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Symmetry selection rules in rotationally inelastic collisions of open-shell diatomic molecules and polyatomic tops: Implications of an irreducible tensor expansion

Millard H. Alexander

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

Stephen L. Davis

Department of Chemistry, George Mason University, Fairfax, Virginia 22030

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An irreducible tensor formalism due to Grawert is applied to collisions of open-shell diatomics and polyatomic tops. Explicit examination of the reduced T -matrix elements within the infinite-order sudden and first-order Born limits allows the derivation of several general symmetry selection rules for a rotationally inelastic process. In particular, both differential and integral cross sections will vanish unless the symmetry indices of the initial and final states satisfy certain conditions, for the following types of transitions: $J = 0 \rightarrow J'M'$; $J, M = 0 \rightarrow J', M' = 0$; and $JM \rightarrow J, -M$. The $M = 0 \rightarrow M' = 0$ selection rule represents the extension, to an arbitrary orientation of the quantization axis, of a selection rule we have derived earlier. A comparison with results of fully quantum studies of collisions of NH_3 and H_2CO with He confirms the predictive accuracy of these rules. We discuss how both the $M = 0 \rightarrow M' = 0$ and $JM \rightarrow J, -M$ selection rules could be directly verified, in experiments involving laser excitation of a particular symmetry level followed by resolution of the fluorescence polarization.

I. INTRODUCTION

Most previous theoretical work on rotational energy transfer has been devoted to collisions of diatomic molecules in $^1\Sigma$ electronic states,¹⁻³ where the orbital motion of the collision partner can couple with just the rotational motion of the nuclei of the molecule. A more complicated but more interesting situation arises when the total angular momentum of the target molecule has a nonzero projection along an internal axis. Examples would be molecular tops,⁴⁻¹⁴ linear polyatomics,^{13,15} or open-shell diatomics.¹⁶⁻²⁵ The degeneracy with respect to the sign of the projection quantum number is usually lifted by some small term in the molecular Hamiltonian, resulting in a doubling of the rotational levels.^{26,27} In a series of recent papers^{10,13,22-24} we have shown how one can develop selection rules for collision induced transitions among the doublet components of the rotational manifold. One of these selection rules^{10,23} applies to cross sections which are fully resolved with respect to the initial and final space fixed rotational projection quantum numbers. In particular, we have shown^{10,23} how the $J, M = 0 \rightarrow J', M' = 0$ cross section vanishes unless the transition connects doublet components of the same symmetry.

This selection rule was derived for the collision frame, where the z axis is taken to be the initial relative velocity vector. It is unclear to what extent this same selection rule would apply to other quantization frames or to cell experiments, in which there would exist a distribution of relative velocity vectors with respect to the laboratory fixed z axis. With relatively few exceptions in previous theoretical work quantization has been done within the collision, not laboratory, frame.^{28,29} As we²⁸ and Monchick³⁰ have discussed earlier, the averaging associated with passage from the collision frame to

the laboratory frame makes it difficult to compare this theoretical work with the models inferred from cell experiments. The validity of our $M = 0 \rightarrow M' = 0$ selection rule^{10,23} in the laboratory frame is an important issue, since we previously suggested²³ that this selection rule could be observed in an optical-optical double resonance experiment of the type reported by Silvers, Gottscho, and Field.³¹

In a previous paper, referred to here as ADI,²⁸ we have used an irreducible tensor expansion of the scattering amplitude, identical to that introduced by Grawert in the theory of atomic collisions,^{32,33} to investigate M dependence in a laboratory frame in collisions of atoms with diatomic molecules in $^1\Sigma$ electronic states. In particular we have shown²⁸ how the entire matrix of $JM \rightarrow J'M'$ cross sections could be expressed in terms of a smaller set of tensor opacities.³⁴ Within the energy sudden limit^{35,36} the latter quantities could be related to degeneracy averaged integral cross sections into the $J=0$ level. Here we extend this tensorial analysis to collisions of molecules having nonzero body-frame projections of the total angular momentum. In particular we show how within the first-order Born^{12,13,19,37} and Infinite-Order-Sudden^{1,2,7,13,22,38-40} (IOS) approximations it is possible to derive several interesting and useful symmetry selection rules bearing on M dependence in both collision and laboratory frames.

The organization of the present article is as follows: In the next section we derive the equations necessary to describe M dependent cross sections in collisions of open-shell diatomics. The application of the Born and IOS approximations is made in Sec. III. These two approximations are then applied in Sec. IV to the formally analogous case of collisions of polyatomic tops. Then, in Sec. V we use the IOS and Born expressions for the

cross sections to discuss general symmetry selection rules. In Sec. VI we analyze, in light of these selection rules, laboratory frame $JM \rightarrow J'M'$ cross sections for the $\text{NH}_3\text{-He}$ system obtained by Davis and Green⁴¹ and collision frame $J=0 \rightarrow J'$ cross sections for $\text{NH}_3\text{-He}$ and $\text{H}_2\text{CO-He}$ collisions reported by Green.^{6,7} Then in Sec. VII we discuss how several of the selection rules derived here could be verified by experiments involving laser excited diatomics. A brief conclusion follows.

II. COLLISION DYNAMICS: DIATOMIC MOLECULES

Full discussions of the quantum scattering of diatomic molecules with nonzero Σ and/or Λ have been given by several authors.^{19-22,25} We shall reproduce here only those equations which are essential to the ensuing development.

In a Hund's case (a) representation, the wave function for a diatomic molecule in a $2^{S+1}\Lambda_\Omega$ electronic state can be written as a product of a wave function describing the vibrational and electronic motion of the rotationless molecule multiplied by a wave function describing the rotational motion, namely^{42,43}

$$|JM\Omega v \Lambda \Sigma\rangle = |JM\Omega\rangle |v \Lambda \Sigma\rangle. \quad (1)$$

Here J denotes the total angular momentum (spin + electronic orbital + rotational) with projection along space- and molecule-fixed axes of M and Ω , respectively; v is the vibrational quantum number; S denotes the spin angular momentum with projection Σ along the molecular axis; and Λ is the projection, also along the molecular axis, of the electronic orbital angular momentum. With no loss of generality we shall restrict ourselves to collisions which are electronically and vibrationally elastic, so that the v index can be suppressed for simplicity. The rotational wave functions $|JM\Omega\rangle$ are proportional to rotation matrix elements.^{43,44}

It will be convenient to use the definite parity states defined by^{22,42,43}

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

where Ω will now be assumed to be a positive number (or zero). The index ϵ can take on the values ± 1 and has been denoted previously by Alexander²² as a "parity index." The total parity of the $|JM\Omega\epsilon\rangle$ functions, defined as the symmetry with respect to inversion of the coordinate system, is given by⁴⁵

$$V_{J'L'\Omega'\epsilon', JL\Omega\epsilon}^J(R) = (-1)^{J+J'+S-\Omega} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2}$$

$$\times \sum_i F_{J\Omega\epsilon, J'\Omega'\epsilon'}^i \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & L & J' \\ L' & J' & l \end{Bmatrix} \left[A_i(R) \begin{pmatrix} J' & l & J \\ -\Omega & 0 & \Omega \end{pmatrix} + \epsilon \delta_{\Omega,0} B_i(R) \begin{pmatrix} J' & l & J \\ -\Omega & 2\Lambda & -\Omega \end{pmatrix} \right], \quad (9)$$

where $\{::\}$ and $\{::\}$ are $3j$ and $6j$ symbols,⁴⁴ respectively, and

$$F_{J\Omega\epsilon, J'\Omega'\epsilon'}^i = \frac{1}{2} [1 + \epsilon \epsilon' (-1)^{J+J'+l+2\Omega}]. \quad (10)$$

In Eq. (9) the $A_i(R)$ and $B_i(R)$ functions arise from the

$$i |JM\Omega\epsilon\rangle = \epsilon (-1)^{J-S+s} |JM\Omega\epsilon\rangle, \quad (3)$$

where $s=1$ for Σ^- states and zero otherwise. In contemporary spectroscopic notation the doublet levels are labeled e and f .⁴⁶ The value of ϵ for the e levels is given by

$$\epsilon = (-1)^{S-s-q}, \quad (4)$$

and for the f levels by

$$\epsilon = -(-1)^{S-s-q}, \quad (5)$$

where $q=0$ for integer spins and $q=\frac{1}{2}$ for half-integer spins.

The collision between a molecule in the $|JM\Omega\epsilon\rangle$ state and a structureless target is usually treated^{19,22} by expanding the overall wave function in eigenfunctions of the total angular momentum J , namely

$$|JL\Omega\epsilon \mathfrak{M}\rangle = \sum_{MM_L} (JMLM_L | \mathfrak{M} \rangle |LM_L\rangle |JM\Omega\epsilon\rangle. \quad (6)$$

Here $(\dots | \dots)$ is a Clebsch-Gordan coefficient,⁴⁴ \mathfrak{M} is the projection of J along the space-fixed z axis, L is the relative orbital angular momentum quantum number, and $|LM_L\rangle$ is the wave function for the angular motion of the structureless particle. The radial expansion coefficients $U_{JL\Omega\epsilon}^J(R)$ of the $|JL\Omega\epsilon \mathfrak{M}\rangle$ functions are solutions to the so-called close-coupled (CC) equations^{19,22,23,25,47,48}:

$$\left[-\frac{\hbar^2}{2m_c} \frac{d^2}{dR^2} + \frac{\hbar^2 L(L+1)}{2m_c R^2} - \mathcal{E}_{J\Omega\epsilon} \right] U_{JL\Omega\epsilon}^J(R) = \sum_{J'L'\Omega'\epsilon'} V_{J'L'\Omega'\epsilon', JL\Omega\epsilon}^J(R) U_{J'L'\Omega'\epsilon'}^J(R). \quad (7)$$

Here m_c is the collision reduced mass and the channel translational energies are given by

$$\mathcal{E}_{J\Omega\epsilon} = E_{\text{tot}} - E_{J\Omega\epsilon}, \quad (8)$$

where E_{tot} is the total energy and $E_{J\Omega\epsilon}$ designates the individual rotational energies. The quantities $V_{J'L'\Omega'\epsilon', JL\Omega\epsilon}^J$ are matrix elements of an effective electrostatic potential, obtained by integration over the electronic coordinates.

The symmetry properties of this potential have been discussed by several authors.¹⁶⁻²² We shall not go into the details here. For the purposes of this article we restrict our attention to the case where $\Omega = \Omega'$. The discussion given earlier by Alexander²² can be easily extended to show that

expansion of the atom-molecule interaction potential.²² We note in Eq. (9) that from the presence of the Kronecker delta and from the selection rules imposed by the denominator of the third $3j$ symbol, that the second term will contribute only in certain cases, as, for ex-

ample, $^1\Pi$, $^3\Pi_{\Omega=1}$, $^1\Delta$, $^3\Delta_{\Omega=2}$, etc.

The CC equations are solved subject to the boundary condition^{22,47}

$$\lim_{R \rightarrow \infty} U_{JL\Omega\epsilon}^J(R) = \delta_{JJ'} \delta_{LL'} \delta_{\Omega\Omega'} \delta_{\epsilon\epsilon'} \exp[-i(k_{J'\Omega'\epsilon'} R - L'\pi/2)] \\ - (k_{J'\Omega'\epsilon'}/k_{J\Omega\epsilon})^{1/2} S_{J'L'\Omega'\epsilon', JL\Omega\epsilon}^J \exp[i(k_{J\Omega\epsilon} R - L\pi/2)], \quad (11)$$

which defines the S matrix. Here the wave vector is defined by $k_{J\Omega\epsilon}^2 = 2m_c \epsilon_{J\Omega\epsilon}/\hbar^2$. As discussed previously,²³ the quantum numbers Ω and ϵ play spectator roles in the angular momentum coupling; therefore the expression for the scattering amplitude is a simple generalization of the expression given earlier^{28,48} for collisions of molecules in $^1\Sigma$ electronic states, namely,

$$f_{JM\Omega\epsilon, J'M'\Omega'\epsilon'}(\hat{R}, \hat{R}') = 2\pi \sum_{J\Omega\epsilon, L\Omega\epsilon} i^{L-L'} (-1)^{L+L'+J+J'} (2J+1) \\ \times \begin{pmatrix} J & L & J \\ M & M_L & -M \end{pmatrix} \begin{pmatrix} J' & L' & J \\ M' & M'_L & -M' \end{pmatrix} Y_{LM}^*(\hat{R}') Y_{L'M'}(\hat{R}) \\ \times T_{JL\Omega\epsilon, J'L'\Omega'\epsilon'}^J. \quad (12)$$

Here Y_{LM} is a spherical harmonic; the T matrix element is $T_{JL\Omega\epsilon, J'L'\Omega'\epsilon'}^J = \delta_{JJ'} \delta_{LL'} \delta_{\Omega\Omega'} \delta_{\epsilon\epsilon'} - S_{JL\Omega\epsilon, J'L'\Omega'\epsilon'}^J$; \hat{R} describes the scattering in the collision frame, with z axis along \mathbf{v}_{rel} ; and \hat{R}' describes the orientation of the collision frame with respect to an external z axis to which the M and M' quantum numbers refer.

In Sec. II of ADI²⁸ we made use of an approach originally introduced by Grawert³² in the field of atomic collisions to expand the scattering amplitude in irreducible tensor components.^{49,50} In the present application these tensor components are denoted by²⁸ $f_{J\Omega\epsilon, J'\Omega'\epsilon'}^{KQ}$, where

$$f_{JM\Omega\epsilon, J'M'\Omega'\epsilon'} = (-1)^{J-M} \sum_{KQ} (2K+1)^{1/2} (-1)^{K-Q} \\ \times \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix} f_{J\Omega\epsilon, J'\Omega'\epsilon'}^{KQ}, \quad (13)$$

or, inversely,

$$f_{J\Omega\epsilon, J'\Omega'\epsilon'}^{KQ} = (2K+1)^{1/2} (-1)^{K-J-Q} \\ \times \sum_{MM'} (-1)^{-M} \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix} f_{JM\Omega\epsilon, J'M'\Omega'\epsilon'}. \quad (14)$$

The tensor order K is limited by the triangle relation in the $3j$ symbols in Eqs. (13) and (14) to the values

$$|J - J'| \leq K \leq J + J'. \quad (15)$$

If Eq. (12) is substituted into Eq. (14), the sums over M , M' , and \mathfrak{R} can be carried out to yield, after some angular momentum algebra,

$$f_{J\Omega\epsilon, J'\Omega'\epsilon'}^{KQ} = 2\pi(2K+1)^{1/2} \sum_{L\Omega\epsilon, L'\Omega'\epsilon'} i^{L-L'} (-1)^{L+L'+J+J'} Y_{LM}^*(\hat{R}') Y_{L'M'}(\hat{R}) \\ \times \begin{pmatrix} L & L' & K \\ M_L & -M'_L & -Q \end{pmatrix} (J'L'\Omega'\epsilon' | T_K | JL\Omega\epsilon). \quad (16)$$

Here the reduced matrix element of the T operator is defined by^{28,51}

$$(J'L'\Omega'\epsilon' | T_K | JL\Omega\epsilon) = (-1)^{J-L'} (2K+1) \\ \times \sum_J (-1)^{-J} (2J+1) \begin{Bmatrix} L' & J' & J \\ J & L & K \end{Bmatrix} T_{JL\Omega\epsilon, J'L'\Omega'\epsilon'}^J. \quad (17)$$

If one squares Eq. (13), integrates over \hat{R} , and averages over all possible values of \hat{R}' , then one obtains, - exactly as in ADI,²⁸ the following expression for the integral M -state resolved cross section appropriate to collision cell experiments:

$$\sigma_{JM\Omega\epsilon, J'M'\Omega'\epsilon'} = \frac{\pi}{k_{J\Omega\epsilon}^2} \sum_{KQ} \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix}^2 P_{J\Omega\epsilon, J'\Omega'\epsilon'}^K. \quad (18)$$

Here the *tensor opacity* $P_{J\Omega\epsilon, J'\Omega'\epsilon'}^K$ is defined by

$$P_{J\Omega\epsilon, J'\Omega'\epsilon'}^K = \frac{1}{2K+1} \sum_{L\Omega\epsilon, L'\Omega'\epsilon'} |(J'L'\Omega'\epsilon' | T_K | JL\Omega\epsilon)|^2. \quad (19)$$

III. FIRST BORN AND IOS APPROXIMATIONS: DIATOMIC MOLECULES

In the following discussion we shall limit ourselves to transitions which are elastic in the projection quantum number Ω . In the Hund's case (a) limit this will restrict us to rotationally inelastic collisions within a single spin-orbit manifold.

If the off-diagonal coupling terms [Eq. (9)] are weak, it may be appropriate to solve the CC equations within the first Born approximation^{19,37} (BA), in which case the inelastic T -matrix element can be written as²²

$$T_{JL\Omega\epsilon, J'L'\Omega'\epsilon'}^{J, BA} = (-1)^{J+J'+J-\Omega} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \sum_I F_I(J\Omega\epsilon, J'\Omega'\epsilon') \\ \times \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & L & J \\ L' & J' & l \end{Bmatrix} \left[\begin{pmatrix} J' & l & J \\ -\Omega & 0 & \Omega \end{pmatrix} I_{JL\Omega\epsilon, J'L'\Omega'\epsilon'}^I(A_I) + \epsilon \delta_{\epsilon, 0} \begin{pmatrix} J' & l & J \\ -\Omega & 2\Lambda & -\Omega \end{pmatrix} I_{JL\Omega\epsilon, J'L'\Omega'\epsilon'}^I(B_I) \right], \quad (20)$$

where⁵²

$$I_{JL\Omega\epsilon, J'L'\Omega'\epsilon'}^I(A_I) = 4im\hbar^{-2} (k_{J\Omega\epsilon} k_{J'\Omega'\epsilon'})^{1/2} \int_0^\infty A_I(R) j_L(k_{J\Omega\epsilon} R) j_{L'}(k_{J'\Omega'\epsilon'} R) R^2 dR, \quad (21)$$

with an analogous expression for $I^I(B_I)$. Here $j_L(x)$ is a spherical Bessel function. Since for $\Omega = \Omega'$ the splitting between the two ϵ doublets is usually much smaller than the collision energy, the I^I factors will be virtually independent of the values of ϵ and ϵ' , so that we can suppress these two indices.

If we substitute Eqs. (20) and (21) into Eq. (17), and use the orthogonality of the $6j$ symbols,⁴⁴ we find that the reduced T -matrix elements are given by, in the case where $\Omega' = \Omega$,

$$(J'L'\Omega\epsilon' || T_K^{BA} || JL\Omega\epsilon) = (-1)^{J'-\Omega} [(2J+1)(2J'+1)]^{1/2} F_{J\Omega\epsilon, J'\Omega\epsilon'}^{K, BA} R_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^{K, BA}, \quad (22)$$

where

$$R_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^{K, BA} = (-1)^{-L'} [(2L+1)(2L'+1)]^{1/2} \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix} \begin{bmatrix} J' & K & J \\ -\Omega & 0 & \Omega \end{bmatrix} \\ \times I_{JL\Omega, J'L'\Omega}^K(A_K) + \epsilon \delta_{\epsilon, 0} \begin{pmatrix} J' & K & J \\ -\Omega & 2\Lambda - \Omega \end{pmatrix} I_{JL\Omega, J'L'\Omega}^K(B_K). \quad (23)$$

From this the tensor opacities [Eq. (19)] will be given by

$$P_{J\Omega\epsilon, J'\Omega\epsilon'}^K = (2J+1)(2J'+1) F_{J\Omega\epsilon, J'\Omega\epsilon'}^K \frac{1}{2K+1} \sum_{LL'} |R_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^{K, BA}|^2. \quad (24)$$

In deriving Eq. (24) we have used the fact that $(F^K)^2 = F^K$, which follows from Eq. (10).

Within the IOS approximation the dynamics are treated by freezing the atom-molecule orientation,^{1,2,22,25,38-40,53} solving a single channel scattering problem to obtain an orientation dependent S function, and then determining matrix elements of this S function between the $|JL\Omega\epsilon\rangle$ states. If the S function is expanded like the interaction potential, then the S -matrix elements are given by an expression entirely equivalent to Eq. (9).²² We have

$$S_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^{\bar{L}, \text{IOS}} = (-1)^{J+J'+J-\Omega} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \\ \times \sum_l F_l(J\Omega\epsilon, J'\Omega\epsilon') \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & L & \bar{J} \\ L' & J' & l \end{pmatrix} \begin{bmatrix} J' & l & J \\ -\Omega & 0 & \Omega \end{bmatrix} S_{\bar{L}}^{\bar{L}} + \epsilon \delta_{\epsilon, 0} \begin{pmatrix} J' & l & J \\ -\Omega & 2\Lambda & -\Omega \end{pmatrix} S_{\bar{L}, 2\Lambda}^{\bar{L}}, \quad (25)$$

where $S_{\bar{L}}^{\bar{L}}$ and $S_{\bar{L}, 2\Lambda}^{\bar{L}}$ are coefficients arising from the expansion of the S function. The index \bar{L} designates the orbital angular momentum which appears in the fixed-orientation scattering problem and is a function of L and L' . For the purposes of the present paper it will not be necessary to specify the exact form of this function. The *inelastic* T -matrix element can be written, within the "correct phase" choice of Khare *et al.*,⁵⁴ as

$$T_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^{\bar{L}, \text{IOS}} = -i^{L+L'-2\bar{L}} S_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^{\bar{L}, \text{IOS}}. \quad (26)$$

The similarity between Eqs. (20) and (25) implies that the steps leading from Eq. (20) to Eq. (22) can be followed exactly, which gives an expression for the reduced T -matrix element in the IOS limit identical to Eq. (22), except with an $R_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^K$ term defined by

$$R_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^{K, \text{IOS}} = -i^{L+L'-2\bar{L}} (-1)^{-L'} [(2L+1)(2L'+1)]^{1/2} \\ \times \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix} \begin{bmatrix} J' & K & J \\ -\Omega & 0 & \Omega \end{bmatrix} S_{\bar{L}}^{\bar{L}} \\ + \epsilon \delta_{\epsilon, 0} \begin{pmatrix} J' & K & J \\ -\Omega & 2\Lambda & -\Omega \end{pmatrix} S_{\bar{L}, 2\Lambda}^{\bar{L}}. \quad (27)$$

The IOS tensor opacities are then given by Eq. (24), but with $R^{K, \text{IOS}}$ [Eq. (27)] replacing $R^{K, BA}$.

The Born and IOS expressions for the tensor opacities can then be introduced into Eq. (18) to obtain an expression for the M -dependent integral cross sections, valid within these two dynamical limits.

We shall defer the analysis of the equations derived

here until we have carried out a similar treatment of collisions of polyatomic molecules.

IV. COLLISION DYNAMICS: POLYATOMIC MOLECULES

We limit ourselves to discussion of the collision of atoms with symmetric and slightly asymmetric tops or linear polyatomics in nondegenerate singlet electronic states. The rotational levels of these systems can be split by the presence of small terms in the total molecular Hamiltonian.²⁷ This doubling is called inversion, K , and l doubling, respectively, and arises from the presence of inversion motion (symmetric tops), the small difference between two moments of inertia (asymmetric tops), or the coupling of rotation with a degenerate bending vibration. The properly symmetrized rotational wave functions can be written, analogously to Eq. (2), as^{6,7,13}

$$|JM\epsilon\rangle = N_k [|JMK\rangle + \epsilon |JM, -k\rangle], \quad (28)$$

where $N_k = [2(1 + \delta_{k,0})]^{-1/2}$. In keeping with usual spectroscopic notation the molecule-frame projection quantum number is designated by the letter k ; we will use lower case to avoid confusion with the tensor order K .

The index ϵ is introduced here exactly as in Eq. (2), in a manner also consistent with two earlier papers by Green on NH_3 -He collisions.^{6,7} As discussed by Green⁸ and Davis and Boggs,⁹ for symmetric tops with inversion doubling, at a given value of J each value of $\epsilon(\pm 1)$ is associated with the doublet level of higher or lower

TABLE I. Relation between the symmetry index [Eq. (28)] and the relative energy of the doublet rotational levels; polyatomic molecules.

System	Higher doublet	Lower doublet
Symmetric top with inversion doubling ^a	$\epsilon = -(-1)^{J+2I}$	$\epsilon = (-1)^{J+2I}$
Near-prolate asymmetric top ^b	$\epsilon = +1$	$\epsilon = -1$
Linear molecule, $k=1^c$	$\epsilon = +1$	$\epsilon = -1$

^aSee Refs. 8 and 9 for a discussion of the symmetry of symmetric top wave functions. The quantum number I designates the spin of the identical symmetric top nuclei.

^bFor a discussion of the symmetry of asymmetric rotor wave functions see G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. 11, 27 (1943). The conventional spectroscopic notation for the rotational levels of an asymmetric top is $J_{k\bar{k}}$, where \bar{k} is the molecule frame projection quantum number in the oblate limit. The relation between the index ϵ and \bar{k} is $\epsilon = (-1)^{J+k\bar{k}}$ (Ref. 13).

^cOne quantum of vibration in doubly degenerate bending mode. Detailed discussions of the rovibrational wave functions for linear polyatomics are given by H. H. Nielsen [Rev. Mod. Phys. 23, 90 (1951)] and on pp. 370–379 of Ref. 27.

energy. The relationships between ϵ and the energy orderings of the doublet states are summarized in Table I. Davis^{9,10} has used an alternative expression for the rotational wave functions of a symmetric top, namely,

$$|JM\bar{k}\bar{\epsilon}\rangle = N_k[|JM\bar{k}\rangle + (-1)^{2I+J}\bar{\epsilon}|JM, -k\rangle], \quad (29)$$

where I is the spin of the identical symmetric top nuclei. The index $\bar{\epsilon}$ is +1 for the lower inversion level and -1 for the upper level. From Table I the relation between the indices ϵ [Eq. (28)] and $\bar{\epsilon}$ [Eq. (29)] is seen to be

$$\bar{\epsilon} = (-1)^{J-2I}\epsilon. \quad (30)$$

The scattering can be treated analogously to the scattering of an open-shell diatomic molecule (Sec. II). In particular Eqs. (16)–(19) can be applied directly. To derive an expression for the reduced T -matrix elements valid in the IOS limit we begin with Eq. (13) of Khare *et al.*,⁵⁴ which relates the IOS T -matrix element in an uncoupled basis to the T -matrix element in the total angular momentum representation. We have

$$T_{JLk\epsilon, J'L'\epsilon'}^{\bar{L}, \text{IOS}} = i^{L+L'-2\bar{L}} \sum_M [(2L+1)(2L'+1)]^{1/2} \times \begin{pmatrix} J & L & \bar{J} \\ M & 0 & -M \end{pmatrix} \begin{pmatrix} J' & L' & \bar{J}' \\ M & 0 & -M \end{pmatrix} T_{\bar{L}M}(Jk\epsilon, J'k'\epsilon'), \quad (31)$$

where we have added the spectator k and ϵ indices appropriate to the present application. Green⁷ has derived an expression for the $T_{\bar{L}M}$ matrix elements for collisions of symmetric or slightly asymmetric tops. Using his expression [Eq. (28) of Ref. 7] in Eq. (31) we find, after some angular momentum algebra,

$$T_{JLk\epsilon, J'L'\epsilon'}^{\bar{L}, \text{IOS}} = -i^{L+L'-2\bar{L}} (-1)^{J'-J-\bar{J}+k'} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \times N_k N_{k'} \sum_i G_{Jk\epsilon, J'k'\epsilon'}^i \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & L & G \\ L' & J' & l \end{Bmatrix} \left[\begin{pmatrix} J' & L & J \\ k' & M^- & -k \end{pmatrix} S_{\bar{L}M^-}^{\bar{L}} + \epsilon' \begin{pmatrix} J' & L & J \\ -k' & M^+ & -k \end{pmatrix} S_{\bar{L}M^+}^{\bar{L}} \right], \quad (32)$$

where $M^\pm = k \pm k'$, and the IOS expansion coefficients $S_{\bar{L}M^\pm}^{\bar{L}}$ are defined by Eq. (16) of Ref. 7 but multiplied here by $[(2l+1)/4\pi]^{1/2}$, and, analogously with Eq. (10), the G_i factor is defined by

$$G_{Jk\epsilon, J'k'\epsilon'}^i = \frac{1}{2} [1 + \epsilon \epsilon' (-1)^{J+J'+k+k'+l}]. \quad (33)$$

Equation (32) is formally similar to Eqs. (20) and (25). Thus if we follow the development leading to Eq. (22), we see that the reduced T -matrix elements will be given by

$$(J'L'k'\epsilon' | T_K^{\text{IOS}} | J L k \epsilon) = (-1)^{J'-J-k'} [(2J+1)(2J'+1)]^{1/2} G_{Jk\epsilon, J'k'\epsilon'}^K R_{JLk\epsilon, J'L'k'\epsilon'}^{K, \text{IOS}}, \quad (34)$$

where, similarly to Eq. (27),

$$R_{JLk\epsilon, J'L'k'\epsilon'}^{K, \text{IOS}} = -i^{L+L'-2\bar{L}} (-1)^{L'-L} N_k N_{k'} [(2L+1)(2L'+1)]^{1/2} \times \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J' & k & J \\ k' & M^- & -k \end{Bmatrix} S_{\bar{L}M^-}^{\bar{L}} + \epsilon' \begin{pmatrix} J' & K & J \\ -k' & M^+ & -k \end{pmatrix} S_{\bar{L}M^+}^{\bar{L}}. \quad (35)$$

To derive an expression for the first Born approximation to the reduced T -matrix elements, we begin with Green's expression^{6,7} for the potential matrix in the total angular momentum representation, which is, in our notation,

$$V_{J'L'k'\epsilon', J L k \epsilon}^J(R) = N_k N_{k'} (-1)^{J+J'+k-k'} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \sum_{lm} \left[\frac{2l+1}{4\pi} \right]^{1/2} \times v_{lm}(R) H_{J\epsilon, J'\epsilon'}^{lm} \begin{pmatrix} L & L' & l \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & L & \bar{J} \\ L' & J' & l \end{Bmatrix} \left[\omega \begin{pmatrix} J' & l & J \\ -k' & \pm m & k \end{pmatrix} + \epsilon \begin{pmatrix} J' & l & J \\ -k' & m & -k \end{pmatrix} \right], \quad (36)$$

where $v_{lm}(R)$ is a particular coefficient in the expansion of the potential and

$$H_{J\epsilon, J'\epsilon'}^{lm} = \frac{1}{2} [1 + \epsilon \epsilon' (-1)^{J+J'+l+m}]. \quad (37)$$

The coefficient ω is given by

$$\omega = 1, \quad k' - k > 0, \\ = (-1)^m, \quad k' - k < 0.$$

Because of the restrictions on the projection quantum numbers in the $3j$ symbols, m is limited to the values $k' - k$, $k' + k$, and $k - k'$.

Since the polyatomic is assumed to be in a singlet electronic state, the body frame projection quantum numbers will be integer, so that

$$H_{J\epsilon, J'\epsilon'}^m = G_{Jk\epsilon, J'k'\epsilon'}^I. \quad (38)$$

Equation (36) can then be written in a form analogous to Eq. (9), namely

$$V_{J'L', k'\epsilon', JLk\epsilon}^J(R) = N_k N_{k'} (-1)^{J+J'-\beta+\kappa} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \sum_i G_{Jk\epsilon, J'k'\epsilon'}^I \\ \times \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & L & J \\ L' & J' & l \end{Bmatrix} \left[C_i(R) \begin{pmatrix} J' & l & J \\ -k' & k-k' & k \end{pmatrix} + \epsilon D_i(R) \begin{pmatrix} J' & l & J \\ -k' & k+k' & -k \end{pmatrix} \right], \quad (39)$$

where

$$D_i(R) = [(2l+1)/4\pi]^{1/2} v_{l, k+k'}, \quad (40)$$

and

$$C_i(R) = [(2l+1)/4\pi]^{1/2} \omega v_{l, k-k'}. \quad (41)$$

The similarity between Eqs. (9) and (39) imply that the development leading from Eq. (20) to Eq. (22) can be followed directly. This yields an expression for the reduced T -matrix elements identical to the IOS expression [Eq. (34)], except that the R^K factors are now given by

$$R_{Jk\epsilon, J'k'\epsilon'}^{K, BA} = (-1)^{-L'} N_k N_{k'} [(2L+1)(2L'+1)]^{1/2} \begin{pmatrix} L' & K & L \\ 0 & 0 & 0 \end{pmatrix} \\ \times \left[\begin{pmatrix} J' & K & J \\ -k' & k'-k & k \end{pmatrix} I_{JLk\epsilon, J'L'k'\epsilon'}^K(C_K) + \epsilon \begin{pmatrix} J' & K & J \\ -k' & k+k' & -k \end{pmatrix} I_{JLk\epsilon, J'L'k'\epsilon'}^K(D_K) \right]. \quad (42)$$

V. GENERAL SELECTION RULES

We shall now use the IOS and Born expressions for the reduced T -matrix elements derived in the preceding two sections [Eqs. (22) and (34)] in a general analysis of M dependence in collisions of molecules with nonzero internal angular momentum.

The reduced T -matrix elements are proportional to either the F^K factor [Eq. (10)] or the G^K factor [Eq. (33)]. For given values of J , J' , ϵ , ϵ' , Ω (or k), and Ω' (or k') these factors will vanish for alternating values of K , and, subsequently, so will the reduced T -matrix elements and tensor opacities [Eq. (19)]. Thus for a given J , J' , Ω (or k) and Ω' (or k'), K values of different parity will contribute to the ϵ -conserving and ϵ -changing transitions, which implies that these two processes will provide completely independent information about the collision dynamics. In the case of diatomics with nonzero Λ and/or Σ nonvanishing reduced T -matrix elements and tensor opacities will occur only for tensor orders for which (in the case where $\Omega = \Omega'$)

$$(-1)^K = \epsilon\epsilon'(-1)^{J+J'+2\Omega}, \quad (43)$$

and, in the case of polyatomic tops, for tensor orders for which

$$(-1)^K = \epsilon\epsilon'(-1)^{J+J'+\kappa+k'}. \quad (44)$$

If Ω (or k) equals 0, then J can equal 0, in which case only the $\epsilon = +1$ level will occur. In this particular case we see from Eq. (15) that only the $K = J'$ tensor order

will contribute. Together with Eq. (43) this implies that for transitions within a single spin-orbit manifold of an open-shell diatomic the index ϵ' must equal +1. In other words, for all collisional transitions out of $J = 0$ e/f symmetry will be conserved. In the case of polyatomic tops a similar argument can be advanced to demonstrate from Eq. (44) that for transitions out of $J = 0$ the index ϵ' must equal $(-1)^{k'}$. Since the above argument does not depend on the value of the projection quantum number M' in Eq. (13), we see that it will apply for all values of M' , and, consequently, to degeneracy averaged differential or integral $J = 0 \rightarrow J'$ cross sections. These degeneracy averaged cross sections are, of course, independent of the choice of quantization axis.²⁸

For the special case of $M = M' = 0$, but J not equal to 0, the symmetry properties of the $3j$ symbol in Eq. (13) imply that $(J + J' + K)$ must be even. Taken together with Eq. (43) this implies that for diatomic molecules with nonzero Σ and/or Λ and transitions within a single spin-orbit manifold the J , $M = 0 \rightarrow J'$, $M' = 0$, ϵ' scattering amplitude will vanish unless

$$\epsilon\epsilon'(-1)^{2\Omega} = +1. \quad (45)$$

Since the projection number M cannot equal zero unless Ω is an integer, Eq. (45) implies that ϵ must equal ϵ' , so that the J , $M = 0 \rightarrow J'$, $M' = 0$ scattering amplitude will vanish unless e/f symmetry is conserved. In an earlier paper²³ we derived an identical selection rule

within the collision frame, where the z axis was taken to be the initial relative velocity vector, \mathbf{v}_{rel} . The derivation was completely general, independent of any dynamical limit and not restricted to $\Delta\Omega=0$ transitions. The expression for the scattering amplitude given by Eqs. (12) and (16) refers to a physical situation in which the quantization axis is aligned at an arbitrary, but fixed, angle \hat{R} with respect to \mathbf{v}_{rel} . Thus within the Born or IOS limits, the $M=0 \rightarrow M'=0$ selection rule applies to all possible choices of quantization axis.

A similar selection rule can be derived for collisions of molecular tops. The reasoning leading to Eq. (45) can be followed to demonstrate that the $J, M=0, k \rightarrow J', M'=0, k'$ cross sections will vanish unless

$$[1 + \epsilon\epsilon'(-1)^{k+k'}] = +1, \quad (46)$$

or

$$\epsilon(-1)^k = \epsilon'(-1)^{k'}. \quad (47)$$

In terms of the symmetry index used by Davis^{3,10} [Eq. (30)] this is equivalent to

$$\bar{\epsilon}(-1)^{J+k} = \bar{\epsilon}'(-1)^{J'+k'}. \quad (48)$$

Again, as in the case of collisions of open-shell diatomics discussed in the preceding paragraph, Eqs. (47) and (48) are equivalent to the selection rule derived by Davis¹⁰ for quantization along \mathbf{v}_{rel} , independent of dynamical limit.

Another similar selection rule can be derived for transitions elastic in J but where the M quantum number changes sign. In this case the $3j$ symbol in Eq. (13),

$$\begin{pmatrix} J & J & K \\ -M & -M & 2M \end{pmatrix},$$

will vanish⁵⁵ unless $(2J+K)$ is even. This implies from Eq. (43), that in the case of open shell diatomics the $JM \rightarrow J, -M$ scattering amplitude will vanish unless Eq. (45) is satisfied. For integer Ω , this implies that e/f symmetry will be conserved; for half-integer Ω , only the $e/f \rightarrow f/e$ transitions will have nonvanishing cross sections. For collisions of polyatomic tops a similar argument implies from Eq. (44) that the $JM \rightarrow J, -M$ scattering amplitude will vanish unless Eq. (47) [or Eq. (48)] is satisfied. As in the case of the $M=0 \rightarrow M'=0$ selection rule, the $JM \rightarrow J, -M$ selection rule derived in this paragraph will apply to any orientation of the quantization axis with respect to \mathbf{v}_{rel} .

From the relation between the reduced T -matrix elements and the integral cross sections appropriate to a cell type experiment [Eqs. (18) and (19)], we see that at least within the Born and IOS limits, the $M=0 \rightarrow M'=0$ and $JM \rightarrow J, -M$ selection rules will also apply to these integral cross sections. This is because these selection rules are present in the scattering amplitude itself, independent of the orientation of the \mathbf{v}_{rel} with respect to the quantization axis. As a corollary, the $M=0 \rightarrow M'=0$ and $JM \rightarrow J, -M$ selection rules will apply to orientation averaged integral cross sections even when the distribution of relative velocity vectors is nonisotropic as, for example, in the experiments discussed by Monchick.³⁰

We see from Eqs. (13), (22), and (34) that a necessary

condition for the validity of both the $J=0, \epsilon = +1 \rightarrow J'\epsilon'$ selection rule for degeneracy averaged cross sections as well as the $M=0 \rightarrow M'=0$ and $JM \rightarrow J, -M$ selection rules for arbitrary quantization axis is that the reduced T -matrix element be factorable as

$$(J'L'\Omega\epsilon' || T_K || JL\Omega\epsilon) = F_{J\Omega\epsilon, J'\Omega\epsilon'}^K h_{JL\Omega\epsilon, J'L'\Omega\epsilon'}^K, \quad (49)$$

where h^K is some function of the superscript and subscript indices. An equivalent expression, with $G_{Jk\epsilon, J'k'\epsilon'}^K$ replacing $F_{J\Omega\epsilon, J'\Omega\epsilon'}^K$, would apply to collisions of a polyatomic top. An examination of the derivation of the Born and IOS T -matrix elements [Eqs. (20), (25), (26), and (32)], presented here and elsewhere,²² indicates that this factorization occurs because the T -matrix elements for the $\Omega \rightarrow \pm\Omega'(k \rightarrow \pm k')$ and $-\Omega \rightarrow \mp\Omega'(-k \rightarrow \mp k')$ transitions are identical to within a phase factor. This may well occur in other dynamical regimes, so that the applicability of either the Born or the IOS approximations to a particular collision system may be only a sufficient rather than necessary condition for the validity of the two selection rules presented earlier in this section.

Another propensity rule can be derived by examining the R^K factors [Eqs. (23), (27), (35), and (42)]. In three earlier papers Alexander^{13,22} used an asymptotic limit⁴⁴ of the second $3j$ symbol in these expressions to demonstrate that in the large- J limit certain degeneracy averaged integral cross sections for transitions in which the index ϵ was conserved would dominate those for transitions in which this index changed. This propensity rule applied to transitions in which either the J or $\Omega(k)$ quantum numbers changed, but not both. Strictly speaking, this propensity rule is also limited to those transitions for which the second term in Eqs. (23), (27), (35), and (42) makes no contributions, although analysis¹³ of computed cross sections for He-NH₃ and He-H₂CO collisions indicated that this restriction could be ignored, since the contribution of the second terms is small in general.

An entirely equivalent argument can be applied here. At large J the square of the second $3j$ symbol in Eqs. (23) and (27) can be written as^{13,22,44}

$$\begin{pmatrix} J & J' & K \\ -\Omega & \Omega & 0 \end{pmatrix}^2 \simeq (2J'+1)^{-1} \left[\frac{(k-J'+J)!}{(k+J'-J)!} \right] [P_K^{J'-J}(\Omega/J)]^2, \quad (50)$$

where $P_K^\nu(x)$ is an associated Legendre polynomial. Since the argument x goes to zero as $J \rightarrow \infty$ and since $P_K^\nu(0)$ vanishes unless $(K-\nu)$ is even,⁵⁶ it follows that in the large J limit the only nonvanishing $R_{J\Omega\epsilon, J'\Omega\epsilon'}^K$ terms [Eqs. (23) and (27)] will be those for which $(K-J'+J)$ is an even number. This taken together with the condition on the nonvanishing of the $F_{J\Omega\epsilon, J'\Omega\epsilon'}^K$ factor [Eq. (43)] implies that in the large J limit the reduced T -matrix elements and tensor opacities will vanish unless

$$\epsilon\epsilon'(-1)^{2(J'+\Omega)} = \epsilon\epsilon' = 1. \quad (51)$$

Here we have used the fact that $(J'+\Omega)$ will always be an integer. This equation implies, by way of Eqs. (16) and (18), that in the large- J limit a propensity toward conservation of the ϵ index will appear in the M dependent scattering amplitude and in the M dependent integral cross sections as well as in the degeneracy averaged

integral cross sections, discussed in our previous papers.²²

A similar argument can be applied to transitions of a polyatomic top which are elastic either in k or J . In the former case the argument of the preceding paragraph can be applied directly, with ω everywhere replaced by k . In the case of transitions elastic in J , but inelastic in k , the relevant asymptotic limit, comparable to Eq. (50), is¹³

$$\lim_{J \rightarrow \infty} \begin{pmatrix} J & K & J \\ \pm k' & M' & k \end{pmatrix}^2 = (2J+1)^{-1} \left[\frac{(K-k \pm k')!}{(K+k \mp k')!} \right] [P_K^{k \mp k'}(\mp k'/J)]^2. \quad (52)$$

At large J the associated Legendre polynomial will vanish unless $(K-k \pm k')$ is even. This taken together with the condition on the nonvanishing of the $G_{Jk\epsilon, J'k'\epsilon'}^K$ factor [Eq. (44)] implies that in the large- J limit the scattering amplitude and tensor opacities for $Jk\epsilon \rightarrow J'k'\epsilon'$ transitions will vanish unless $\epsilon = \epsilon'$. Here we have explicitly used the fact that for polyatomics in singlet electronic states the J and k quantum numbers will be integers. Thus we have demonstrated, again invoking Eqs. (16) and (18), that a propensity toward conservation of the ϵ index will be apparent for M dependent differential and integral cross sections, for either $\Delta J, \Delta k = 0$ or $\Delta J = 0, \Delta k$ transitions, exactly as in the case of the degeneracy averaged cross sections, discussed in an earlier paper.¹³

The propensity toward conservation of the ϵ index, discussed in the two preceding paragraphs, is, strictly speaking, valid only at large J . It will become apparent whenever the angular momenta are large enough that the $3j$ symbols in Eqs. (50) and (52) display a clear alternation with even and odd values of K . In a previous paper Alexander has shown¹³ how this onset could be estimated for given values of $J, J', \Omega(k), \Omega'(k')$, and K .

VI. TENSOR OPACITIES AND CROSS SECTIONS FOR NH_3 -He AND H_2CO -He COLLISIONS

Recently Davis and Green^{11,41} have calculated laboratory frame $JMk\epsilon \rightarrow J'M'k'\epsilon'$ cross sections for collisions of NH_3 with He at $E_{\text{tot}} = 126$ and 226 cm^{-1} , assuming an isotropic distribution of relative velocity vectors. From these M -dependent integral cross sections the appropriate tensor opacities can be extracted from Eq. (18) by a least-squares procedure, as we have discussed previously.²⁸ For each transition the square deviation, defined by

$$\sum_{MM'} \left[\sigma_{JMk\epsilon, J'M'k'\epsilon'} - \frac{\pi}{k^2_{Jk\epsilon}} \sum_{KQ} \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix}^2 P_{Jk\epsilon, J'k'\epsilon'}^K \right]^2 = \Delta(P_{Jk\epsilon, J'k'\epsilon'}^1, P_{Jk\epsilon, J'k'\epsilon'}^2, \dots), \quad (53)$$

is minimized with respect to each $P_{Jk\epsilon, J'k'\epsilon'}^K$. This results in a set of linear equations which can be easily solved.

The resulting tensor opacities for $E_{\text{tot}} = 226 \text{ cm}^{-1}$ are listed in Table II. The values at $E_{\text{tot}} = 126 \text{ cm}^{-1}$ show virtually the same qualitative behavior and will not be presented or discussed. We see at first glance that the set of tensor opacities, either even or odd, which are predicted to vanish by Eq. (44) are in reality extremely

TABLE II. Tensor opacities for $Jk\epsilon \rightarrow J'k'\epsilon'$ transitions; NH_3 -He collisions at $E_{\text{tot}} = 226 \text{ cm}^{-1}$.^a

J	k	ϵ	J'	k'	ϵ'	$K=1$	2	3	4	5
1	1	1	2	1	1	44.81	0.053	4.863		
					-1	0.123	1.659	0.047		
			3	1	1		1.462	0.038	0.886	
					-1		0.016	13.10	0.033	
			2	2	1	0.000	0.178	0.021		
					-1	0.030	0.007	21.87		
			3	2	1		0.002	8.471	0.008	
					-1		0.098	0.012	16.26	
2	1	1	3	1	1	48.46	0.011	1.487	0.010	0.379
					-1	0.140	1.038	0.027	2.146	0.019
			2	2	1	0.000	0.061	0.008	18.13	0.006
					-1	0.127	0.005	0.289	0.026	11.43
			3	2	1	0.010	1.658	0.006	1.786	0.0003
					-1	0.043	0.015	27.04	0.015	1.351
2	2	1	3	1	1	0.056	0.113	0.017	14.73	0.007
					-1	0.036	0.008	9.913	0.004	1.31
			3	2	1	30.58	0.087	15.03	0.030	0.216
					-1	0.097	3.071	0.058	1.356	0.004

^aTensor opacities defined by Eq. (19) with Ω, Ω' replaced by k, k' . The range of values of the tensor order is limited by Eq. (15).

small. As discussed in the preceding section we also expect a propensity toward conservation of the ϵ index for the $\Delta J, \Delta k = 0$ and $\Delta J = 0, \Delta k$ transitions, so that the dominant tensor opacities for the $\epsilon \rightarrow \epsilon$ transitions would be predicted to be larger than those for the $\epsilon \rightarrow -\epsilon$ transitions. This does in fact occur for the $J=1, k=1 \rightarrow 2, 1; 2, 1 \rightarrow 2, 2; 2, 1 \rightarrow 3, 1$; and $2, 2 \rightarrow 3, 2$ transitions, although not for the $1, 1 \rightarrow 3, 1$ transition. In this latter case, where $\Delta J = 2$, the values of J and J' are not large enough for an alternation of the $3j$ symbol in Eq. (35) to be apparent.¹³

We notice also that in general for a given transition one or two of the tensor opacities are significantly larger than all the others. This implies that most of the dynamical information contained in the matrix of $JM \rightarrow J'M'$ cross sections can be reduced to only one or two parameters, even fewer than the range of values of the tensor order K [Eq. (15)]. In contrast to the case of He-CO collisions, analyzed in AD I,²⁸ the largest tensor opacities do not always correspond to the smallest values of the tensor order. It is also worthwhile noting that the representation of the entire matrix of $JM \rightarrow J'M'$ cross sections by a few tensor opacities applies only to laboratory frame quantization. In AD I²⁸ we discuss how, in the collision frame, interference occurs between the various tensor orders which is washed out by the orientation averaging which takes place when one passes to laboratory frame quantization.

We turn now to the examination of the $M=0 \rightarrow M'=0$ cross sections. For the He- NH_3 system these are listed in Table III for all the $Jk\epsilon \rightarrow J'k'\epsilon'$ transitions investigated by Davis and Green⁴¹ at $E_{\text{tot}} = 126$ and 226 cm^{-1} . In both cases one of the $\epsilon \rightarrow \epsilon'$ cross sections is much larger than the other, entirely in agreement with the selection rule contained in Eq. (47). Although this selection rule was derived within the IOS and Born limits, it appears

to have excellent predictive validity here, for both collision energies. By contrast, in a study of He-NH₃ collisions at $E = 190 \text{ cm}^{-1}$ Green⁷ found that the accuracy of the IOS approximation for the actual calculation of cross sections was somewhat erratic. This situation is reminiscent of our study of He-LiH collisions.⁵⁷ Although the accuracy of the IOS cross sections was somewhat disappointing, the more accurate coupled states^{2,3,6,21,22,38,58} (CS) cross sections could be well interrelated by the IOS scaling relation.

As discussed in the preceding section the $M=0 \rightarrow M' = 0$ selection rule which is apparent in the laboratory frame cross sections displayed in Table III was derived earlier by Davis¹⁰ within the collision frame. At that time it was anticipated that averaging over the orientations of \mathbf{v}_{rel} , with respect to z , would obscure, to some extent, this selection rule. We see from Table III that this does not occur to any significant degree, at least for NH₃-He collisions.

Let us look now for evidence of the $JM \rightarrow J, -M$ selection rule developed in the preceding section. In Table IV we list the NH₃-He $JM \rightarrow J, -M, k' \epsilon'$ cross sections for $J=1, 2$ and $k=1, 2$ at $E_{\text{tot}} = 226 \text{ cm}^{-1}$ calculated by Davis and Green.⁴¹ In all cases one of the $\epsilon \rightarrow \epsilon'$ cross sections is much larger than the other, entirely in agreement with the selection rule contained in Eq. (47). Again, although the $JM \rightarrow J, -M$ selection rule was derived within the IOS and Born limits, it appears to have excellent predictive validity. It is interesting that the $JM \rightarrow J, -M$ selection rule appears stronger in the case of the transitions which are inelastic in the k quantum number, because in the $k=k'$ case the allowed $\epsilon' = \epsilon$ transitions have relatively small cross sections themselves.

In the preceding section we also demonstrated that within the Born and IOS limits, the degeneracy averaged $J=0, \epsilon = +1 \rightarrow J'\epsilon'$ cross sections will vanish

TABLE III. Laboratory frame cross sections (in Å²) for ϵ -conserving and ϵ -changing $J, M=0, k \epsilon \rightarrow J', M'=0, k'\epsilon'$ transitions; NH₃-He collisions.^a

J	k	J'	k'	$E_{\text{tot}} \approx 126 \text{ cm}^{-1b}$		$E_{\text{tot}} \approx 226 \text{ cm}^{-1b}$	
				$\epsilon' = \epsilon$	$\epsilon' = -\epsilon$	$\epsilon' = \epsilon$	$\epsilon' = -\epsilon$
$\Delta k = 0$							
1	1	2	1	1.658	0.005	2.583	0.008
1	1	3	1	0.006	0.0001	0.0073	0.0014
2	1	3	1	0.424	0.0017	2.106	0.007
2	2	3	2	0.410	0.0016	1.500	0.005
$\Delta k = 1$							
1	1	2	2	0.0005	0.643	0.0007	0.759
1	1	3	2	0.0001	0.059	0.0003	0.421
2	1	3	2	0.0004	0.185	0.0005	0.544
2	2	2	1	0.0002	0.179	0.0004	0.326
2	2	3	1	0.0004	0.037	0.0027	0.205

^aCross sections from Ref. 41. Note that the symmetry index ϵ [Eq. (28)] is related by Eq. (30) to the similar index used by Davis in previous work (Refs. 9 and 10).

^bTotal energy.

TABLE IV. Laboratory frame cross sections (in Å²) for ϵ -conserving and ϵ -changing $JM \epsilon \rightarrow J, -M, k'\epsilon'$ transitions; NH₃-He collisions at $E_{\text{tot}} = 226 \text{ cm}^{-1}$.^a

J	M	k	k'	$\epsilon' = \epsilon$	$\epsilon' = -\epsilon$
$\Delta k = 0$					
1	1	1	1	0.055	0.003
2	2	1	1	0.081	0.001
2	1	1	1	0.064	0.001
2	2	2	2	0.016	0.001
2	1	2	2	0.103	0.007
$\Delta k = 1$					
2	2	2	1	0.0003	0.595
2	1	2	1	0.0005	0.352

^aCross sections from Ref. 41. Note that the symmetry index [Eq. (28)] is related by Eq. (30) to the similar index used by Davis in previous work (Refs. 9 and 10).

unless $\epsilon' = +1$ (for an open-shell diatomic) or unless $\epsilon' = (-1)^{k'}$ (for a polyatomic top). To test the validity of this selection rule we display in Table V degeneracy averaged $J=0, \epsilon = +1 \rightarrow J'\epsilon'$ cross sections and thermal rate constants for collisions of He with NH₃ and H₂CO taken from CC and CS calculations by Green and co-workers.⁵⁻⁷ We see that the selection rule is extremely well obeyed. Furthermore, the ratio between the forbidden [$\epsilon = -(-1)^{k'}$] and allowed [$\epsilon = (-1)^{k'}$] cross sections decreases as the energy (or temperature) in-

TABLE V. Degeneracy averaged cross sections and rate constants for ϵ -conserving and ϵ -changing $Jk \epsilon = 001 \rightarrow J'k'\epsilon'$ transitions in NH₃-He and N₂CO-He collisions.

System	J'	k'	ϵ'	$E_{\text{tot}} (\text{cm}^{-1})$	$\sigma_{000 \rightarrow J'k'\epsilon'} (\text{\AA}^2)$
NH ₃ ^a	3	3	+1	100	0.12
			-1		0.93
	3	3	+1	190	0.0017
			-1		2.65
	4	3	+1		0.0003
			-1		0.18
H ₂ CO ^b	2	2	+1	200	2.1
			-1		0.0
	3	2	+1		1.5
			-1		0.0
$T (\text{K})$					
H ₂ CO ^c	2	2	+1	10.0	4.5
			-1		0.00035
	3	2	+1		1.3
			-1		0.00017
	2	2	+1	70.0	950
			-1		0.028
	3	2	+1		620
			-1		0.012

^aClose-coupling cross sections from Ref. 6.

^bCoupled states cross sections from Ref. 7.

^cThermal rate constants from Ref. 5.

creases, particularly for $\text{NH}_3\text{-He}$, which is what we would expect, since the sudden limit will be more appropriate at higher energy.

VII. EXPERIMENTAL VERIFICATION OF SELECTION RULES

In an earlier paper we described an optical-optical double resonance experiment which could provide a direct demonstration of the $M=0 \rightarrow M'=0$ selection rule in a $^1\Pi$ electronic state.²³ At the time that paper was written we were unsure to what extent the passage from the collision frame to the laboratory frame would obliterate this selection rule. The results of the present article indicate in fact that this selection rule will also apply to laboratory frame quantization in a cell experiment, if the collision dynamics fall within the Born or IOS regimes.

Direct experimental verification of the $JM \rightarrow J, -M$ selection rule in an open-shell diatomic is also possible. Suppose a heteronuclear diatomic molecule with a $^2\Sigma^+$ ground state and a $^2\Pi$ excited state is pumped by a circularly polarized laser tuned to one of the Q -branch ($J'' = \frac{1}{2}$) lines of a particular $^2\Pi_{1/2} \leftarrow X^2\Sigma^+$ vibrational band.²⁶ Only the $M = \frac{1}{2}$ sublevel, in a laboratory frame, of either the $f(\epsilon = -1)$ or $e(\epsilon = +1)$ Λ doublets will be populated. In this case since Ω is half-integer the $JM \rightarrow J, -M$ selection rule implies that collisions will not transfer population directly to the $M = -\frac{1}{2}$ sublevel of the same Λ doublet. The polarization of this simple two-level system is defined as⁵⁹

$$P = (n_{+1/2} - n_{-1/2}) / (n_{+1/2} + n_{-1/2}), \quad (54)$$

where n_M is the population in the M sublevel. Circularly polarized excitation will produce a polarization of unity in the pumped Λ doublet. The implication of the $JM \rightarrow J, -M$ selection rule is that this polarization will remain constant, or, in other words, no elastic collisional depolarization will occur. Experimental verification depends only on resolving the circular polarization of the resonance fluorescence, in a manner similar to previous experiments by McCaffery and co-workers.⁶⁰ Alternatively, an equivalent experiment could be carried out by pumping the $f(\epsilon = +1)$ or $e(\epsilon = -1)$ spin doublets of the $J = \frac{1}{2}$ level of a $^2\Sigma^+$ state by a circularly polarized laser tuned to a Q -branch line of a $^2\Sigma^+ \leftarrow ^2\Pi_{1/2}$ vibrational band²⁶ (e.g., the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition in OH). Again, we expect that collisional depolarization of the pumped spin doublet will not occur.

VIII. CONCLUSIONS

In the present article we have used an irreducible tensor formalism, introduced originally by Grawert³² and used by us,²⁸ as well as Elbel,⁴⁹ in recent discussions of collisions of diatomic molecules in $^1\Sigma^+$ electronic states, to treat collisions involving diatomic molecules in electronic states of nonzero Λ and/or Σ and collisions involving molecular tops. The scattering amplitude for a situation in which the quantization axis is arbitrarily oriented with respect to the initial relative velocity vector can be written as a sum of tensor components, which are themselves sums of reduced T -

matrix elements. After averaging over scattering angle and orientation we find that the M dependent integral cross sections, where quantization refers to a laboratory fixed axis system, can be written as sums of tensor opacities weighted by squares of angular momentum coupling coefficients. The entire matrix of $JM \rightarrow J'M'$ cross sections can be represented by only $2 \min(J, J') + 1$ tensor opacities. Explicit expressions for the reduced T -matrix elements were obtained within the first-order Born and infinite-order-sudden (IOS) limits. Examination of these expressions led to the following conclusions:

(1) For a particular value of the angular momentum (J), projection (Ω or k) and symmetry (ϵ) quantum numbers of the initial and final states, only even or only odd tensor orders will contribute.

(2) Furthermore, for transitions which are elastic in either the $\Omega(k)$ or, in the case of molecular tops, the J quantum numbers, at large J the nonvanishing tensor opacities will be much larger in the case of transitions in which the symmetry index ϵ is conserved. This represents an extension, to M resolved differential and integral cross sections, of a propensity rule recently derived by Alexander.^{13,22}

(3) A particular consequence of point (1) above is that degeneracy averaged as well as M -resolved cross sections for $J=0 \rightarrow J'$ transitions will vanish unless e/f symmetry⁴⁶ is conserved (for diatomic molecules) or unless the symmetry index of the final rotational state is equal to $(-1)^{k'}$ (for molecular tops).

(4) In the particular case of $M=0 \rightarrow M'=0$ transitions, differential and integral cross sections for all values of J and J' are predicted to be zero unless the initial and final symmetry indices satisfy certain conditions. For open-shell diatomic molecules these conditions imply that e/f symmetry will be conserved for $M=0 \rightarrow M'=0$ transitions. For polyatomic tops the condition is that $\epsilon(-1)^k = \epsilon'(-1)^{k'}$. These two selection rules are identical to those derived earlier for quantization along \mathbf{v}_{rel} . They are here extended to arbitrary space-frame orientations of the quantization axis and, in particular, to the case of laboratory frame quantization which would occur in a collision cell experiment.

(5) In the particular case of $JM \rightarrow J, -M$ transitions, differential and integral cross sections are predicted to be zero, for all values of J , unless $\epsilon = \epsilon'(-1)^{2\Omega}$, in the case of open-shell diatomics, or unless $\epsilon(-1)^k = \epsilon'(-1)^{k'}$, in the case of polyatomic tops. For open-shell diatomics this implies that e/f symmetry will be conserved for $JM \rightarrow J, -M$ transitions if Ω is integer, and that e/f symmetry will be reversed if Ω is half integer. As in point (4) above this selection rule is valid for arbitrary quantization axes and applies also to laboratory frame quantization in a collision cell experiment.

A comparison with tensor opacities and cross sections obtained from accurate close-coupling and coupled-states calculations on the $\text{NH}_3\text{-He}$ and $\text{H}_2\text{CO-He}$ systems substantiated (Tables II-V) the qualitative predictions summarized in the preceding paragraph. To

judge from these tables, and as discussed in Sec. V, the validity of these predictions may well extend to collision regimes which are not well described by the IOS or Born approximations, provided that the reduced T -matrix elements are factorable as in Eq. (49).

We have shown, in Sec. VII and previously,²³ how the selection rules outlined in conclusions (4) and (5) could be directly verified, in experiments involving laser excitation with resolution of the fluorescence polarization.

The theoretical treatment of the scattering of an open shell diatomic (Secs. II and III) was restricted to a Hund's case (a) representation of the molecular wave function. It would be interesting to carry out a similar analysis of M dependence for a case (b) or intermediate case molecule, where the proper wave functions are linear combinations of case (a) wave functions.^{21,23,24} In an earlier article we were able to show²³ that the selection rule for conservation of e/f symmetry (conservation of the ϵ index) in $M=0 \rightarrow M'=0$ transitions for quantization along v_{rel} , was valid for molecules in both $^1\Pi$ [case (a)] and $^3\Sigma$ [case (b)] electronic states. The case (b) IOS formalism has already been presented for molecules in $^2\Pi$, $^2\Sigma$,²⁴ and $2s+1\Sigma$ ²⁵ electronic states. Alexander and Dagdigian²⁴ have recently used a semiclassical limit²⁴ of the key $3j$ symbol to derive propensity rules for M dependent and degeneracy averaged cross sections in collisions of molecules in $^3\Sigma$ states, for the general case of intermediate coupling.

We emphasize again that the selection rules discussed in Sec. V are completely general in the sense that they were derived independently of any consideration of the interaction potential, and will thus apply to all systems, at least when the Born or IOS limits are valid. We expect that this type of general collisional selection rule will be invaluable in the interpretation of future state resolved experiments on rotational energy transfer in open-shell diatomics and polyatomic tops.

Note added in proof. Recent close-coupled calculations of cross sections for collisions of Ar with NO ($X^2\Pi_{1/2}$) [T. Orlikowski and M. H. Alexander (to be published)] at $E_{tot} = 282 \text{ cm}^{-1}$ strongly confirm the $JM \rightarrow J, -M$ selection rule for open-shell diatomics.

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