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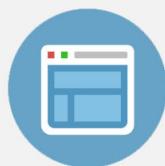Rotationally inelastic collisions between a diatomic molecule in a 2+ electronic state and a structureless target
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# Rotationally inelastic collisions between a diatomic molecule in a $^2\Pi$ electronic state and a structureless target

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We present the full close-coupling formulation of the collision between a diatomic molecule in a $^2\Pi$ state in the Hund's case (a) limit and a structureless target. Due to the possibility of transitions between spin-orbit and/or $\Lambda$-doubling states the scattering displays an additional degree of complexity not seen in rotationally inelastic collisions of $^1\Sigma^+$ molecules. The well-known coupled states and infinite-order-sudden (IOS) approximation techniques can be applied in a straightforward manner. The factorization and scaling relations between the various cross sections, which are valid in the energy sudden limit, are explored. For transitions within either spin-orbit manifold ($\Omega = 1/2$, $\Omega = 3/2$), these scaling relations allow both matrices of cross sections, for parity conserving and parity violating transitions, to be expressed in terms of the cross sections for parity conserving transitions out of the $\Omega = 1/2$, $J = 1/2$ level. Under conditions in which either a Born or sudden formulation of the collision dynamics is appropriate, we show that at large values of the total angular momentum, transitions which conserve the parity index of the molecular wave functions will be strongly favored, a propensity rule which has been seen in previous experimental studies of rotational relaxation in $^2\Pi$ molecules. A scaling relation is also derived for the cross sections for transitions between the two spin-orbit manifolds. For these processes, however, the propensity toward conservation of the parity index only occurs in the case of transitions which are elastic in the total angular momentum. The IOS formulation of the collision dynamics is then extended to a Hund's case (b) representation of the molecular wave function. Although a complete factorization is no longer possible, one can still show that at large $J$ there will exist a strong propensity toward conservation of the alignment between S (the spin-angular momentum of the molecule) and N (the vector sum of the nuclear rotational angular momentum R and the $z$-component $\Lambda$ of the electronic orbital angular momentum). In the case (b) limit a propensity toward conservation of the parity index will still exist, but less strongly than in the case (a) limit.

## I. INTRODUCTION

For several decades now there has been much theoretical interest in rotationally inelastic collisions between atoms and diatomic molecules.[1-3] The large bulk of this work has been devoted to collisions of molecules in $^1\Sigma^+$ electronic states, where the orbital motion of the molecule with respect to the atom can couple just with the rotational motion of the molecule itself. As our knowledge of rotationally inelastic processes progresses, we are led to investigate the more complicated case of collisions involving molecules with nonvanishing electronic spin and orbital angular momenta. Early work along these lines[4,5] dealt with collisions of molecules in $^1\Pi$ electronic states, motivated by the experimental studies of Ottinger, Bergmann, Demtroder, Zare, and their co-workers.[6,7] The first papers[4,5] were devoted primarily to characterizing the nature of the interaction potential. These were followed by a number of studies,[8-12] both formal and numerical, dealing with collisions of OH and CH, which are of considerable astrophysical importance. In particular, Dixon and Field[9] have presented the general formalism for the quantum treatment of the scattering of $\Pi$-state molecules, and have carried out distorted-wave Born calculations of relative cross sections for the scattering of OH and CH with several collision partners.

Inspired by the experimental work by Lengel and Crosley[13] on rotational relaxation in the $A\,^2\Sigma^+$ state of OH, and by the ongoing molecular beam investigation by Dagdigian[14] of inelastic collisions of CaCl in the $X\,^2\Sigma^+$ state, we have recently published[15] an article laying the formal groundwork for the theoretical study of colli-

sions of $^2\Sigma^+$ molecules. In particular, we demonstrated that within the energy sudden limit it was possible to rigorously predict that at large values of the total angular momentum the rotationally inelastic cross sections would tend to zero unless the parity index of the molecular wave function was conserved, a propensity rule deduced empirically by Lengel and Crosley.[13] The discussion by Gottscho[16] of recent experimental evidence for similar propensity rules in collisions of $^2\Pi$ molecules subsequently motivated us to extend our investigation to the latter systems. The results of this study are contained in the present article.

To elucidate these propensity rules, it is first necessary to proceed through the full close-coupling (CC) formulation of the dynamics of an inelastic collision between a $^2\Pi$ diatomic and a structureless target, and then introduce the coupled-states[1-3,17-19] (CS) decoupling approximation, which has proven to be of high accuracy in the study of rotationally inelastic collisions between atoms and $^1\Sigma^+$ diatomics. Although the CC formalism is already contained in the paper by Dixon and Field[9] and the CS formalism, applied to a $^2\Pi$ molecule in a Hund's case (b) representation, is contained in an as yet unpublished paper by Dewangan and Flower,[12] we include a recapitulation here to establish notation and to prepare for the introduction of the infinite-order-sudden[18,20-23] (IOS) decoupling approximation, which represents a further simplification of the CS equations. Subsequently, we shall use the factorization of the $S$ matrix, which is possible within the energy sudden limit,[2,3,23-29] to explore the scaling relations and propensity rules which will characterize the collisions of $^2\Pi$ diatomics.

The organization of this paper is as follows: In the next section we review the full close-coupling formulation of the dynamics of the collision between a structureless particle and a diatomic molecule in a $^2\Pi$ electronic state described in a Hund's case (a) basis. The CS and IOS approximations, still in a case (a) basis, are presented in Secs. III and IV, respectively. The factorization properties, scaling relations, and propensity rules, which apply in the energy sudden limit, are explored in Sec. V for transitions within a single spin-orbit manifold and in Sec. VI for transitions between the two spin-orbit manifolds. In Sec. VII we demonstrate that the same propensity rules are equally valid when the scattering is treated within the Born approximation. Then in Sec. VIII the IOS formulation of the dynamics is extended to a Hund's case (b) description of the states of the isolated diatomic and the appropriate propensity rules extracted. We close with a brief discussion.

## II. CLOSE COUPLING FORMULATION OF COLLISION DYNAMICS

The wave functions for a diatomic molecule in a $^2\Pi$ electronic state can be written in a Hund's case (a) representation as a product of a wave function describing the vibrational and electronic motion of the rotationless diatomic multiplied by a wave function describing the rotational motion; namely,[30,31]

$$|JM\Omega v\Lambda S\Sigma\rangle = |JM\Omega\rangle|v\Lambda S\Sigma\rangle . \tag{1}$$

Here, $J$ denotes the total angular momentum (spin plus rotational) with projection along space- and molecule-fixed axes of $M$ and $\Omega$, respectively; $v$ is the vibrational quantum number; $S$ denotes the spin angular momentum with projection $\Sigma$ along the molecular axis; and $\Lambda$ is the projection of the electronic orbital angular momentum along the molecular axis. For a $^2\Pi$ molecule, $\Lambda = \pm 1$ and $\Sigma = \pm\frac{1}{2}$ so that $\Lambda$ and $\Sigma$ can be parallel, leading to a state with $|\Omega| = \frac{3}{2}$, or antiparallel, leading to a state with $|\Omega| = \frac{1}{2}$. For doublets, $S = \frac{1}{2}$ and will be suppressed as an index in the development which follows.

It will be convenient to use the definite parity states defined by

$$|JM\bar{\Omega}\epsilon v\rangle = 2^{-1/2}(|JM\bar{\Omega}\rangle|v,\Lambda=1,\Sigma=\bar{\Omega}-1\rangle$$
$$+ \epsilon|JM,-\bar{\Omega}\rangle|v,\Lambda=-1,\Sigma=-\bar{\Omega}+1\rangle) , \tag{2}$$

where $\bar{\Omega} \equiv |\Omega|$, and where $\epsilon = \pm 1$ and refers to the parity of the wave function with respect to inversion of the space-fixed axis system, so that[31]

$$i_{SF}|JM\bar{\Omega}\epsilon v\rangle = \epsilon(-1)^{J+S}|JM\bar{\Omega}\epsilon v\rangle . \tag{3}$$

Within current spectroscopic nomenclature,[32] the $\epsilon = +1$ levels are designated as f and the $\epsilon = -1$ levels as e. The rotational wave functions $|JM\Omega\rangle$ which appear in Eq. (1) can be written as rotation matrix elements; namely,[31]

$$|JM\Omega\rangle = [(2J+1)/8\pi^2]^{1/2}D^{J*}_{M\Omega}(\alpha\beta\gamma) , \tag{4}$$

where the Euler angles refer to the space fixed orientation of the diatomic and the definition of these angles follows that of Brink and Satchler.[33]

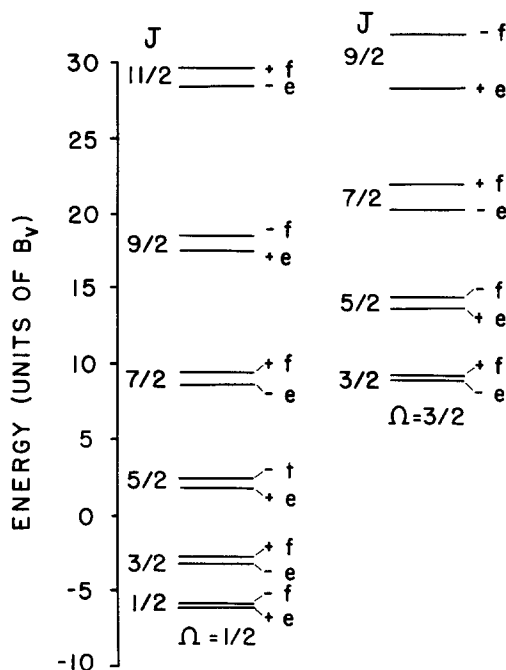The rotational energies can be written as[30,34,35]



FIG. 1. Illustrative spectrum of rotational energy levels of a diatomic molecule in a $^2\Pi$ electronic state in a Hund's case (a) basis. For purposes of illustration, in Eqs. (5) and (6) the rotational constants were chosen identical for both manifolds, the spin-orbit constant $A_v$ was chosen to be equal to $14B_v$, the values of p and q were both taken to be $0.2B_v$. In general, p and q will be much smaller. The $\Lambda$ doubling splitting shown here has been exaggerated for visual clarity. The zero of energy corresponds to setting $T_v = 0$ in Eqs. (5) and (6). The parity [Eq. (3)] of the $\Lambda$ doubling levels is indicated. The f levels correspond to a parity index $\epsilon = +1$, and the e levels, to a parity index $\epsilon = -1$.

$$E_{J,\bar{\Omega}=3/2,\epsilon v} = T_v + \frac{1}{2}A_v + B_v[J(J+1) - \tfrac{7}{4}]$$
$$+ \frac{1}{2}\epsilon(B_v/A_v)(2q+pB_v/A_v)(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+\tfrac{3}{2}) , \tag{5}$$

and

$$E_{J,\bar{\Omega}=1/2,\epsilon v} = T'_v - \frac{1}{2}A_v + B'_v[J(J+1)+\tfrac{1}{4}] + \frac{1}{2}\epsilon p(J+\tfrac{1}{2}) . \tag{6}$$

Here, $T_v$ is the vibrational term, $A_v$ the spin-orbit constant, and $B_v$ the rotational constant. The prime signs in Eq. (6) indicate possible differences between the phenomenological spectroscopic constants for the two spin-orbit states.[31] The last term on the right-hand side on Eqs. (5) and (6) describes the slight splitting between the parity levels, which is designated as $\Lambda$ doubling and arises from orbit-rotation and spin-orbit coupling with nearby $^2\Sigma^+$ electronic states. The magnitude of this splitting is governed by the parameters p and q in Eqs. (5) and (6), which can be evaluated using second order perturbation theory.[31] Figure 1 presents a qualitatively correct representation of the rotational levels in a $^2\Pi$ state.

Consider the interaction between a $^2\Pi$ diatomic and a spherical atom in a singlet state. If the electronic wave function of the atom is designated in the molecule frame by the ket $|\beta\rangle$, then the total wave function for the atom can be written as

$$|LM_L\beta\rangle = |LM_L\rangle|\beta\rangle , \tag{7}$$

where $|LM_L\rangle$ is a spherical harmonic, assumed to be expressed in space-frame coordinates, which describes the orbital motion of the atom about the center-of-mass of the diatomic. The complete wave function for the atom–molecule system can be expressed as a linear combination of products of the $|LM_L\beta\rangle$ functions [Eq. (7)] and the $|JM\bar{\Omega}\epsilon v\rangle$ functions [Eq. (2)]; namely,

$$|JM\bar{\Omega}\epsilon vLM_L\beta\rangle = 2^{-1/2}|LM_L\rangle(|JM\bar{\Omega}\rangle|\beta v, \Lambda = 1, \Sigma = \bar{\Omega} - 1\rangle$$

$$+ \epsilon|JM, -\bar{\Omega}\rangle|\beta v, \Lambda = -1, \Sigma = -\bar{\Omega} + 1\rangle) . \qquad (8)$$

It will be more convenient to expand in terms of eigenfunctions of the total angular momentum $\mathcal{J}$ and its projection $\mathfrak{M}$ defined by

$$|JL\bar{\Omega}\epsilon v\beta\mathcal{J}\mathfrak{M}\rangle = \sum_{MM_L}(JMLM_L|JL\mathcal{J}\mathfrak{M})|JM\bar{\Omega}\epsilon vLM_L\beta\rangle , \qquad (9)$$

where $(\cdots|\cdots)$ is a Clebsch–Gordan coefficient.

Following the initial work of Arthurs and Dalgarno[36] on collisions of atoms with diatomic molecules in $^1\Sigma^+$ states, we can expand the complete wave function for the atom–molecule system in terms of the $|JL\bar{\Omega}\epsilon v\beta\rangle$ states. For notational simplicity, the $\beta$ index will be suppressed, since we will only consider collisions which are elastic in the electronic state of the atom. The expansion coefficients, denoted as $U_{JL\bar{\Omega}\epsilon v}^{\mathcal{J}\mathfrak{M}}(R)$ are functions of the distance $R$ between the atom and the center-of-mass of the diatomic, and are solutions to a set of coupled differential equations—the close-coupled (CC) equations—defined by

$$\left[-\frac{\hbar^2}{2m_c}\frac{d^2}{dR^2} + \frac{\hbar^2L(L+1)}{2m_cR^2} + \langle JL\bar{\Omega}\epsilon v\mathcal{J}\mathfrak{M}|V|JL\bar{\Omega}\epsilon v\mathcal{J}\mathfrak{M}\rangle - \mathcal{E}_{J\bar{\Omega}\epsilon v}\right]U_{JL\bar{\Omega}\epsilon v}^{\mathcal{J}\mathfrak{M}}(R)$$

$$= -\sum_{\substack{J'L'\bar{\Omega}'\epsilon' \\ \bar{\Omega}'v'}}' \langle J'L'\bar{\Omega}'\epsilon'v'\mathcal{J}\mathfrak{M}|V|JL\bar{\Omega}\epsilon v\mathcal{J}\mathfrak{M}\rangle U_{J'L'\bar{\Omega}'\epsilon'v'}^{\mathcal{J}\mathfrak{M}}(R) , \qquad (10)$$

where the prime on the summation indicates that the diagonal term $(J'L'\bar{\Omega}'\epsilon'v' = JL\bar{\Omega}\epsilon v)$ is excluded; where $m_c$ is the collision reduced mass; and where

$$\mathcal{E}_{J\bar{\Omega}\epsilon v} = E_{tot} - E_{J\bar{\Omega}\epsilon v} , \qquad (11)$$

the latter quantity being defined by Eqs. (5) and (6).

The matrix elements of the interaction potential which appear in Eq. (10) are obtained by integration over all coordinates except $R$. Within the Born–Oppenheimer approximation, the integration over the electronic coordinates can be carried out first to yield an effective potential which is a function of $r$, the diatomic bond length $R$, and the angles $\tilde{\theta}$ and $\tilde{\phi}$ which describe the orientation of $\mathbf{R}$ with respect to $\mathbf{r}$. We will assume further that the integration runs over the vibrational motion of the diatomic, so that the resulting potential will apply only to the rotational motions of the atom–molecule system. Additionally, we will assume that the interaction potential does not contain any spin-dependent terms. The effective potential can be defined by

$$V_{\Lambda'\Lambda}^{v'v}(R, \tilde{\theta}, \tilde{\phi}) = \delta_{\Sigma\Sigma'}\langle\bar{\Omega}'v'\Lambda'\Sigma'|V|\bar{\Omega}v\Lambda\Sigma\rangle , \qquad (12)$$

where tildes will indicate the molecule frame coordinate

system. For the sake of simplicity the vibrational indices will be suppressed from now on unless needed. As has been discussed by Green and Zare,[5] Shapiro and Kaplan,[10] and Dixon and Field,[9] the dependence on the azimuthal angle $\tilde{\phi}$, which does not arise in the description of collisions between structureless atoms and molecules in $\Sigma$ electronic states, occurs here because the wave function for a molecule in a $\Pi$ electronic state is not cylindrically symmetric, but has an azimuthal dependence of $\exp(i\Lambda\tilde{\phi}_e)$, where $\tilde{\phi}_e$ describes the orientation of the entire electronic wave function. Thus, the overall azimuthal dependence of the potential defined by Eq. (12) is given by $\exp[-i(\Lambda' - \Lambda)\tilde{\phi}]$.

The reader should note that the potential defined by Eq. (12) is constructed by integration over the *adiabatic* electronic states of the system, which correlate asymptotically to the product of an atom in state $|\beta\rangle$ and a $^2\Pi$ diatomic molecule in the $|\Lambda S\Sigma\rangle$ state. It is this type of electronically adiabatic potential which will be accessible through a typical *ab initio* calculation.

Using Eqs. (8), (9), and (12), one can show that the expression for the potential matrix elements is given by

$$\langle J'L'\bar{\Omega}'\epsilon'\mathcal{J}\mathfrak{M}|V|JL\bar{\Omega}\epsilon\mathcal{J}\mathfrak{M}\rangle = \sum_{\substack{MM_L \\ M'M'_L}} \tfrac{1}{2}(JMLM_L|JL\mathcal{J}\mathfrak{M})(J'M'L'M'_L|J'L'\mathcal{J}\mathfrak{M})$$

$$\times [\delta_{\bar{\Omega}\bar{\Omega}'}(\langle L'M'_LJ'M'\bar{\Omega}|V_{1,1}|LM_LJM\bar{\Omega}\rangle + \epsilon\epsilon'\langle L'M'_LJ'M', -\bar{\Omega}|V_{-1,-1}|LM_LJM, -\bar{\Omega}\rangle)$$

$$+ (1 - \delta_{\bar{\Omega}\bar{\Omega}'})(\epsilon\langle L'M'_LJ'M'\bar{\Omega}'|V_{1,-1}|LM_LJM, -\bar{\Omega}\rangle + \epsilon'\langle L'M'_LJ'M', -\bar{\Omega}'|V_{-1,1}|LM_LJM\bar{\Omega}\rangle)] . \qquad (13)$$

As stated above, the vibrational indices have been suppressed. The integration in Eq. (13) extends over the angles describing the orientation of the atom and the diatomic molecule. This integration can be accomplished by expanding the $V_{\Lambda'\Lambda}$ terms as

$$V_{\Lambda'\Lambda}(R, \tilde{\theta}, \tilde{\phi}) = \sum_{l\mu}[4\pi/(2l+1)]^{1/2}A_{l\mu}^{\Lambda'\Lambda}(R)Y_{l\mu}(\tilde{\theta}, \tilde{\phi}) . \qquad (14)$$

For given values of $\Lambda$ and $\Lambda'$ only the $\mu = -\Lambda' + \Lambda$ term will contribute. As $\Lambda, \Lambda' = \pm 1$ for a $\Pi$ electronic state, it

follows that the only nonvanishing $A_{l\mu}^{\Lambda'\Lambda}$ terms are $A_{l;0}^{1;1}$, $A_{l;0}^{-1;-1}$, $A_{l;-2}^{1;-1}$, and $A_{l;2}^{-1;1}$. Since the only $\Lambda$ dependence of the $V_{\Lambda'\Lambda}$ potentials is contained in the $\exp[-i(\Lambda'-\Lambda)\tilde{\phi}]$ term and since the coefficients in Eq. (14) can be taken to be real, it is clear that the four sets of nonvanishing $A_{l\mu}^{\Lambda'\Lambda}$ coefficients are related by

$$A_{l;0}^{1;1}(R) = A_{l;0}^{-1;-1}(R) \tag{15}$$

and

$$A_{l;-2}^{1;-1}(R) = A_{l;2}^{-1;1}(R) \ . \tag{16}$$

Because the $|JM\Omega\rangle$ [Eq. (4)] and $|LM_L\rangle$ functions are defined in a space-fixed axis system, the integration in Eq. (13) can be most easily done by expanding the potential [Eq. (14)] in the space frame as

$$V_{\Lambda'\Lambda}(R, \theta, \phi) = \sum_{lm\mu} [4\pi/(2l+1)]^{1/2} A_{l\mu}^{\Lambda'\Lambda}(R) D_{m\mu}^{l}(\alpha\beta\gamma) Y_{lm}(\theta, \phi) \ , \tag{17}$$

where the Euler angles are the same as in Eq. (4), and the angles $\theta$, $\phi$ describe the orientation of R in the space frame.

If we substitute Eq. (17) into Eq. (13) and use Eqs. (15) and (16) as well as the known expressions for integrals involving the product of three rotation matrix elements and/or spherical harmonics,[33,37] we find, after some straightforward angular momentum algebra, the following expression for the potential matrix elements:

$$\langle J'L'\bar{\Omega}'\epsilon'\mathcal{J}\mathfrak{M}|V|JL\bar{\Omega}\epsilon\mathcal{J}\mathfrak{M}\rangle = (-1)^{J+J'+\mathcal{J}-\bar{\Omega}}[(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \sum_l \tfrac{1}{2}[1-\epsilon\epsilon'(-1)^{J+J'+l}]$$

$$\times \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & L & \mathcal{J} \\ L' & J' & l \end{Bmatrix} \left[ \delta_{\bar{\Omega}\bar{\Omega}'} A_{l0}^{1;1}(R) \begin{pmatrix} J' & l & J \\ -\bar{\Omega} & 0 & \bar{\Omega} \end{pmatrix} - \epsilon(1-\delta_{\bar{\Omega}\bar{\Omega}'})A_{l;-2}^{1;-1}(R) \begin{pmatrix} J' & l & J \\ -\bar{\Omega}' & 2 & -\bar{\Omega} \end{pmatrix} \right] \ . \tag{18}$$

In going through the derivation of this equation one must remember that for doublet states the angular momentum quantum numbers $J$, $M$, $J'$, $M'$, $\bar{\Omega}$, $\bar{\Omega}'$, $\mathcal{J}$, $\mathfrak{M}$ will all be half-integer, so that terms of the form $(-1)^{J+J}$ will equal negative unity. Equation (18) can be shown to be a generalization, to the case of definite parity states, of the expression given by Dixon and Field[9] for potential matrix elements between individual $|JL\Omega\mathcal{J}\mathfrak{M}\rangle$ states.

Several observations are important: For transitions *within* a given spin-orbit manifold ($\bar{\Omega}' = \bar{\Omega}'$) nonvanishing contributions to the potential matrix elements arise only from the first term in the square brackets on the far right of Eq. (18) and, specifically, only from the $\mu = 0$ terms in the expansion of the potential. For transitions *between* the two spin-orbit manifolds ($\bar{\Omega}' = \bar{\Omega} \pm 1$) nonvanishing contributions arise only from the second term in the square brackets and, specifically, from the $\mu = -2$ terms in the expansion. Thus, in the structure of the potential matrix there is no interference between the $\mu = 0$ and $\mu = -2$ terms. This kind of interference, specifically a variation in magnitude with the parity index $\epsilon$, does occur in the case of collisions of molecules in $^1\Pi$ electronic states. This has been discussed previously by several authors,[4,5,9,10] but is absent here due to the $\delta_{\Sigma\Sigma'}$ selection rule contained in Eq. (12). Also, it is worth noting that since $l$ must be greater than 2 in the last $3j$ symbol in Eq. (18), only the $l \geq 2$ terms in the expansion of the potential will contribute to transitions between the two spin-orbit manifolds. Finally, the first term in square brackets after the summation sign in Eq. (18) vanishes except for certain combinations of values of $\epsilon$, $\epsilon'$, $J$, $J'$, and $l$, so that certain selection rules are imposed on the coupling potential matrix, as has been discussed by Dixon and Field,[9] as well as in our previous paper[15] on collisions of molecules in $^2\Sigma^+$ electronic states. These selection rules are summarized in Table I.

The CC equations (10) are solved subject to the boundary condition[1,36]

$$\lim_{R\to\infty} U_{JL\bar{\Omega}\epsilon}^{\mathcal{J}\mathfrak{M}}(R) = \delta_{jj'}\delta_{LL'}\delta_{\bar{\Omega}\bar{\Omega}'}\delta_{\epsilon\epsilon'} \exp[-i(k_{J''\bar{\Omega}''\epsilon''}R$$

$$- L''\pi/2)] - (k_{J''\bar{\Omega}''\epsilon''}/k_{J\bar{\Omega}\epsilon})^{1/2}$$

$$\times S_{J''L''\bar{\Omega}''\epsilon'',JL\bar{\Omega}\epsilon}^{\mathcal{J}} \exp[i(k_{J\bar{\Omega}\epsilon}R - L\pi/2)] \ , \tag{19}$$

where

$$k_{J\bar{\Omega}\epsilon} = (2m_c \mathcal{E}_{J\bar{\Omega}\epsilon}/\hbar^2)^{1/2} \ . \tag{20}$$

The scattering amplitude can be then constructed exactly as in the Arthurs–Dalgarno formulation of collisions involving $^1\Sigma^+$ diatomics[36] as

$$f_{JM\bar{\Omega}\epsilon \to J'M'\bar{\Omega}'\epsilon'} = \sum_{\mathcal{J}LL'} i^{L-L'}[(2L+1)\pi]^{1/2}(2\mathcal{J}+1) \begin{pmatrix} J & \mathcal{J} & L \\ M & -M & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} J' & \mathcal{J} & L' \\ M' & -M & M'_L \end{pmatrix} T_{JL\bar{\Omega}\epsilon,J'L'\bar{\Omega}'\epsilon'}^{\mathcal{J}} Y_{L'M'_L}(\hat{R}) \ , \tag{21}$$

TABLE I. Selection rules for nonzero coupling.[a]

| $l$ | Nonzero coupling | |
| --- | --- | --- |
| | $\epsilon = \epsilon'$ | $\epsilon = \epsilon'$ |
| even | $\Delta J$ = even[b] | $\Delta J$ = odd |
| odd | $\Delta J$ = odd | $\Delta J$ = even |

[a]For a given value of $l$, and for given values of the parity indices $\epsilon$ of the initial and final states, the potential matrix elements [Eqs. (18) and (27)] will vanish unless the difference $\Delta J$ between the initial and final values of the total molecular angular momentum is either even or odd as listed in the table.
[b]$\Delta J = J - J'$.

where

$$T^{\mathscr{J}}_{JL\bar{\Omega}\epsilon,J'L'\bar{\Omega}'\epsilon'}$$

$$= \delta_{JJ'}\delta_{LL'}\delta_{\bar{\Omega}\bar{\Omega}'}\delta_{\epsilon\epsilon'} - S^{\mathscr{J}}_{JL\bar{\Omega}\epsilon,J'L'\bar{\Omega}'\epsilon'} \ . \tag{22}$$

The integral cross section for the $J\bar{\Omega}\epsilon \rightarrow J'\bar{\Omega}'\epsilon$ transition, summed over $M'$ and averaged over $M$, is given by the expression

$$\sigma_{J\bar{\Omega}\epsilon \rightarrow J'\bar{\Omega}'\epsilon'} = \frac{\pi}{(2J+1)k^2_{J\bar{\Omega}\epsilon}} \sum_{\mathscr{J}} (2\mathscr{J}+1)$$

$$\times \sum_{LL'} |T^{\mathscr{J}}_{JL\bar{\Omega}\epsilon,J'L'\bar{\Omega}'\epsilon'}|^2 \ . \tag{23}$$

We note that there exist several additional degrees of inelasticity here which are not present in collisions of $^1\Sigma^+$ diatomics, namely, the parity index and the value of $\bar{\Omega}$. Collisions can be inelastic in any one or more of the $\bar{\Omega}$, $\epsilon$, or $J$ indices. A brief physical interpretation of these effects is worthwhile. We follow, in spirit, the discussion given by Green and Zare for collisions of $^1\Pi$ molecules.[5]

In the isolated $^2\Pi_\Omega$ molecule in Hund's case (a), $\Lambda$ and $\Sigma$ are coupled to form $\Omega$, the total projection of L and S along the internuclear axis. This resultant $\Omega$ is then coupled with R, the angular momentum associated with the rotation of the nuclei, to form J, the total rotational angular momentum. Neither $\Omega$ nor R is fixed in direction; both precess around J. The $\mu = 0$ terms in the expansion of the potential are cylindrically symmetric about the molecular axis, and thus do not affect any change in $\Lambda$ but can only cause a change in the magnitude and/or orientation of R; so, after the target has receded, the subsequent recoupling with $\Omega$ to form J can result in changes both in $|J|$ and $\epsilon$. The $\mu = 2$ terms in the expansion of the potential will cause a change in the orientation of $\Lambda$, as well as R, although S is still unaffected because the potential does not contain any spin-dependent terms. The subsequent recoupling, both of $\Lambda$ and S to form $\Omega$, and $\Omega$ and R to form J, can result in changes in $|J|$, $|\Omega|$, and $\epsilon$.

## III. COUPLED STATES APPROXIMATION

The prime difficulty in implementing CC calculations arises from the large number of coupled equations which must be solved simultaneously, due to the projection degeneracy of the rotational quantum number.[1-3,38] This is further complicated in the present application by the necessity of including both parity indices and both spin-orbit components. A possible simplification, which should be valid in the weak coupling limit, is to utilize a solution of the CC equations based on perturbation theory. This approach, the Born approximation,[39] has been followed by Dixon and Field[9] in their study of collisions involving OH in the $X^2\Pi$ ground state and will be discussed below in Sec. VII.

Alternatively, for atom–diatom systems in which the interaction potential is primarily short ranged, a significant reduction in dimensionality with little loss in accuracy can be achieved by the block diagonalization of the CC equations which constitutes the coupled states (CS) approximation.[2,3,17-19,40-42] This is carried out by first replacing the centrifugal terms in the CC equations (10) by an average value $\hbar^2 \bar{L}(\bar{L}+1)/2m_c R^2$. Then, the potential matrix can be block diagonalized, while preserving the diagonality of the centrifugal terms, by a transformation to a new basis defined by

$$|Jv\bar{\Omega}\epsilon\mathscr{J}\mathfrak{M}\rangle = \sum_L B^{J\mathscr{J}}_{vL} |JL\bar{\Omega}\epsilon\mathscr{J}\mathfrak{M}\rangle \ , \tag{24}$$

where, as discussed by DePristo and Alexander,[43]

$$B^{J\mathscr{J}}_{vL} = (-1)^v (2L+1)^{1/2} \begin{pmatrix} L & J & \mathscr{J} \\ 0 & v & -v \end{pmatrix} \ . \tag{25}$$

The potential matrix in the new basis then becomes

$$\langle J'v'\bar{\Omega}'\epsilon'\mathscr{J}\mathfrak{M} | V | Jv\bar{\Omega}\epsilon\mathscr{J}\mathfrak{M}\rangle$$

$$= \sum_{LL'} B^{J'\mathscr{J}}_{v'L'} B^{J\mathscr{J}}_{vL} \langle J'L'\bar{\Omega}'\epsilon'\mathscr{J}\mathfrak{M} | V | JL\bar{\Omega}\epsilon\mathscr{J}\mathfrak{M}\rangle \ . \tag{26}$$

With Eqs. (8), (9), (13), and (18), and some angular momentum algebra, one can show that the result is

$$\langle J'v'\bar{\Omega}'\epsilon'\mathscr{J}\mathfrak{M} | V | Jv\bar{\Omega}\epsilon\mathscr{J}\mathfrak{M}\rangle = \delta_{vv'}(-1)^{v+1-\bar{\Omega}}[(2J+1)(2J'+1)]^{1/2} \sum_l \tfrac{1}{2}[1 - \epsilon\epsilon'(-1)^{J+J'+l}]$$

$$\times \begin{pmatrix} J' & l & J \\ v & 0 & -v \end{pmatrix} \left[ \delta_{\bar{\Omega}\bar{\Omega}'} A^{1;1}_{l;0}(R) \begin{pmatrix} J' & l & J \\ -\bar{\Omega} & 0 & \bar{\Omega} \end{pmatrix} - \epsilon(1-\delta_{\bar{\Omega}\bar{\Omega}'}) A^{1;-1}_{l;-2}(R) \begin{pmatrix} J' & l & J \\ -\bar{\Omega}' & 2 & -\bar{\Omega} \end{pmatrix} \right] \ . \tag{27}$$

Since the potential matrix elements are independent of $\mathscr{J}$ (and its projection $\mathfrak{M}$), these indices can be dropped. In contrast to the situation which occurs in collisions involving $^1\Sigma^+$ molecules, the $v$ index is now *half-integer*. Since both terms in square brackets after the summation sign in Eq. (27) are identical to the comparable terms in Eq. (18), the entire discussion following Eq. (18) which concerns selection rules and the importance of various terms in the expansion of the potential applies equally within the CS approximation.

Within this approximation, the CC equations (10) are replaced by

$$\left[ -\frac{\hbar^2}{2m_c}\frac{d^2}{dR^2} + \frac{\hbar^2 \bar{L}(\bar{L}+1)}{2m_c R^2} + \langle Jv\bar{\Omega}\epsilon | V | Jv\bar{\Omega}\epsilon\rangle - \mathscr{E}_{J\bar{\Omega}\epsilon} \right] U^{\bar{L}v}_{J\bar{\Omega}\epsilon}(R)$$

$$= -\sum_{J'\epsilon'\bar{\Omega}'} {}' \langle J'v\,\bar{\Omega}'\epsilon' | V | Jv\bar{\Omega}\epsilon\rangle U^{\bar{L}v}_{J'\bar{\Omega}'\epsilon'}(R) \ . \tag{28}$$

These are solved subject to the boundary condition

$$\lim_{R\to\infty} U^{\bar{L}v}_{J\bar{\Omega}\epsilon}(R) = \delta_{JJ''}\delta_{\bar{\Omega}\bar{\Omega}''}\delta_{\epsilon\epsilon''} \exp[-i(k_{J''\bar{\Omega}''\epsilon''}R - \bar{L}\pi/2)]$$

$$- (k_{J''\bar{\Omega}''\epsilon''}/k_{J\bar{\Omega}\epsilon})^{1/2} S^{\bar{L}v}_{J''\bar{\Omega}''\epsilon'',J\bar{\Omega}\epsilon} \exp[i(k_{J\bar{\Omega}\epsilon}R - \bar{L}\pi/2)] \ . \tag{29}$$

The relation between the CS and CC $T$ matrices can be obtained by reversing the transformation implicit in Eq.

(24). We will introduce an overall phase factor which corresponds to the so-called "correct phase" choice, discussed by Khare et al.[44] Accordingly, we have

$$T^{\mathcal{J}}_{JL\bar{\Omega}\epsilon,J'L'\bar{\Omega}'\epsilon'} = i^{L+L'-2\bar{L}} \sum_{\nu} [(2L+1)(2L'+1)]^{1/2}$$

$$\times \begin{pmatrix} L & J & \mathcal{J} \\ 0 & \nu & -\nu \end{pmatrix} \begin{pmatrix} L' & J' & \mathcal{J} \\ 0 & \nu & -\nu \end{pmatrix} T^{\bar{L}\nu}_{J\bar{\Omega}\epsilon,J'\bar{\Omega}'\epsilon'} \ . \tag{30}$$

The expression for the degeneracy averaged integral cross section is given in terms of the CS $T$ matrix elements by the expression[45]

$$\sigma_{J\bar{\Omega}\epsilon \to J'\bar{\Omega}'\epsilon'} = \frac{\pi}{(2J+1)k^2_{J\bar{\Omega}\epsilon}} \sum_{\bar{L}} (2\bar{L}+1) \sum_{\nu} |T^{\bar{L}\nu}_{J\bar{\Omega}\epsilon,J'\bar{\Omega}'\epsilon'}|^2 \ . \tag{31}$$

As stated in the introduction, Dewangan and Flower,[12] in an article still in press (and which we have not seen), have developed the CS approximation for the collision of a $^2\Pi$ molecule in a Hund's case (b) basis.

## IV. INFINITE ORDER SUDDEN APPROXIMATION

In cases where the potential is short ranged and where, furthermore, the collision energy is high compared to the spacing between individual levels, the CS equations can be further simplified within the infinite-order-sudden (IOS) approximation, presented first by Pack.[18,20] In the application of this method to collisions of $^2\Pi$ molecules, it will be convenient to work not with the definite parity states [Eq. (2)] but with the $|JM\Omega v\Lambda\Sigma\rangle$ states defined by Eq. (1), which we shall denote as definite $\Omega$ states. Analogously to Eqs. (8) and (9), these states can be multiplied by the $|LM_L\beta\rangle$ functions describing the motion of the atom and linear combinations taken which are eigenfunctions of the total angular momentum. We find

$$|JL\Omega v\Lambda\Sigma\beta\mathcal{J}\mathfrak{M}\rangle = |JL\Omega\mathcal{J}\mathfrak{M}\rangle|\beta v\Lambda\Sigma\rangle \ , \tag{32}$$

where we recall that the second ket on the right-hand side of this equation describes the motion of all the electrons as well as the vibrational motion of the diatomic, and where

$$|JL\Omega\mathcal{J}\mathfrak{M}\rangle = \sum_{MM_L} (JMLM_L|JL\mathcal{J}\mathfrak{M})|LM_L\rangle|JM\Omega\rangle \ . \tag{33}$$

In the definite $\Omega$ basis, the CC equations have a structure analogous to Eq. (10) and are written as

$$\left[ -\frac{\hbar^2}{2m_c} \frac{d^2}{dR^2} + \frac{\hbar^2 L(L+1)}{2m_c R^2} + \langle JL\Omega v\Lambda\Sigma\mathcal{J}\mathfrak{M}|V|JL\Omega v\Lambda\Sigma\mathcal{J}\mathfrak{M}\rangle - \mathcal{E}_{J\Omega v} \right] U^{\mathcal{J}\mathfrak{M}}_{JL\Omega v\Lambda\Sigma}(R)$$

$$= -\sum_{\substack{J'L'\Omega' \\ v'\Lambda'\Sigma'}}' \langle J'L'\Omega'v'\Lambda'\Sigma'\mathcal{J}\mathfrak{M}|V|JL\Omega v\Lambda\Sigma\mathcal{J}\mathfrak{M}\rangle U^{\mathcal{J}\mathfrak{M}}_{J'L'\Omega'v'\Lambda'\Sigma'}(R) \ , \tag{34}$$

where $\beta$ index has been suppressed and where the channel energies are defined by Eqs. (5) and (6) *without* the terms reflecting the $\Lambda$ doubling splitting. In Eq. (34) the potential matrix elements are given by

$$\langle J'L'\Omega'v'\Lambda'\Sigma'\mathcal{J}\mathfrak{M}|V|JL\Omega v\Lambda\Sigma\mathcal{J}\mathfrak{M}\rangle = \langle J'L'\Omega'\mathcal{J}\mathfrak{M}|V_{\Lambda'\Lambda}|JL\Omega\mathcal{J}\mathfrak{M}\rangle \ , \tag{35}$$

where $V_{\Lambda'\Lambda}$ is defined by Eq. (12). Equations (10) and (34) are, strictly speaking, equivalent only if the small splitting of the channel energies due to $\Lambda$ doubling is neglected, an approximation which is completely consistent with the energy sudden limit.

Equation (8) can be used to derive the relationship between the elements of the $S$ matrix in the definite parity and definite $\Omega$ bases. We find

$$S^{\mathcal{J}}_{JL\bar{\Omega}\epsilon,J'L'\bar{\Omega}'\epsilon'} = \tfrac{1}{2}[\delta_{\bar{\Omega}\bar{\Omega}'}(S^{\mathcal{J}}_{JL,\Omega=\bar{\Omega},\Lambda=1,\Sigma=\bar{\Omega}-1,J'L',\Omega'=\bar{\Omega},\Lambda'=1,\Sigma'=\bar{\Omega}-1} + \epsilon\epsilon'S^{\mathcal{J}}_{JL,\Omega=-\bar{\Omega},\Lambda=-1,\Sigma=-\bar{\Omega}+1,J'L',\Omega'=-\bar{\Omega},\Lambda'=-1,\Sigma'=-\bar{\Omega}+1}) + (1-\delta_{\bar{\Omega}\bar{\Omega}'})$$

$$\times (\epsilon'S^{\mathcal{J}}_{JL,\Omega=\bar{\Omega},\Lambda=1,\Sigma=\bar{\Omega}-1,J'L',\Omega'=-\bar{\Omega}',\Lambda'=-1,\Sigma'=-\bar{\Omega}'+1} + \epsilon S^{\mathcal{J}}_{JL,\Omega=-\bar{\Omega},\Lambda=-1,\Sigma=-\bar{\Omega}+1,J'L',\Omega'=\bar{\Omega}',\Lambda'=1,\Sigma'=\bar{\Omega}'-1})] \ , \tag{36}$$

where the vibrational indices are now suppressed.

In deriving Eq. (36), we have explicitly used the fact that because the interaction potential does not contain any spin dependent terms, the elements of the $S$ matrix in the definite $\Omega$ basis will vanish unless $\Sigma = \Sigma'$.

It is also possible to achieve the coupled states simplification within the definite $\Omega$ basis by first replacing the centrifugal terms in Eq. (32) by an average value $\hbar \bar{L}(\bar{L}+1)/2m_c R^2$ and then by applying to the $|JL\Omega v\Lambda\Sigma\beta\mathcal{J}\mathfrak{M}\rangle$ states [Eq. (34)] the transformation defined by Eqs. (24) and (25). If, furthermore, the individual channel energies are replaced by an average value $\bar{\mathcal{E}}$, then, as Secrest[21] and Hunter[22] have shown, the CS equations become completely uncoupled, so that the scattering problem is reduced to the solution of an infinite set of angle-dependent, one-dimensional equations; namely,

$$\left[ -\frac{\hbar^2}{2m_c} \frac{d^2}{dR^2} + \frac{\hbar^2 \bar{L}(\bar{L}+1)}{2m_c R^2} + V_{\Lambda'\Lambda}(R,\bar{\theta},\bar{\phi}) - \bar{\mathcal{E}} \right] U^{\bar{L}}_{\Lambda'\Lambda}(R;\bar{\theta},\bar{\phi}) = 0 \ , \tag{37}$$

where $V_{\Lambda'\Lambda}(R,\bar{\theta},\bar{\phi})$ is just the interaction potential in the molecule-frame coordinate system, defined by Eq. (12). In contrast to the description of collisions involving molecules in $\Sigma$ electronic states, both the potential and the solutions have an additional dependence on the azimuthal angle.

These IOS equations are solved subject to the boundary condition

$$\lim_{R\to\infty} U^{\bar{L}}_{\Lambda'\Lambda}(R,\bar{\theta},\bar{\phi}) = \bar{k}^{-1/2}\{\exp[-i(\bar{k}R - \bar{L}\pi/2)$$

$$- S^{\bar{L}}_{\Lambda'\Lambda}(\bar{\theta},\bar{\phi})\exp[i(\bar{k}R - \bar{L}\pi/2)]\} \ , \tag{38}$$

where $\bar{k}$ is the wave vector corresponding to the average

energy $\bar{\mathscr{E}}$. The individual $S$ matrix elements in the definite $\Omega$ basis are obtained as matrix elements of the angle dependent IOS $S^L_{\Lambda'\Lambda}(\bar{\theta}, \tilde{\phi})$ function; namely,

$$S^{\mathscr{J}}_{JL\Omega\Delta\mathcal{E},J'L'\Omega'\Lambda'\mathcal{E}'}$$
$$= \delta_{\mathcal{E}\mathcal{E}'}\langle J'L'\Omega'\mathscr{J}\mathfrak{M}|S^L_{\Lambda'\Lambda}(\bar{\theta}, \tilde{\phi})|JL\Omega\mathscr{J}\mathfrak{M}\rangle \ . \quad (39)$$

These can be related to $S$ matrix elements between definite parity states by means of Eq. (36), and, ultimately, to $T$ matrix elements by means of the relation

$$T^{\mathscr{J}}_{JL\bar{\Omega}\epsilon,J'L'\bar{\Omega}'\epsilon'} = i^{L+L'-2\bar{L}}(\delta_{JJ'}\delta_{LL'}\delta_{\bar{\Omega}\bar{\Omega}'}\delta_{\epsilon\epsilon'}$$
$$- S^{\mathscr{J}}_{JL\bar{\Omega}\epsilon,J'L'\bar{\Omega}'\epsilon'}) \ , \quad (40)$$

where, as we have discussed in Sec. III, the factor of $i^{L+L'-2\bar{L}}$ corresponds to the "correct phase" defined by Khare et al.[44]

The formal evaluation of the matrix elements of the $S^L_{\Lambda'\Lambda}(\bar{\theta}, \tilde{\phi})$ function can be facilitated by an expansion in spherical harmonics, as in Eq. (14),

$$S^L_{\Lambda'\Lambda}(\bar{\theta}, \tilde{\phi}) = \sum_{l\mu}[4\pi/(2l+1)]^{1/2}S^{L,\Lambda'\Lambda}_{l\mu}Y_{l\mu}(\bar{\theta}, \tilde{\phi}) \ . \quad (41)$$

We remember from Sec. II that for $\Lambda'=\Lambda$ the potential is independent of $\tilde{\phi}$. For this reason the $S$ function $S^L_{\Lambda'\Lambda}$ will also be independent of $\tilde{\phi}$ for $\Lambda'=\Lambda$; so, only the $\mu=0$ terms in Eq. (41) will be nonvanishing in this case. For notational simplicity we will rewrite Eq. (41) for the $\Lambda=\Lambda'$ case as

$$S^L_{\Lambda\Lambda}(\bar{\theta}, \tilde{\phi}) = \sum_l S^L_l P_l(\cos\bar{\theta}) \ . \quad (42)$$

For $\Lambda'=-\Lambda$, the dependence of the potential on the azimuthal angle is given by $\exp[i(\Lambda'-\Lambda)\tilde{\phi}]$. Thus, it follows from Eq. (37) that

$$S^L_{\Lambda'\Lambda}(\bar{\theta}, \tilde{\phi}) = S^L_{\Lambda\Lambda'}(\bar{\theta}, -\tilde{\phi}) \ , \quad (43)$$

and, furthermore, since $|\Lambda'|=|\Lambda|=1$ for states of $\Pi$ symmetry,

$$S^L_{\Lambda'\Lambda}(\bar{\theta}, \pi/2) = S^L_{\Lambda\Lambda'}(\bar{\theta}, \pi/2) \ . \quad (44)$$

It can be shown that the latter symmetry relation can be satisfied only if the index $\mu$ in Eq. (41) is restricted to even values. With this restriction, the symmetry relation (43) implies that the coefficients in Eq. (41) obey the relation

$$S^{L,\Lambda'\Lambda}_{l\mu} = S^{L,\Lambda\Lambda'}_{l,-\mu} \ . \quad (45)$$

This is equivalent to re-expressing Eq. (41) for the case $\Lambda'=-\Lambda$ in terms of one set of coefficients; namely,

$$S^L_{1,-1}(\bar{\theta}, \tilde{\phi}) = \sum_{l\mu}[4\pi/(2l+1)]^{1/2}S^L_{l\mu}Y_{l\mu}(\bar{\theta}, \tilde{\phi}) \quad (46)$$

and

$$S^L_{-1,1}(\bar{\theta}, \tilde{\phi}) = \sum_{l\mu}[4\pi/(2l+1)]^{1/2}S^L_{l,-\mu}Y_{l\mu}(\bar{\theta}, \tilde{\phi}) \ . \quad (47)$$

With expansions (42), (46), and (47), the matrix elements of the $S$ function between definite $\Omega$ states [defined by Eq. (39)] and, ultimately, between definite parity states can be evaluated by following the steps taken in proceeding from Eqs. (14)–(18). We find

$$\langle J'L'\bar{\Omega}'\epsilon'\mathscr{J}\mathfrak{M}|S^L|JL\bar{\Omega}\epsilon\mathscr{J}\mathfrak{M}\rangle = (-1)^{J+J'+\mathscr{J}-\bar{\Omega}}[(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2}\sum_l \tfrac{1}{2}[1-\epsilon\epsilon'(-1)^{J+J'+l}]\begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{Bmatrix} J & L & \mathscr{J} \\ L' & J' & l \end{Bmatrix}\left[\delta_{\bar{\Omega}\bar{\Omega}'}S^L_{l,0}\begin{pmatrix} J' & l & J \\ -\bar{\Omega} & 0 & \bar{\Omega} \end{pmatrix} - \epsilon(1-\delta_{\bar{\Omega}\bar{\Omega}'})S^L_{l,-2}\begin{pmatrix} J' & l & J \\ -\bar{\Omega}' & 2 & -\bar{\Omega} \end{pmatrix}\right] \ . \quad (48)$$

The integral inelastic cross sections can be evaluated using Eq. (23) and some angular momentum algebra. For the case of transitions within either of the two spin-orbit states $(\bar{\Omega}'=\bar{\Omega})$, we will define the quantity

$$\sigma_l = \frac{\pi}{k^2}\sum_{LL'}\frac{1}{2l+1}\begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2|S^L_l|^2 \quad (49)$$

in terms of which the degeneracy averaged cross section can be written

$$\sigma_{J\bar{\Omega}\epsilon \to J'\bar{\Omega}\epsilon'} = \sum_l(2J'+1)\begin{pmatrix} J' & l & J \\ -\bar{\Omega} & 0 & \bar{\Omega} \end{pmatrix}^2$$
$$\times \tfrac{1}{2}[1-\epsilon\epsilon'(-1)^{J+J'+l}]\sigma_l \ . \quad (50)$$

In a similar manner, for the case of transitions between the two spin-orbit manifolds $(\bar{\Omega}'=\bar{\Omega}\pm 1)$ we will define the quantity

$$\sigma_{12} = \frac{\pi}{k^2}\sum_{LL'}\frac{1}{2l+1}\begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2|S^L_{l,-2}|^2 \quad (51)$$

in terms of which the degeneracy averaged cross section can be written

$$\sigma_{J\bar{\Omega}\epsilon \to J',\bar{\Omega}'=\bar{\Omega}\pm 1,\epsilon'} = \sum_{l\geq 2}(2J'+1)\begin{pmatrix} J' & l & J \\ -\bar{\Omega}' & 2 & -\bar{\Omega} \end{pmatrix}^2$$
$$\times \tfrac{1}{2}[1-\epsilon\epsilon'(-1)^{J+J'+l}]\sigma_{12} \ . \quad (52)$$

The restriction of the summation in Eq. (52) reflects the fact that the $3j$ symbol vanishes for $l<2$. We note that the combinations of values of $\epsilon$, $\epsilon'$, $J$, $J'$, and $l$, which give nonvanishing contributions to the sum in both Eqs. (50) and (52), are limited by the triangular relation contained in the $3j$ symbols and by the selection rules discussed in connection with Eq. (18) and listed in Table I.

At this point, with the formalism presented, it is worthwhile to examine in detail several aspects of the application of the IOS method to collisions of $^2\Pi$ molecules. As stated earlier, the small error introduced by the neglect of the $\Lambda$ doubling splitting, which is made when the definite $\Omega$ and definite parity representations are set equivalent, will be completely overshadowed by the error introduced by the neglect of the much larger rotational and/or spin-orbit energy gaps, which is the

keystone of any energy sudden approximation. For collisions within the $\overline{\Omega} = \frac{3}{2}$ or $\overline{\Omega} = \frac{1}{2}$ manifolds the application of the IOS method appears straightforward. For many systems the collision energy will be sufficiently in excess of the pure rotational energy splittings to justify the imposition of the energy sudden limit. The $V_{\Lambda\Lambda}$ coupling potential is independent of $\tilde{\phi}$, as is the IOS $S$ function [Eq. (42)], so that the calculations of the $S$ function will be no more difficult than comparable calculations for the scattering of a $^1\Sigma^+$ or $^2\Sigma^+$ diatomic.

The application of the IOS method will be more complicated, however, for intermultiplet transitions $\overline{\Omega} = \frac{1}{2}$ $\rightleftharpoons \overline{\Omega} = \frac{3}{2}$. On one hand, the spin-orbit splitting and, consequently, the inelastic energy gaps may be large enough to invalidate the use of an energy sudden limit. Also, since the $V_{\Lambda'\Lambda}$ potential will be $\tilde{\phi}$ dependent, one must characterize the dependence of the $S$ function on both $\tilde{\theta}$ and $\tilde{\phi}$, which will necessitate roughly the square of the number of calculations which would be required when $\tilde{\theta}$ is the only independent variable. In this respect, the increase in computational effort is comparable to the extension of the IOS method from atom + rigid-rotor collisions to the collision of two rigid rotors,[46] or, perhaps more analogously, to the collision of an atom with a symmetric top.[47] Since only the $\mu = -2$ term is needed [Eq. (51)], it may be that the $\tilde{\phi}$ dependence of the $S_{\Lambda\Lambda'}^{\bar{l}}$ function can be adequately characterized by a small number of integration points. One important complexity arises here from the imaginary component in the $V_{\Lambda'\Lambda}$ potential for $\Lambda' = -\Lambda$, so that Eq. (37) must be solved with complex arithmetic. The problem is similar to the application of a one-dimensional optical model with complex potential.[48] This implies, of course, that the $S$ function defined by Eq. (38) is no longer constrained to unit modulus.

## V. FACTORIZATION PROPERTIES AND SCALING RELATIONS: TRANSITIONS WITHIN A SINGLE SPIN-ORBIT MANIFOLD

Equation (50) is the generalization to collisions of $^2\Pi$ diatomics of an analogous relationship for collisions of $^1\Sigma^+$ molecules; namely,

$$\sigma_{J \to J'} = \sum_l (2J'+1) \begin{pmatrix} J' & l & J \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma_l \ . \tag{53}$$

This equation was first explored within the IOS approximation by Goldflam, Green, and Kouri,[23,25] and then later shown[27,28] to apply whenever an energy sudden limit is assumed. Equation (50) is entirely analogous to the equation given earlier by Green[47] for collisions of atoms with symmetric top molecules, and, furthermore, for $\overline{\Omega} = \frac{1}{2}$, Eq. (50) is identical to the relationship derived previously by us[15] for rotationally inelastic collisions of diatomic molecules in $^2\Sigma^+$ electronic states.

There are several interesting insights which can be deduced from Eq. (50). First, due to the way in which $\epsilon$ and $\epsilon'$ enter into the right-hand side of Eq. (50), it is clear that the cross sections are independent of either a reversal or change in sign in the parity indices of the initial and final states. In other words,

$$\sigma_{J\bar{\Omega}\epsilon \to J'\bar{\Omega}\epsilon'} = \sigma_{J,\bar{\Omega},-\epsilon \to J',\bar{\Omega},-\epsilon'} \tag{54}$$

and

$$\sigma_{J\bar{\Omega}\epsilon \to J'\bar{\Omega}\epsilon'} = \sigma_{J'\bar{\Omega}\epsilon' \to J'\bar{\Omega}\epsilon} \ . \tag{55}$$

These two relationships are identical to equations presented earlier[15] for collisions of $^2\Sigma^+$ diatomics. Also, it is apparent that the inelastic cross sections within the $\overline{\Omega} = \frac{3}{2}$ and $\overline{\Omega} = \frac{1}{2}$ manifolds can be related to one another, since both sets of cross sections can be expressed in terms of the same $\sigma_l$ cross sections, which are independent of $\overline{\Omega}$ [Eq. (49)].

This relationship can be made explicit by setting $J = \overline{\Omega} = \frac{1}{2}$ in Eq. (50), which gives

$$\sigma_{(1/2)(1/2)\epsilon \to J'(1/2)\epsilon'} = (2J'+1)\sum_l \begin{pmatrix} J' & l & \frac{1}{2} \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2$$
$$\times \tfrac{1}{2}[1 - \epsilon\epsilon'(-1)^{J'+l+1/2}]\sigma_l \ . \tag{56}$$

From the discussion immediately following Eq. (52), we conclude that for $\epsilon = \epsilon'$ only $l = J' - \frac{1}{2}$ gives a nonzero contribution, so that

$$\sigma_{(1/2)(1/2)\epsilon \to J'(1/2)\epsilon} = (2J'+1)\begin{pmatrix} J' & J'-\frac{1}{2} & \frac{1}{2} \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2 \sigma_{l=J'-1/2} \ . \tag{57}$$

Evaluation of the $3j$ symbol leads to the following expression for $\sigma_l$:

$$\sigma_l = [(2l+1)/(l+1)]\sigma_{(1/2)(1/2)\epsilon \to J'=l+1/2, (1/2)\epsilon} \ . \tag{58}$$

Similarly, if $\epsilon' = -\epsilon$ in Eq. (56), only the value $l = J' + \frac{1}{2}$ gives a nonzero contribution. This yields, in an entirely equivalent manner, an alternative relation for $\sigma_l$; namely,

$$\sigma_l = [(2l+1)/l]\sigma_{(1/2)(1/2)\epsilon \to J'=l-1/2,1/2,-\epsilon} \ . \tag{59}$$

Either of Eqs. (58) and (59) can be reintroduced back into Eq. (50) to give an expression for all cross sections within both the $\overline{\Omega} = \frac{1}{2}$ and $\overline{\Omega} = \frac{3}{2}$ manifolds in terms of cross sections out of the $J = \overline{\Omega} = \frac{1}{2}$ level. If Eq. (58) is chosen, we find

$$\sigma_{J\bar{\Omega}\epsilon \to J'\bar{\Omega}\epsilon'} = (2J'+1)\sum_l [(2l+1)/(l+1)]\begin{pmatrix} J' & l & J \\ -\overline{\Omega} & 0 & \overline{\Omega} \end{pmatrix}^2$$
$$\times \tfrac{1}{2}[1 - \epsilon\epsilon'(-1)^{J+J'+l}]\sigma_{(1/2)(1/2)\epsilon \to l+1/2, (1/2)\epsilon} \ , \tag{60}$$

which can be written more compactly as

$$\sigma_{J\bar{\Omega}\epsilon \to J'\bar{\Omega}\epsilon'} = \sum_l g_l(J, \epsilon, J', \epsilon'; \overline{\Omega})\sigma_{(1/2)(1/2)\epsilon \to l+1/2, (1/2)\epsilon} \ , \tag{61}$$

where the definition of $g_l(J, \epsilon, J', \epsilon'; \overline{\Omega})$ is obvious. Because of Eq. (55) this equation could be equally well written as

$$\sigma_{J\bar{\Omega}\epsilon \to J'\bar{\Omega}\epsilon'} = \sum_l g_l(J, \epsilon, J', \epsilon'; \overline{\Omega})\sigma_{(1/2)(1/2)\epsilon' \to l+1/2, (1/2)\epsilon'} \ . \tag{62}$$

For low-lying values of $J$ and $J'$, we list in Table II the numerical values of the $g_l$ factors which relate all the intramultiplet cross sections to those out of the $J = \overline{\Omega} = \frac{1}{2}$ level. There are several worthwhile observations. First, experimental measurement of even a small subset of cross sections within a given spin-orbit

TABLE II.  Scaling factors relating inelastic $J\bar{\Omega}\epsilon \to J'\,\bar{\Omega}\epsilon\,'$ cross sections to the $J=\tfrac12$, $\bar{\Omega}=\tfrac12$, $\epsilon \to J''$, $\bar{\Omega}=\tfrac12$, $\epsilon$ cross sections.[a]

| $J'$ | $\epsilon\,'$ | $J=1/2$ $\epsilon=-1$[b] | $3/2$ $-1$[b] | $5/2$ $-1$[b] | $7/2$ $-1$[b] |
|---|---|---|---|---|---|
| | | | $\bar{\Omega}=\tfrac12$ | | |
| $1/2$ | $+1$ | $\tfrac12 A$ | c | c | c |
| $3/2$ | $-1$ | $A$ | $\cdots$ | c | c |
| $3/2$ | $+1$ | $\tfrac23 B$ | $\tfrac{1}{10}A+\tfrac{9}{20}C$ | c | c |
| $5/2$ | $-1$ | $B$ | $\tfrac{9}{10}A+\tfrac{3}{10}C$ | $\cdots$ | c |
| $5/2$ | $+1$ | $\tfrac34 C$ | $\tfrac17 B+\tfrac{18}{35}D$ | $\tfrac{3}{70}A+\tfrac{2}{15}C+\tfrac{25}{63}E$ | c |
| $7/2$ | $-1$ | $C$ | $\tfrac67 B+\tfrac27 D$ | $\tfrac67 A+\tfrac13 C+\tfrac{10}{63}E$ | $\cdots$ |
| $7/2$ | $+1$ | $\tfrac45 D$ | $\tfrac16 C+\tfrac59 E$ | $\tfrac{4}{63}B+\tfrac{12}{77}D+\tfrac{100}{231}F$ | $\tfrac{1}{42}A+\tfrac{3}{44}C+\tfrac{25}{182}E+\tfrac{1225}{3432}G$ |
| | | | $\bar{\Omega}=\tfrac32$ | | |
| $3/2$ | $+1$ | d | $\tfrac{9}{10}A+\tfrac{1}{20}C$ | c | c |
| $5/2$ | $-1$ | d | $\tfrac{6}{10}A+\tfrac{9}{20}C$ | $\cdots$ | c |
| $5/2$ | $+1$ | d | $\tfrac67 B+\tfrac{3}{35}D$ | $\tfrac{27}{70}A+\tfrac{49}{120}C+\tfrac{25}{252}E$ | c |
| $7/2$ | $-1$ | d | $\tfrac{10}{21}B+\tfrac{18}{35}D$ | $\tfrac57 A+\tfrac37 E$ | $\cdots$ |
| $7/2$ | $+1$ | d | $\tfrac56 C+\tfrac19 E$ | $\tfrac{10}{21}B+\tfrac{128}{385}D+\tfrac{10}{77}F$ | $\tfrac{3}{14}A+\tfrac{49}{132}C+\tfrac{289}{1638}E+\tfrac{147}{1144}G$ |

[a]Shown are all nonzero values of the quantity $g_l\,(J,\ \epsilon,\ J',\ \epsilon\,';\ \bar{\Omega})$ [Eq. (61)] with the appropriate value of $l$ indicated by the upper case letters $A,\ B,\ C,\ D,\ E,\ F,\ G$ which correspond, respectively, to $l=1,\ 2,\ 3,\ 4,\ 5,\ 6,$ and 7.

[b]Cross sections for transitions out of the $\epsilon=+1$ level can be obtained from the symmetry relation Eq. (54).

[c]Cross sections for downward transitions $(J'<J)$ can be obtained from the tabulated entries via microreversibility, which in the sudden approximation is expressed as $\sigma_{J'\bar{\Omega}\epsilon'\to J\bar{\Omega}\epsilon}=[(2J+1)/(2J'+1)]\,\sigma_{J\bar{\Omega}\epsilon\to J'\bar{\Omega}\epsilon'}$.

[d]For $\bar{\Omega}=\tfrac32$, $J$ must be $\geq\tfrac32$.

manifold can often, at least within the sudden approximation, provide enough information to determine a far larger portion of the entire cross section matrix for both manifolds.

Secondly, it appears that for transitions in which the parity index changes, for a given value of $\Delta J=|J'-J|$, the scaling factors for a given value of $l$ display a marked decrease as $J$ increases. It is instructive to examine the limiting behavior as $J\to\infty$. This can be done by first using a known large-$J$ limit[49] of the Clebsch–Gordan coefficient $\langle l0J\bar{\Omega}|lJJ'\bar{\Omega}\rangle$ to write

$$\lim_{J,J'\to\infty}\begin{pmatrix} J' & l & J \\ -\bar{\Omega} & 0 & \bar{\Omega}\end{pmatrix}=(-1)^{J'-2J+\bar{\Omega}}(2J'+1)^{-1/2}d^l_{J'-J,0}(x)$$

$$=(-1)^{J'-2J+\bar{\Omega}}(2J'+1)^{-1/2}[(l-J'+J)!\,/$$

$$(l+J'-J)!\,]^{1/2}P_l^{J'-J}(x)\ . \tag{63}$$

Here, $d^l_{\mu,\nu}(x)$ is a rotation matrix element and $P_l^{\nu}(x)$ is an associated Legendre polynomial with argument[49] $x=\bar{\Omega}/J$. Since $x\to0$ as $J\to\infty$, the large-$J$ limit of Eq. (60) can be written as

$$\lim_{J,J'\to\infty}\sigma_{J\bar{\Omega}\epsilon\to J'\bar{\Omega}\epsilon'}=\sum_l\frac{(2l+1)(l-J'+J)!}{(l+1)(l+J'-J)!}[P_l^{J'-J}(0)]^2$$

$$\times\tfrac12[1-\epsilon\epsilon'(-1)^{J+J'+l}]\sigma_{(1/2)(1/2)\epsilon\to l+1/2,(1/2)\epsilon}\ . \tag{64}$$

Since[50]

$$P_l^m(0)=2^m\pi^{-1/2}\cos[\tfrac12\pi(l-m)]$$

$$\times\Gamma[\tfrac12(l+m+1)]/\Gamma[\tfrac12(l-m+2)]\ , \tag{65}$$

it is clear from the cosine factor that the associated Legendre polynomial with argument 0 in Eq. (64) will vanish unless the quantity $(l-J'+J)$ is even. Because $J'$ is half-integer, this implies that the quantity $(l+J'+J)$ must be odd. But, the factor $1-\epsilon\epsilon'(-1)^{J+J'+l}$ implies that if $(l+J'+J)$ is odd, then each term in the summation over $l$ will vanish unless the initial and final parity indices are equal.

This discussion implies the existence of a propensity rule which will become stronger at larger $J$, whereby transitions which conserve the parity index (e → e or f → f) will be favored over transitions in which the parity index is changed (e → f, f → e). An entirely equivalent propensity rule was found to be valid for collisions of $^2\Sigma^+$ diatomics. Physically, this propensity rule implies that at large $J$, the collisions become completely ineffective in decoupling $\Omega$ from $R$. It is satisfying to observe that this is exactly the same propensity rule which was deduced empirically by Linton[51] and by Bernath[52] from their experimental studies of energy transfer in collisions of YO($A\,^2\Pi$) and CaF($A\,^2\Pi$) with Ar.

We note that our demonstration of the existence of such a propensity rule depends only on the validity of the sudden limit, and does not depend on considerations re-

lated to the presence or absence of certain terms in the expansion of the potential [Eq. (14)], as, for example, in the qualitative discussion by Gottscho[16] of the phenomenological propensity rules reported by Linton[51] and Bernath.[52]

It is worthwhile to examine the approach to the limit given by Eq. (64) for the particular case $J'=J$, $\epsilon'=-\epsilon$. In this case only the $l$ odd terms will contribute. To evaluate the limiting behavior, we express the Legendre polynomial in Eq. (63) in terms of the hypergeometric function[50]

$$P_{2n+1}^0(x) = (-1)^n[(2n+1)!/2^{2n}(n!)^2]$$
$$\times F(-n, n+\tfrac{3}{2}, \tfrac{3}{2}, x^2) . \tag{66}$$

Since $\lim_{x\to 0} F(a, b, c, x^2) = 1$,[50] we have

$$\lim_{x\to 0}[P_{2n+1}^0(x)]^2 = \{[(2n+1)!]^2/[2^{4n}(n!)^4]\}x^2 . \tag{67}$$

Using this limit in Eq. (64), we find

$$\lim_{J\to\infty} \sigma_{J\bar{\Omega}\epsilon\to J\bar{\Omega},-\epsilon}$$
$$= \sum_{l\,\text{odd}} \frac{(l!)^2(2l+1)\bar{\Omega}^2}{2^{2l-2}(l+1)J^2\{[(l-1)/2]!\}^4}\sigma_{(1/2)(1/2)\epsilon\to l+1/2,(1/2)\epsilon} . \tag{68}$$

This indicates that for the transitions which are elastic in $J$ but inelastic in the parity index, the cross sections approach zero inversely as the square of $J$. Due to the presence of the $\bar{\Omega}^2$ factor in the numerator of Eq. (68), this limit is approached nine times faster for the $\bar{\Omega} = \tfrac{1}{2}$ manifold than for the $\bar{\Omega} = \tfrac{3}{2}$ manifold. This behavior can be shown to be general for all the $\epsilon\to-\epsilon$ transitions, so that the propensity rule discussed in the preceding paragraph can be expected to become experimentally apparent at much lower $J$ in the $\bar{\Omega} = \tfrac{1}{2}$ manifold.

## VI. FACTORIZATION PROPERTIES AND SCALING RELATIONS: TRANSITIONS BETWEEN SPIN-ORBIT MANIFOLDS

The scaling relations within the energy sudden limit appropriate to transitions between the $\bar{\Omega} = \tfrac{1}{2}$ and $\bar{\Omega} = \tfrac{3}{2}$ manifolds derive from Eq. (52). We notice first that the symmetry with respect to $\epsilon$ and $\epsilon'$, exemplified in Eqs. (54) and (55), is preserved so that

$$\sigma_{J\bar{\Omega}\epsilon\to J',\bar{\Omega}\pm1,\epsilon'} = \sigma_{J\bar{\Omega},-\epsilon\to J',\bar{\Omega}\pm1,-\epsilon'} \tag{69}$$

and

$$\sigma_{J\bar{\Omega}\epsilon\to J',\bar{\Omega}\pm1,\epsilon'} = \sigma_{J\bar{\Omega}\epsilon'\to J',\bar{\Omega}\pm1,\epsilon} . \tag{70}$$

We note also from Eq. (52) that in the energy sudden limit, the $\bar{\Omega} = \tfrac{1}{2} \rightleftharpoons \bar{\Omega} = \tfrac{3}{2}$ cross sections satisfy the microreversibility relation

$$(2J+1)\sigma_{J\bar{\Omega}\epsilon\to J',\bar{\Omega}\pm1,\epsilon'} = (2J'+1)\sigma_{J',\bar{\Omega}\pm1,\epsilon'\to J\bar{\Omega}\epsilon} . \tag{71}$$

By substitution of $J=\bar{\Omega}=\tfrac{1}{2}$ in Eq. (52), we can derive explicit expressions for the $\sigma_{l2}$ factors analogous to Eqs. (58) and (59). We find

$$\sigma_{l2} = [(2l+1)/(l-1)]\sigma_{(1/2)(1/2)\epsilon\to l+1/2,(3/2)\epsilon} \tag{72}$$

and

$$\sigma_{l2} = [(2l+1)/(l+2)]\sigma_{(1/2)(1/2)\epsilon\to l-1/2,3/2,-\epsilon} . \tag{73}$$

If Eq. (73) is introduced into Eq. (52), we find

$$\sigma_{J,\bar{\Omega}=1/2,\epsilon\to J',\bar{\Omega}=3/2,\epsilon'}$$
$$= (2J'+1)\sum_{l\geqslant2}[(2l+1)/(l+2)]\begin{pmatrix} J' & l & J \\ -\tfrac{3}{2} & 2 & -\tfrac{1}{2} \end{pmatrix}^2$$
$$\times \tfrac{1}{2}[1-\epsilon\epsilon'(-1)^{J+J'+l}]\sigma_{(1/2)(1/2)\epsilon\to l-1/2,3/2,-\epsilon} , \tag{74}$$

which can be written more compactly as

$$\sigma_{J,\bar{\Omega}=1/2,\epsilon\to J',\bar{\Omega}=3/2,\epsilon'}$$
$$= \sum_{l\geqslant2} h_l(J, \epsilon, J', \epsilon')\sigma_{(1/2)(1/2)\epsilon\to l-1/2,3/2,-\epsilon} , \tag{75}$$

where the definition of $h_l(J, \epsilon, J', \epsilon')$ is obvious. Table III lists the nonzero values of the $h_l(J, \epsilon, J', \epsilon')$ coefficients for low-lying values of $J$ and $J'$.

It is interesting to investigate whether propensity rules, similar to those discussed in the preceding section, can be derived for the intermultiplet transitions. Following the development leading to Eq. (64), we first use the asymptotic expansion of the $3j$ symbol in Eq. (74), which is

$$\lim_{J,J'\to\infty} \begin{pmatrix} J' & l & J \\ -\tfrac{3}{2} & 2 & -\tfrac{1}{2} \end{pmatrix} = (-1)^{J'-2J+3/2}(2J'+1)^{-1/2}d_{J'-J,2}^l(x) , \tag{76}$$

where $x=\cos^{-1}[3/2J']$, and, in the limit, $x$ goes to $\pi/2$. In general, the $d_{mn}^l$ rotation matrix elements do not vanish for $x=\pi/2$, so that a general propensity rule does not emerge. In the case where $J'=J$, the first subscript equals zero, so that the rotation matrix element becomes proportional for $x=\pi/2$ to the associated Legendre polynomial $P_l^2(0)$, which, from Eq. (65), vanishes if $l$ is odd. For transitions in which the parity index is not conserved, the only nonvanishing contributions to the sum in Eq. (74) occur for $l$ odd. Thus, in this one case $(J'=J)$ the cross sections associated with the $\epsilon\to-\epsilon$ transition will vanish in the large $J$ limit; i.e.,

$$\lim_{J\to\infty} \sigma_{J\bar{\Omega}\epsilon\to J,\bar{\Omega}\pm1,-\epsilon} = 0 . \tag{77}$$

An interesting result emerges from Eq. (74) in the case when $J=\tfrac{1}{2}$, $J'=\tfrac{3}{2}$, $\epsilon=\epsilon'$. The triangular relation in the $3j$ symbol limits $l$ to the values of $l=1$ or 2. However, the former is not allowed by the range of the summation, and for $l=2$ the term $[1-\epsilon\epsilon'(-1)^{J+J'+l}]$ vanishes when $\epsilon=\epsilon'$. Thus, within the sudden limit, there will be no collisional coupling between the lowest e or lowest f levels of the two spin-orbit manifolds.

To our knowledge, published experimental studies[53] of collisional transfer between the two spin-orbit manifolds of a $^2\Pi$ state have not yet been carried out with a degree of rotational and $\Lambda$ doubling state resolution sufficient to establish the existence of the type of propensity role discussed here.

## VII. PROPENSITY RULES WITHIN THE BORN APPROXIMATION

It is worthwhile to investigate what propensity rules apply under conditions in which the sudden approximation is completely inappropriate, as, for example, in a weak coupling limit. Under these conditions, one might use the Born approximation, as has been applied (in a distorted wave framework) by Dixon and Field[9] to collisions of OH and CH. Within the quantum

TABLE III. Scaling factors relating inelastic $J$, $\overline{\Omega}=\frac{1}{2}$, $\epsilon \rightarrow J'$, $\Omega=\frac{3}{2}$, $\epsilon'$ cross sections to the $J=\frac{1}{2}$, $\overline{\Omega}=\frac{1}{2}$, $\epsilon \rightarrow J'$, $\Omega=\frac{3}{2}$, $-\epsilon$ cross sections.[a]

| $J'$ | $\epsilon'$ | $J=1/2$ $\epsilon=-1$[b] | $3/2$ $\epsilon=-1$ | $5/2$ $\epsilon=-1$ | $7/2$ $\epsilon=-1$ |
|---|---|---|---|---|---|
| 3/2 | $-1$ | $0^c$ | $\frac{1}{2}B$ | d | d |
| 3/2 | $+1$ | $B$ | $\frac{2}{5}C$ | d | d |
| 5/2 | $-1$ | $\frac{1}{4}B$ | $\frac{1}{10}C$ | $\frac{27}{56}B+\frac{5}{28}D$ | d |
| 5/2 | $+1$ | $C$ | $\frac{4}{7}B+\frac{15}{28}D$ | $\frac{1}{10}C+\frac{5}{14}E$ | d |
| 7/2 | $-1$ | $\frac{2}{5}C$ | $\frac{5}{28}B+\frac{1}{70}D$ | $\frac{2}{15}C+\frac{8}{105}E$ | $\frac{10}{21}B+\frac{16}{77}D+\frac{7}{66}F$ |
| 7/2 | $+1$ | $D$ | $\frac{3}{5}C+\frac{3}{5}E$ | $\frac{10}{21}B+\frac{289}{1155}D+\frac{14}{33}F$ | $\frac{8}{165}C+\frac{32}{273}E+\frac{140}{429}G$ |
| 9/2 | $-1$ | $\frac{1}{2}D$ | $\frac{3}{10}C$ | $\frac{25}{168}B+\frac{25}{924}D+\frac{1}{33}F$ | $\frac{5}{33}C+\frac{4}{39}E+\frac{25}{429}G$ |
| 9/2 | $+1$ | $E$ | $\frac{25}{44}D+\frac{7}{11}F$ | $\frac{169}{330}C+\frac{25}{78}E+\frac{200}{429}G$ | $\frac{100}{231}B+\frac{361}{2002}D+\frac{25}{132}F+\frac{105}{286}H$ |

[a]Shown are all nonzero values of the quantity $h_l$ $(J,\ \epsilon,\ J',\ \epsilon')$ [Eq. (75)] with the appropriate value of $l$ indicated by the upper case letters $B$, $C$, $D$, $E$, $F$, $G$, $H$ which correspond, respectively, to $l=2$, 3, 4, 5, 6, 7, and 8.
[b]Cross sections for transitions out of the $\epsilon=+1$ level can be obtained from the symmetry relation Eq. (69).
[c]This cross section is identically zero [see the discussion following Eq. (77)].
[d]Cross sections for downward transitions $(J'<J)$ and for $\overline{\Omega}=\frac{3}{2}\rightarrow\overline{\Omega}=\frac{1}{2}$ transitions can be obtained from the tabulated entries via microreversibility [Eq. (71)].

Born approximation, the $T$ matrix element of Eq. (22) is given by[39,54,55]

$$T^{\mathcal{I}}_{JL\overline{\Omega}\epsilon,J'L'\overline{\Omega}'\epsilon'} = 4 \mathrm{im}_c \hbar^{-2}(k_{J\overline{\Omega}\epsilon}k_{J'\overline{\Omega}'\epsilon'})^{1/2}$$

$$\times \int_0^\infty \langle J'L'\overline{\Omega}'\epsilon'\mathcal{I}\mathfrak{M}|V|JL\overline{\Omega}\epsilon\mathcal{I}\mathfrak{M}\rangle$$

$$\times j_{L'}(k_{J'\overline{\Omega}'\epsilon'}R)j_L(k_{J\overline{\Omega}\epsilon}R)R^2\,dR\ , \tag{78}$$

where $j_l(x)$ is a spherical Bessel function and the matrix element of the potential is defined by Eq. (18). Since Eqs. (18) and (48) are formally similar, the development leading from Eqs. (48)–(50) can be followed to evaluate the inelastic cross section from Eq. (23). In the case of transitions within either of the two spin-orbit manifolds $(\overline{\Omega}'=\overline{\Omega})$, we find

$$\sigma^B_{J\overline{\Omega}\epsilon \rightarrow J'\overline{\Omega}\epsilon'} = \frac{\pi}{(2J+1)k^2_{J\overline{\Omega}\epsilon}}\sum_l(2J'+1)$$

$$\times \begin{pmatrix} J' & l & J \\ -\overline{\Omega} & 0 & \overline{\Omega} \end{pmatrix}^2 \frac{1}{2}[1-\epsilon\epsilon'(-1)^{J+J'+l}]$$

$$\times \sum_{LL'}\frac{1}{2l+1}\begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2 |I_l(J'L'\epsilon',JL\epsilon;\overline{\Omega})|^2\ , \tag{79}$$

where

$$I_l(J'L'\epsilon',JL\epsilon;\overline{\Omega}) = 4\mathrm{im}_c\hbar^{-2}(k_{J\overline{\Omega}\epsilon}k_{J'\overline{\Omega}\epsilon'})^{1/2}$$

$$\times \int_0^\infty A^{1,1}_{l0}(R)j_{L'}(k_{J'\overline{\Omega}\epsilon'}R)j_L(k_{J\overline{\Omega}\epsilon}R)R^2\,dR\ . \tag{80}$$

When we compare Eqs. (79) and (50), we see that the common factor of

$$\frac{1}{2}[1-\epsilon\epsilon'(-1)^{J+J'+l}]\begin{pmatrix} J' & l & J \\ -\overline{\Omega} & 0 & \overline{\Omega} \end{pmatrix}^2$$

will imply, by virtue of the argument following Eq. (65), the same propensity rule at large $J$ as in the energy sudden limit; namely, that the Born cross sections will

tend to zero if the initial and final parity indices are different. The establishment of this propensity rule is independent of the specific form of the $I_l$ integral [Eq. (80)]. Thus, it will apply equally well when the collision dynamics are treated within the distorted–wave Born approximation, since the only difference between the latter and pure Born approximation lies in the definition of the $I_l$ integrals.[39]

Similarly, for collisions between the two spin-orbit manifolds the Born cross section is given by the expression

$$\sigma^B_{J\overline{\Omega}\epsilon \rightarrow J',\overline{\Omega}'=\overline{\Omega}\pm1,\epsilon'} = \frac{\pi}{(2J+1)k^2_{J\overline{\Omega}\epsilon}}\sum_{l\geq2}(2J'+1)$$

$$\times \begin{pmatrix} J' & l & J \\ -\overline{\Omega}' & 2 & -\overline{\Omega} \end{pmatrix}^2 \frac{1}{2}[1-\epsilon\epsilon'(-1)^{J+J'+l}]\sum_{LL'}\frac{1}{(2l+1)}$$

$$\times \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2 |J_l(J'L'\overline{\Omega}'\epsilon',JL\overline{\Omega}\epsilon)|^2\ , \tag{81}$$

where

$$J_l(J'L'\overline{\Omega}'\epsilon',JL\overline{\Omega}\epsilon) = 4\mathrm{im}_c\hbar^{-2}(k_{J\overline{\Omega}\epsilon}k_{J'\overline{\Omega}'\epsilon'})^{1/2}$$

$$\times \int_0^\infty A^{1,-1}_{l,-2}(R)j_{L'}(k_{J'\overline{\Omega}'\epsilon'}R)j_L(k_{J\overline{\Omega}\epsilon}R)R^2\,dR\ . \tag{82}$$

Again, the discussion surrounding Eq. (76) can be applied directly here to demonstrate that the cross sections associated with the $J\rightarrow J$, $\epsilon\rightarrow-\epsilon$ transitions will vanish in the large $J$ limit, exactly as predicted in Sec. VI within a sudden formulation of the collision dynamics.

## VIII. SUDDEN LIMIT FOR HUND'S CASE (b) COUPLING

If the spin-orbit splitting is very small compared to the rotational spacing, or, in most cases, when the angular momentum becomes very large, it becomes

more accurate to use a Hund's case (b) representation of the states of the diatomic.[35] In terms of the $|JM\Omega v\Lambda S\Sigma\rangle$ case (a), states [Eq. (1)] the case (b) states are defined, following Hougen,[30] as

$$|JM\alpha\Lambda\Sigma\rangle = (2J+1)^{-1/2}[(J+\tfrac{1}{2}-\alpha)^{1/2}|JM, \Omega = \Lambda + \Sigma, \Lambda\Sigma\rangle$$
$$-\alpha(J+\tfrac{1}{2}+\alpha)^{1/2}|JM, \Omega = \Lambda - \Sigma, \Lambda, -\Sigma\rangle] ,$$
(83)

where $\alpha = \pm 1$ and is an index related to the coupling of S with J; so,

$$N = J + \alpha/2 ,$$
(84)

where **N** is the vector addition of the nuclear rotational and electronic orbital angular momenta. Definite parity combinations can be taken defined by

$$|JM\alpha\epsilon\rangle = 2^{-1/2}[|JM\alpha\Lambda\Sigma\rangle + \epsilon|JM\alpha, -\Lambda, -\Sigma\rangle] .$$
(85)

For notational simplicity we have suppressed the $v$ and S indices in Eqs. (83) and (85). In conventional spectroscopic notation,[32,35] the states with $\alpha = +1$ are labeled $F_2$ states and those with $\alpha = -1$ are labeled $F_1$ states. A subscript e or f is added depending on whether the

parity index $\epsilon$ is $-1$ or $+1$, respectively. The parity designation is consistent with that used in the case (a) limit.[32]

From Eqs. (83) and (85), we see that the definite parity states in the case (b) limit can be written in terms of the definite parity case (a) states [Eq. (2)] as

$$|JM\alpha\epsilon\rangle = (2J+1)^{-1/2}[(J+\tfrac{1}{2}-\alpha)^{1/2}|JM, \overline{\Omega} = \tfrac{3}{2}, \epsilon\rangle$$
$$-\alpha(J+\tfrac{1}{2}+\alpha)^{1/2}|JM, \overline{\Omega} = \tfrac{1}{2}, \epsilon\rangle] .$$
(86)

Subsequently, the complete atom–molecule wave functions in the total $\mathscr{J}$ representation can be written, in a manner similar to Eq. (9), as

$$|JL\alpha\epsilon\mathscr{JM}\rangle = (2J+1)^{-1/2}[(J+\tfrac{1}{2}-\alpha)^{1/2}|JL, \overline{\Omega} = \tfrac{3}{2}, \epsilon\mathscr{JM}\rangle$$
$$-\alpha(J+\tfrac{1}{2}+\alpha)^{1/2}|JL, \overline{\Omega} = \tfrac{1}{2}, \epsilon\mathscr{JM}\rangle] ,$$
(87)

where we have suppressed the $v$ and $\beta$ indices.

From Eqs. (48) and (87), we see that the S matrix element between Hund's case (b) states becomes, in the IOS approximation

$$\langle J'L'\alpha'\epsilon'\mathscr{JM}|S^{\mathscr{J}}|JL\alpha\epsilon\mathscr{JM}\rangle = (-1)^{J+J'+\mathscr{J}}[(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2}$$

$$\times \sum_l \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & L & \mathscr{J} \\ L' & J' & l \end{Bmatrix} [f_l^{\mathscr{J}}(J'\alpha'\epsilon', J\alpha\epsilon) + c_l^{\mathscr{J}}(J'\alpha'\epsilon', J\alpha\epsilon)] ,$$
(88)

where

$$f_l^{\mathscr{J}} = [(2J+1)(2J'+1)]^{-1/2}(i/2)[1 - \epsilon\epsilon'(-1)^{J+J'+l}]$$

$$\times S_l^{\mathscr{J}}\left[(J+\tfrac{1}{2}-\alpha)^{1/2}(J'+\tfrac{1}{2}-\alpha')^{1/2}\begin{pmatrix} J' & l & J \\ -\tfrac{3}{2} & 0 & \tfrac{3}{2} \end{pmatrix} - \alpha\alpha'(J+\tfrac{1}{2}+\alpha)^{1/2}(J'+\tfrac{1}{2}+\alpha')^{1/2}\begin{pmatrix} J' & l & J \\ -\tfrac{1}{2} & 0 & \tfrac{1}{2} \end{pmatrix}\right]$$
(89)

and

$$c_l^{\mathscr{J}} = [(2J+1)(2J'+1)]^{-1/2}(i/2)\epsilon(1 - \delta_{l0})(1 - \delta_{l1})[1 - \epsilon\epsilon'(-1)^{J+J'+l}]$$

$$\times S_{l,-2}^{\mathscr{J}}\left[-\alpha(J+\tfrac{1}{2}+\alpha)^{1/2}(J'+\tfrac{1}{2}-\alpha')^{1/2}\begin{pmatrix} J' & l & J \\ -\tfrac{3}{2} & 2 & -\tfrac{1}{2} \end{pmatrix} + \alpha'(J+\tfrac{1}{2}-\alpha)^{1/2}(J'+\tfrac{1}{2}+\alpha')^{1/2}\begin{pmatrix} J' & l & J \\ -\tfrac{1}{2} & 2 & -\tfrac{3}{2} \end{pmatrix}\right] .$$
(90)

With algebra similar to that used in going from Eqs. (48)–(50), one can show that in the Hund's case (b) limit the degeneracy averaged integral cross section for the transition from state $|J\alpha\epsilon\rangle$ to state $|J'\alpha'\epsilon'\rangle$ is given by

$$\sigma_{J\alpha\epsilon \to J'\alpha'\epsilon'} = \sum_l (2J'+1)\sigma_l ,$$
(91)

where

$$\sigma_l = \frac{\pi}{\overline{k}^2}\sum_{LL'}\frac{1}{2l+1}\begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2$$
$$|f_l^{\mathscr{J}}(J'\alpha'\epsilon', J\alpha\epsilon) + c_l^{\mathscr{J}}(J'\alpha'\epsilon', J\alpha\epsilon)|^2 .$$
(92)

It is obvious that the resemblance is only superficial between Eqs. (91) and (92) on the one hand, and Eqs. (49) and (50) on the other. In the Hund's case (b) limit, the $\sigma_l$ factors [Eq. (92)] are no longer independent of the initial and final quantum states, so that the factorization is incomplete. Additionally, we see from Eqs. (88)–(90) and (92), that there will be an interference be-

tween the $S_l^{\mathscr{J}}$ and $S_{l,-2}^{\mathscr{J}}$ terms in the expansion of the IOS S functions [Eqs. (42)–(47)], which does not occur in the case (a) limit discussed previously. This indicates that in the case (b) limit the symmetry with respect to the parity index $\epsilon$ contained in Eqs. (69) and (70) is no longer present.

Nevertheless, although a complete factorization is not possible in the case (b) limit, we can extract propensity rules, valid at large J, analogous to those discussed in Secs. V and VI above. To do so, we apply the large-J limit presented in Eqs. (63) and (65) to both 3j symbols in Eq. (89), and use the discussion immediately following Eq. (65) to show that

$$\lim_{J,J'\to\infty} f_l^{\mathscr{J}}(J'\alpha'\epsilon', J\alpha\epsilon) = 0 , \text{ if } \alpha \neq \alpha' \text{ or if } \epsilon \neq \epsilon' .$$
(93)

A similar large-J limit can be derived for the $c_l^{\mathscr{J}}$ coefficients. In addition to using Eq. (76) and the discussion immediately following Eq. (65), we will use the standard recursion relation[56]

$$[(J - \tfrac{1}{2})(J + \tfrac{3}{2})]^{1/2} \begin{pmatrix} J' & l & J \\ -\tfrac{1}{2} & 2 & -\tfrac{3}{2} \end{pmatrix} + [(J' - \tfrac{1}{2})(J' + \tfrac{3}{2})]^{1/2}$$

$$\times \begin{pmatrix} J' & l & J \\ -\tfrac{3}{2} & 2 & -\tfrac{1}{2} \end{pmatrix} + [(l+2)(l-1)] \begin{pmatrix} J' & l & J \\ -\tfrac{1}{2} & 1 & -\tfrac{1}{2} \end{pmatrix} = 0 \tag{94}$$

to show that for $J, J' \gg l$

$$\begin{pmatrix} J' & l & J \\ -\tfrac{1}{2} & 2 & -\tfrac{3}{2} \end{pmatrix} \simeq - \begin{pmatrix} J' & l & J \\ -\tfrac{3}{2} & 2 & -\tfrac{1}{2} \end{pmatrix} . \tag{95}$$

We find then

$$\lim_{J, J' \to \infty} c_l^{\bar{l}}(J'\alpha'\epsilon', J\alpha\epsilon) = 0, \quad \text{if } \alpha \neq \alpha' \text{ or if } J = J', \epsilon \neq \epsilon' . \tag{96}$$

The restriction that $J$ must equal $J'$ in Eq. (96) is justified by the discussion immediately following Eq. (76).

Equations (93) and (96) contain the propensity rules for the case (b) limit. Let us look first at the selection rule on the initial and final values of the $\alpha$ index. A brief physical interpretation can be made, similar to the interpretation of the case (a) limit, at the end of Sec. II and to the discussion contained in our paper on collisions of $^2\Sigma^+$ molecules.[15] In the case (b) limit, N and S are coupled to form J and both precess around J. Since $J < N$ for the $\alpha = -1$ ($F_1$) states [Eq. (84)], it follows that N and S form an acute angle for the $\alpha = -1$ states (N·S $< 0$), and vice versa for the $\alpha = +1$ ($F_2$) states. Because the interaction potential does not contain any spin dependent terms, the collision cannot affect either the magnitude or orientation of S. However, the collision can result in a change in the magnitude and/or orientation of N, so that after the collision partner has receded, the subsequent recoupling with S to form J can result in changes in both |J| and $\alpha$. Physically, the selection rule on $\alpha$ contained in Eqs. (93) and (96) implies that at large $J$ ($N$) the collisions become completely ineffective in decoupling S from N. This propensity rule is physically equivalent to the propensity rule deduced earlier for collisions of $^2\Sigma^+$ molecules.[15] Similarly, it is well known that for an electric dipole $^2\Pi - ^2\Pi$ transition in the Hund's case (b) limit the satellite branches with $\Delta N \neq \Delta J$ ($F_1 \rightleftarrows F_2$) are forbidden.[35]

The selection rule for changes in the parity index, which was rigorous in the case (a) limit, is no longer so in the case (b) limit, except for the special case of collisions elastic in $J$. Nonetheless, since the $f_l^{\bar{l}}$ factor does vanish in the large-$J$ limit for $\epsilon \neq \epsilon'$, it is likely that, in general, at large $J$ the cross sections for transitions in which the parity index changes will be smaller than cross sections for transitions in which the parity index is conserved. Similarly, it can also be shown in the discussion in Sec. VII, that application of the Born approximation to collisions involving a $^2\Pi$ molecule in the case (b) limit results in propensity rules identical to those derived earlier in this section within the sudden approximation. Although we will not present any details, for reasons of brevity, the argument involves use of Eq. (78), but with case (b) matrix elements of the potential. These are formally similar to the matrix elements of the S function [Eq. (88)].

## IX. CONCLUSION

This article has presented the exact and several approximate treatments of the dynamics of rotationally inelastic collisions of diatomic molecules in $^2\Pi$ states with structureless targets. We have shown how the various formalisms developed previously for collisions of $^1\Sigma^+$ diatomics can be easily extended to encompass the additional doublings of the rotational manifold which arise from the presence of the nonzero spin and electronic orbital angular momenta. In particular, the scaling relations which appear naturally when any sudden approximation is involved, and which were derived in the Hund's case (a) limit within the infinite order sudden approximation in Secs. V and VI, take on additional richness in the case of $^2\Pi$ collisions because they predict some degree of connection between cross sections for parity conserving and parity violating collisions and between cross sections for transitions within either of the two spin-orbit manifolds. However, there is no relation between these cross sections and those for transitions between the two spin-orbit manifolds, which are induced by a different component in the interaction potential. Again, still within the case (a) limit, we have demonstrated that under conditions in which either the Born or sudden approximations is appropriate, and for transitions within either of the two spin-orbit manifolds, those transitions which conserve the parity index of the molecular wave function will be strongly favored as the value of the rotational angular momentum $J$ increases. We have also shown that this propensity rule will become more quickly apparent in the $\bar{\Omega} = \tfrac{1}{2}$ manifold. For transitions between the two spin-orbit manifolds, the large-$J$ propensity towards conservation of the parity index will apply only to transitions which are elastic in $J$.

In the Hund's case (b) limit, it does not seem that useful scaling relations can be developed, since the factorization of the S matrix elements is not as complete as in the Hund's case (a) limit. Nevertheless, we were able to show that at large $J$ there will exist, at least in the sudden and Born limits, a strong propensity for conservation of the alignment of N with S. By contrast to the case (a) limit, the propensity toward conservation of the parity index will become less marked in the case (b) limit, except for transitions which are elastic in $J$.

Propensity rules for a molecule with intermediate coupling could be explored using the techniques outlined in Sec. VII, except that the mixing coefficients of the $\Omega = \Lambda + \Sigma$ and $\Omega = \Lambda - \Sigma$ states in Eq. (78) would not be equal in magnitude in the large-$J$ limit. The only rigorous propensity rule which would survive is the conservation of the parity index for transitions which are elastic in $J$. In most systems, one would expect to observe propensities in the inelastic cross sections which would correspond to the most appropriate Hund's limit, either case (a) or case (b).

One direction in which the present study could be extended is toward the exploration of factorization relations and propensity rules for collisions of $\Pi$ state molecules with different multiplicities. We expect for the case of $^1\Pi$ molecules that there will be an interference

between the $S_l^{\bar{I}}$ and $S_{l,-2}^{\bar{I}}$ terms in the expansion of the IOS $S$ function, since a similar interference occurs in the matrix elements of the potential.[57] This may imply that a complete factorization will not be possible, as in the case (b) limit discussed in Sec. VIII where mixing of the $S_l^{\bar{I}}$ and $S_{l,-2}^{\bar{I}}$ terms took place.

Another direction for further study is the implementation of actual calculations of cross sections for a model system. The interaction potential could be taken either from *ab initio* calculations,[58] or, alternatively, adapted from a known interaction potential for a chemically similar $^1\Sigma^+$+atom system. Even in the latter case the scattering calculations could provide meaningful insights into the relative strength of parity conserving versus parity violating transitions and on the range of validity of the sudden scaling relations, or of the IOS or Born approximations themselves. In the case (a) limit, we would expect the energy sudden limit to apply to transitions within either of the two spin-orbit manifolds, but not necessarily between the two. For these transitions, the inelastic energy gaps could be substantial, if the spin-orbit coupling is large, except, perhaps, for particular combinations of the initial and final vibrational quantum numbers selected to minimize the energy mismatch. Over the past few years, DePristo and co-workers[59] have developed a highly successful energy correction to the sudden scaling relations for systems in which the criteria for application of the sudden approximation are not met. Recently, Richard and De-Pristo[60] have applied the energy corrected sudden (ECS) scaling theory to collisions of an atom with a symmetric top. Since this system is formally similar to the one studied here, we expect that the ECS scaling theory could be applied to the present case of collisions involving $^2\Pi$ molecules for transitions between the two spin-orbit manifolds, in the case (a) limit, or for transitions within a particular spin-orbit manifold but at large $J$, where the energy gaps represent a significant fraction of the total energy.

We believe that the scaling relations and propensity rules derived in this article will be useful in the interpretation of experimental studies of rotationally inelastic collisions involving $^2\Pi$ molecules. Experimental determination of state-to-state cross sections could provide a stringent test of the validity of these sudden limit predictions. As mentioned above, Gottscho[16] has observed that several recent experimental studies of the pressure dependence of fluorescence from $^2\Pi$ molecules give evidence for the propensity toward parity conservation discussed in Sec. V. Theoretical studies, such as the one presented here, will provide the proper framework for the interpretation and understanding of this kind of experimental data.

*Note added in proof*: Since the time this article was submitted and revised, it has come to our attention that equations similar to some of those in Secs. IV–VI have been derived by V. N. Ostrovsky and V. I. Ustinov [J. Phys. B **14**, 1139 (1981)] in an application of the sudden approximation to collisions of *electrons* with diatomic molecules, although no investigation was made of the propensity toward conservation of the parity index, discussed here.

Also, in a subsequent manuscript [M. H. Alexander, "Propensity rules in rotationally inelastic collisions of symmetric top molecules or linear polyatomic molecules with structureless atoms," J. Chem. Phys. (in press)] we demonstrated how to obtain an estimate of the minimum value of $J$ for which this propensity will become apparent. This is done by comparison of the $3j$ symbol squared in Eq. (50) calculated for the minimum values of $l$ which will contribute in the case of $\epsilon \rightarrow \epsilon$ transitions ($l = |J' - J|$) and $\epsilon \rightarrow -\epsilon$ transitions ($l = |J' - J| + 1$). As an example, for $J \rightarrow J + 1$ transitions within the $\bar{\Omega} = \frac{1}{2}$ manifold we find that $\epsilon$ conservation will be apparent when $J \gtrsim \frac{3}{2}$, and for $\bar{\Omega} = \frac{3}{2}$, when $J \gtrsim \frac{7}{2}$.

## ACKNOWLEDGMENTS

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