

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

Millard H. Alexander

Citation: *The Journal of Chemical Physics* **76**, 3637 (1982); doi: 10.1063/1.443401

View online: <http://dx.doi.org/10.1063/1.443401>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/76/7?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

Rotationally inelastic collisions between a molecule in a 2 electronic state and a 2 S atom: Sudden factorization, scaling, and symmetry relations

*J. Chem. Phys.* **85**, 1859 (1986); 10.1063/1.451188

Rotationally inelastic collisions between a diatomic molecule in a 2S+1 electronic state and a 2 S atom: The optimal choice for the totalJ representation

*J. Chem. Phys.* **83**, 5060 (1985); 10.1063/1.449719

Propensity rules in rotationally inelastic collisions of diatomic molecules in 3 electronic states

*J. Chem. Phys.* **79**, 302 (1983); 10.1063/1.445578

Erratum: Rotationally inelastic collisions between a diatomic molecule in a 2+ electronic state and a structureless target [*J. Chem. Phys.* 76, 3637 (1982)]; Rotationally inelastic collisions between a diatomic molecule in a 2 electronic state and a structureless target [*J. Chem. Phys.* 76, 5974 (1982)]

*J. Chem. Phys.* **78**, 1625 (1983); 10.1063/1.445496

Rotationally inelastic collisions between a diatomic molecule in a 2 electronic state and a structureless target

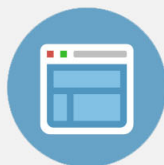
*J. Chem. Phys.* **76**, 5974 (1982); 10.1063/1.442951

---



## Re-register for Table of Content Alerts

Create a profile.



Sign up today!



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

Millard H. Alexander

Department of Chemistry, University of Maryland, College Park, Maryland 20742

(Received 30 November 1981; accepted 24 December 1981)

We present the full close-coupling formulation of the collision between a diatomic molecule in a  $^2\Sigma^+$  state and a structureless target. Due to the possibility of transitions which are inelastic in the parity index of the doublet 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 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. These allow the entire matrix of cross sections, both parity conserving and parity violating, to be expressed in terms of the cross sections for parity conserving transitions out the lowest ( $J = 1/2$ ) level. Within the sudden limit it is also possible to 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  $^2\Sigma^+$  molecules. If the doublet states are unresolved, the sudden scaling relations become identical to those derived previously for collisions of  $^1\Sigma^+$  molecules.

## I. INTRODUCTION

Over the past twenty years there has been an enormous interest in rotationally inelastic collisions,<sup>1-3</sup> stimulated by the development not only of efficient computer codes to solve the quantum mechanical scattering equations,<sup>1,4,5</sup> but also of accurate quantum approximation techniques,<sup>2,3,6-14</sup> which have greatly extended the range of systems for which cross sections may be determined theoretically. Concurrently, technical developments have facilitated the experimental study of rotationally inelastic collisions with quantum state resolution.<sup>15-22</sup> Most of the previous work, both experimental and theoretical, has involved the collisions of molecules in  $^1\Sigma^+$  electronic states, where the orbital motion of the molecule with respect to its collision partner can couple with only the rotational motion of the molecule itself. As our understanding of rotationally inelastic processes increases we are led to consider the more complicated case of collisions involving diatomic molecules with nonvanishing electronic spin and orbital angular momentum. Recently, several groups<sup>23-28</sup> have investigated rotational energy transfer in collisions of molecules in  $\Pi$ -states, of considerable astrophysical importance.

We look here at collisions between diatomic molecules in  $^2\Sigma^+$  electronic states and structureless targets. Conceptually, the problem is only slightly more complicated than collisions of  $^1\Sigma^+$  molecules, but allows a new type of inelastic phenomenon, namely collisions which are elastic in  $N$ , the rotational angular momentum of the nuclei, but *inelastic* in the parity of the molecular wave function. These correspond to a recoupling of  $N$  with  $S$ , the spin angular momentum. Experimental studies,<sup>29,30</sup> first by Lengel and Crosley,<sup>29</sup> of rotational relaxation in the  $A^2\Sigma^+$  state of OH,<sup>30</sup> and the experiments underway in Dagdikian's laboratory<sup>31</sup> on the scattering of state selected beams of CaCl in the  $X^2\Sigma^+$  state provided the motivation for the research reported in the present article. This paper is purely formal and is meant to

provide the theoretical framework for future computational studies of particular  $^2\Sigma^+$  systems, using *ab initio* or model interaction potentials.

In the next section we review the description of the wave functions for a  $^2\Sigma^+$  diatomic and develop the fully quantum, close-coupling description of the rotationally inelastic collision dynamics, assuming that there are no spin dependent terms in the interaction potential. In Sec. III we show how the well-known coupled states (CS) approximation,<sup>2,3,7-9</sup> which has proven to be of high accuracy for inelastic collisions between atoms and  $^1\Sigma^+$  diatomics, can be easily adapted to  $^2\Sigma^+$  atom collisions. This particular extension of the CS method to collisions involving particles other than diatomic molecules in  $^1\Sigma^+$  electronic states can be compared to several earlier studies: the work of Secrest, Green, Lester, and their co-workers<sup>32</sup> on collisions between atoms and polyatomic tops, and the work of Fitz and Kouri<sup>33</sup> on collisions of  $^1\Sigma^+$  molecules with atoms in  $^2P$  states.

Imposition of an energy sudden limit within the CS approximation leads to the infinite order sudden (IOS) approximation,<sup>8,12-14</sup> first developed for collisions of  $^1\Sigma^+$  molecules by Pack.<sup>8</sup> The application of the IOS approximation to collisions of  $^2\Sigma^+$  diatomics is discussed in Sec. IV. The factorization properties and scaling relations which characterize the energy sudden limit, and which have been extensively exploited for atom  $^1\Sigma^+$  collisions,<sup>2,3,14,34-39</sup> are examined in Sec. V for the case of atom  $^2\Sigma^+$  collisions. In particular, these relations predict some degree of interrelation between transitions in which the parity index of the molecular wave function is conserved and those in which the parity index is changed. We explore in Sec. VI the simplifications which occur, still in the sudden limit, if the doublet states associated with each value of  $N$ , the nuclear rotational angular momentum, are unresolved. In this case the simpler  $^1\Sigma^+$  factorization relations are recovered. A brief discussion follows.

## II. CLOSE COUPLING FORMULATION OF COLLISION DYNAMICS

The wave functions for a diatomic molecule in a  $^2\Sigma^+$  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<sup>40,41</sup>

$$|JM\Omega^2\Sigma^+vS\Sigma\rangle = |JM\Omega\rangle |^2\Sigma^+vS\Sigma\rangle. \quad (1)$$

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; and  $S$  denotes the spin angular momentum with projection  $\Sigma$  along the molecular axis. For a  $^2\Sigma^+$  molecule  $S = \frac{1}{2}$  and there is no electronic orbital angular momentum, so that  $\Omega = \Sigma = \pm \frac{1}{2}$ . It will be convenient to use the definite parity states, defined by<sup>41</sup>

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

where  $\epsilon = \pm 1$  and is related to the parity of the wave function with respect to inversion of the space fixed axis system, so that<sup>41</sup>

$$i_{SF} |JM\epsilon^2\Sigma^+vS\Sigma\rangle = \epsilon(-1)^{J+S} |JM\Omega\epsilon^2\Sigma^+vS\Sigma\rangle. \quad (3)$$

In conventional spectroscopic notation<sup>42</sup> the  $\epsilon = +1$  states are designated as  $f$  or  $F_2$  levels; the  $\epsilon = -1$  states, as  $e$  or  $F_1$  levels. The rotational wave functions  $|JM\Omega\rangle$  which appear in Eq. (1) can be written as rotation matrix elements, namely,

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

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.<sup>43</sup>

The rotational energies of the parity doublets are given by the expression<sup>41</sup>

$$E_{J\epsilon} = B_v(J + \epsilon/2)(J + \epsilon/2 + 1) - (\epsilon/2)\gamma(J + \epsilon + 1/2), \quad (5)$$

where  $B_v$  is the rotational constant and  $\gamma$  is the spin-rotation constant. Typically  $\gamma$  is much smaller than  $B_v$ . The rotational angular momentum of the nuclei  $N$  is given by

$$N = J + \epsilon/2, \quad (6)$$

so that the expression for the rotational energies, Eq. (5), can be written in the more familiar form<sup>44</sup>

$$E_N = N(N+1)B_v - (\epsilon/2)\gamma[N + (\epsilon+1)/2], \quad (7)$$

the  $\epsilon = -1$  level being higher in energy (for positive  $\gamma$ ). Note that for  $N=0$  only the  $\epsilon = -1$  level occurs. Figure 1 displays a representative pattern of rotational energy levels. The presence of the electronic spin in a  $^2\Sigma^+$  state acts to split the rotational levels into doublets, with a spacing which increases linearly with  $N$ , namely<sup>44</sup>

$$E_{N,\epsilon=-1} - E_{N,\epsilon=+1} = (N+1/2)\gamma. \quad (8)$$

In the Hund's case (b) limit, conventionally used for molecules in  $^2\Sigma$  states,<sup>44</sup> the states are labeled by  $J$ ,

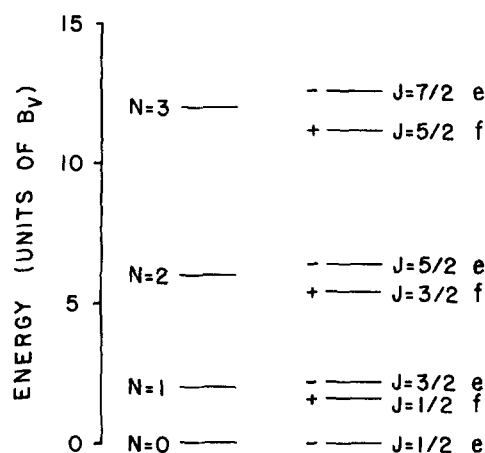


FIG. 1. Schematic description of the rotational energy levels of a diatomic molecule in a  $^2\Sigma^+$  electronic state. In the absence of the spin-rotation interaction, the rotational levels are indexed only in  $N$  the rotational angular momentum of the nuclei. The resulting spectrum, shown on the left-hand side, is equivalent to the spectrum of a  $^1\Sigma^+$  molecule. The level diagram on the right displays the doublet structure which occurs when the spin-rotation interaction is included [Eq. (5)]. For purposes of illustration the spin-rotation constant  $\gamma$  was taken to be  $0.4B_v$ . For most molecules the relative value of  $\gamma$  will be much smaller.

$M$ ,  $N$ ,  $v$ , and  $S$ , and are defined by Eq. (2), with the relation between  $N$ ,  $J$ , and  $\epsilon$  given by Eq. (6).<sup>41</sup>

Consider the interaction between a  $^2\Sigma^+$  diatomic and a spherical atom in a singlet state. We shall include only electrostatic terms in the total Hamiltonian. Since there is no orbital electronic angular momentum in a  $^2\Sigma^+$  electronic state, the wave function of the diatomic is cylindrically symmetric about the molecular axis. Thus when the interaction Hamiltonian is integrated over the electronic coordinates, within the Born-Oppenheimer approximation, the resulting potential for the motion of the nuclei is a function only of the diatomic bond length  $r$ ; the distance  $R$  between the atom and the center-of-mass of the diatomic; and the angle between  $r$  and  $R$ . This can be expanded in the usual series<sup>1,3,45</sup>

$$V(r, R, \mathbf{r} \cdot \mathbf{R}) = \sum_i V_i(r, R) P_i(\cos \tilde{\theta}), \quad (9)$$

where tildes will indicate the molecule frame coordinate system. If the molecule is treated as a rigid rotor the dependence on  $r$  can be neglected. For simplicity this will be done here; the vibrational degree of freedom can be added back to the following equations in a straightforward manner.

Following the initial work of Arthurs and Dalgarno for collisions of atoms with  $^1\Sigma^+$  diatomics,<sup>45</sup> we expand the wave function for the rotational motion of the nuclei in terms of eigenfunctions of the total angular momentum  $\mathcal{J}$ , namely

$$U_{JL}^{JM}(\mathbf{R}) |JL\epsilon\mathcal{J}\mathcal{M}\rangle, \quad (10)$$

where

$$|JL\epsilon\mathfrak{M}\rangle = \sum_{MM_L} 2^{-1/2} \langle JMLM_L | JL\epsilon\mathfrak{M}\rangle \times |LM_L\rangle [ |JM\Omega\rangle + \epsilon |JM, -\Omega\rangle ]. \quad (11)$$

Here  $(\dots | \dots)$  is a Clebsch-Gordan coefficient<sup>43,46</sup>;  $|JM\Omega\rangle$  is defined by Eq. (4), and  $|LM_L\rangle$ , the wave function for the orbital motion of the atom, is a spherical harmonic in a space fixed axis system.

The functions  $U_{JL\epsilon}^{\mathfrak{M}}(R)$  are solutions to a set of coupled differential equations—the close-coupled (CC) equations—defined by

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2 L(L+1)}{2\mu R^2} + \langle JL\epsilon\mathfrak{M} | V | JL\epsilon\mathfrak{M}\rangle - \delta_{J\epsilon} \right] U_{JL\epsilon}^{\mathfrak{M}}(R) = - \sum_{J' L' \epsilon'}' \langle J' L' \epsilon' \mathfrak{M} | V | JL\epsilon\mathfrak{M}\rangle U_{J' L' \epsilon'}^{\mathfrak{M}}(R), \quad (12)$$

where the prime on the summation indicates that the diagonal term is excluded, where  $\mu$  is the collision re-

duced mass, and where

$$\delta_{J\epsilon} = E_{\text{tot}} - E_{J\epsilon}. \quad (13)$$

The potential matrix elements in Eq. (12) are obtained by integration over the angles describing the orientation of the atom and the diatomic molecule. Since the  $|JM\Omega\rangle$  [Eq. (4)] and  $|LM_L\rangle$  functions are defined in a space fixed axis system, this integration can be most easily done by expanding the potential [Eq. (9)] in the space frame as

$$V(\hat{r}, R) = \sum_{lm} [4\pi/(2l+1)] V_l(R) Y_{lm}^*(\hat{r}) Y_{lm}(\hat{r}), \quad (14)$$

where as discussed above, we have suppressed the dependence on  $r$  the bond length of the diatomic. Using Eqs. (2) and (4) as well as known expressions for integrals involving the product of three rotation matrix elements and/or spherical harmonics,<sup>43,46</sup> we find, after a bit of straightforward algebra, the following expression for the potential matrix elements:

$$\langle J' L' \epsilon' \mathfrak{M} | V | JL\epsilon\mathfrak{M}\rangle = (-1)^{J+J'+\mathfrak{M}} [(2L+1)(2L'+1)(2J+1)(2J'+1)]^{1/2} \times \sum_l V_l(R) \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \begin{Bmatrix} J & L & \mathfrak{J} \\ L' & J' & l \end{Bmatrix} (-i/2) [1 - \epsilon\epsilon'(-1)^{J+J'+\mathfrak{M}}], \quad (15)$$

where  $\{\dots\}$  and  $\{\dots\}$  are  $3j$  and  $6j$  symbols, respectively. Here we have explicitly used the fact that  $\Omega = \pm \frac{1}{2}$  for  $^2\Sigma^+$  states. In deriving Eq. (15) one must remember that for  $^2\Sigma^+$  states the angular momentum quantum numbers  $J, M, J', M', \mathfrak{J}, \mathfrak{M}$  will all be half-integer, so that terms of the form  $(-1)^{J+J'}$  will equal negative unity. The last term on the right-hand side of Eq. (15) 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.<sup>26</sup> These selection rules are summarized in Table I.

The CC equations (12) are solved subject to the boundary condition<sup>1,45</sup>

$$\lim_{R \rightarrow \infty} U_{JL\epsilon}^{\mathfrak{M}}(R) = \delta_{J J'} \delta_{L L'} \delta_{\epsilon \epsilon'} \exp[-i(k_{J\epsilon} R - L'\pi/2)] - (k_{J\epsilon}/k_{J\epsilon'})^{1/2} S_{J' L' \epsilon', J L \epsilon} \exp[i(k_{J\epsilon} R - L\pi/2)], \quad (16)$$

where

$$k_{J\epsilon} = (2\mu \delta_{J\epsilon} / \hbar^2)^{1/2}. \quad (17)$$

The scattering amplitude can be then constructed exactly as in the Arthurs-Dalgarno formulation of collisions involving  $^1\Sigma^+$  diatomics<sup>45</sup> as

$$f_{J M \epsilon \rightarrow J' M' \epsilon'} = \sum_{\mathfrak{J} L L'} i^{L-L'} [(2L+1)\pi]^{1/2} (2\mathfrak{J}+1) \times \begin{pmatrix} J & \mathfrak{J} & L \\ M & -M & 0 \end{pmatrix} \begin{pmatrix} J' & \mathfrak{J} & L' \\ M' & -M & M'_L \end{pmatrix} T_{J L \epsilon, J' L' \epsilon'}^{\mathfrak{J}} Y_{L' M'_L}(\hat{R}), \quad (18)$$

where

$$T_{J L \epsilon, J' L' \epsilon'}^{\mathfrak{J}} = \delta_{J J'} \delta_{L L'} \delta_{\epsilon \epsilon'} - S_{J' L' \epsilon', J L \epsilon}^{\mathfrak{J}}. \quad (19)$$

The integral cross section for the  $J\epsilon \rightarrow J'\epsilon'$  transition,

summed over  $M'$  and averaged over  $M$ , is given by the expression

$$\sigma_{J\epsilon \rightarrow J'\epsilon'} = \frac{\pi}{(2J+1)k_{J\epsilon}^2} \sum_{\mathfrak{J}} (2\mathfrak{J}+1) \sum_{L L'} |T_{J L \epsilon, J' L' \epsilon'}^{\mathfrak{J}}|^2. \quad (20)$$

We note that there exists an additional degree of inelasticity here which is not present in collisions of  $^1\Sigma^+$  diatomics, namely the parity index of the initial and final states. Collisions can be inelastic in  $\epsilon$  and elastic in  $J$ , and vice versa, or inelastic in both  $\epsilon$  and  $J$ . 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.<sup>24</sup> In the isolated  $^2\Sigma^+$  molecule  $N$  and  $S$  are coupled to form  $J$ , the total rotational angular momentum. Neither  $N$  nor  $S$  are fixed in direction; both precess around  $J$ . Since  $J < N$  for the  $\epsilon = -1$  parity states [Eq. (6)], it follows that  $N$  and  $S$  form an acute angle for the  $\epsilon = -1$  ( $e$ ) states ( $N \cdot S < 0$ ), and vice versa for the  $\epsilon = +1$  ( $f$ ) states. Since the interaction potential does not contain any spin dependent terms, the collision can not 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 target has receded, the subsequent recoupling with  $S$  to form  $J$  can result in changes both in  $|J|$  and  $\epsilon$ . From a spectroscopic point of view the collisions in which  $N$  changes but  $\epsilon$  remains constant are analogous to the normal  $P$  and  $R$  branches of a  $^2\Sigma^+ \rightarrow ^2\Sigma^+$  transition.<sup>44</sup> On the other hand, collisions in which both  $N$  and  $\epsilon$  change correspond to the satellite branches<sup>44</sup> of a  $^2\Sigma^+ \rightarrow ^2\Sigma^+$  transition.

### 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.<sup>1-3,6</sup> 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.<sup>2,3,7-9,47-50</sup> This is carried out by first replacing the centrifugal terms in the CC equations (12) by an average value  $\hbar^2 \bar{L}(\bar{L}+1)/2\mu R^2$ . 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

$$|J\nu\epsilon\mathfrak{M}\rangle = \sum_L B_{\nu L}^{J\mathfrak{J}} |JL\epsilon\mathfrak{M}\rangle, \quad (21)$$

where, as discussed by DePristo and Alexander,<sup>50</sup>

$$B_{\nu L}^{J\mathfrak{J}} = (-1)^\nu (2L+1)^{1/2} \begin{pmatrix} L & J & \mathfrak{J} \\ 0 & \nu & -\nu \end{pmatrix}. \quad (22)$$

The potential matrix in the new basis then becomes

$$\begin{aligned} \langle J'\nu'\epsilon'\mathfrak{M}' | V | J\nu\epsilon\mathfrak{M} \rangle \\ = \sum_{L,L'} B_{\nu' L'}^{J'\mathfrak{J}'} B_{\nu L}^{J\mathfrak{J}} \langle J'L'\epsilon'\mathfrak{M}' | V | JL\epsilon\mathfrak{M} \rangle. \end{aligned} \quad (23)$$

With Eqs. (15) and (22) and some angular momentum algebra one can show that the result is

$$\begin{aligned} \langle J'\nu'\epsilon'\mathfrak{M}' | V | J\nu\epsilon\mathfrak{M} \rangle &= \delta_{\nu\nu'} (-1)^{\nu+\nu'} [(2J+1)(2J'+1)]^{1/2} \\ &\times \sum_i V_i(R) \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \begin{pmatrix} J' & l & J \\ \nu & 0 & -\nu \end{pmatrix} \\ &\times (-i/2) [1 - \epsilon\epsilon'(-1)^{J+J'+1}]. \end{aligned} \quad (24)$$

Since the potential matrix elements are independent of  $\mathfrak{J}$  (and its projection  $\mathfrak{M}$ ), these indices will be dropped. The only difference between Eq. (24) and the expression for the CS potential matrix elements for collisions of  $^1\Sigma^+$  molecules lies in the presence of the  $\Omega = \pm \frac{1}{2}$  factors in the first  $3j$  symbol. The reader should also note that in contrast to the situation which occurs in collisions involving  $^1\Sigma^+$  molecules, the  $\nu$  index is now half-integer.

Within the CS approximation the CC equations (12) are replaced by

$$\begin{aligned} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2 \bar{L}(\bar{L}+1)}{2\mu R^2} + \langle J\nu\epsilon | V | J\nu\epsilon \rangle - \mathcal{E}_{J\epsilon} \right] U_{J\epsilon}^{\bar{\nu}}(R) \\ = - \sum_{J'\epsilon'}' \langle J'\nu'\epsilon' | V | J\nu\epsilon \rangle U_{J'\epsilon'}^{\bar{\nu}}(R). \end{aligned} \quad (25)$$

These are solved subject to the boundary condition:

$$\begin{aligned} \lim_{R \rightarrow \infty} U_{J\epsilon}^{\bar{\nu}}(R) &= \delta_{J,J'} \delta_{\epsilon,\epsilon'} \exp[-i(k_{J,\epsilon,\epsilon'} R - \bar{L}\pi/2)] \\ &- (k_{J,\epsilon,\epsilon'}/k_{J\epsilon})^{1/2} S_{J,\epsilon,\epsilon'}^{\bar{\nu}} \exp[i(k_{J\epsilon} R - \bar{L}\pi/2)]. \end{aligned} \quad (26)$$

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

Eq. (22). We will introduce an overall phase factor which corresponds to the so called "correct phase" choice, discussed by Khare *et al.*<sup>51</sup> Accordingly, we have

$$\begin{aligned} T_{JL\epsilon, J'L'\epsilon'}^{\mathfrak{J}} &= i^{L+L'-2\bar{L}} \sum_{\nu} [(2L+1)(2L'+1)]^{1/2} \\ &\times \begin{pmatrix} L & J & \mathfrak{J} \\ 0 & \nu & -\nu \end{pmatrix} \begin{pmatrix} L' & J' & \mathfrak{J} \\ 0 & \nu & -\nu \end{pmatrix} T_{J\epsilon, J'\epsilon'}^{\bar{\nu}}. \end{aligned} \quad (27)$$

The expression for the degeneracy averaged integral cross section is given in terms of the CS  $T$ -matrix elements by the expression<sup>52</sup>

$$\sigma_{J\epsilon \rightarrow J'\epsilon'} = \frac{\pi}{(2J+1)\hbar^2 k_{J\epsilon}^2} \sum_L (2L+1) \sum_{\nu} |T_{J\epsilon, J'\epsilon'}^{\bar{\nu}}|^2. \quad (28)$$

#### 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 by replacing the individual channel energies  $\mathcal{E}_{J\epsilon}$  in Eq. (25) by an average value  $\bar{\mathcal{E}}$ . As Secrest and Hunter have shown,<sup>12,13</sup> this permits the complete uncoupling of the equations, so that the scattering problem is reduced to the solution of an infinite set of angle-dependent one-dimensional equations, namely

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2 \bar{L}(\bar{L}+1)}{2\mu R^2} + V(R, \cos \bar{\theta}) - \bar{\mathcal{E}} \right] U^{\bar{L}}(R; \bar{\theta}) = 0, \quad (29)$$

where  $V(R, \cos \bar{\theta})$  is just the interaction potential expressed in a molecule frame coordinate system [Eq. (9)]. These infinite order-sudden (IOS) equations are solved subject to the boundary condition

$$\begin{aligned} \lim_{R \rightarrow \infty} U^{\bar{L}}(R; \bar{\theta}) &= \exp[-i(\bar{k}R - \bar{L}\pi/2)] \\ &- S^{\bar{L}}(\bar{\theta}) \exp[i(\bar{k}R - \bar{L}\pi/2)], \end{aligned} \quad (30)$$

where  $\bar{k}$  is the wave vector corresponding to the average energy  $\bar{\mathcal{E}}$ .

The individual  $T_{JL\epsilon, J'L'\epsilon'}^{\mathfrak{J}}$   $T$ -matrix elements are obtained as matrix elements of the angle dependent IOS  $S^{\bar{L}}(\bar{\theta})$  function, namely

$$\begin{aligned} T_{JL\epsilon, J'L'\epsilon'}^{\mathfrak{J}} &= i^{L+L'-2\bar{L}} [\delta_{J,J'} \delta_{L,L'} \delta_{\epsilon,\epsilon'} \\ &- \langle J'L'\epsilon' | S^{\bar{L}}(\bar{\theta}) | JL\epsilon \rangle], \end{aligned} \quad (31)$$

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.*<sup>51</sup> The formal evaluation of the matrix elements of the  $S^{\bar{L}}(\bar{\theta})$  function can be facilitated by an expansion in Legendre polynomials, as in Eq. (9),

$$S^{\bar{L}}(\bar{\theta}) = \sum_i S_i^{\bar{L}} P_i(\cos \bar{\theta}). \quad (32)$$

Consequently, the development leading to Eq. (15) can be followed exactly, which gives

$$\begin{aligned} \langle J'L'\epsilon'\mathfrak{M}' | S^{\bar{L}}(\bar{\theta}) | JL\epsilon\mathfrak{M} \rangle &= (-1)^{J+J'+1} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \\ &\times \sum_i S_i^{\bar{L}} \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \begin{pmatrix} J & L & \mathfrak{J} \\ L' & J' & l \end{pmatrix} (-i/2) [1 - \epsilon\epsilon'(-1)^{J+J'+1}]. \end{aligned} \quad (33)$$

TABLE I. Selection rules for nonzero coupling.<sup>a</sup>

$l$	Nonzero coupling	
	$\epsilon = \epsilon'$	$\epsilon = -\epsilon'$
Even	$\Delta J = \text{even}^b$	$\Delta J = \text{odd}$
Odd	$\Delta J = \text{odd}$	$\Delta J = \text{even}$

<sup>a</sup>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. (15) and (24)] 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.

<sup>b</sup> $\Delta J = J - J'$ .

The integral inelastic cross sections can be evaluated using Eqs. (20) and (33). If we define the quantity

$$\sigma_l = \frac{\pi}{k^2} \sum_{L, L'} \frac{1}{2l+1} \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2 |S_l|^2, \quad (34)$$

then one can show, with a little angular momentum algebra, that the degeneracy averaged *inelastic* integral cross sections are given by the expression

$$\sigma_{J\epsilon \rightarrow J'\epsilon'} = \sum_l (2J' + 1) \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2 \times \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{J+J'+l}] \sigma_l. \quad (35)$$

In deriving Eq. (35) we have also used the fact that

$$\frac{1}{4} [1 - \epsilon\epsilon'(-1)^{J+J'+l}]^2 = \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{J+J'+l}]. \quad (36)$$

The individual  $\sigma_l$  terms make a nonvanishing contribution to the cross section only for certain combinations of the values of  $\epsilon$ ,  $\epsilon'$ ,  $J$ ,  $J'$ , and  $l$ . These values are governed by the triangular relation contained in the  $3j$  symbol in Eq. (35) and by the selection rules discussed in connection with Eqs. (15) and (24) and listed in Table I. An expression analogous to Eq. (35) for atom-symmetric top collisions has been derived previously by Green.<sup>53</sup>

## V. FACTORIZATION PROPERTIES AND SCALING RELATIONS

Equation (35) is the generalization to collisions of  $^2\Sigma^+$  diatomics of an analogous relationship for collisions of  $^1\Sigma^+$  molecules, namely,

$$\sigma_{J \rightarrow J'} = \sum_l (2J' + 1) \begin{pmatrix} J' & l & J \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma_l. \quad (37)$$

This relationship was first explored within the IOS approximation by Goldflam, Green, and Kouri<sup>14,35</sup> and then later shown<sup>37,38</sup> to apply whenever an energy sudden limit is assumed.

There are several interesting insights, specific to the collision of  $^2\Sigma^+$  molecules, which can be deduced from Eq. (35). First, due to the way in which  $\epsilon$  and  $\epsilon'$  enter into the right-hand side of Eq. (35) it is clear that the

cross sections are independent of either a reversal of or change in sign in the parity indices of the initial and final states. In other words

$$\sigma_{J\epsilon \rightarrow J'\epsilon'} = \sigma_{J, -\epsilon \rightarrow J', -\epsilon'} \quad (38)$$

and

$$\sigma_{J\epsilon \rightarrow J'\epsilon'} = \sigma_{J\epsilon' \rightarrow J'\epsilon}. \quad (39)$$

If, alternatively, we follow a Hund's case (b) notation and label the initial and final states by the values of  $N$ , the rotational angular momentum of the nuclei, then, by means of Eq. (6), it is easy to show that Eq. (38) is equivalent to the relation

$$\sigma_{N, \epsilon \rightarrow N', \epsilon'} = \sigma_{N-1, \epsilon \rightarrow N'-1, \epsilon'} \quad (40)$$

In the particular case when  $N = N'$ , this relation becomes

$$\sigma_{N, \epsilon \rightarrow N, \epsilon'} = \sigma_{N-1, \epsilon \rightarrow N-1, \epsilon'}. \quad (41)$$

This relationship is somewhat unexpected, for it predicts an equality between two transitions only one of which is *elastic* in  $N$ . Figure 1 may be useful to the reader in exploring the relationship between Eqs. (38)–(41). Equation (38) is also equivalent, if we convert to a labeling in  $N$ , to the relation

$$\sigma_{N, \epsilon \rightarrow N', \epsilon'} = \sigma_{N-1, \epsilon \rightarrow N'-1, \epsilon'}. \quad (42)$$

which implies that rotationally inelastic cross sections within the two parity manifolds are equivalent, provided that the rotational ladder is shifted down by one step in the case of the states with the negative parity index ( $\epsilon = -1$ ,  $e$  levels).

A third set of relations can be derived by setting  $J = \frac{1}{2}$  in Eq. (35), which gives

$$\sigma_{(1/2)\epsilon \rightarrow J'\epsilon'} = (2J' + 1) \sum_l \begin{pmatrix} J' & l & \frac{1}{2} \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2 \times \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{J'+l+1/2}] \sigma_l. \quad (43)$$

From the discussion immediately following Eq. (36) we conclude that for  $\epsilon = \epsilon'$  only  $l = J' - \frac{1}{2}$  gives a nonzero contribution, so that

$$\sigma_{(1/2)\epsilon \rightarrow J'\epsilon} = (2J' + 1) \begin{pmatrix} J' & J' - \frac{1}{2} & \frac{1}{2} \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2 \sigma_{l=J'-1/2}. \quad (44)$$

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

$$\sigma_l = [(2l+1)/(l+1)] \sigma_{(1/2)\epsilon \rightarrow J=l+1/2, \epsilon}. \quad (45)$$

Similarly, if  $\epsilon' = -\epsilon$  in Eq. (43) 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,

$$\sigma_l = [(2l+1)/l] \sigma_{(1/2)\epsilon \rightarrow J=l-1/2, -\epsilon}. \quad (46)$$

Either of Eqs. (45) or (46) can be reintroduced back into Eq. (35) to give an expression for all cross sections in terms of cross sections out of the  $J = \frac{1}{2}$  level. If Eq. (45) is chosen we find

$$\sigma_{J\epsilon \rightarrow J'\epsilon'} = (2J' + 1) \sum_l [(2l+1)/(l+1)] \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2 \times \frac{1}{2} [1 - \epsilon\epsilon'(-1)^{J+J'+l}] \sigma_{(1/2)\epsilon \rightarrow l+1/2, \epsilon}, \quad (47)$$

TABLE II. Scaling factors relating inelastic  $J\epsilon \rightarrow J'\epsilon'$  cross sections to the  $J=\frac{1}{2}$ ,  $\epsilon \rightarrow J'$ ,  $\epsilon$  cross sections.<sup>a</sup>

$J'$	$\epsilon'$	$J=1/2$ $\epsilon=-1^b$	$3/2$ $-1^b$	$5/2$ $-1^b$	$7/2$ $-1^b$
1/2	+1	$\frac{1}{2}A$	c	c	c
3/2	-1	A	...	c	c
3/2	+1	$\frac{2}{3}B$	$\frac{1}{10}A + \frac{9}{20}C$	c	c
5/2	-1	B	$\frac{9}{10}A + \frac{3}{10}C$	...	c
5/2	+1	$\frac{3}{4}C$	$\frac{1}{7}B + \frac{18}{35}D$	$\frac{3}{70}A + \frac{2}{15}C + \frac{25}{63}E$	c
7/2	-1	C	$\frac{6}{7}B + \frac{2}{7}D$	$\frac{6}{7}A + \frac{1}{3}C + \frac{10}{63}E$	...
7/2	+1	$\frac{4}{5}D$	$\frac{1}{6}C + \frac{5}{9}E$	$\frac{4}{63}B + \frac{12}{77}D + \frac{100}{231}F$	$\frac{1}{42}A + \frac{3}{44}C + \frac{25}{182}E + \frac{1225}{3432}G$

<sup>a</sup>Shown are all nonzero values of the quantity  $g_l(J, \epsilon, J', \epsilon')$  [Eq. (48)] with the appropriate value of  $l$  indicated by the upper case letters A, B, C, D, E, F which correspond, respectively, to  $l=1, 2, 3, 4, 5$ , and 6.

<sup>b</sup>Cross sections for transitions out of the  $\epsilon=+1$  level can be obtained from the symmetry relation Eq. (38).

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

which can be written more compactly as

$$\sigma_{J\epsilon \rightarrow J'\epsilon'} = \sum_l g_l(J, \epsilon, J', \epsilon') \sigma_{(1/2)\epsilon \rightarrow (1/2)\epsilon'} \quad (48)$$

where the definition of  $g_l(J, \epsilon, J', \epsilon')$  is obvious. Because of Eq. (39), this equation can be equally well written as

$$\sigma_{J\epsilon \rightarrow J'\epsilon'} = \sum_l g_l(J, \epsilon, J', \epsilon') \sigma_{(1/2)\epsilon' \rightarrow (1/2)\epsilon} \quad (49)$$

A new set of relations between cross sections can be obtained by setting Eqs. (45) and (46) equal, which gives

$$l\sigma_{(1/2)\epsilon \rightarrow (1/2)\epsilon'} = (l+1)\sigma_{(1/2)\epsilon \rightarrow (1/2)\epsilon'} \quad (50)$$

If we label with  $N$ , rather than  $J$ , Eq. (50) leads to the following relations:

$$\sigma_{N=0, \epsilon \rightarrow -1 \rightarrow N, \epsilon \rightarrow -1} = [(N+1)/N]\sigma_{N=0, \epsilon \rightarrow -1 \rightarrow N, \epsilon \rightarrow +1} \quad (51)$$

and

$$\sigma_{N=1, \epsilon \rightarrow +1 \rightarrow N, \epsilon \rightarrow +1} = [N/(N-1)]\sigma_{N=1, \epsilon \rightarrow +1 \rightarrow N-2, \epsilon \rightarrow -1} \quad (52)$$

which relate certain cross sections for transitions in which the parity index is changed, to cross sections for transitions in which the parity index is conserved. As is clear from Fig. 1, only the  $\epsilon=-1$  parity level exists for  $N=0$ . Equation (51) demonstrates that for a given value of  $N'$  the two  $N=0 \rightarrow N'$  cross sections (parity conserving and parity violating) can be simply related. Equations (40) and (51) taken together lead to the interesting relation

$$\begin{aligned} \sigma_{N=1, \epsilon \rightarrow +1 \rightarrow N=1, \epsilon \rightarrow -1} &= \sigma_{N=0, \epsilon \rightarrow -1 \rightarrow N=2, \epsilon \rightarrow +1} \\ &= \frac{2}{3}\sigma_{N=0, \epsilon \rightarrow -1 \rightarrow N=2, \epsilon \rightarrow -1} \end{aligned} \quad (53)$$

Equation (47) relates all inelastic cross sections to those out of the  $J=\frac{1}{2}$ ,  $\epsilon$  level. For low-lying values of  $J$  and  $J'$  we list in Table II the numerical values of the  $g_l$  factors [Eq. (48)] which relate  $\sigma_{J\epsilon \rightarrow J'\epsilon'}$  to the  $J=\frac{1}{2}$ ,  $\epsilon \rightarrow J'$  cross sections. There are several worthwhile observations. First, experimental measurement of even a small subset of cross sections can often, at least within the sudden approximation, provide enough information to determine a far larger portion of the entire cross section matrix.

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  $J \rightarrow \infty$ . This can be done by first expressing Eq. (47) as

$$\begin{aligned} \sigma_{J\epsilon \rightarrow J'\epsilon'} &= \sum_l (J^{\frac{1}{2}} l 0 | J l J'^{\frac{1}{2}})^2 [(2l+1)/(l+1)] \\ &\times \frac{1}{2} [1 - \epsilon \epsilon' (-)^{J+J'+l}] \sigma_{(1/2)\epsilon \rightarrow (1/2)\epsilon'} \end{aligned} \quad (54)$$

We then use a large  $J$  limit of the Clebsch-Gordan coefficient<sup>54</sup> to write

$$\begin{aligned} (J^{\frac{1}{2}} l 0 | J l J'^{\frac{1}{2}})^2 &\approx [d_{J', -J, 0}^l(x)]^2 \\ &= [(l-J'+J)! / (l+J'-J)!] [P_l^{J'-J}(x)]^2 \end{aligned} \quad (55)$$

Here  $d_{\mu, \nu}^l(x)$  is a rotation matrix element and  $P_l^m(x)$  is an associated Legendre polynomial with argument<sup>54</sup>  $x=1/(2J')$ .

Since  $x \rightarrow 0$  as  $J \rightarrow \infty$  the large  $J$  limit of Eq. (54) can be written as

$$\lim_{J \rightarrow \infty} \sigma_{J \leftarrow J', \epsilon'} = \sum_l \frac{(2l+1)(l-J'+J)!}{(l+1)(l+J'-J)!} [P_l^{J'-J}(0)]^2 \times \frac{1}{2} [1 - \epsilon \epsilon' (-1)^{J+J'+l}] \sigma_{(1/2)\epsilon \rightarrow l+1/2, \epsilon} \quad (56)$$

Since<sup>55</sup>

$$P_l^m(0) = 2^m \pi^{-1/2} \cos[\frac{1}{2}\pi(l-m)] \times \Gamma[\frac{1}{2}(l+m+1)] / \Gamma[\frac{1}{2}(l-m+2)] \quad (57)$$

it is clear that the associated Legendre polynomial with argument 0 in Eq. (56) will vanish unless the quantity  $(l-J'+J)$  is even. Because  $J'$  is a 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 ( $e \rightarrow e$  or  $f \rightarrow f$ ) will be favored over transitions in which the parity index is changed ( $e \rightarrow f, f \rightarrow e$ ). An entirely equivalent propensity rule will be valid if we index in  $N$  rather than  $J$ . Physically, this propensity rule implies that at large  $J$  (or  $N$ ), the collisions become completely ineffective in decoupling  $S$  from  $N$ . It is satisfying to observe that this is exactly the same propensity rule which was found empirically by Lengel and Crosley<sup>29</sup> in their experimental study of rotational energy transfer in the  $A^2\Sigma^+$  state of OH, and surmised by Broida and Carrington, in early work<sup>56</sup> on energy transfer in the  $A^2\Sigma^+$  state of NO. 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 related to the presence or absence of certain terms in the expansion of the potential [Eq. (9)], which would be the case if the Born approximation were used to derive propensity rules.

It is worthwhile to examine the limit given by Eq. (56) for the case  $J' = J+1$ ,  $\epsilon' = \epsilon$ . Explicit introduction of Eq. (57) into Eq. (56) yields the expression

$$\lim_{J \rightarrow \infty} \sigma_{J \leftarrow J+1, \epsilon} = \sum_{l \text{ odd}} \frac{(2l+1)(l!)^2}{l(l+1)^2 2^{2l-2} [(l-1)/2]!} \sigma_{(1/2)\epsilon \rightarrow l+1/2, \epsilon} \quad (58)$$

or, more explicitly,

$$\lim_{J \rightarrow \infty} \sigma_{J \leftarrow J+1, \epsilon} = \frac{3}{4} \sigma_{(1/2)\epsilon \rightarrow (3/2)\epsilon} + \frac{21}{64} \sigma_{(1/2)\epsilon \rightarrow (7/2)\epsilon} + \frac{55}{256} \sigma_{(1/2)\epsilon \rightarrow (11/2)\epsilon} + \dots \quad (59)$$

## VI. LACK OF $J$ -STATE RESOLUTION

It is worthwhile to consider a situation in which the initial and final nuclear rotational states are resolved but not the parity doublets. The overall cross section for a transition between  $N$  states is obtained by summing and averaging over the unresolved  $J = N - \epsilon/2$ ,  $\epsilon \rightarrow J' = N' - \epsilon'/2$ ,  $\epsilon'$  transitions. Within the IOS approximation this can be written, with the help of Eq. (35), as

$$\sigma_{N \rightarrow N'} = \sum_l \sum_{J=N-1/2}^{N+1/2} \sum_{J'=N'-1/2}^{N'+1/2} w_J (2J'+1) \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2 \times \frac{1}{2} [1 - \epsilon \epsilon' (-1)^{J+J'+l}] \sigma_l \quad (60)$$

where  $w_J$  denotes the fractional weight associated with state  $J$ . For the purposes of discussion we shall assume that this is purely statistical, so that

$$w_J = (2J+1) / \left[ \sum_{J=N-1/2}^{N+1/2} (2J+1) \right] \quad (61)$$

It will be convenient to switch from  $J$  to  $N$  as a label [Hund's case (b)], so that Eq. (61) becomes

$$w_N = (2N+1 - \epsilon) / (4N+2) \quad (62)$$

and Eq. (60) becomes

$$\sigma_{N \rightarrow N'} = \sum_l (2N'+1) f_l(N, N') \sigma_l \quad (63)$$

where we have introduced the quantity

$$f_l(N, N') = \frac{1}{4(2N+1)(2N'+1)} \sum_{\epsilon, \epsilon' = -1}^{+1} (2N+1 - \epsilon)(2N'+1 - \epsilon') \times [1 - \epsilon \epsilon' (-1)^{N+N'+l - (\epsilon + \epsilon')/2}] \times \begin{pmatrix} N' - \epsilon'/2 & l & N - \epsilon/2 \\ -\frac{1}{2} & 0 & +\frac{1}{2} \end{pmatrix}^2 \quad (64)$$

The summations can be simplified by the realization that

$$[1 - \epsilon \epsilon' (-1)^{N+N'+l - (\epsilon + \epsilon')/2}] = [1 + (-1)^{N+N'+l}] \quad (65)$$

To evaluate the resulting summation over  $\epsilon$  and  $\epsilon'$  we make use of the identity<sup>57</sup>

$$\begin{pmatrix} N' \pm \frac{1}{2} & l & N \pm \frac{1}{2} \\ -\frac{1}{2} & 0 & +\frac{1}{2} \end{pmatrix}^2 = (2N+1)(2N'+1) \begin{pmatrix} N & l & N' \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} l & N' & N \\ \frac{1}{2} & N \pm \frac{1}{2} & N' \pm \frac{1}{2} \end{matrix} \right\} \quad (66)$$

and then introduce explicit expressions for the  $6j$  symbols. After a little algebra the following result emerges:

$$f_l(N, N') = \begin{pmatrix} N' & l & N \\ 0 & 0 & 0 \end{pmatrix}^2 \quad (67)$$

so that the  $J$ -unresolved  $N \rightarrow N'$  cross section can be written as

$$\sigma_{N \rightarrow N'} = \sum_l (2N'+1) \begin{pmatrix} N' & l & N \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma_l \quad (68)$$

We recognize that this expression is entirely equivalent to Eq. (37), the sudden factorization relation appropriate to collisions of  $^1\Sigma^+$  molecules. As might be expected, when the resolution of the parity doublets is lost, the inelastic collision dynamics becomes equivalent to that of a  $^1\Sigma^+$  diatomic, where the only internal angular momentum arises from the rotation of the nuclei. As Goldflam *et al.* have shown,<sup>35</sup> substitution of the value of  $N=0$  into Eq. (68) leads to the identification of  $\sigma_l$  with the cross section for the  $N=0 \rightarrow N=l$  transition, namely,



$$\sigma_I = \sigma_{N=0 \rightarrow I} \quad (69)$$

This relation is entirely analogous to Eqs. (45) and (46). Thus, as has been discussed by several authors,<sup>2,3,14,34-36,39</sup> all  $N \rightarrow N'$  cross sections can be expressed in terms of cross sections out of the  $N=0$  level, since from Eqs. (68) and (69) we have

$$\sigma_{N \rightarrow N'} = \sum_{\bar{N}} (2N' + 1) \begin{pmatrix} N' & \bar{N} & N \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma_{0 \rightarrow \bar{N}} \quad (70)$$

An interesting corollary in the case of collisions involving  $^2\Sigma^+$  molecules is that even if it is impossible to resolve experimentally the full  $J$ -state dependence of the cross sections, nevertheless experimental  $N=0 \rightarrow \bar{N}$  cross sections can be used to predict this dependence, at least within the sudden approximation. This follows from introduction of Eq. (69) into Eq. (35) to yield

$$\sigma_{J \rightarrow J'} = \sum_{\bar{N}} (2J' + 1) \begin{pmatrix} J' & \bar{N} & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2 \times \frac{1}{2} [1 - \epsilon \epsilon' (-1)^{J+J'+\bar{N}}] \sigma_{N=0 \rightarrow \bar{N}} \quad (71)$$

## VII. DISCUSSION

This article has presented the exact and several approximate treatments of the dynamics of rotationally inelastic collisions of diatomic molecules in  $^2\Sigma^+$  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 doublet character of the rotational levels. In particular the scaling relations which appear naturally when any sudden approximation is involved, and which were derived within the infinite order sudden approximation in Secs. IV and V, take on additional richness in the case of  $^2\Sigma^+$  collisions, since they predict some degree of connection between cross sections for parity conserving and parity violating collisions. Additionally, these scaling relations can be used to demonstrate that, at least within the sudden approximation, cross sections for transitions in which the doublet structure is not resolved can be used directly to predict the full  $J$ -dependence of the inelastic cross sections. Also, we have demonstrated that in the sudden limit, transitions which conserve the parity index of the molecular wave function are strongly favored as the value of the rotational angular momentum  $J$  increases.

The spin-orbit and orbit-rotation terms in the total molecular Hamiltonian will act to mix  $^2\Sigma^+$  and  $^2\Pi$  electronic states.<sup>41</sup> If the  $^2\Pi$  states lie nearby, then this mixing will result in a sizeable admixture of  $^2\Pi$  character into the electronic wave function, which should be taken into account in a description of the scattering. This can be done by expanding the electronic wave function as a linear combination of  $^2\Sigma^+$  and  $^2\Pi_{\Omega}$  components, and then deriving the close-coupled equations as in Sec. II. The coupled-states and infinite order-sudden simplifications can be made, but the resulting equations are considerably more complex than in the case of the scattering of pure  $^2\Sigma^+$  molecules, treated here. In particular, this additional complexity appears to preclude the development of useful factorization relations.

One direction in which the present study could be pursued is in the implementation of actual calculations of cross sections for a model system. The interaction potential could be taken either from *ab initio* calculations, 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. In connection with this last point, we point out that over the past few years DePristo and co-workers<sup>58</sup> have developed a highly successful methodology for extending the sudden scaling relations to systems in which the criteria for application of the sudden approximation are not met. This approach could easily be adapted to the present case of collisions involving  $^2\Sigma^+$  molecules.

Also, the present article, and in particular Sec. V which deals with the sudden factorization and scaling relations, should be useful in the interpretation of experimental studies of rotationally inelastic collisions involving  $^2\Sigma^+$  molecules. As discussed above, these scaling relations can be used to extract some degree of detailed state-to-state information from data obtained from partially unresolved experiments. Conversely, experiments with full  $J$ -state resolution will provide a stringent test of the validity of the sudden scaling relations and, ultimately, of the accuracy of calculations based on the formalism presented here. Gottscho<sup>59</sup> has recently observed that several experimental studies, other than the work of Lengel and Crosley<sup>29</sup> discussed here, have given evidence of strong propensity rules for transition in which the parity of the molecular wave function can be selected and resolved. Theoretical studies, such as the one presented here, can provide the proper framework for the interpretation and understanding of these kinds of propensity rules.

## ACKNOWLEDGMENTS

The author would like to thank his colleague, Paul Dagdigian, for his encouragement of the research reported here. This work was supported in part by the National Science Foundation, grants CHE78-08729 and CHE81-08464, and by the U.S. Army Research Office, grant DAAG29-81-K-0102.

<sup>1</sup>D. Secrest, in *Atom-Molecule Collision Theory: A Guide for the Experimentalist*, edited by R. B. Bernstein (Plenum, New York, 1979), p. 265.

<sup>2</sup>D. J. Kouri, in *Atom-Molecule Collision Theory: A Guide for the Experimentalist*, edited by R. B. Bernstein (Plenum, New York, 1979), p. 301.

<sup>3</sup>A. S. Dickinson, *Comput. Phys. Commun.* **17**, 51 (1979).

<sup>4</sup>See, for example, the articles by W. A. Lester, Jr., D. Secrest, and R. G. Gordon in *Meth. Comp. Phys.* **10**, 81, 211, 293 (1971).

<sup>5</sup>L. D. Thomas, M. H. Alexander, B. R. Johnson, W. A. Lester, Jr., J. C. Light, K. D. McLenithan, G. A. Parker, M. J. Redmon, T. G. Schmalz, D. Secrest, and R. B. Walker, *J. Comput. Phys.* **41**, 407 (1981).

<sup>6</sup>H. Rabitz, in *Modern Theoretical Chemistry*, edited by W.

- H. Miller (Plenum, New York, 1976), Vol. I, p. 33.
- <sup>7</sup>P. McGuire and D. J. Kouri, *J. Chem. Phys.* **60**, 2488 (1974).
- <sup>8</sup>R. T Pack, *J. Chem. Phys.* **60**, 633 (1974).
- <sup>9</sup>M. Tamir and M. Shapiro, *Chem. Phys. Lett.* **31**, 166 (1975); **39**, 79 (1976).
- <sup>10</sup>A. E. DePristo and M. H. Alexander, *J. Chem. Phys.* **63**, 3552 (1975); **64**, 3009 (1976).
- <sup>11</sup>G. A. Parker and R. T Pack, *J. Chem. Phys.* **66**, 2850 (1977).
- <sup>12</sup>D. Secrest, *J. Chem. Phys.* **62**, 710 (1975).
- <sup>13</sup>L. W. Hunter, *J. Chem. Phys.* **62**, 2855 (1975).
- <sup>14</sup>R. Goldflam, S. Green, and D. J. Kouri, *J. Chem. Phys.* **67**, 4149 (1977).
- <sup>15</sup>Recent reviews include J. P. Toennies, *Annu. Rev. Phys. Chem.* **27**, 225 (1976); M. Faubel and J. P. Toennies, *Adv. At. Mol. Phys.* **13**, 229 (1977).
- <sup>16</sup>U. Borkenhagen, H. Malthan, and J. P. Toennies, *J. Chem. Phys.* **71**, 1722 (1979).
- <sup>17</sup>P. J. Dagdigian, B. E. Wilcomb, and M. H. Alexander, *J. Chem. Phys.* **71**, 1670 (1979); P. J. Dagdigian and B. E. Wilcomb, *ibid.* **72**, 6462 (1980); P. J. Dagdigian and M. H. Alexander, *ibid.* **72**, 6513 (1980).
- <sup>18</sup>U. Buck, F. Huisken, and J. Schleusener, *J. Chem. Phys.* **68**, 5654 (1978); U. Buck, F. Huisken, J. Schleusener, and J. Schaefer, *J. Chem. Phys.* **72**, 1512 (1980); **74**, 535 (1981).
- <sup>19</sup>W. R. Gentry and C. F. Giese, *J. Chem. Phys.* **67**, 5389 (1977).
- <sup>20</sup>D. E. Pritchard, N. Smith, R. D. Driver, and T. A. Brunner, *J. Chem. Phys.* **70**, 2115 (1979).
- <sup>21</sup>B. A. Esche, R. E. Kutina, N. C. Lang, J. C. Polanyi, and A. M. Rulis, *Chem. Phys.* **41**, 183 (1979); J. A. Barnes, M. Keil, R. E. Kutina, and J. C. Polanyi, *J. Chem. Phys.* **76**, 913 (1982).
- <sup>22</sup>K. Bergmann, R. Engelhardt, U. Hefter, and J. Witt, *J. Chem. Phys.* **71**, 2726 (1979); K. Bergmann, U. Hefter, and J. Witt, *ibid.* **72**, 4777 (1980).
- <sup>23</sup>H. Klar, *J. Phys. B* **6**, 2139 (1973).
- <sup>24</sup>S. Green and R. N. Zare, *Chem. Phys.* **7**, 62 (1975).
- <sup>25</sup>S. I. Chu, *Astrophys. J.* **206**, 6110 (1976).
- <sup>26</sup>R. N. Dixon and D. Field, *Proc. R. Soc. London Ser. A* **368**, 99 (1979).
- <sup>27</sup>M. Shapiro and H. Kaplan, *J. Chem. Phys.* **71**, 2182 (1979).
- <sup>28</sup>D. P. Dewangan and D. R. Flower, *J. Phys. B* **14**, 2179 (1981).
- <sup>29</sup>R. K. Lengel and D. R. Crosley, *J. Chem. Phys.* **67**, 2085 (1977).
- <sup>30</sup>D. Stepowski and M. J. Cottureau, *J. Chem. Phys.* **74**, 6674 (1981).
- <sup>31</sup>P. J. Dagdigian, work in progress, 1981.
- <sup>32</sup>S. Green, *J. Chem. Phys.* **64**, 3463 (1976); B. J. Garrison and W. A. Lester, Jr., *ibid.* **66**, 531 (1977); T. G. Heil and D. Secrest, *ibid.* **69**, 219 (1978).
- <sup>33</sup>D. E. Fitz and D. J. Kouri, *J. Chem. Phys.* **74**, 3933 (1981).
- <sup>34</sup>S. I. Chu and A. Dalgarno, *Proc. R. Soc. London Ser. A* **342**, 191 (1975).
- <sup>35</sup>R. Goldflam, D. J. Kouri, and S. Green, *J. Chem. Phys.* **67**, 5661 (1977).
- <sup>36</sup>S. S. Bhattacharyya and A. S. Dickinson, *J. Phys. B* **L521** (1979).
- <sup>37</sup>V. Khare, *J. Chem. Phys.* **68**, 4631 (1978).
- <sup>38</sup>M. H. Alexander, *J. Chem. Phys.* **71**, 5212 (1979).
- <sup>39</sup>D. E. Fitz and D. J. Kouri, *Chem. Phys.* **47**, 195 (1980).
- <sup>40</sup>J. T. Hougen, *Natl. Bur. Stand. U. S. Monogr.* **115**, (1970).
- <sup>41</sup>R. N. Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, *J. Mol. Spectrosc.* **46**, 37 (1973).
- <sup>42</sup>J. 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).
- <sup>43</sup>D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. (Oxford University, Oxford, England, 1975).
- <sup>44</sup>G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, Princeton, N.J., 1950).
- <sup>45</sup>A. M. Arthurs and A. Dalgarno, *Proc. R. Soc. London Ser. A* **256**, 540 (1960).
- <sup>46</sup>A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, N.J., 1960).
- <sup>47</sup>P. McGuire, *J. Chem. Phys.* **65**, 3275 (1976).
- <sup>48</sup>Y. Shimoni and D. J. Kouri, *J. Chem. Phys.* **66**, 2841 (1977).
- <sup>49</sup>G. A. Parker and R. T Pack, *J. Chem. Phys.* **66**, 2850 (1977).
- <sup>50</sup>A. E. DePristo and M. H. Alexander, *Chem. Phys.* **19**, 181 (1977).
- <sup>51</sup>V. Khare, D. E. Fitz, and D. J. Kouri, *J. Chem. Phys.* **73**, 2802 (1980).
- <sup>52</sup>D. J. Kouri and Y. Shimoni, *J. Chem. Phys.* **67**, 86 (1977).
- <sup>53</sup>S. Green, *J. Chem. Phys.* **70**, 816 (1979).
- <sup>54</sup>Reference 43, p. 33.
- <sup>55</sup>M. Abramowitz and I. Stegun, *Natl. Bur. Stand. (U.S.) Appl. Math. Ser.* **55** (1965), Eq. (8.6.1).
- <sup>56</sup>H. P. Broida and T. Carrington, *J. Chem. Phys.* **38**, 136 (1962).
- <sup>57</sup>Reference 43, p. 141.
- <sup>58</sup>A. E. DePristo, S. D. Augustin, R. Ramaswamy, and H. Rabitz, *J. Chem. Phys.* **71**, 850 (1979); A. E. DePristo and H. Rabitz, *ibid.* **72**, 4685 (1980); A. E. DePristo, *ibid.* **74**, 5037 (1981).
- <sup>59</sup>R. A. Gottscho, *Chem. Phys. Lett.* **81**, 66 (1981).