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# On the physical origin of propensity rules in collisions involving molecules in $^2\Sigma$ electronic states

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A general quantum treatment of the collision dynamics of  $^{2S+1}\Sigma$ -state diatomic molecules is developed, with particular emphasis given to the physical origin of the collisional propensity for conservation of the e/f molecular symmetry label. State-resolved integral cross sections are expressed as a weighted sum of tensor opacities which are related to the probability that a collision will reorient the nuclear rotational angular momentum vector. Previous derivations of the propensity rules for collisions of  $^{2S+1}\Sigma$ -state diatomic molecules were restricted to the sudden or Born approximations. Here a general derivation is developed that is free of dynamical approximations, and that clearly establishes the direct connection between the observed propensity for the conservation of the e/f molecular symmetry and the collisional propensity for the conservation of the orientation of the nuclear rotational angular momentum vector. A power-law model suggested by previous semiempirical fits to cross sections for  $^1\Sigma^+$ -state molecules is extended to open-shell molecules. This simple model allows us to predict semiquantitatively the degree to which the e/f symmetry index is conserved without performing a full dynamical calculation.

## I. INTRODUCTION

Recent work<sup>1-9</sup> has provided a clear theoretical justification for the existence of general propensity rules<sup>1-21</sup> which govern collision induced transitions between fine-structure levels in open-shell molecules, which are energetically distinct because of the coupling between the nuclear rotational angular momentum  $N$  and the spin  $S$  and/or orbital electronic angular momentum of the electrons.<sup>22</sup> Much of this work, both theoretical<sup>1,3-9</sup> as well as experimental,<sup>5,6,8,10-13</sup> has dealt with collisions involving molecules in  $\Sigma$  electronic states. Within a Hund's case (b) representation,<sup>22</sup> the fine-structure levels are labeled by  $N$  and  $J$ , where the total molecular angular momentum  $J$  is defined by the vector addition of  $N$  and  $S$ . In a  $^2\Sigma^+$  molecule the spin doublet levels corresponding to the parallel ( $J = N + 1/2$ ) and antiparallel ( $J = N - 1/2$ ) coupling of  $N$  and  $S$  are labeled e and f, respectively.<sup>23</sup> The relation between  $N$ ,  $J$ , and the e/f label is clarified by Fig. 1.

The atom-molecule intermolecular potential is electrostatic in origin, and therefore independent of the electronic spin. Thus a collision cannot directly affect the orientation of  $S$ . Since the transition from an e to an f level in a  $^2\Sigma$  electronic state necessitates a  $180^\circ$  reorientation of  $N$  with respect to  $S$  (Fig. 1), the observed propensity toward conservation of the e/f symmetry label has been interpreted,<sup>1,5,8,10,12,13</sup> originally by Lengel and Crosley,<sup>10</sup> as a manifestation of a collisional propensity toward conservation of the orientation of  $N$ . Unfortunately, this qualitative physical picture did not emerge explicitly in our earlier theoretical predictions of these propensity rules, which were based<sup>1,3</sup> on the asymptotic behavior<sup>24,25</sup> of the vector coupling coefficients which appear in the sudden-limit<sup>26-30</sup> expressions for the relevant inelastic cross sections.

In fact, even within an *exact* quantum mechanical formalism the collisional propensity toward the conservation of the e/f molecular symmetry index can be related directly to the degree to which the orientation of  $N$  is conserved during the collision. This relation follows, as was anticipated in our earlier publication<sup>5</sup> on collision-induced transitions between molecular hyperfine levels, from application of both the angular momentum vector recoupling scheme proposed by Corey and McCourt<sup>31</sup> for collisions of molecules in  $\Sigma$  electronic states with nonzero electronic spin and the "translational-internal" coupling scheme,<sup>32-37</sup> first introduced into the field of molecular collisions by Curtiss and co-workers.<sup>33</sup> As will be outlined in Sec. II, utilization of these two coupling schemes allows us to write the cross section for a particular  $NJ \rightarrow N'J'$  transition as a sum over an angular momentum transfer index. Each term in the sum factors into a product of a spin-dependent geometrical factor and a spin-independent tensor opacity.<sup>37</sup> All effects on rotational transitions due to the nonzero electronic spin in the open-shell molecule are accounted for through the geometrical term.

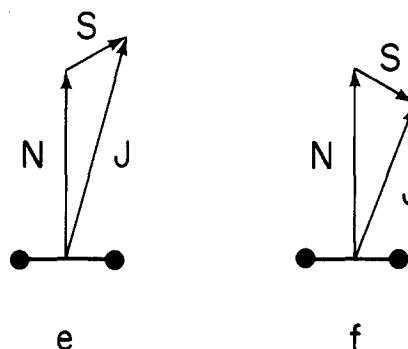


FIG. 1. Vector model description of the angular momenta in the e and f levels of a  $^2\Sigma^+$  molecule (see Refs. 6 and 22). The identification of the e and f labels is reversed for a  $^2\Sigma^-$  molecule.

<sup>a)</sup> NATO Post-doctoral Research Fellow.

The tensor opacities, which contain all the dependence on the intermolecular dynamics, are related<sup>32,38-40</sup> to the probability that a collision will reorient the nuclear rotational angular momentum vector  $\mathbf{N}$ . As will be demonstrated in the next section, the physical origin of the experimentally observed propensity toward  $e/f$  conservation is due to the dependence of the geometrical factors and the spin-independent tensor opacities on the angular momentum transfer index. In our initial description<sup>1,31</sup> of the collision dynamics of open-shell molecules this factorization of the cross section was evident only within the sudden approximation.

This formal work provides the conceptual framework for a *qualitative* discussion, within an exact treatment of the collision dynamics, of the physical origin of the collisional propensities governing rotational energy transfer in multiplet- $\Sigma$  state diatomic molecules. Unfortunately, it does not allow the *extent* of the conservation of the  $e/f$  molecular symmetry to be ascertained without performing a full dynamical calculation.

In an extension of work by Goldflam, Kouri, and Green,<sup>29</sup> Derouard,<sup>39</sup> and Pritchard and co-workers,<sup>41</sup> we shall assume that the overall *qualitative* behavior of these spin-independent tensor opacities can be accurately described as the product of the square of a Wigner  $3j$  symbol<sup>24,25</sup> multiplied by the magnitude of the reorientation of  $\mathbf{N}$  raised to a power. This description is motivated by the well-known factorization<sup>1,29,31,40</sup> of the tensor opacities within the sudden limit and a power-law model<sup>39,41</sup> for the base cross sections for transitions out of the ground rotational state. As will be described in Sec. III, upon the introduction of algebraic expressions for the  $3j$  and  $6j$  symbols, we can obtain explicit expressions for the ratio of  $e \rightarrow f$  to  $e \rightarrow e$  cross sections which are valid asymptotically in the large- $N$  limit. These expressions depend upon only one free parameter. Physically reasonable choices for this parameter lead to *quantitative* predictions for the degree of collisional conservation of the  $e/f$  molecular symmetry. In Sec. IV we use these asymptotic expressions to demonstrate how the degree to which the collision reorients  $\mathbf{N}$  is related directly to the degree to which the  $e/f$  molecular symmetry label is conserved. A brief conclusion follows. The Appendix contains a derivation of a new asymptotic expansion of an important vector coupling coefficient.

## II. DYNAMICS OF INELASTIC COLLISIONS INVOLVING $2\Sigma$ MOLECULES

In our earlier treatment of collisions of a  $2\Sigma^+$  molecule with hyperfine structure,<sup>5</sup> we expanded the atom-molecule wave function in eigenfunctions of the total angular momentum  $\mathcal{J}$ , which are defined by the vector coupling scheme

$$\mathbf{N} + \mathbf{S} = \mathbf{J}, \quad \mathbf{J} + \mathbf{L} = \mathcal{J}, \quad (1)$$

where  $\mathbf{N}$ ,  $\mathbf{S}$ , and  $\mathbf{J}$  have been defined in the Introduction and  $\mathbf{L}$  designates the relative orbital angular momentum of the collision partners. As discussed in the Introduction, the atom-molecule interaction potential is electrostatic in origin, and therefore independent of the electronic spin  $\mathbf{S}$ . The anisotropy of the electrostatic interaction strongly couples  $\mathbf{N}$  to  $\mathbf{L}$  with  $\mathbf{S}$  playing only a spectator role in the collision

dynamics.<sup>1,3,6,12,13,31</sup> Thus, guided by an important recent paper by Corey and McCourt,<sup>31</sup> and by earlier work on atomic collisions by Omont,<sup>32</sup> we can exploit this collisional mechanism to rigorously decouple the electronic spin angular momentum from the nuclear rotational and relative orbital angular momenta by utilizing a total- $\mathcal{J}$  representation defined by the coupling scheme

$$\mathbf{N} + \mathbf{L} = \mathbf{j}, \quad \mathbf{j} + \mathbf{S} = \mathcal{J}. \quad (2)$$

As discussed in detail in Ref. 31, the dynamical problem is now reduced formally to the collision of a molecule without electronic spin, with the intermediate angular momentum  $\mathbf{j}$  playing the same role as the total angular momentum in the case of a collision of a  $1\Sigma$ -state diatomic molecule. The orthogonal transformation connecting these two total- $\mathcal{J}$  representations defines a Wigner  $6j$  symbol and the crucial  $T_{N'S'J'L,NSJL}^{\mathcal{J}}$  matrix elements governing an  $NJ \rightarrow N'J'$  fine-structure transition in  $2\Sigma^+$  state molecules can be constructed from spin-independent  $T$ -matrix elements  $T_{N'L',NL}^j$  via<sup>5,31,40</sup>

$$T_{N'S'J'L,NSJL}^{\mathcal{J}} = (-1)^{J'+L'-J+L} [JJ']^{1/2} \sum_j [j] \times \left\{ \begin{matrix} S & N & J \\ L & \mathcal{J} & j \end{matrix} \right\} \left\{ \begin{matrix} S & N' & J' \\ L' & \mathcal{J} & j \end{matrix} \right\} T_{N'L',NL}^j, \quad (3)$$

where  $\{\dots\}$  is a  $6j$  symbol<sup>24,25</sup> and  $[X_1 \dots X_n]$  designates the product of  $(2X_i + 1)$  degeneracy factors. We<sup>5,36,37,40,42</sup> and others<sup>32-35,38,39,43,44</sup> have shown how it is convenient to work with irreducible tensorial components of the  $T$  matrix, given by<sup>40</sup>

$$\langle N'S'J'L' || T^K || NSJL \rangle = (2K+1)(-1)^{J'+L'} \sum_{\mathcal{J}} (-1)^{\mathcal{J}} (2\mathcal{J}+1) \times \left\{ \begin{matrix} J & J' & K \\ L' & L & \mathcal{J} \end{matrix} \right\} T_{N'S'J'L',NSJL}^{\mathcal{J}}, \quad (4)$$

where the reduced matrix elements of the  $2^K$ -pole tensor are defined by the Wigner-Eckart theorem.<sup>24,25</sup> This decomposition has been designated by Hunter, Snider, and co-workers<sup>33,34</sup> as the "translational-internal" coupling scheme.

Substitution of Eq. (3) into Eq. (4) and evaluation of the resultant summation over  $\mathcal{J}$  and  $j$  via a Racah-Elliott relation<sup>25</sup> and the orthogonality properties of the  $6j$  symbols yields<sup>5,40</sup>

$$\langle N'S'J'L' || T^K || NSJL \rangle = [JJ']^{1/2} (-1)^{S+J+N'+K} \times \left\{ \begin{matrix} N & N' & K \\ J' & J & S \end{matrix} \right\} \langle N'L' || T^K || NL \rangle. \quad (5)$$

The spin-independent reduced  $T$ -matrix element  $\langle N'L' || T^K || NL \rangle$  is defined in terms of the spin-independent total- $j$   $T$ -matrix elements  $T_{N'L',NL}^j$  by an equation formally equivalent to Eq. (4). For experiments in which the initial relative velocity vectors of the collision partners are isotropically distributed with respect to a laboratory fixed axis of quantization the integral cross section for  $M$ -resolved  $NJM \rightarrow N'J'M'$  transitions is given by

$$\sigma_{NJM \rightarrow N'J'M'} = \frac{\pi}{k^2} \sum_{KQ} \begin{pmatrix} J' & K & J \\ -M' & Q & M \end{pmatrix}^2 \times P^K(N'SJ', NSJ), \quad (6)$$

where  $\begin{pmatrix} \dots \end{pmatrix}$  is a  $3j$  symbol<sup>24,25</sup> and the tensor opacity  $P^K(N'SJ', NSJ)$  is defined in terms of reduced  $T$ -matrix elements by

$$P^K(N'SJ', NSJ) = \frac{1}{2K+1} \sum_{L'L} |\langle N'SJ'L' \| T^K \| NSJL \rangle|^2. \quad (7)$$

Through Eq. (5) we can express the tensor opacities for fine-structure transitions in terms of spin-independent tensor opacities, i.e.,

$$P^K(N'SJ', NSJ) = [JJ'] \begin{Bmatrix} N & N' & K \\ J' & J & S \end{Bmatrix}^2 P^K(N', N), \quad (8)$$

where the spin-independent tensor opacities  $P^K(N', N)$  are defined in terms of the spin-independent reduced  $T$ -matrix elements  $\langle N'L' \| T^K \| NL \rangle$  by an equation equivalent to Eq. (7). We can therefore write the integral cross section for  $M$ -resolved transitions as<sup>5,40</sup>

$$\sigma_{NJM \rightarrow N'J'M'} = \frac{\pi}{k^2} [JJ'] \sum_{KQ} \begin{pmatrix} J' & K & J \\ -M' & Q & M \end{pmatrix}^2 \times \begin{Bmatrix} N & N' & K \\ J' & J & S \end{Bmatrix}^2 P^K(N', N), \quad (9)$$

and similarly, the degeneracy-averaged integral cross section as

$$\sigma_{NJ \rightarrow N'J'} = \frac{\pi}{k^2} (2J'+1) \sum_K \begin{Bmatrix} N & N' & K \\ J' & J & S \end{Bmatrix}^2 P^K(N', N). \quad (10)$$

Expressing the integral cross sections in terms of the spin-independent tensor opacities leads to the physical origin of the  $e/f$  conserving collisional propensities in  $^2\Sigma$ -state molecules. Each term in Eq. (10) factors into a spin-independent tensor opacity times the square of a  $6j$  symbol. The  $6j$  symbol describes the coupling between the nuclear rotational angular momentum  $N$  and the unpaired electronic spin  $S$  to form the total molecular angular momentum  $J$ , along with the coupling between the pre- and post-collisional nuclear rotational angular momentum  $N$  and  $N'$ , as well as the total molecular angular momentum  $J$  and  $J'$ , to form a  $K$ th rank tensor.

Further insight into the dynamically exact Eqs. (9) and (10) can be gained by exploring the relation between the tensor order  $K$  and the angular momentum transferred during the collision. As has been discussed previously,<sup>8,36,42,45</sup> within any dynamical approximation that implicitly assumes that the  $T$  operator is local in the internal rotational and relative orbital subspaces (as, for example, the coupled states,<sup>46,47</sup> energy sudden,<sup>26-30</sup> or Born<sup>48</sup> approximations), the  $T$  operator can be expanded as a scalar contraction of  $K$ th rank tensors  $A^K(\hat{J})$  and  $A^K(\hat{L})$  that operate in the  $J$  and  $L$  subspaces, respectively. We have

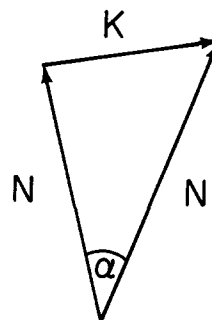


FIG. 2. In a vector coupling model the angular momentum transfer index is defined by  $K = |N - N'|$ . Classically,  $K$  is related to the nuclear rotational angular momentum reorientation angle  $\alpha$ .

$$T = \sum_K A^K(\hat{J}) \cdot A^K(\hat{L}), \quad (11)$$

or, equivalently, in the spin-independent representation

$$T = \sum_K B^K(\hat{N}) \cdot B^K(\hat{L}). \quad (12)$$

Here the  $Q$ th component of the operators in Eq. (12) are defined by<sup>24,32,49,50</sup>

$$B_Q^K(\hat{N}) = \sum_{NN'} C^K(N, N') b_Q^K(N, N'), \quad (13)$$

with

$$b_Q^K(N, N') = (-1)^{K-N-Q} \sum_{MM'} (-1)^{-M} [K]^{1/2} \times \begin{pmatrix} N & N' & K \\ -M & M' & -Q \end{pmatrix} |NM\rangle \langle N'M'|. \quad (14)$$

The  $C^K(N, N')$  are expansion coefficients independent of  $M$  and  $M'$ . The operators  $B^K(\hat{L})$ ,  $A^K(\hat{J})$ , and  $A^K(\hat{L})$  are defined by equations analogous to Eqs. (13) and (14). Because the bra vectors  $\langle N'M'|$  transform under rotations contragrediently to the ket vectors  $|NM\rangle$  this coupling scheme can be summarized formally by the vector equation<sup>49,50</sup>

$$\mathbf{K} = \mathbf{N} - \mathbf{N}' = \mathbf{L} - \mathbf{L}' = \mathbf{J} - \mathbf{J}'. \quad (15)$$

Therefore, in the decomposition of the  $T$  operator in

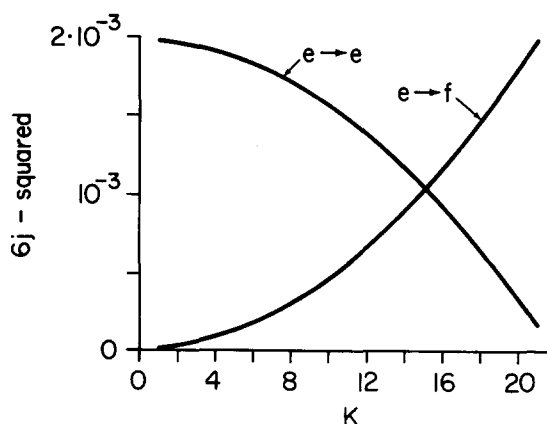


FIG. 3. Numerical values of the square of the  $6j$  symbol in Eq. (10),  $\begin{Bmatrix} N & N' & K \\ J' & J & S \end{Bmatrix}^2$ , for  $S = 1/2$ ,  $N = 10$ , and  $N' = 11$ , as a function of the tensor order  $K$ . The curves correspond to the values of  $J$  appropriate to an  $e \rightarrow e$  transition ( $N, J = N + 1/2 \rightarrow N', J' = N' + 1/2$ ) and to an  $e \rightarrow f$  transition ( $N, J = N + 1/2 \rightarrow N', J' = N' - 1/2$ ). The  $6j$  symbols are defined only for integer values of  $K$ . However, for visual clarity the points have been joined by continuous curves.

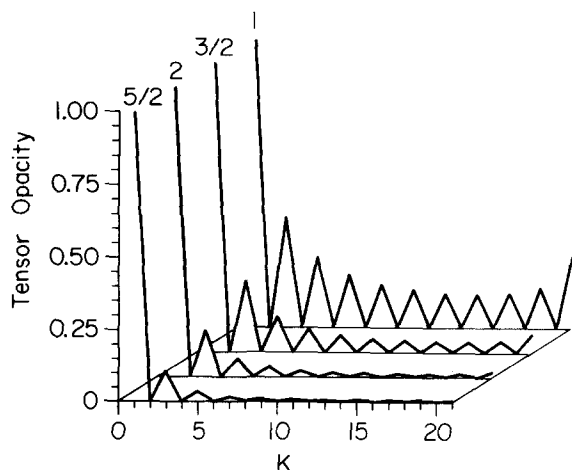


FIG. 4. Numerical values of the tensor opacities  $P^K(N, N')/P^{K=1}(N, N')$  [Eq. (19)] for  $N = 10$  and  $N' = 11$  as a function of the tensor order  $K$ . Although the tensor opacities are defined only for integer values of  $K$ , for visual clarity the points have been joined by continuous curves. Curves are displayed for four values ( $1, 3/2, 2, 5/2$ ) of the power-law parameter  $\gamma$  [Eq. (18)]. Our previous calculations on  $\text{CaCl}(X^2\Sigma^+) + \text{Ar}$  collisions (Ref. 6) as well as extensive studies of collisions of molecules in  $^1\Sigma$  electronic states (Ref. 41) suggest that values of  $\gamma$  in the range  $3/2 - 2$  are most physically reasonable.

Eqs. (4), (11), and (12) the tensor order  $K$  can be identified as the amount of angular momentum transferred during the collision. Classically, the angular momentum transfer index is related to the nuclear rotational angular momentum reorientation angle  $\alpha$  defined in Fig. 2 [cf. Eq. (15)] and the tensor opacities are therefore related to the probability that a collision will reorient the nuclear rotational angular momentum vector.<sup>39,40</sup> The low order tensor opacities, and therefore small collisional transfers of angular momentum, correlate with small nuclear rotational angular momentum reorientation angles. Thus the final expression for the integral cross section [Eq. (10)] can be interpreted<sup>40</sup> as the weighted sum of probabilities associated with increasingly large degrees of angular momentum transfer, with the constraint that

$$\max[|J - J'|, |N - N'|] \leq K \leq \min[J + J', N + N'] \quad (16)$$

Examination of the exact algebraic expression<sup>25</sup> for the  $6j$  symbol in Eq. (10) indicates, as illustrated in Fig. 3, that for  $e \rightarrow e$  transitions ( $N, J = N + 1/2 \rightarrow N', J' = N' + 1/2$ ) the  $6j$  symbol is strongly peaked at the lowest allowed values of  $K$  whereas for  $e \rightarrow f$  transitions ( $N, J = N + 1/2 \rightarrow N', J' = N' - 1/2$ ) the  $6j$  symbol is peaked at the largest allowed values of  $K$ . Therefore, for  $e/f$  conserving transitions the angular momentum coupling described by the  $6j$  symbol in Eq. (10) preferentially weights collisions that cause a small reorientation of  $N$ . Conversely, in  $e/f$  changing transitions collisions that cause large reorientations of  $N$  are weighted more heavily. As illustrated in Fig. 4, for most molecular systems the tensor opacities are strongly peaked at low values of  $K$ . This is because the majority of collisions are grazing encounters which allow only a small reorientation of  $N$ . This is in accord with the discussion, presented earlier,<sup>1,5,8,10,12,13</sup> of the physical origin of the collisional propensity toward  $e/f$  conservation, namely that  $e/f$  changing

transitions will result primarily from collisions in which  $N$  is significantly reoriented.

### III. LARGE- $N$ LIMITING EXPRESSIONS FOR CROSS SECTIONS

As we shall demonstrate in this section, if the spin-independent tensor opacities in Eqs. (8)–(10) are described by the flexible parametric form suggested by Pritchard and co-workers,<sup>41</sup> then we can derive explicit expressions for the ratio of the  $e/f$  changing to  $e/f$  conserving cross sections for a given  $N \rightarrow N'$  transition. The development is as follows.

Within the energy sudden limit the spin-independent tensor opacities take particularly simple forms, and are proportional to cross sections out of the lowest accessible rotational level.<sup>1,4,29,31,40</sup> We have<sup>29</sup>

$$\frac{\pi}{k^2} P^K(N, N') = [NN'K] \begin{pmatrix} N' & K & N \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma_{K \rightarrow 0} \quad (17)$$

Pritchard and co-workers<sup>41</sup> have suggested that the base cross sections in Eq. (17) can be written as

$$\sigma_{K \rightarrow 0} = a(K + 1/2)^{-\gamma}, \quad (18)$$

where  $a$  and  $\gamma$  are constants. We will assume that even if the energy sudden limit is not strictly valid, the spin-free tensor opacities can be well represented in a form suggested by Eqs. (17) and (18), namely

$$\begin{aligned} \frac{\pi}{k^2} P^K(N, N') &= a_{N, N'} [NN'K] \\ &\times \begin{pmatrix} N' & K & N \\ 0 & 0 & 0 \end{pmatrix}^2 (K + 1/2)^{-\gamma_{NN'}}, \end{aligned} \quad (19)$$

where the parameters  $a$  and  $\gamma$  are no longer constrained to be independent of the initial and final rotational levels. Introducing Eq. (19) into Eq. (10), we obtain the following expression for the degeneracy averaged integral cross sections:

$$\begin{aligned} \sigma_{N \rightarrow N', J'}(\gamma) &= 2a(2J' + 1)(2N' + 1)(2N + 1) \\ &\times \sum_{K=|N-N'|}^{N+N'} \begin{pmatrix} N' & K & N \\ 0 & 0 & 0 \end{pmatrix}^2 \\ &\times \left\{ \begin{matrix} N & N' & K \\ J' & J & S \end{matrix} \right\}^2 (K + 1/2)^{1-\gamma}. \end{aligned} \quad (20)$$

For notational simplicity we have suppressed the  $N$  and  $N'$  indices on the  $a$  and  $\gamma$  parameters.

We shall now develop asymptotic approximations to Eq. (20) which are valid when  $N$  is large.

#### A. $e \rightarrow f$ transitions

As discussed in Sec. II, and illustrated in Fig. 3, for  $e \rightarrow f$  transitions ( $N, J = N + 1/2 \rightarrow N', J' = N' - 1/2$ ) the  $6j$  symbol in Eq. (20) is largest for the largest allowed values of  $K$ . We can therefore make use of the well-known semiclassical limit of the  $3j$  symbol in Eq. (20), namely,<sup>51-57</sup>

$$\begin{aligned} \begin{pmatrix} N + \Delta & K & N \\ 0 & 0 & 0 \end{pmatrix}^2 &= \frac{1}{\pi} [1 + (-1)^{K+2N+\Delta}] \\ &\times \{(\kappa^2 - \Delta^2)[- \kappa^2 + (2N + \Delta + 1)^2]\}^{-1/2}, \end{aligned} \quad (21)$$

where  $\kappa = K + 1/2$ . With this, and the well-known algebraic expression<sup>25</sup> for the  $6j$  symbol in Eq. (20), we obtain the following general expression for the cross section for  $e \rightarrow f$  transitions:

$$\sigma_{Ne \rightarrow N+\Delta, f}(\gamma) = \frac{2a(N+\Delta)(N+\Delta+1/2)}{\pi(N+1)(N+\Delta+1)(N+\Delta+3/2)} \times \sum_{\kappa=\Delta}^{2N+\Delta} \frac{[\kappa^2 - (\Delta+1/2)^2]\kappa^{1-\gamma}}{[(\kappa^2 - \Delta^2)[-\kappa^2 + (2N+\Delta+1)^2]^{1/2}} \quad (22)$$

$$g(N, \Delta, m, \gamma) = \frac{(2N-m)(1+2\Delta-m+2N)(1/2+\Delta-m+2N)^{1-\gamma}}{[(1/2+m)(1/2-m+2N)(1/2+2\Delta-m+2N)(3/4+\Delta-m/2+2N)]^{1/2}} \quad (24)$$

Since the  $3j$  symbol with zero projection quantum numbers in Eq. (20) vanishes whenever  $(N+N'+K)$  is odd, the summation in Eq. (23) is restricted to even values of  $m$ . This is designated by the prime following the summation sign. In the transformation from Eq. (22) to Eq. (24), as well as in the transformations described in the rest of this section, we have made extensive use of the SMP symbolic manipulation program<sup>58</sup> running on a VAX-11/785.

To simplify Eq. (23) further we shall make use of the following trapezoidal rule approximation:

$$\sum_{m=0}^{2N} 'f(m) \simeq \frac{1}{2} [f(m=0) + f(m=2N)] + \int_0^{2N} f(m) dm, \quad (25)$$

which should become increasingly accurate as  $N \rightarrow \infty$ . Unfortunately, it is not possible to use Eq. (25) directly by setting  $f(m)$  equal to the summand  $g(N, \Delta, m, \gamma)$  in Eq. (23), since in general the resulting integral cannot be evaluated in closed form. The approach that we follow is, for a given value of  $\gamma$ , to replace  $g(N, \Delta, m, \gamma)$  by a function  $f(N, \Delta, m, \gamma)$  which becomes asymptotically exact as  $N \rightarrow \infty$  and for which the integral *can* be evaluated. We have done this for four values of  $\gamma$  (1, 3/2, 2, 5/2) which span the *physically realistic* range of values seen<sup>6,39,41</sup> in previous studies of

We can simplify this by expanding the factor which precedes the summation in a power series in  $1/N$ , and by making the variable substitution  $m = 2N + \Delta - K$ . We then obtain

$$\sigma_{Ne \rightarrow N+\Delta, f}(\gamma) \simeq \frac{2^{1/2}a}{\pi} \left( \frac{1}{N} - \frac{3}{N^2} + \frac{13+4\Delta}{2N^3} \right) \times \sum_{m=0}^{2N} 'g(N, \Delta, m, \gamma), \quad (23)$$

where

rotationally inelastic atom-molecule collisions. The results are as follows.

For  $\gamma = 1$  we can accurately approximate the summand as

$$g(N, \Delta, m, 1) \simeq f(N, \Delta, m, 1) = (b + cm + dm^2)/(1/2 + m)^{1/2}, \quad (26)$$

where the coefficients  $b$ ,  $c$ , and  $d$  are defined by a Taylor series expansion of  $(1/2 + m)^{1/2}g(N, \Delta, m, 1)$  about  $m = 0$ , namely,

$$b = \left[ 1 + \frac{1+4\Delta}{16N} - \frac{(1+4\Delta)(29+20\Delta)}{512N^2} \right] (2N)^{1/2}, \quad (27)$$

$$c = \left( -3 + \frac{7+12\Delta}{16N} - \frac{205+808\Delta+464\Delta^2}{512N^2} \right) \times \frac{1}{4(2N)^{1/2}}, \quad (28)$$

and

$$d = \left[ -5 + \frac{3(13+20\Delta)}{16N} \right] \frac{1}{32(2N)^{3/2}}. \quad (29)$$

Similarly, for  $\gamma = 3/2$  an excellent approximation to the summand in Eq. (23) was found to be

$$g(N, \Delta, m, 3/2) \simeq f(N, \Delta, m, 3/2) = \left[ \frac{(2N-m)(1+2\Delta-m+2N)}{(1/2+m)(1/2+\Delta-m+2N)(3/4+\Delta-m/2+2N)} \right]^{1/2}. \quad (30)$$

A Taylor series expansion about  $m = 0$  gives

$$f(N, \Delta, m, 3/2) = (b + cm) \left( \frac{2N-m}{1/2+m} \right)^{1/2}, \quad (31)$$

with

$$b = \left[ \frac{1+2\Delta+2N}{(1/2+\Delta+2N)(3/4+\Delta+2N)} \right]^{1/2} \quad (32)$$

and

$$c = \frac{5+18\Delta+20N+40\Delta N+16\Delta^2+16N^2}{16[(1/2+\Delta+2N)^3(3/4+\Delta+2N)^3(1+2\Delta+2N)]^{1/2}}. \quad (33)$$

For  $\gamma = 2$  and  $\gamma = 5/2$  excellent approximations to the summand in Eq. (23) were found to be

$$g(N, \Delta, m, 2) \simeq f(N, \Delta, m, 2) \\ = [(1/2 + m)(3/4 + \Delta - m/2 + 2N)]^{-1/2} \quad (34)$$

and

$$g(N, \Delta, m, 5/2) \simeq f(N, \Delta, m, 5/2) \\ = \frac{b + cm}{[(1/2 + m)(1/2 + \Delta - m/2 + 2N)]^{1/2}}, \quad (35)$$

with

$$b = \left(1 - \frac{3 + 4\Delta}{16N}\right) \frac{1}{(2N)^{1/2}} \quad (36)$$

and

$$c = \frac{1}{8 \cdot 2^{1/2} \cdot N^{3/2}}. \quad (37)$$

In each of these cases the integrals of  $f(N, \Delta, m, \gamma)$  can be evaluated in closed form,<sup>59</sup> so that Eq. (25) can be used directly to evaluate the sum. Since  $f(N, \Delta, m, 3/2)$  [Eqs. (31)–(33)] is strongly peaked at  $m = 0$ , a better approximation for  $\gamma = 3/2$  is obtained by evaluating the first three terms in the sum in Eq. (25) exactly, and then using the integral approximation for the remainder. This involves replacing Eq. (25) by

$$\sum_{m=0}^{2N} f(m) \simeq f(0) + f(2) + f(4) \\ + \frac{1}{2} \left[ f(6) + f(2N) + \int_6^{2N} f(m) dm \right]. \quad (38)$$

In all four cases, after the summation was evaluated by Eq. (25) ( $\gamma = 1, 2, 5/2$ ) or by Eq. (38) ( $\gamma = 3/2$ ), the resulting algebraic expressions were expanded in power series in  $1/N$ . This led, after some further algebra, to the following asymptotic expressions for the  $e \rightarrow f$  cross sections:

$$\lim_{N \rightarrow \infty} \sigma_{Ne \rightarrow N + \Delta, f}(\gamma = 1) \\ = a \left[ 2^{1/2} \frac{23}{16\pi} + \frac{0.30246\Delta - 1.6357}{N} \right], \quad (39)$$

$$\lim_{N \rightarrow \infty} \sigma_{Ne \rightarrow N + \Delta, f}(\gamma = 3/2) = \frac{a}{N^{1/2}} \\ \times \left( \frac{17}{32} + \frac{0.07413}{N^{1/2}} - \frac{1.5137 - 0.01563\Delta}{N} \right), \quad (40)$$

$$\lim_{N \rightarrow \infty} \sigma_{Ne \rightarrow N + \Delta, f}(\gamma = 2) \\ = \frac{a}{N} \left( \frac{1}{2} - \frac{1.42042 + 0.15916\Delta}{N} \right), \quad (41)$$

$$\lim_{N \rightarrow \infty} \sigma_{Ne \rightarrow N + \Delta, f}(\gamma = 5/2) = \frac{a}{N^{3/2}} \\ \times \left[ \frac{9}{16} - 0.1989 \left( \frac{1 + 2\Delta}{N} \right)^{1/2} - \frac{1.7812 + 0.09375\Delta}{N} \right]. \quad (42)$$

## B. $e \rightarrow e$ transitions

We turn now to the derivation of asymptotic expressions for  $e \rightarrow e$  cross sections ( $N, J = N + 1/2 \rightarrow N', J' = N' + 1/2$ ). Since, as discussed in Sec. II, the  $6j$  symbol in Eq. (20) is peaked at  $K = |N - N'|$ , we cannot use the asymptotic expansion for the  $3j$  symbol given by Eq. (21), because it is not accurate for the smallest allowed values of  $K$ . Instead we use an alternate asymptotic expression derived in the Appendix, namely,

$$\begin{pmatrix} N & \Delta + d & N + \Delta \\ 0 & 0 & 0 \end{pmatrix}^2 \simeq \frac{(2\Delta + d)d!}{[(\Delta + \frac{1}{2}d)!(\frac{1}{2}d)!2^{\Delta+d}]^2} \\ \times \left( \frac{1}{2N} - \frac{\Delta + 1}{4N^2} \right). \quad (43)$$

This approximation, combined with the well-known algebraic expansion<sup>25</sup> for the  $6j$  symbol in Eq. (20) leads to the following expression for the  $e \rightarrow e$  cross sections, which is valid at large  $N$ :

$$\sigma_{Ne \rightarrow N + \Delta, e}(\gamma) = 2a \left( \frac{1}{4N^2} - \frac{\Delta + 3}{8N^3} \right) \\ \times \sum_{d=0}^{2N} \frac{(2\Delta + d)d!}{[(\Delta + \frac{1}{2}d)!(\frac{1}{2}d)!2^{\Delta+d}]^2} \\ \times (r + sd - d^2)(d + \Delta + 1/2)^{1-\gamma}, \quad (44)$$

where

$$r = 2(1 + 2N)(1 + \Delta + N) \quad (45)$$

and

$$s = -2(1 + \Delta). \quad (46)$$

The summation in Eq. (44) can be evaluated accurately by explicit evaluation of the first 5 terms ( $d = 0, 2, 4, 6, 8$ ), combined with the trapezoidal rule approximation [Eq. (25)] for the remaining  $d = 10$  to  $d = 2N$  terms. In the integration we make use of the known asymptotic limit<sup>60</sup>

$$\lim_{n \rightarrow \infty} \frac{(2n)!}{(2^n n!)^2} = (\pi n)^{-1/2} \left( 1 - \frac{1}{8n} + \frac{1}{128n^2} \right) \quad (47)$$

to simplify the ratio of factorials. We then obtain

$$\sum_{d=10}^{2N} \frac{(2\Delta + d)d!}{[(\Delta + \frac{1}{2}d)!(\frac{1}{2}d)!2^{\Delta+d}]^2} \\ \times (r + sd - d^2)(d + \Delta + 1/2)^{1-\gamma} \\ \simeq \frac{1}{2} \left[ f(10) + f(2N) + \int_{10}^{2N} f(x) dx \right], \quad (48)$$

where

$$f(x) = \frac{2}{\pi x} \left[ 1 - \frac{1 + 2\Delta}{2x} + \frac{(1 + 2\Delta)(1 + 6\Delta)}{8x^2} \right] \\ \times \frac{r + sx - x^2}{(x + \Delta + 1/2)^{r-1}}. \quad (49)$$

The integration involves integrals of the form

$$\int x^n (x + y)^{-m/2} dx, \quad (50)$$

with  $-3 < n < 1$  and  $m = 0, 1, 2, 3$ , which can all be evaluated in closed form.<sup>59</sup> When the resulting algebraic expressions

TABLE I. Coefficients in asymptotic expansion of  $e \rightarrow e$  cross sections.\*

Coefficient	$\gamma = 1$	$\gamma = 3/2$	$\gamma = 2$	$\gamma = 5/2$
$A_{\gamma,1}$	0.5403	1.615	0.9137	0.645 0
$A_{\gamma,2}$	0.1201	1.170	0.4864	0.255 6
$A_{\gamma,3}$	-0.1259	0.9622	0.3296	0.143 2
$A_{\gamma,4}$	-0.2937	0.8384	0.2495	0.094 24
$B_{\gamma,1}$	1.066	0.8076	-0.1798	0.322 5
$B_{\gamma,2}$	1.234	1.170	-0.1502	0.255 6
$B_{\gamma,3}$	1.244	1.443	-0.1422	0.214 8
$B_{\gamma,4}$	1.163	1.677	-0.1377	0.188 5

\* See Eq. (51).

are expanded in a power series in  $1/N$ , the  $e \rightarrow e$  cross sections for  $\gamma = 1, 3/2, 2, 5/2$  can be written in the general form

$$\sigma_{Ne \rightarrow N+\Delta, e}(\gamma) = a \left[ A_{\gamma, \Delta} + \frac{B_{\gamma, \Delta}}{N} + \delta_{\gamma,1} \frac{\ln N}{\pi} \left( 2 + \frac{\Delta}{N} \right) - \delta_{\gamma,3/2} \frac{8}{3\pi} \left( \frac{2}{N} \right)^{1/2} \right], \quad (51)$$

where  $A_{\gamma, \Delta}$  and  $B_{\gamma, \Delta}$  are constants. Values for these coefficients are given in Table I.

As an indication of the accuracy of the asymptotic approximations to the  $N \rightarrow N'$  cross sections [Eqs. (39)–(42) and (51)], Fig. 5 presents, for the representative case of  $\Delta = 2$ , a comparison of the cross sections predicted by the asymptotic expansions with the exact values obtained by direct numerical evaluation of Eq. (20). Beyond  $N = 20$  the accuracy is excellent.

## V. DISCUSSION

Examination of the asymptotic expansions for the  $e \rightarrow e$  [Eq. (51)] and  $e \rightarrow f$  cross sections [Eqs. (39)–(42)] yields important insight into the physics of these inelastic processes. It is most worthwhile to examine the *ratio* of the  $e \rightarrow f$  to  $e \rightarrow e$  cross sections for a given  $N \rightarrow N'$  transition, since this quantity is independent of the value of the parameter  $a_{NN'}$  in Eq. (19). From Eqs. (39)–(42) and (51) we see that this ratio, which we designate

$$R_{N, N+\Delta}(\gamma) = \frac{\sigma_{Ne \rightarrow N+\Delta, f}(\gamma)}{\sigma_{Ne \rightarrow N+\Delta, e}(\gamma)}, \quad (52)$$

is given by

$$\lim_{N \rightarrow \infty} R_{N, N+\Delta}(\gamma = 1) = \frac{2^{1/2} 23}{16(2 \ln N + \pi A_{1, \Delta})}, \quad (53)$$

$$\lim_{N \rightarrow \infty} R_{N, N+\Delta}(\gamma = 3/2) = \left[ \frac{17}{32} + \frac{0.63772 + 0.07413 A_{3/2, \Delta}}{A_{3/2, \Delta} N^{1/2}} \right] \frac{1}{A_{3/2, \Delta} N^{1/2}}, \quad (54)$$

$$\lim_{N \rightarrow \infty} R_{N, N+\Delta}(\gamma = 2) = \frac{1}{2A_{2, \Delta} N}, \quad (55)$$

$$\lim_{N \rightarrow \infty} R_{N, N+\Delta}(\gamma = 5/2) = \left[ \frac{9}{16} - 0.1982 \left( \frac{1+2\Delta}{N} \right)^{1/2} \right] \frac{1}{A_{5/2, \Delta} N^{3/2}}. \quad (56)$$

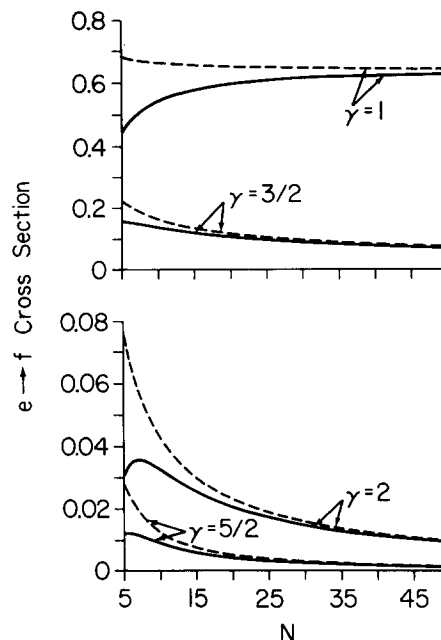


FIG. 5. Comparison of exact cross sections for  $Ne \rightarrow N + \Delta, f$  transitions [Eq. (20), solid curves] with values predicted by the asymptotic expressions given by Eqs. (39)–(42) (dashed curves) for  $\Delta = 2$  with values of the power-law parameter  $\gamma$  [Eq. (18)] of 1, 3/2, 2, and 5/2. The cross sections are, of course, defined only for integer values of  $N$ . For visual clarity the points have been joined by continuous curves. In all cases the cross sections are given in units of the constant  $a$  in Eq. (18).

The accuracy of our asymptotic expansions is illustrated by Fig. 6, which presents a comparison of the cross section ratios predicted by these expressions with the exact values obtained from direct numerical evaluation of Eq. (20). Beyond  $N = 10$  the accuracy is fully satisfactory.

We observe, either from Fig. 6 or from the examination of Eqs. (52)–(56), that as the power-law parameter  $\gamma$  increases, and the  $(K + 1/2)^{1-\gamma}$  term in the tensor opacities

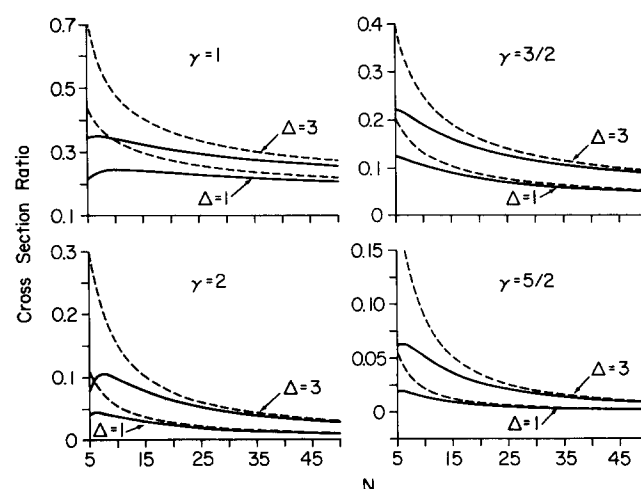


FIG. 6. Comparison of the ratio of the  $Ne \rightarrow N + \Delta, f$  to the  $Ne \rightarrow N + \Delta, e$  cross sections as a function of  $N$  for  $\Delta = 1$  and  $\Delta = 3$  and for values of the power-law parameter  $\gamma$  [Eq. (18)] of 1, 3/2, 2, and 5/2. The cross sections and hence the cross section ratios are, of course, defined only for integer values of  $N$ . For visual clarity the points have been joined by continuous curves. The solid curves represent the exact values obtained by direct numerical evaluation of Eq. (20) while the dashed curves represent the values predicted by the asymptotic expressions given by Eqs. (53)–(56).



[Eq. (19)] becomes increasingly peaked at low values of the tensor order, the  $e \rightarrow f/e \rightarrow e$  cross section ratio *diminishes*. Furthermore, the rate at which the ratio decreases as  $N$  increases becomes increasingly pronounced as  $\gamma$  increases. We also observe that except for the case of  $\gamma = 1$  the cross section ratio *increases* with  $\Delta$ , because the  $A_{\gamma,\Delta}$  coefficients (Table I), which appear in the denominator of Eqs. (54)–(56), *decrease* with  $\Delta$ . This indicates that the increase with  $\Delta$  of the cross section ratio arises primarily not because of an increase in the  $e \rightarrow f$  cross sections, which themselves become independent of  $\Delta$  at large  $N$  [Eqs. (39)–(42)], but rather because of the dramatic decrease in the  $e \rightarrow e$  cross sections as  $\Delta$  increases.

The decrease in the  $e \rightarrow e$  cross sections with increasing  $\Delta$  is consistent with the body of earlier work on collisions of  $^1\Sigma$  molecules<sup>41</sup>: the smallest collisional transfers of angular momentum are the most favored, since only small changes in the magnitude of  $N$  can occur during weak, grazing collisions. It is significant that this behavior does *not* characterize  $e \rightarrow f$  transitions, most likely because  $e \rightarrow f$  transitions occur predominately by “hard” collisions, accompanied by considerable reorientation of  $N$ .

As discussed in the Introduction, the explanation first advanced<sup>1,5,8,10,12,13</sup> to support the experimental observation of  $e/f$  conservation is that collisions hard enough to result in a significant reorientation of  $N$  and a consequent sizable probability for  $e \rightarrow f$  transfer will be relatively improbable events in most molecular encounters. A quantitative connection between this picture and the dependence on  $N$  of the asymptotic expansions for the cross section ratios derived in Sec. III is provided by the representation of the density operator of the initial state in terms of state multipoles.<sup>24,61</sup>

As discussed in Sec. II, the recoupling algorithm of Corey and McCourt<sup>31</sup> allows us to treat the dynamics of the collision in a spin-independent representation, so for the purposes of the study of the collisional reorientation of  $N$  it is sufficient to work within a basis of spin-independent rotor functions  $|NM\rangle$ . In the absence of coherences in the initial state the distribution of initial  $M$  states or final  $M'$  states can be written in terms of the diagonal elements of the density operator  ${}^N\rho_{M,M} = \langle NM | \rho | NM \rangle$ . In a spherical, rather than Cartesian, basis one defines state multipoles, namely,<sup>24,32,35,61</sup>

$$\rho_Q^\kappa(N) = (2\kappa + 1)^{1/2} (-1)^{\kappa-Q-N} \sum_{M,M'} (-1)^M \times \begin{pmatrix} N & N & \kappa \\ -M & M' & Q \end{pmatrix} {}^N\rho_{M,M'} \quad (57)$$

The  $\kappa = 0, 1$ , and  $2$  multipoles describe, respectively, the *population*, the *orientation* vector, and the *alignment* tensor of the excited state. In the absence of coherences only the  $Q = 0$  moments are nonzero. In the semiclassical large- $N$  limit  $\rho^1(N)$  and  $\rho^2(N)$  are proportional, respectively, to the first and second Legendre moments of  $N$ .<sup>62–64</sup>

Rather than examine directly how collisions will reorient  $N$ , one can *equivalently* investigate the degree to which collisions alter the multipole moments of  $N$ . If the collision preserves the orientation of  $N$ , then the multipole moments of the initial density matrix will be transferred unchanged by

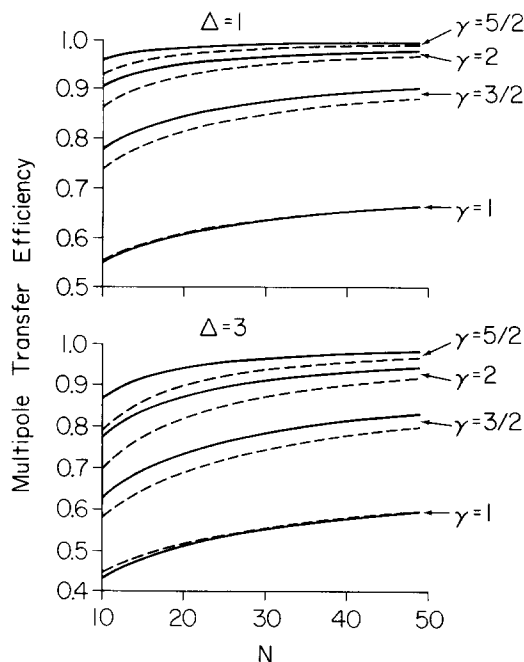


FIG. 7. Multipole transfer efficiencies [Eq. (58)] for the  $\kappa = 1$  multipole (solid curves) and  $\kappa = 2$  multipole (dashed curves) of the initial density matrix appropriate to an  $N \rightarrow N + \Delta$  transition with  $\Delta = 1$  and  $\Delta = 3$ . The tensor opacities are given by Eq. (19) with values of the power-law parameter  $\gamma = 1, 3/2, 2, 5/2$ .

the collision. In a previous paper<sup>42</sup> we have shown that the degree to which the  $\kappa$ th state multipole, normalized to the zeroth moment (the population), is preserved by the collision can be expressed in terms of *multipole transfer efficiencies*.<sup>65</sup> If the initial relative velocity vectors of the collision partners are isotropic, the multipole transfer efficiencies are defined in terms of the tensor opacities as follows<sup>42,65</sup>:

$$E_\kappa(N, N') = (-1)^{\kappa-N-N'} \times \frac{[NN']^{1/2} \sum_K (-1)^{-K} \begin{Bmatrix} N & N' & \kappa \\ N & N' & K \end{Bmatrix} P^K(N, N')}{\sum_K P^K(N, N')} \quad (58)$$

These multipole transfer efficiencies can be computed easily using the power-law expression for the tensor opacities [Eq. (19)]. The dependence on  $N$  and the power-law parameter  $\gamma$  is illustrated in Fig. 7 for the  $\kappa = 1$  and  $\kappa = 2$  multipoles for both  $N \rightarrow N + 1$  ( $\Delta = 1$ ) and  $N \rightarrow N + 3$  ( $\Delta = 3$ ) transitions. We observe first that the multipole transfer efficiencies all tend toward unity as  $N$  increases, which indicates that less reorientation occurs as the magnitude of  $N$  increases, as is to be expected physically from a simple gyroscopic model. Secondly, the  $\kappa = 1$  transfer efficiencies are slightly larger than the  $\kappa = 2$  values, which indicates, again as might be expected, that the higher multipole moments of the density matrix are a more sensitive measure of the effect of collisions. Finally, and most relevant to the present discussion, we observe that for a given value of  $N$  both the  $\kappa = 1$  and  $\kappa = 2$  multipole transfer efficiencies approach unity as the power-law parameter increases. In other words, as the tensor opacities become more sharply peaked at small values of the tensor order  $K$  (Fig. 4), the less the collision will reorient  $N$ . Again, we recall that the develop-

ment of Sec. II, as well as the definition of the multipole transfer efficiencies in terms of the tensor opacities [Eq. (57)], is based on the assumption of an isotropic distribution of initial relative velocity vectors, so that the collisional reorientation of  $\mathbf{N}$  refers specifically to a laboratory frame.

A comparison of Figs. 6 and 7 illustrates clearly the connection between the relative magnitude of  $e \rightarrow f$  changing cross sections and the degree of the collisional reorientation of  $\mathbf{N}$ : *As anticipated originally by Lengel and Crosley,<sup>10</sup> the stronger the tendency to conserve the orientation of the nuclear rotational angular momentum vector, the greater will be the propensity toward conservation of the e/f symmetry label.*

## V. SUMMARY

In the present paper we have given a derivation of the collisional propensity rules in  $^{2S+1}\Sigma$ -state diatomic molecules that is free of dynamical approximations and clearly establishes the connection, as originally put forth by Lengel and Crosley,<sup>10</sup> between the observed propensity for conservation of the e/f molecular symmetry index and the collisional propensity towards conservation of the orientation of the nuclear rotational angular momentum vector. Our derivation is based on an application of the angular momentum vector recoupling scheme proposed by Corey and McCourt<sup>31</sup> for collisions of molecules in  $^{2S+1}\Sigma$  electronic states and the translational-internal coupling scheme,<sup>32–37</sup> first introduced into the field of molecular collisions by Curtiss and co-workers.<sup>33</sup> Within this representation the cross section for a fine-structure transition can be written as a sum over an angular momentum transfer index. Classically, this angular momentum transfer index is directly related to the degree to which the nuclear rotational angular momentum is reoriented by the collision.<sup>39,40</sup>

While this formal work provides an extremely useful conceptual framework for an analysis of rotational energy transfer in open-shell molecules, it unfortunately does not allow the degree to which the e/f symmetry index is conserved to be determined without first performing a full dynamical calculation. We therefore introduced a flexible parametric representation for the crucial tensor opacities that govern the collision dynamics of  $^{2S+1}\Sigma$ -state molecules. The form of this parametrization was suggested by previous power-law fits<sup>41</sup> of cross sections for collisions of  $^1\Sigma^+$  diatomic molecules. For  $^2\Sigma$ -state molecules, this allowed us to extract analytic expressions for the large- $N$  behavior of both the  $e \rightarrow e$  and  $e \rightarrow f$  cross sections for various physically reasonable choices of the power-law parameter. Although the simple parametric form for the tensor opacities chosen here is probably not sufficiently flexible to provide a *quantitative* fit to the individual cross sections for a given  $^2\Sigma$ -state molecule + atom system,<sup>6</sup> nevertheless it clearly has sufficient flexibility to describe *qualitatively* the behavior of the relevant tensor opacities for most of those systems. Thus the conclusions drawn here about the relation between the propensity toward e/f conservation and the tendency toward conservation of the orientation of  $\mathbf{N}$  will apply, at least *qualitatively*, to all  $^2\Sigma$ -state molecule + atom systems.

Additionally, the analytic expressions for the cross sections [Eqs. (39)–(42) and (51)] as well as the cross section

ratios [Eqs. (53)–(56)], may prove to be useful in kinetic modeling studies of nonequilibrium systems involving  $^2\Sigma$ -state molecules, where it is important to have a simple functional representation of the quantum number dependence of relaxation cross sections.

Finally, the work reported here clearly illustrates the power and relevance of symbolic interpreters in molecular dynamics. By greatly extending the range of parameters and quantum number space in which useful analytic approximations to cross sections can be developed, these programs should become a most useful tool in understanding the physics of molecular collisions.

## ACKNOWLEDGMENTS

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## APPENDIX: A NEW ASYMPTOTIC EXPANSION FOR THE SQUARE OF THE 3j/SYMBOL WITH ZERO PROJECTION QUANTUM NUMBERS

The known algebraic expression<sup>25</sup> for the  $3j$  symbol with zero projection quantum numbers can be rewritten to give

$$\begin{pmatrix} N & \Delta + d & N + \Delta \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{(2\Delta + d)!d!}{[(\Delta + \frac{1}{2}d)!(\frac{1}{2}d)!2^{\Delta+d}]^2} \times q(\Delta + 1/2d) \prod_{t=1}^{\Delta+1/2d} p(t), \quad (\text{A1})$$

where

$$p(t) = (N + t)/(2N + 2t - 1) \quad (\text{A2})$$

and

$$q(\Delta + \frac{1}{2}d) = 1/(2N + 2\Delta + d + 1). \quad (\text{A3})$$

The functions  $p$  and  $q$  can be expanded in power series in  $1/N$  to give

$$\begin{pmatrix} N & \Delta + d & N + \Delta \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{(2\Delta + d)!d!}{[(\Delta + \frac{1}{2}d)!(\frac{1}{2}d)!2^{\Delta+d}]^2} \times \left[ \frac{1}{2N} - \frac{\Delta + 1}{4N^2} + \mathcal{O}(N^{-3}) \right]. \quad (\text{A4})$$

For a fixed value of  $N$ , Eq. (A4) is most accurate at low values of  $\Delta$ .

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