the sudden S functions in terms of the appropriate $d_{mo}^l(\theta)$ reduced rotation matrix elements. It is the dependence of the sudden S -matrix elements, in Eqs. (47)–(51), on the angular momentum quantum numbers which will allow us to derive propensity rules for the various possible inelastic processes.

The IOS approximation to the degeneracy averaged electronically elastic but rotationally inelastic integral cross sections $\sigma_{J\epsilon^2\Sigma \rightarrow J'\epsilon^2\Sigma}$, $\sigma_{J\epsilon^2\Pi_{\Omega} \rightarrow J'\epsilon^2\Pi_{\Omega}}$, and $\sigma_{J\epsilon^2\Pi_{\Omega} \rightarrow J'\epsilon^2\Pi_{\Omega \pm 1}}$ are given, respectively, by Eq. (35) of Ref. 5 and Eqs. (47) and (48) of Ref. 6, and will not be repeated here.⁶² The Σ – Π electronically inelastic cross section can now be obtained from Eqs. (44) and (49)–(51):

$$\sigma_{J\epsilon^2\Pi_{\Omega} \rightarrow J'\epsilon^2\Sigma} = \sum_{l \geq 1} \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{J'+J+l}] (2J' + 1) \times \left[\begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix}^2 \delta_{\Omega, 1/2} + \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & -1 & \frac{3}{2} \end{pmatrix}^2 \delta_{\Omega, 3/2} \right] \sigma_l^{\Sigma}, \quad (52)$$

where the “base” cross sections are defined by

$$\sigma_l^{\Sigma} = \frac{\pi}{k^2} \sum_{L, L'} \frac{(2L+1)(2L'+1)}{(2l+1)} \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2 |S_l^{\Sigma}|^2. \quad (53)$$

The restriction on the summation in Eq. (52) reflects the fact that the $3j$ symbols vanish for $l < 1$. The individual σ_l^{Σ} terms make a nonzero contribution to the cross section only for

certain combinations of ϵ , ϵ' , J , J' , and l . These values are governed by the triangle inequality contained in the $3j$ symbols and the selection rules summarized in Table I of Ref. 5 and Table I of Ref. 6, which are imposed by the phase factor in square brackets in Eq. (52).

VI. SUDDEN LIMIT FACTORIZATION PROPERTIES AND SCALING RELATIONS

A. Pure Hund's case (a) basis

There are several interesting insights which can be deduced from Eq. (52), which is the sudden scaling relation appropriate to collision induced $^2\Pi$ – $^2\Sigma$ transitions. First, exactly as in the case of transitions entirely within an electronic state of $^2\Sigma$ or $^2\Pi$ symmetry,^{5,6} the cross sections will be independent of either a reversal or change in sign in the symmetry indices of the initial and final states. In other words,

$$\sigma_{J\epsilon^2\Pi_{\Omega} \rightarrow J'\epsilon^2\Sigma} = \sigma_{J, -\epsilon, ^2\Pi_{\Omega} \rightarrow J', -\epsilon', ^2\Sigma} \quad (54a)$$

$$= \sigma_{J\epsilon^2\Pi_{\Omega} \rightarrow J'\epsilon^2\Sigma}. \quad (54b)$$

The base cross sections in Eq. (52), which are *independent* of Ω , can as in the case of transitions within a $^2\Sigma$ or $^2\Pi$ manifold,^{5,6} be expressed in terms of cross sections into (or out of) the $J = 1/2$ level. If J' is set equal to $1/2$ in Eq. (52), the sum over l collapses to two terms, one of which vanishes because of the phase factor in square brackets. By evaluation of the $3j$ symbol, one can derive the following expressions for the base cross sections:

$$\sigma_l^{\Sigma} = [(2l+1)(l+1)/(l+2\Omega-1)] \times \sigma_{J=l+1/2, \epsilon^2\Pi_{\Omega} \rightarrow J'=1/2, \epsilon^2\Sigma}, \quad (55a)$$

$$= [(2l+1)l/(l+2-2\Omega)] \times \sigma_{J=l-1/2, \epsilon^2\Pi_{\Omega} \rightarrow J'=1/2, -\epsilon, ^2\Sigma}. \quad (55b)$$

Either of Eqs. (55a) or (55b) can be reintroduced into Eq. (52) to give an expression for *all* electronically inelastic $^2\Sigma$ – $^2\Pi_{\Omega}$ cross sections in terms of cross sections out of a single Λ doublet in either the $\Omega = 1/2$ or $\Omega = 3/2$ Π -state manifolds.

Equations (55a) and (55b) further imply a relationship between the ϵ -conserving and ϵ -changing $\Pi_{\Omega} \rightarrow \Sigma$, $J = 1/2$ cross sections, namely,

$$\sigma_{J\epsilon^2\Pi_{1/2} \rightarrow J'=1/2, \epsilon^2\Sigma} = \left(\frac{J-1/2}{J+1/2} \right)^2 \sigma_{J-1, \epsilon, ^2\Pi_{1/2} \rightarrow J'=1/2, -\epsilon, ^2\Sigma} \quad (56a)$$

and

$$\sigma_{J\epsilon^2\Pi_{3/2} \rightarrow J'=1/2, \epsilon^2\Sigma} = \left[\frac{(J-1/2)(J+3/2)}{(J+1/2)(J-3/2)} \right] \sigma_{J-1, \epsilon^2\Pi_{3/2} \rightarrow J'=1/2, -\epsilon, ^2\Sigma}. \quad (56b)$$

Thus, in the high- J limit the ϵ -conserving $J\Pi_{\Omega} \rightarrow J' = 1/2$, Σ cross sections are identical to the ϵ -changing $J-1$, $\Pi_{\Omega} \rightarrow J' = 1/2$ Σ cross sections.

We can also use Eqs. (55a) and (55b) to explicitly relate the cross sections for $^2\Pi_{3/2} \rightarrow ^2\Sigma$ transitions to those for $^2\Pi_{1/2} \rightarrow ^2\Sigma$ transitions. We find that

$$\sigma_{J\epsilon^2\Pi_{3/2} \rightarrow J' = 1/2, \epsilon^2\Sigma} = \left[1 + \frac{2}{J - \frac{1}{2}} \right] \sigma_{J\epsilon^2\Pi_{1/2} \rightarrow J' = 1/2, \epsilon^2\Sigma} \quad (57a)$$

and

$$\sigma_{J\epsilon^2\Pi_{3/2} \rightarrow J' = 1/2, -\epsilon^2\Sigma} = \left[1 - \frac{2}{J + \frac{3}{2}} \right] \sigma_{J\epsilon^2\Pi_{1/2} \rightarrow J' = 1/2, -\epsilon^2\Sigma} \quad (57b)$$

These last two equations imply, at least for transitions into or out of the $J = 1/2$ levels of the Σ rotational manifold, that the cross sections for Σ - $\Pi_{3/2}$ ϵ -conserving transitions are greater than those for Σ - $\Pi_{1/2}$ ϵ -conserving transitions. This ordering is reversed for ϵ -changing transitions. The ratios decrease as J increases, dropping from a value of 3 at $J = 3/2$, down to unity in the high- J limit.

B. Intermediate and Hund's case (b) coupling

When the spin-orbit coupling is large compared with the rotational spacing, the molecular states of Π electronic symmetry can be accurately described in the pure Hund's case (a) representation assumed above. For light molecules or for large J the spin-orbit coupling is small compared to the rotational spacing and the molecular states are more appropriately expressed in terms of a Hund's case (b) representation. In general, the $^2\Pi$ molecular wave functions can be written as a linear combination of the $\Omega = 1/2$ and $3/2$ pure case (a) basis functions defined in Eq. (1)^{44,45,63}:

$$|JMF_1\epsilon\Pi v\rangle = \cos\theta_J |JM\frac{1}{2}\epsilon\Pi v\rangle + \sin\theta_J |JM\frac{3}{2}\epsilon\Pi v\rangle \quad (58)$$

and

$$|JMF_2\epsilon\Pi v\rangle = -\sin\theta_J |JM\frac{1}{2}\epsilon\Pi v\rangle + \cos\theta_J |JM\frac{3}{2}\epsilon\Pi v\rangle \quad (59)$$

F_1 and F_2 designate the lower and higher energy levels, and the Λ doublets are still designated by the spectroscopic labels⁴⁵ e if $\epsilon = +1$ and f if $\epsilon = -1$. The angle θ_J , which describes the degree of mixing of the pure case (a) wave functions, can be obtained by diagonalizing the 2×2 molecular Hamiltonian matrix given in the lower right-hand corner of Table II.⁴⁴ In the pure case (a) limit, θ_J equals zero for a regular and $\pi/2$ for an inverted² state. In the pure case (b) limit, θ_J equals $\pi/4$ at high J .

The exact quantum formulation developed in Sec. IV could equally well be based on the intermediate coupled Π -state basis functions [Eqs. (58) and (59)]. This would lead to expressions for the potential matrix elements formally equivalent to Eq. (47) but with the transformation matrix $D(J)$ obtained, as discussed above, by diagonalizing only the 2×2 Π subspace of the molecular Hamiltonian. In the sudden limit the electronically inelastic cross sections in this intermediate coupled basis are given by

$$\sigma_{J\epsilon^2\Pi_{F_1} \rightarrow J'\epsilon^2\Sigma} = \sum_{l=1}^{\infty} \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{J+J'+l}] (2J'+1) G_l^{\epsilon}(J'J) \sigma_l^1, \quad (60)$$

where

$$\begin{aligned} G_l^{\epsilon}(J'J) &= \cos^2\theta_J \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix}^2 + 2\epsilon \sin\theta_J \cos\theta_J \\ &\times \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & -1 & \frac{3}{2} \end{pmatrix} \\ &+ \sin^2\theta_J \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & -1 & \frac{3}{2} \end{pmatrix}^2 \end{aligned} \quad (61)$$

The expression for $G_l^{\epsilon}(J'J)$ is given by Eq. (61) but with $\cos\theta_J$ replaced by $-\sin\theta_J$ and $\sin\theta_J$ replaced by $\cos\theta_J$, consistent with Eqs. (58) and (59).

The $G_l^{\epsilon}(J'J)$ factors have an asymmetric dependence on ϵ and ϵ' , so that the cross sections are no longer invariant with respect to a reversal or change in sign of the symmetry indices of the initial and final states, as was true in the pure case (a) limit [Eq. (54)]. However, because the σ_l^1 base cross sections which appear in Eq. (60) are still independent of Ω , the electronically inelastic cross sections can be completely factorized regardless of the strength of the mixing of the pure case (a) basis. Arguments identical to those leading to Eq. (55) allow one to write the base cross sections in terms of scattering out of either the F_1 or F_2 states. Specifically, choosing the F_1 state, we can express the σ_l^1 factor in terms of ϵ -conserving cross sections as

$$\begin{aligned} \sigma_l^1 &= \frac{(2l+1)(l+1)}{[\epsilon l^{1/2} \cos\theta_J + (l+1)^{1/2} \sin\theta_J]^2} \\ &\times \sigma_{J=1+1/2, \epsilon^2\Pi_{F_1} \rightarrow J'=1/2, \epsilon^2\Sigma} \end{aligned} \quad (62a)$$

or, alternatively, in terms of ϵ -changing cross sections as

$$\begin{aligned} \sigma_l^1 &= \frac{(2l+1)l}{[\epsilon(l+1)^{1/2} \cos\theta_J + (l-1)^{1/2} \sin\theta_J]^2} \\ &\times \sigma_{J=1-1/2, \epsilon^2\Pi_{F_1} \rightarrow J'=1/2, -\epsilon^2\Sigma} \end{aligned} \quad (62b)$$

Equations (62a) and (62b) reduce to Eqs. (55a) and (55b) in the pure case (a) limit.

VII. IMPLICATIONS OF THE QUANTUM SCATTERING FORMALISM

A. Conservation of s/a symmetry in collisions of homonuclear diatomic molecules

As discussed in Sec. II, in the particular case of collisions involving homonuclear diatomic molecules, in the expansion of the V_{Σ} , V_{Π} , and V_2 diabatic potentials only the *even* l terms will be nonzero, and in the expansion of the V_1 potential only the *even* l terms will be nonzero if the Π and Σ electronic wave functions have *identical* inversion symmetry but only the *odd* l terms will be nonzero if the Π and Σ electronic wave functions have *opposite* inversion symmetry. This taken together with the phase factor in square brackets in Eq. (33) implies that in the case of states of identical electronic inversion symmetry the coupling between two Π levels, between two Σ levels, or between Π and Σ levels will be nonzero only if both levels have the *same* parity $[\epsilon(-1)^{J-1/2+\epsilon}]$ ⁴⁰. On the other hand, in the case of opposite electronic inversion symmetry, the coupling between Π and Σ levels will be nonzero only if the two levels have *oppo-*

site parity. As is apparent from Table I, this implies that *there will be no coupling between levels of opposite s/a labeling*. Since the electrostatic coupling potential vanishes, conservation of the s/a label will be a rigorous collisional selection rule for collisions involving homonuclear diatomic molecules.

An alternative derivation of the s/a conservation rule is possible. In a homonuclear diatomic molecule levels of different s/a symmetry correspond to different values of the total nuclear spin I .³¹ (In the case of atoms with zero nuclear spin, such as ${}^{12}\text{C}$ or ${}^{16}\text{O}$, only one of the s/a doublets will exist.) If one neglects both molecular hyperfine coupling as well as any coupling between the nuclear spin of the molecule and that of the collision partner, then I will remain a spectator during the collision, so that $\Delta I = 0$ will be a rigorous selection rule. Because each value of I corresponds to a unique s or a level, this argument also implies conservation of s/a symmetry.

This selection rule is an extension of the well-known $\Delta J = \text{even}$ selection rule⁶⁴ in collisions of homonuclear diatomic molecules in ${}^1\Sigma^+$ electronic states. Recently, Katayama¹⁶ has seen evidence of this s/a selection rule in an optical-optical double resonance study of transitions between the $A\ {}^2\Pi_u$ and $X\ {}^2\Sigma_g^+$ states of N_2^+ .

B. Applicability of Franck-Condon approximations

In the interpretation of their experimental study of collision induced $A\ {}^2\Pi \rightarrow X\ {}^2\Sigma^+$ transitions in CN, Katayama and co-workers have proposed¹² that the $\Pi \rightarrow \Sigma$ integral cross sections can be written as

$$\sigma_{\Pi \rightarrow \Sigma} \sim \sigma_{\text{el}} |\langle v|v' \rangle|^2 \exp(-\Delta E/kT), \quad (63)$$

where σ_{el} designates an "intrinsic" cross section for electronic relaxation, ΔE is the energy separation of the initial and final vibrational levels, and T is the translational temperature. The dependence on the initial and final rotational angular momenta, symmetry indices, or fine-structure level (in the Π state) was explicitly ignored. A linear dependence on the Franck-Condon factor has also been suggested by Freed.⁶⁵ The appropriateness of this approximation can now be addressed.

As we have seen [Eq. (33)] within a Franck-Condon approximation the electrostatic potential matrix elements can be factored into the product of the vibrational overlap multiplied by a term containing the dependence on all other quantum numbers and indices. This factorization of the potential implies a linear dependence of the cross section on the Franck-Condon factor (the square of the vibrational overlap) both in the first-order Born limit,⁶⁶ where the inelastic S -matrix elements will be directly proportional to the square of the integral of $V_{JL\Omega\epsilon\Lambda v, J'L'\epsilon'\Lambda'v'}(R)$ [Eq. (33)], and, as we have seen in Sec. V, in the "vibrationally frozen" sudden limit, where the S -matrix elements are isomorphic with the potential matrix elements in the total- J basis [Eq. (33)]. However, we do not expect either of these dynamical approximations to be valid for typical atom-molecule systems: the first because the collisions will tend to be dominated by the expected strong repulsive anisotropy and thus will not be well described within a perturbative, weak collision limit; and the

second because the vibrational motion will not be frozen during the time scale of a typical collision. Thus a Franck-Condon approximation, despite its attractiveness and possible phenomenological success,¹² cannot be justified on the basis of a rigorous description of the collision dynamics.

VIII. COLLISIONAL PROPENSITY RULES

A. Pure Hund's case (a) basis

For rotationally inelastic collisions *within* a ${}^2\Pi$ or ${}^2\Sigma$ electronic state, we have previously provided^{5,6} a clear theoretical justification for the general collisional propensity rule that, at large values of J , transitions which *conserve* the symmetry index ϵ of the molecular wave function will be strongly favored. In this section we shall demonstrate that it is possible to derive similar propensity rules for *electronically inelastic* collisions.

To do so we proceed by simplifying the sudden limit expression for the Π - Σ cross sections [Eq. (52)] in the limit that J becomes large, but still small enough that a Hund's case (a) description is valid. We use the well-known large- J limit⁴³ of the $3j$ symbols in Eq. (52) to write

$$\lim_{J', J \rightarrow \infty} (2J' + 1) \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & \pm 1 & \frac{1}{2} \mp 1 \end{pmatrix}^2 = [d_{J', -J, \pm 1}^{J'}(x)]^2, \quad (64)$$

where $x = \cos^{-1}[1/(2J')]$. In the high- J limit x goes to $\pi/2$. Since the $d_{mn}^{J'}$ reduced rotation matrix elements do not vanish in general for $x = \pi/2$, a propensity rule valid for all J and J' , similar to those derived previously,^{5,6} does not emerge. However, in the case where $J' = J$, the first subscript equals zero, so that for $x = \pi/2$ the reduced rotation matrix element becomes proportional⁴³ to the associated Legendre polynomial $P_l^1(0)$. Thus the large- J limit of the rotationally elastic cross section can be written as

$$\lim_{J \gg 1/2} \sigma_{J\epsilon^2\Pi_{\Omega} \rightarrow J\epsilon'^2\Sigma} = \sum_{l=1}^{\infty} \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{2J+l}] [(l-1)!/(l+1)!] [P_l^1(0)]^2 \sigma_l^1. \quad (65)$$

Since⁶⁷

$$P_l^1(0) = 2\pi^{-1/2} \cos[\frac{1}{2}\pi(l-1)] \Gamma[\frac{1}{2}(l+2)] / \Gamma[\frac{1}{2}(l+1)], \quad (66)$$

it follows from the cosine factor that the associated Legendre polynomial with argument zero will vanish unless l is odd. Since J is half-integer, the phase factor $1 - \epsilon\epsilon'(-1)^{2J+l}$ in Eq. (65) implies that each term in the summation over l will vanish unless the initial and final symmetry indices ϵ and ϵ' are *different*.

This discussion implies the existence of a propensity rule, which will become stronger at larger J , whereby transitions with $\Delta J = 0$ in which the symmetry index is *changed* (${}^2\Sigma^+ - {}^2\Pi_{\Omega}: e \leftrightarrow f$; ${}^2\Sigma^- - {}^2\Pi_{\Omega}: e \leftrightarrow e$ or $f \leftrightarrow f$) will be favored over transitions which *conserve* the symmetry index (${}^2\Sigma^+ - {}^2\Pi_{\Omega}: e \leftrightarrow e$ or $f \leftrightarrow f$; ${}^2\Sigma^- - {}^2\Pi_{\Omega}: e \leftrightarrow f$).

B. Hund's case (b) basis

In the high- J limit, where for most molecules a Hund's case (b) description is appropriate, an additional collisional

propensity emerges, as will become apparent from an analysis of Eqs. (60) and (61). The well-known recursion relation for the $3j$ symbols⁴³ implies that for small $\Delta J = J' - J$,

$$\lim_{J', J \gg l} \begin{pmatrix} J' & l & J \\ \frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix} = - \lim_{J', J \gg l} \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix}. \quad (67)$$

If a pure Hund's case (a) representation remains valid, Eq. (67) along with Eq. (52) implies that cross sections for $\Sigma \rightarrow \Pi_{1/2}$ and $\Sigma \rightarrow \Pi_{3/2}$ transitions will be identical in the high- J limit provided only values of l small relative to J and J' make a significant contribution to the summation in Eq. (52). This is consistent with the fact that the multiplicative factor in Eq. (57) relating the $\Sigma \rightarrow \Pi_{1/2}$ and $\Sigma \rightarrow \Pi_{3/2}$ base cross sections is unity in the high- J limit.

In the pure case (b) limit $\theta_J = \pi/4$; Eq. (67) therefore implies that Eq. (61) can be simplified to

$$\begin{aligned} \lim_{J', J \gg l} G_1^\epsilon(J'lJ) &= \lim_{J', J \gg l} G_2^{-\epsilon}(J'lJ) \\ &= [1 - \epsilon(-1)^{J'+l+J}] \\ &\quad \times \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix}^2. \end{aligned} \quad (68)$$

Thus, Eq. (60) can be written as

$$\begin{aligned} \lim_{J, J' \gg 1/2} \sigma_{J\epsilon^2\Pi_{F_1} \rightarrow J'\epsilon'^2\Sigma} \\ = \sum_{l=1} \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{J+J'+l}] [1 \mp \epsilon(-1)^{J+J'+l}] \\ \times \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix}^2 \sigma_l^1 \end{aligned} \quad (69)$$

where the minus and plus signs inside the second set of square brackets are associated with transitions out of the F_1 and F_2 levels, respectively.

The combined effect of the two factors in square brackets in Eq. (69) implies that in the high- J Hund's case (b) limit transitions from the F_1 Λ -doublet levels of the ${}^2\Pi$ state into the $\epsilon' = -1$ spin-doublet levels of either a ${}^2\Sigma^+$ or ${}^2\Sigma^-$ state will be forbidden, and, similarly, that transitions from the F_2 Λ doublets into the $\epsilon' = +1$ spin-doublet levels will be forbidden. In terms of the e/f labels, this restriction can be written as ${}^2\Pi_{F_1} e/f \rightarrow {}^2\Sigma^+ f, {}^2\Sigma^- e$ and ${}^2\Pi_{F_2} e/f \rightarrow {}^2\Sigma^+ e, {}^2\Sigma^- f$. Equation (69) also implies that the allowed ${}^2\Pi_{F_1} \rightarrow {}^2\Sigma$ and ${}^2\Pi_{F_2} \rightarrow {}^2\Sigma$ transitions have identical cross sections, except for a reversal in the sign of ϵ . In other words

$$\sigma_{J\epsilon^2\Pi_{F_1} \rightarrow J'\epsilon'^2\Sigma} = \sigma_{J, -\epsilon, {}^2\Pi_{F_2} \rightarrow J'\epsilon', -1, {}^2\Sigma}. \quad (70)$$

The selection rule for transitions with $\Delta J = 0$, derived in the preceding subsection, remains valid in the Hund's case (b) limit. Combined with the selection rule derived in the preceding paragraph, this implies the net result that for $\Delta J = 0$ transitions in the case (b) limit only the $F_1 f \rightarrow {}^2\Sigma^+ e ({}^2\Sigma^- f)$ and $F_2 e \rightarrow {}^2\Sigma^+ f ({}^2\Sigma^- e)$ transitions will occur.

The collisional selection rules valid in the Hund's case (a) and case (b) limits are summarized schematically in Fig. 1. As the value of J increases, through the region where an intermediate coupling description of the wave function is

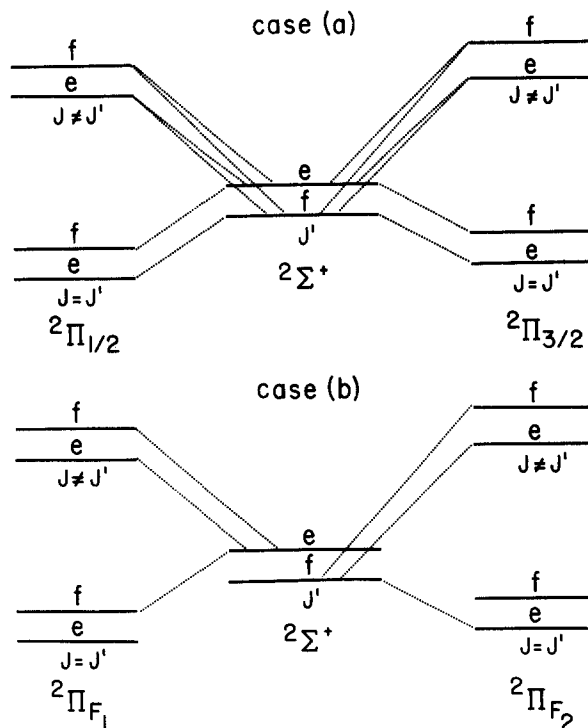


FIG. 1. Allowed ${}^2\Pi J \rightarrow {}^2\Sigma^+ J'$ transitions (dotted lines). The upper and lower panels refer to the situation where the ${}^2\Pi$ state can be well described in Hund's case (a) or Hund's case (b), respectively. In the case (b) limit the ${}^2\Pi_{F_1}$ and F_2 manifolds correspond to $J = N + 1/2$ and $J = N - 1/2$, respectively. For the ${}^2\Sigma^+$ state the e and f levels correspond to $J = N + 1/2$ and $J = N - 1/2$, respectively. For ${}^2\Pi \rightarrow {}^2\Sigma^+$ transitions with $\Delta J = 0$, a distinct propensity toward changing the e/f label will appear both in the case (a) and case (b) limits. Added to this, in the case (b) limit will be an additional propensity rule: transitions into the e -labeled levels of the ${}^2\Sigma^+$ state will originate from the F_1 Π -state manifold, while transitions into the f -labeled levels will originate from the F_2 Π -state manifold.

most appropriate, the cross sections for transitions which are allowed in Hund's case (a) but forbidden in case (b) will become progressively smaller.

We observe in Fig. 1 that in the case (b) limit the $\epsilon = +1$ spin-doublet levels (${}^2\Sigma^+ e$ or ${}^2\Sigma^- f$) will be populated by collisions out of only the ${}^2\Pi_{F_1}$ rotational manifold, while the $\epsilon = -1$ spin-doublet levels (${}^2\Sigma^+ f$ or ${}^2\Sigma^- e$) will be populated by collisions out of only the ${}^2\Pi_{F_2}$ rotational manifold. In the Hund's case (b) limit both the ${}^2\Pi_{F_1}$ Λ -doublet levels and the $\epsilon = +1$ ${}^2\Sigma$ spin-doublet level are characterized by $J = N + S$, while both the ${}^2\Pi_{F_2}$ Λ -doublet levels and the $\epsilon = -1$ ${}^2\Sigma$ spin-doublet level are characterized by $J = N - S$.^{31,44,45} [For a ${}^2\Pi$ state in the case (b) limit N corresponds to the sum of the electronic orbital and nuclear rotational angular momenta.] Thus, the collisional selection rule derived earlier in this subsection, and illustrated in Fig. 1(b), corresponds physically to a model in which S is a spectator during the collision, so that changes in the magnitude of N can occur but not changes in the relative orientation of N and S . This is, of course, the same model that we have used^{5,8} to explain the collisional propensity rules seen in experimental studies of collisional transfer between fine- and hyperfine-structure levels of molecules in ${}^2\Sigma$ electronic states.^{5,8,68,69}

In the case of homonuclear diatomic molecules, the case (b) collisional propensity rule discussed above becomes

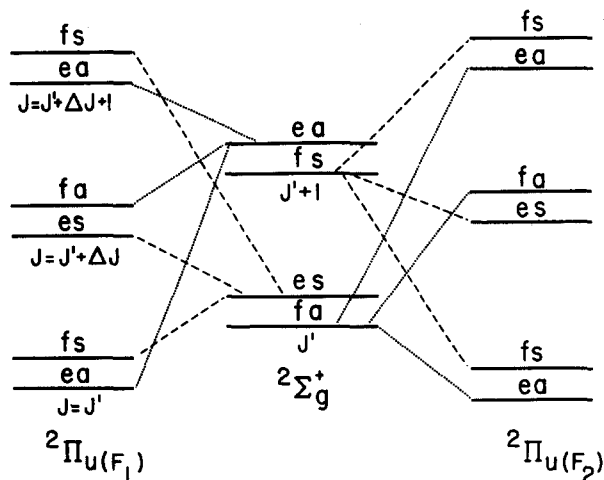


FIG. 2. Allowed ${}^2\Pi_u J \rightarrow {}^2\Sigma_g^+ J'$ transitions in the high- J limit, where a case (b) description of the ${}^2\Pi$ state is appropriate. The dashed and dotted lines denote $s \leftrightarrow s$ and $a \leftrightarrow a$ transitions, respectively. The ${}^2\Pi_{F_1}$ levels as well as the e levels in the ${}^2\Sigma_g^+$ state correspond to $J = N + 1/2$; the ${}^2\Pi_{F_2}$ levels as well as the f levels in the ${}^2\Sigma_g^+$ state correspond to $J = N - 1/2$. The assignment of the e/f and s/a symmetry labels is clarified in Table I. Without loss of generality the quantity ΔJ which appears in the assignment of the rotational quantum numbers to the Π -state levels has been taken to be odd. Three propensity rules are apparent: (1) s/a permutation-inversion symmetry will be rigorously conserved; (2) for transitions with $\Delta J = 0$ the e/f -changing processes will be strongest; and (3) transitions into the e -labeled levels of the ${}^2\Sigma_g^+$ state will originate from the F_1 Π -state manifold, while transitions into the f -labeled levels will originate from the F_2 Π -state manifold.

further restricted by the rigorous selection rule governing conservation of the permutation-inversion symmetry labels (Sec. VII). Thus, as is illustrated in Fig. 2, in the case (b) limit only *one* of each of the paired F_1 or F_2 Λ -doublet levels will contribute to a given $J \Pi \rightarrow J' \Sigma$ transition. Equivalently, a given Λ -doublet level will contribute to $J \Pi \rightarrow J' \Sigma$ transitions only for $(J' + 1/2)$ odd or $(J' + 1/2)$ even, but not both. As in the case of collisions involving heteronuclear molecules, described above, the F_1 Π -state levels will transfer population only into the $\epsilon = +1$ spin-doublet level of the ${}^2\Sigma$ state, *regardless of the inversion or reflection symmetry*, and the F_2 levels will transfer population only into the $\epsilon = -1$ spin-doublet levels.

IX. CONCLUSION

In the present article we have developed the exact quantum description of electronically inelastic collisional mixing between ${}^2\Pi$ and ${}^2\Sigma$ states of a diatomic molecule. This formulation of the collision dynamics is free of any approximations and based on a complete description of the electrostatic coupling potential. Our major contributions are as follows:

(1) The description of the way in which the electrostatic matrix elements required in an asymptotically exact *adiabatic* basis suitable for a scattering calculation can be obtained from an *ab initio* calculation of the *electronically adiabatic* atom-molecule wave functions of A' and A'' symmetry.

(2) The formulation of the appropriate quantum close-coupling equations. This allowed us to demonstrate both that s/a permutation-inversion symmetry will be rigorously conserved in collisions involving homonuclear diatomic molecules, as seen experimentally by Katayama; and that

use of Franck-Condon approximations is not justified by rigorous theoretical considerations.

(3) The extension of the infinite-order sudden approximation to treat electronically *inelastic* collisions, both within vibrationally frozen and vibrationally adiabatic limits. As in the case of electronically *elastic* atom-molecule collisions, in the sudden limit the cross sections for various inelastic transitions are interrelated by a number of useful scaling relations.

(4) The demonstration, again within the sudden limit, of the following two new collisional propensity rules: (a) For ${}^2\Pi \rightarrow {}^2\Sigma$ transitions with $\Delta J = 0$ the cross sections will become vanishingly small for transitions which *conserve* the symmetry index of the molecular wave function, in direct contrast to the situation for transitions *within* a ${}^2\Pi$ or ${}^2\Sigma$ electronic state. (b) For ${}^2\Pi \rightarrow {}^2\Sigma$ transitions with J large enough that a Hund's case (b) description of the Π state is appropriate, transitions will be forbidden from the F_1 Π -state manifold into the $\epsilon = -1$ Σ -state spin-doublet levels, and from the F_2 Π -state manifold into the $\epsilon = +1$ Σ -state spin-doublet levels. This propensity rule is consistent with a physical model in which the electronic spin S is a spectator during the collision so that the relative orientation of N and S is preserved.

As mentioned earlier, the conservation of s/a symmetry in collisions of homonuclear diatomic molecules has already been observed experimentally in N_2^+ . It is exciting to anticipate that future experiments will confirm the two new propensity rules summarized in Eq. (4) above. Strictly speaking, these propensity rules, as derived here, are valid only within a sudden limit. However, following recent work^{68,69} on collisions of molecules in ${}^2\Sigma$ electronic states, we believe that it may ultimately be possible to derive the present propensity rules for electronically inelastic collisions within a more rigorous dynamical framework.

For purposes of brevity we have ignored the effect of non-Born-Oppenheimer mixing of the ${}^2\Pi$ and ${}^2\Sigma$ states of the isolated molecule, except for the short discussion in Sec. IV of how the close-coupled equations could be extended to incorporate this effect. Thus the scaling relations and propensity rules derived here apply only to situations where these spectroscopic perturbations are negligible (rotational levels far from regions of large mixing; homonuclear molecules where mixing is precluded by the inversion symmetry of the electronic wave functions). In subsequent work we shall extend the present theory to deal explicitly with regions of strong non-Born-Oppenheimer mixing. In anticipation of this we mention that the case (b) limit propensity rule derived here—that collisions will tend to preserve the orientation of N and S —will not be affected by the presence of non-Born-Oppenheimer mixing in the isolated molecule.

Ideally, it would be exciting to carry out the necessary *ab initio* electronic calculations to obtain the intermolecular potential for an atom-molecule system of interest (CN-He, N_2^+-He). The present paper would then provide the theoretical framework for the quantitative calculation of cross sections, which ultimately could be compared to experiment. Also, it will be important to extend the present work to deal with electronically inelastic collisions between states of

singlet or triplet multiplicity, processes that have been of considerable experimental interest.^{17-22,26-30} All this work will provide invaluable insight into the way in which collisions lead to changes in molecular electronic states.

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APPENDIX A: REDUCTION OF THE ELECTROSTATIC COUPLING MATRIX ELEMENTS IN THE CASE OF HOMONUCLEAR DIATOMIC MOLECULES

We shall refer, wherever possible, to our earlier derivation⁴⁶ of the electrostatic coupling matrix elements in collisions involving molecules in Π electronic states. We assume that the electronic wave function can be expanded in terms of molecular orbitals expressed formally as linear combinations of atomic orbitals, all centered at the midpoint of the molecular figure axis, namely,

$$|\lambda\rangle = \sum_{kL} U_{kL\lambda}(\rho) Y_{L\lambda}(\hat{\rho}), \quad (A1)$$

where $\rho \equiv (\rho, \hat{\rho})$ designates the coordinates of the electron and k and L index the atomic orbitals of azimuthal symmetry λ . To ascertain the symmetry properties of the potential matrix elements, it is sufficient to consider only those electrons in unfilled orbitals. Let us assume ${}^2\Pi$ and ${}^2\Sigma^+$ electronic states arising from one electron in an unfilled orbital. Then, following Ref. 46, we can write the electrostatic matrix element $\langle \Lambda' | V_{el} | \Lambda \rangle$ in Eq. (5) more fully as

$$\langle \Lambda' | V_{el} | \Lambda \rangle = \sum D_{0\mu}^{L\Lambda'}(0\beta 0) \int Y_{L'\Lambda'}^*(\hat{\rho}) Y_{L\Lambda}(\hat{\rho}) \times C_{\mu}(\hat{\rho}) d\hat{\rho} f_{LL'}(R, r), \quad (A2)$$

where $C_{\mu}(\hat{\rho})$ designates an unnormalized spherical harmonic⁴³ and where the summation extends over the indices, l, μ, L , and L' . Here the function $f_{LL'}$ arises from an integration over all the electronic degrees of freedom, *except* $\hat{\rho}$, of the unpaired electron. Equation (A2) can be compared to Eq. (6) of Ref. 46. Since we have assumed a single unpaired electron, obviously $\lambda = \Lambda$ and $\lambda' = \Lambda'$.

The integral over $\hat{\rho}$ can be performed⁴³ to give

$$\langle \Lambda' | V_{el} | \Lambda \rangle = (-1)^{\Lambda'} \sum_{LL'} D_{0, \Lambda' - \Lambda}^{L\Lambda'}(0\beta 0) \times [(2L + 1)(2L' + 1)]^{1/2} f_{LL'}(R, r) \times \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & l & L \\ -\Lambda' & \Lambda' - \Lambda & \Lambda \end{pmatrix}. \quad (A3)$$

For a homonuclear molecule, the symmetry properties of the spherical harmonics in Eq. (A1) imply that only even L will contribute for a *gerade* electronic wave function and only odd L for an *ungerade* wave function. This, coupled with the

restriction, imposed by the properties⁴³ of the first $3j$ symbol in Eq. (A3), that $(L' + l + L)$ be even, implies that only the *even* l terms in Eqs. (5) and (A3) will be nonzero for g - g or u - u coupling, while only the *odd* l terms will be nonzero for g - u coupling.

In the case of electronic wave functions involving more than one unpaired electron, in particular for Σ^- states, an entirely equivalent formal analysis can be performed by making use of Slater determinants involving the orbitals defined in Eq. (A1) (See, for example, the Appendix of Ref. 46.) The restriction on the values of l in Eq. (5) remains unchanged, and depends only on the inversion symmetry of the total electronic wave functions of the two states which are coupled.

APPENDIX B: EVALUATION OF EXPANSION COEFFICIENTS FOR THE ADIABATIC MIXING ANGLE

Multiplying both sides of Eq. (25) by $\sin \theta d^2_{20}(\theta)$ and integrating over θ , we obtain, using the known orthogonality of the $d^j_{mm'}$, reduced rotation matrix elements with differing j ,⁴³

$$C_2 = \frac{5}{2} \int_0^\pi \chi(\theta) d^2_{20}(\theta) \sin \theta d\theta. \quad (B1)$$

Equation (26) can be obtained from Eq. (B1) by introducing the known expression for $d^2_{20}(\theta)$, integrating by parts, and utilizing the fact that $\chi(\theta)$ vanishes at the endpoints of the integration.

Differentiating both sides of Eq. (25) with respect to θ , and multiplying by $\sin \theta$ yields, when one uses a known recursion relation for the $d^j_{mm'}$ matrix elements,⁷⁰

$$\sin \theta d\chi(\theta)/d\theta = \sum_{l=2}^{\infty} [2/(2l+1)] \{ -(l+1)(l^2-4)^{1/2} d^{l-1}_{20}(\theta) + l[(l+1)^2-4]^{1/2} d^{l+1}_{20}(\theta) \} C_l. \quad (B2)$$

Equation (27) can be obtained from Eq. (B2) by multiplying both sides by $\sin \theta$, integrating over θ , and using the orthogonality relation⁴³ for the $d^j_{mm'}$ matrix elements.

¹S. Green and R. N. Zare, Chem. Phys. 7, 62 (1975).

²R. N. Dixon and D. Field, Proc. R. Soc. London Ser. A 366, 99, 225 (1979).

³M. Shapiro and H. Kaplan, J. Chem. Phys. 71, 2182 (1979).

⁴V. N. Ostrovsky and V. I. Ustimov, J. Phys. B 14, 1139 (1981); 17, 99 (1984).

⁵M. H. Alexander, J. Chem. Phys. 76, 3637 (1982).

⁶M. H. Alexander, J. Chem. Phys. 76, 5974 (1982).

⁷M. H. Alexander and S. L. Davis, J. Chem. Phys. 79, 227 (1983); M. H. Alexander and P. J. Dagdigan, *ibid.* 79, 302 (1982); M. H. Alexander and B. Pouilly, *ibid.* 79, 1545 (1983).

⁸G. C. Corey and F. R. McCourt, J. Phys. Chem. 87, 2723 (1983).

⁹H. E. Radford and H. P. Broida, J. Chem. Phys. 38, 644 (1963).

¹⁰D. W. Pratt and H. P. Broida, J. Chem. Phys. 50, 2181 (1969).

¹¹N. Duric, P. Erman, and M. Larsson, Phys. Scr. 18, 39 (1978).

¹²D. H. Katayama, T. A. Miller, and V. E. Bondybey, J. Chem. Phys. 71, 1662 (1979).

¹³V. E. Bondybey and T. A. Miller, J. Chem. Phys. 69, 3597 (1978).

¹⁴D. H. Katayama and J. A. Welsh, J. Chem. Phys. 79, 3627 (1983); Chem. Phys. Lett. 106, 74 (1984).

¹⁵D. H. Katayama, T. A. Miller, and V. E. Bondybey, J. Chem. Phys. 72, 5469 (1980).

- ¹⁶D. H. Katayama, J. Chem. Phys. **81**, 3495 (1984); Phys. Rev. Lett. **54**, 657 (1985).
- ¹⁷G. N. Hays and H. J. Oskam, J. Chem. Phys. **59**, 1507 (1973).
- ¹⁸M. F. Golde and B. A. Thrush, Proc. R. Soc. London Ser. A **330**, 121 (1972); E. M. Gartner and B. A. Thrush, *ibid.* **346**, 103 (1975).
- ¹⁹F. Heidner, D. G. Sutton, and S. N. Suchard, Chem. Phys. Lett. **37**, 243 (1976); see also B. A. Garetz, J. I. Steinfeld, and L. L. Poulsen, *ibid.* **38**, 365 (1976).
- ²⁰N. Sadeghi and D. W. Setser, Chem. Phys. Lett. **77**, 308 (1981); **82**, 44 (1981); J. Chem. Phys. **79**, 2710 (1983).
- ²¹A. Rotem, I. Nadler, and S. Rosenwaks, Chem. Phys. Lett. **83**, 281 (1981); J. Chem. Phys. **76**, 2109 (1982).
- ²²W. Benesch, J. Chem. Phys. **78**, 2978 (1983).
- ²³W. M. Gelbart and K. F. Freed, Chem. Phys. Lett. **18**, 470 (1973).
- ²⁴A. J. Kotlar, R. W. Field, J. I. Steinfeld, and J. A. Coxon, J. Mol. Spectrosc. **80**, 82 (1980).
- ²⁵M. H. Alexander, J. Chem. Phys. **76**, 429 (1982).
- ²⁶M. H. Alexander and M. Osmolovsky, J. Chem. Phys. **77**, 839 (1982); B. Pouilly, J.-M. Robbe, and M. H. Alexander, J. Phys. Chem. **88**, 140 (1984).
- ²⁷C. R. Jones and H. P. Broida, J. Chem. Phys. **59**, 6677 (1973); R. W. Field, C. R. Jones, and H. P. Broida, *ibid.* **60**, 4377 (1974).
- ²⁸C. J. Hsu, W. D. Krugh, and H. B. Palmer, J. Chem. Phys. **60**, 5118 (1974).
- ²⁹R. W. Field, R. A. Gottscho, J. G. Pruett, and J. J. Reuther, in *Proceedings of the 14th International Conference on Free Radicals* (Association for Science Documents Information, Japan, 1979), p. 39.
- ³⁰H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, New York, in press), Chap. 5.
- ³¹G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, Princeton, 1968).
- ³²F. Rebertus and W. A. Lester, Jr., J. Chem. Phys. **64**, 3879 (1976).
- ³³F. Rebertus and W. A. Lester, Jr., J. Chem. Phys. **67**, 3367 (1977).
- ³⁴R. T. Pack, J. Chem. Phys. **60**, 633 (1974).
- ³⁵D. Secrest, J. Chem. Phys. **62**, 710 (1975).
- ³⁶L. W. Hunter, J. Chem. Phys. **62**, 2855 (1975).
- ³⁷R. Goldflam, S. Green, and D. J. Kouri, J. Chem. Phys. **67**, 4149 (1977); R. Goldflam, D. J. Kouri, and S. Green, *ibid.* **67**, 5661 (1977).
- ³⁸D. J. Kouri, in *Atom-Molecule Collision Theory: A Guide for the Experimentalists*, edited by R. B. Bernstein (Plenum, New York, 1979), p. 301.
- ³⁹R. N. Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, J. Mol. Spectrosc. **46**, 37 (1973).
- ⁴⁰M. Larsson, Phys. Scr. **23**, 835 (1981).
- ⁴¹Note that this expression for the parity and the assignment of the symmetry index ϵ to the e and f levels has been corrected from Refs. 5 and 6, which made use of an erroneous expression for the parity of the spin eigenfunctions, as discussed by Larsson (Ref. 40).
- ⁴²J. M. Brown, J. T. Hougen, K. P. Huber, J. W. C. Johns, I. Kopp, H. Lefebvre-Brion, A. R. Merer, D. A. Ramsay, J. Rostas, and R. N. Zare, J. Mol. Spectrosc. **55**, 500 (1975).
- ⁴³D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. (Clarendon, Oxford, 1968).
- ⁴⁴J. T. Hougen, Natl. Bur. Stand. (U.S.) Monogr. **115**, (1970).
- ⁴⁵M. H. Alexander and P. J. Dagdigian, J. Chem. Phys. **80**, 4325 (1984).
- ⁴⁶M. H. Alexander, Chem. Phys. **92**, 337 (1985).
- ⁴⁷The following discussion of the relation between the *adiabatic* electrostatic matrix elements and the results of an *ab initio* calculation of the corresponding atom-molecule potential surfaces, as well as the subsequent discussion of the sudden S functions in Sec. V, have been specialized to Σ^+ states. With the appropriate permutation of the electronic wave function symmetry index η and the A' and A'' group theoretic labels an entirely equivalent discussion applies to Σ^- states.
- ⁴⁸G. C. Nielson, G. A. Parker, and R. T. Pack, J. Chem. Phys. **66**, 1396 (1977).
- ⁴⁹S. L. Davis, B. Pouilly, and M. H. Alexander, Chem. Phys. **91**, 81 (1984).
- ⁵⁰See the discussion immediately prior to Eq. (28) in Ref. 32.
- ⁵¹This can be shown easily from Eq. (8.7.1) of M. Abramowitz and I. A. Stegun, Natl. Bur. Stand. (U.S.) Appl. Math. Ser. **55**, (1965).
- ⁵²D. Secrest, in *Atom-Molecule Collision Theory: A Guide for the Experimentalist*, edited by R. B. Bernstein (Plenum, New York, 1979), p. 265.
- ⁵³W. A. Lester, Jr., Methods Comput. Phys. **10**, 211 (1971).
- ⁵⁴S. C. Leasure and J. M. Bowman, Chem. Phys. Lett. **48**, 179 (1977).
- ⁵⁵R. Schinke and P. McGuire, Chem. Phys. **31**, 391 (1978).
- ⁵⁶S. Green, J. Chem. Phys. **70**, 4686 (1979).
- ⁵⁷D. Clary, J. Chem. Phys. **75**, 209 (1981).
- ⁵⁸G. A. Pfeffer and D. Secrest, J. Chem. Phys. **78**, 3052 (1982).
- ⁵⁹D. R. Flower and D. J. Kirkpatrick, J. Phys. B **15**, 1701 (1982).
- ⁶⁰F. A. Gianturco, U. T. Lamanna, and G. Petralla, Il Nuovo Cimento D **3**, 561 (1984).
- ⁶¹V. J. Khare, D. E. Fitz, and D. J. Kouri, J. Chem. Phys. **73**, 2802 (1980).
- ⁶²The S_l^L coefficients of Ref. 5 and the S_l^L and $-S_{l-2}^L$ coefficients of Ref. 6 are, respectively, equivalent to the S_l^Z , S_l^H , and S_l^Z coefficients defined here.
- ⁶³M. H. Alexander, J. Chem. Phys. **80**, 3485 (1984).
- ⁶⁴K. Takayanagi, Adv. At. Mol. Phys. **1**, 149 (1965).
- ⁶⁵K. F. Freed, Adv. Chem. Phys. **47**, 291 (1981).
- ⁶⁶See, for example, G. G. Balint-Kurti, in *Theoretical Chemistry*, MTP International Review of Science, Physical Chemistry, Series 2 (Butterworths, London, 1975), Vol. 1.
- ⁶⁷Reference 51, Eq. (8.6.1).
- ⁶⁸M. H. Alexander and P. J. Dagdigian, J. Chem. Phys. **80**, 4325 (1985).
- ⁶⁹M. H. Alexander, J. E. Smedley, and G. C. Corey (unpublished).
- ⁷⁰D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonsky, *Kvantovaya Teoriya Uglovogo Momenta* (Nauka, Leningrad, 1975), p. 82.