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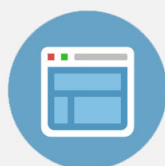
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# Propensity rules for rotationally inelastic collisions of symmetric top molecules or linear polyatomic molecules with structureless atoms

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Using an asymptotic expansion of the angular momentum coupling coefficients which appear in the infinite-order-sudden formulation of collisions between symmetric top molecules and structureless atoms [S. Green, *J. Chem. Phys.* **70**, 816 (1979)], we demonstrate that in certain cases, transitions which conserve the "parity index" of the rotational wave function will be strongly favored over those in which the parity index changes. This propensity rule will apply both to transitions which are inelastic in  $J$  but elastic in  $K$ , the projection of  $J$  along the molecular axis, as well as to transitions which are elastic in  $J$  but inelastic in  $K$ . Identical propensity rules will emerge within a Born treatment of the collision dynamics. These rules are completely general and independent of the particular form of the atom-molecule potential. The propensity toward conservation of the parity index will also be apparent in collisions of slightly asymmetric tops and  $l$ -doubled linear polyatomic molecules. A simple criteria is developed to determine the minimum value of  $J$  for which these propensity rules will be valid. Examination of accurate close-coupling and coupled-states cross sections for the  $\text{NH}_3$ -He and  $\text{H}_2\text{CO}$ -He systems confirms the accuracy of the new propensity rules. These rules can be used to predict intensity changes in four-level double resonance experiments; excellent agreement is obtained in a comparison with available experimental data for collisions of both HCN and  $\text{NH}_3$  with He, Ar, Xe, and  $\text{H}_2$ .

## I. INTRODUCTION

Although most previous theoretical work on rotational energy transfer has been devoted to collisions of diatomic molecules in  $^1\Sigma^+$  electronic states,<sup>1-3</sup> there has been continued interest in collisions between atoms and symmetric top molecules.<sup>4-11</sup> Motivation for the study of these systems arises from their astrophysical importance<sup>12</sup> and from the body of experimental data now available,<sup>13-21</sup> primarily from microwave or microwave-infrared double resonance studies, a technique pioneered by Oka, Wilson, and their co-workers.<sup>13-17</sup> Augustin and Miller<sup>4</sup> used classical and semiclassical  $S$ -matrix techniques to determine rotationally inelastic cross sections for the  $\text{H}_2\text{CO}$ -He system. Quantum mechanical studies within the exact close-coupling formalism, and within the coupled-states and infinite-order-sudden decoupling approximations, have been reported by Green, Garrison, Lester, and Miller<sup>5,6</sup> for  $\text{H}_2\text{CO}$ -He collisions and by Green<sup>7-9</sup> for  $\text{NH}_3$ -He collisions. Davis and Boggs<sup>10</sup> have determined cross sections for the  $\text{NH}_3$ -He system using an impact parameter version of the close-coupled and coupled-states methods. Recently, Dixon and Field<sup>11</sup> have extended the quantum formalism to include spin-dependent interactions between the atom and the symmetric top.

Despite this extensive work, both theoretical and experimental, it has been difficult to extract general "propensity" rules which could explain the variation in magnitude of the cross sections for transitions between the various levels.<sup>13,15,17,19</sup> This difficulty has been particularly pronounced for collisions of symmetric tops with structureless atoms, where it is not possible to apply simple multipole selection rules. In two recent papers<sup>22</sup> devoted to rotationally inelastic collisions of diatomic molecules in  $^2\Sigma^+$  and  $^2\Pi$  electronic states, we have demonstrated the existence of a marked propensity toward conservation of the parity index of the

$\Lambda$ -doubled (or spin-doubled) rotational wave functions. This propensity becomes more pronounced as the rotational quantum number increases.

Because of the formal similarity between the equations governing the scattering of  $^2\Sigma^+$  (or  $^2\Pi$ ) diatomics and those governing the scattering of symmetric and slightly asymmetric tops, we were led to search for similar propensity rules which would apply to the latter systems. We have been able to show, as will be summarized here, that it is possible to extract propensity rules for transitions which are inelastic in  $J$ , the total rotational quantum number of the top, but elastic in  $K$ , the projection of  $J$  along the symmetry axis of the top, and for transitions which are elastic in  $J$  but inelastic in  $K$ . The same propensity rules apply also to collisions of structureless atoms with linear polyatomics, since the  $l$  doubling of the latter produces a doublet structure formally similar to that of an asymmetric top.

The organization of this article is as follows: In the next section, we review the treatment of the collision dynamics within the infinite-order-sudden approximation,<sup>1,2,23-25</sup> developed by Pack<sup>23</sup> and applied to collisions of symmetric top molecules by Green.<sup>8</sup> This allows us to demonstrate the propensity toward conservation of the parity index, both for transitions elastic in  $K$  (discussed in Sec. III) and for transitions elastic in  $J$  but inelastic in  $K$  (discussed in Sec. IV). The collisional selectivity becomes increasingly rigorous as  $J$  increases; we explore, in Secs. III and IV, at what minimum value of  $J$  one could expect to observe the onset of these propensity rules. In Sec. V, we demonstrate how identical propensity rules can be also derived within a Born treatment<sup>26</sup> at the dynamics. A comparison with accurate quantum rate constants for the  $\text{H}_2\text{CO}$ -He and  $\text{NH}_3$ -He systems is made in Sec. VI; the propensity rules are seen to be remarkably accurate, even

at low values of  $J$ .

In Sec. VII, we use these propensity rules to predict the expected intensity changes in the four-level double resonance experiments of the type developed by Oka.<sup>15</sup> The experimental data obtained for collisions of  $\text{NH}_3$  with noble gas atoms, first by Oka,<sup>13-15</sup> and more recently by Shimizu, Kano, and co-workers<sup>18,19</sup> conform, with very few exceptions, to our predictions. The extension to collisions of atoms with linear polyatomics is made in Sec. VIII; our predictions are confirmed by the experiments of Cohen and Wilson<sup>17</sup> on collisions of HCN with noble gases. Then, in Sec. IX we speculate whether the propensity rules developed here can be expected to emerge within a purely classical treatment of the collision dynamics. Finally, Sec. X contains a brief conclusion.

## II. SUDDEN TREATMENT OF THE COLLISION DYNAMICS

As stated in the Introduction, we will follow the notation and development of the infinite-order-sudden treatment of the dynamics of atom-symmetric top collisions presented earlier by Green.<sup>8</sup> We shall assume that the molecule possesses an  $n$ -fold axis of rotation and that the two parity doublets corresponding to each rotational level are split slightly by the inversion motion of the nuclei or, for slightly asymmetric tops, by the difference in the rotational constants. In the latter case, we shall assume that the asymmetry is small enough that the rotational motion can be described by a single symmetric top wave function. For both systems, the rotational wave functions are described in a basis of "primitive" functions, which we denote as  $|JMK\rangle$ , where  $J$  denotes the rotational angular momentum with projection along space- and body-fixed  $z$  axes of  $M$  and  $K$ , respectively. In the coordinate representation, these functions are proportional to rotation matrix elements.<sup>27,28</sup>

For symmetric tops with inversion doubling, we follow Green's analysis<sup>9</sup> and write the properly symmetrized rotational functions as

$$|JMK\epsilon\rangle = N_K [ |JMK\rangle |I_+\rangle + \epsilon |JM, -K\rangle |I_-\rangle ], \quad (1)$$

where  $N_K = (2 - \delta_{K0})^{-1/2}$ . Here,  $|I_+\rangle$  and  $|I_-\rangle$  denote normalized linear combinations of the nuclear spin functions (given by Green<sup>9</sup> for  $\text{NH}_3$ ), which are not explicitly needed in a discussion of rotationally inelastic collisions and will thus be dropped in the ensuing development. The "parity index"  $\epsilon$  in Eq. (1) can take on the values  $\pm 1$  (except for  $K=0$ , when the  $\epsilon = -1$  function vanishes). When the inversion motion of the nuclei is added, the parity index becomes tied to the inversion doublets through the relation<sup>9</sup>

$$\nu = (-1)^{J+1}\epsilon, \quad (2)$$

with  $\nu = +1$  corresponding to the upper inversion level and  $\nu = -1$ , to the lower. The parity of the inversion-rotation wave functions, defined as the symmetry with respect to inversion of the space frame coordinate system,<sup>29</sup> is given by<sup>9,30</sup>

$$i_{SF} |JMK\epsilon\rangle |\nu\rangle = (-1)^{J+K+1} \epsilon |JMK\epsilon\rangle |\nu\rangle. \quad (3)$$

For slightly asymmetric tops, we shall assume that the rotational wave functions can be adequately described as a linear combination of the  $|JMK\rangle$  and  $|JM, -K\rangle$  functions, as was first given by Wang,<sup>31</sup> namely,

$$|JMK\epsilon\rangle = N_K [ |JMK\rangle + \epsilon |JM, -K\rangle ]. \quad (4)$$

For a near-prolate asymmetric top, the parity of these functions is given by the relation<sup>32</sup>

$$i_{SF} |JMK\epsilon\rangle = (-1)^{J+K} \epsilon |JMK\epsilon\rangle. \quad (5)$$

The  $\epsilon = -1$  levels are the lower energy components of the  $K$  doublets for all values of  $K$ .<sup>33</sup> The conventional spectroscopic notation for the rotational levels of an asymmetric top is  $J_{KK'}$ , where  $K'$  is the projection quantum number in the oblate limit.<sup>33</sup> The relation between the parity index  $\epsilon$  and  $K'$  is

$$\epsilon = (-1)^{J+K+K'}. \quad (6)$$

In the subsequent text, the reader should be careful not to confuse the *parity* of the rotational wave functions and the *parity index*  $\epsilon$ .

Within the infinite-order-sudden approximation,<sup>34</sup> the cross section for a transition from the  $JK\epsilon$  to  $J'K'\epsilon'$  levels, summed and averaged over the projection quantum numbers, is given by, in Green's notation,<sup>8</sup>

$$\sigma_{JK\epsilon \rightarrow J'K'\epsilon'} = N_K^2 N_{K'}^2 (2J'+1) \sum_L \left\{ \begin{pmatrix} J' & L & J \\ K' & M' & -K \end{pmatrix}^2 [1 + \epsilon\epsilon' P(L)]^2 Q(L, M^*, M') + \begin{pmatrix} J' & L & J \\ K' & M' & -K \end{pmatrix} \begin{pmatrix} J' & L & J \\ -K' & M' & -K \end{pmatrix} \right. \\ \left. \times [1 + \epsilon\epsilon' P(L)] [\epsilon' + \epsilon P(L)] 2 \text{Re}[Q(L, M^*, M')] + \begin{pmatrix} J' & L & J \\ -K' & M' & -K \end{pmatrix}^2 [\epsilon' + \epsilon P(L)]^2 Q(L, M^*, M') \right\}, \quad (7)$$

where  $M^* = K + K'$ ,  $M' = K - K'$ , and

$$P(L) = (-1)^{J+J'+K+K'+L}. \quad (8)$$

The quantities  $Q(L, M, M')$  are defined by<sup>8</sup>

$$Q(L, M, M') = \frac{\pi}{k^2} \sum_l (2l+1) \left[ \frac{1}{4\pi} S_{LM}^{l*} S_{LM}^l - \delta_{L0} \right], \quad (9)$$

where  $k$  is the collision wave vector and

$$S_{LM}^l = \int Y_{LM}^*(\bar{\theta}, \bar{\phi}) S^l(\bar{\theta}, \bar{\phi}) \sin \bar{\theta} d\bar{\theta} d\bar{\phi}. \quad (10)$$

Here, the sudden  $S$  function  $S^l(\bar{\theta}, \bar{\phi})$ , where the tildes indicate a molecule frame coordinate system, is obtained by solution of a single-channel scattering problem where the orientation of the incoming projectile and the molecular target, specified by  $\bar{\theta}$  and  $\bar{\phi}$ , remains unchanged during the collision.<sup>8,34</sup> The  $S$  function has the same symmetries as the atom-molecule potential,<sup>8</sup> which implies, in particular, that the  $Q(L, M, M')$ , which from Eq. (9) are tensor products of moments of the  $S$  function, vanish unless both  $M$  and  $M'$  are integer mul-

ticles of  $n$ , the order<sup>35</sup> of the subgroup corresponding to rotation about the principal axis of the molecule. Also, it is clear from the  $3j$  symbols in Eq. (7) that the  $Q(L, M, M')$  are defined only for  $L \geq \max(M, M')$ .

Since

$$\epsilon' + \epsilon P(L) = \epsilon' [1 + \epsilon \epsilon' P(L)] \quad (11)$$

and

$$[1 + \epsilon \epsilon' P(L)]^2 = 2[1 + \epsilon \epsilon' P(L)], \quad (12)$$

we can factor out the quantity  $[1 + \epsilon \epsilon' P(L)]$  in Eq. (7) to give

$$\begin{aligned} \sigma_{J K \epsilon \rightarrow J' K' \epsilon'} = 4N_K^2 N_{K'}^2 (2J' + 1) \sum_L \frac{1}{2} [1 + \epsilon \epsilon' P(L)] & \left\{ \begin{pmatrix} J' & L & J \\ K' & M' & -K \end{pmatrix}^2 Q(L, M', M') \right. \\ & \left. + 2\epsilon' \begin{pmatrix} J' & L & J \\ K' & M' & -K \end{pmatrix} \begin{pmatrix} J' & L & J \\ -K' & M' & -K \end{pmatrix} \operatorname{Re}[Q(L, M', M')] + \begin{pmatrix} J' & L & J \\ -K' & M' & -K \end{pmatrix}^2 Q(L, M', M') \right\}. \end{aligned} \quad (13)$$

For notational convenience, we shall refer to the quantity  $\frac{1}{2}[1 + \epsilon \epsilon' P(L)]$  as the *parity factor*, which can take on the values 0 or 1.

### III. PROPENSITY RULES, $\Delta K = 0$ TRANSITIONS

For transitions within the same  $K$  stack, Eq. (13) reduces to, specifically excluding the  $K = 0$  stack,

$$\begin{aligned} \sigma_{J K \epsilon \rightarrow J' K' \epsilon'}^K = (2J' + 1) \sum_L \frac{1}{2} [1 + \epsilon \epsilon' P(L)] & \left\{ \begin{pmatrix} J' & L & J \\ K & 0 & -K \end{pmatrix}^2 Q(L, 0, 0) \right. \\ & \left. + 2\epsilon' \begin{pmatrix} J' & L & J \\ K & 0 & -K \end{pmatrix} \begin{pmatrix} J' & L & J \\ -K & 2K & -K \end{pmatrix} \operatorname{Re}[Q(L, 2K, 0)] + \begin{pmatrix} J' & L & J \\ -K & 2K & -K \end{pmatrix}^2 Q(L, 2K, 2K) \right\}. \end{aligned} \quad (14)$$

Due to the symmetry of the  $Q(L, M, M')$  factors, the last two terms in Eq. (14) vanish if  $2K$  is not an integer multiple of  $n$ , in which case we find

$$\begin{aligned} \sigma_{J K \epsilon \rightarrow J' K' \epsilon'}^K = (2J' + 1) \sum_L \frac{1}{2} [1 + \epsilon \epsilon' P(L)] & \\ \times \begin{pmatrix} J' & L & J \\ K & 0 & -K \end{pmatrix}^2 Q(L, 0, 0) & \quad (15) \end{aligned}$$

In the particular case of collisions involving  $\text{NH}_3$ , this simplification will occur for transitions within the *para*- $\text{NH}_3$  stacks ( $K = 3n \pm 1$ ). Note, however, that this simplification will never apply for a molecule with a twofold axis of rotation (e.g.,  $\text{H}_2\text{CO}$ ).

At large values of the angular momenta  $J$  and  $J'$ , we can replace the  $3j$  symbol in Eq. (15) by the asymptotic expression<sup>28</sup>

$$\begin{aligned} \lim_{J, J' \rightarrow \infty} \begin{pmatrix} J' & L & J \\ K & 0 & -K \end{pmatrix} = (2J' + 1)^{-1/2} (-1)^{K+L-J} & \\ \times \left[ \frac{(L - J' + J)!}{(L + J' - J)!} \right]^{1/2} P_L^{J'-J}(K/J') & \quad (16) \end{aligned}$$

where  $P_L^m$  is an associated Legendre polynomial. At large  $J'$ , the argument  $K/J'$  tends to zero for  $K$  fixed, so that

$$\begin{aligned} \lim_{J, J' \rightarrow \infty} \begin{pmatrix} J' & L & J \\ K & L & -K \end{pmatrix}^2 = (2J' + 1)^{-1} \left[ \frac{(L - J' + J)!}{(L + J' - J)!} \right] & \\ \times [P_L^{J'-J}(0)]^2. & \quad (17) \end{aligned}$$

Since<sup>36</sup>

$$P_L^m(0) = 2^m \pi^{-1/2} \cos[\frac{1}{2}\pi(l - m)] \Gamma[\frac{1}{2}(l + m + 1)] / \Gamma[\frac{1}{2}(l - m + 2)], \quad (18)$$

it is clear from the cosine factor that the  $3j$  symbol in Eq. (15) will vanish unless the quantity  $(L - J' + J)$  is even. From Eq. (8), if  $(L - J' + J)$  is even, then for transitions within a given  $K$  stack, the parity factor  $[1 + \epsilon \epsilon' P(L)]$  will vanish if the initial and final parity indices are different. This implies a propensity rule, which will become increasingly rigorous as  $J$  and  $J'$  increase, that the cross sections for transitions which conserve the parity index will become increasingly dominant relative to the cross sections for the same  $J \rightarrow J'$  transition but where the parity index changes. Specifically, for collisions of atoms with a rotor with inversion doubling, as, for example,  $\text{NH}_3$ , because of the relation between the index  $\epsilon$  and the parity [Eq. (3)], for odd  $\Delta J$ , the large  $J$  propensity will be toward parity changing transitions, whereas for even  $\Delta J$ , the propensity will be toward parity conserving transitions.

It is useful to try to ascertain at what value of  $J$  we can reasonably expect this propensity to become apparent. From the triangular relation contained in the  $3j$  symbol in Eq. (15) and from the necessity that the parity factor be nonvanishing, we see that for transitions in which the parity index is conserved, the lowest value of  $L$  which will contribute in Eq. (15) will be  $L = |J' - J|$  and, for transitions in which the parity index changes,  $L = |J' - J| + 1$ . If we assume that the  $Q(L, 0, 0)$  factors are roughly the same for these two values of  $L$ , then an estimate of the ratio of the two  $J \rightarrow J'$  cross sections will be given by

$$\begin{aligned} \sigma_{J K \epsilon \rightarrow J' K' \epsilon}^K / \sigma_{J K \epsilon \rightarrow J' K' \epsilon}^K \approx R(J, J', K) = & \begin{pmatrix} J' & |J' - J| + 1 & J \\ K & 0 & -K \end{pmatrix}^2 \\ / \begin{pmatrix} J' & |J' - J| & J \\ K & 0 & -K \end{pmatrix}^2. & \quad (19) \end{aligned}$$

TABLE I. Minimum rotational quantum numbers for onset of propensity toward conservation of the parity index; transitions within a given  $K$  stack.<sup>a</sup>

$K^b$	$J_{\min}$				
	$\Delta J=1$	$\Delta J=2$	$\Delta J=3$	$\Delta J=4$	$\Delta J=5$
1	2	3	3	3	3
2	4	5	6	7	7
3	7	9	10	11	12
4	9	12	14	15	17
5	12	15	17	19	21
6	14	18	21	24	26
7	17	21	25	28	30
8	19	24	29	32	35
9	22	28	32	36	40
10	24	31	36	40	44

<sup>a</sup>Indicated are values of  $J_{\min}$  such that the estimated cross section ratio  $R(J, J+\Delta J, K)$  [Eq. (19)] will be less than  $\delta=0.5$  for  $J \geq J_{\min}$  [Eq. (21)].

<sup>b</sup>No entries are listed for  $K=0$ , since only the  $\epsilon=+1$  levels occur for this stack.

In the Appendix, we show how the asymptotic limit of the  $3j$  symbols [Eq. (16)] can be used to obtain the limit

$$\lim_{J, J' \rightarrow \infty} R(J, J', K) = (2\Delta J + 1)K^2/J_\zeta^2, \quad (20)$$

where  $J_\zeta = \min(J, J')$  and  $\Delta J = |J' - J|$ . Obviously, this ratio eventually goes to zero, as implied by the discussion of the preceding paragraph. The onset of the validity of this propensity rule can be considered to occur whenever the smaller of the two rotational quantum numbers ( $J'$  and  $J$ ) is greater than some minimal value  $J_{\min}$ , for which

$$R(J_{\min}, J_{\min} + \Delta J; K) \leq \delta, \quad (21)$$

where  $\delta$  is some number less than unity. If the limiting value of the ratio [Eq. (20)] is used, we find

$$J_{\min} \approx K[(2\Delta J + 1)/\delta]^{1/2}, \quad (22)$$

which indicates that the onset of the propensity rule developed here can be expected to occur at successively higher values of  $J$  as  $K$  increases, or, alternatively, as the change in rotational quantum number increases. Table I presents the values of  $J_{\min}$  determined for  $\delta=0.5$

by actual computation of the  $3j$  symbols in Eq. (19). The values agree very closely with those predicted by Eq. (22).

For inelastic transitions within the  $K$  stacks for which  $2K$  equals an integer multiple of  $n$ , the  $Q(L, 2K, 2K)$  terms do not vanish, so that it becomes necessary to examine the asymptotic behavior of the 3rd  $3j$  symbol in Eq. (14). Analogously to Eq. (16), one can show that<sup>28</sup>

$$\lim_{J, J' \rightarrow \infty} \begin{pmatrix} J' & L & J \\ -K & 2K & -K \end{pmatrix} = (-1)^{J'+K} (2J'+1)^{-1/2} d_{J',-J,2K}^L(\beta), \quad (23)$$

where  $\beta = \cos^{-1}(K/J')$  and  $d_{m,m'}^L(\beta)$  is a rotation matrix element. In the asymptotic limit,  $\beta \rightarrow \pi/2$ . Since in general the  $d_{m,m'}^L$  rotation matrix elements do not vanish for  $\beta = \pi/2$ , the third term in curly brackets in Eq. (14) will always contribute. Thus, the propensity rule derived earlier in this section will not, strictly speaking, apply to transitions within the  $2K=Nn$  stacks (only the *ortho* stacks in the case of  $\text{NH}_3$ , but both the *ortho* and *para* stacks in the case of  $\text{H}_2\text{CO}$ ). However, the contribution to Eq. (14) from the  $Q(L, 2K, 2K)$  terms will be nonvanishing only for  $L \geq 2K$ . To judge from Green's IOS calculations,<sup>8</sup> and from the analysis of Green's cross sections done by Richard and DePristo,<sup>37</sup> the  $Q(L, M, M')$  factors can be expected to decrease significantly in magnitude as  $L$  increases. Thus, although the cross sections for transitions in which the parity index changes will not *rigorously* vanish in the large  $J$  limit for transitions within the  $K$  stacks with  $2K=Nn$ , we can still expect a significant propensity toward conservation of the parity index. This argument can be expected to become increasingly valid as  $K$  increases, and  $2K$  becomes much larger than 1.

#### IV. PROPENSITY RULES: $\Delta K \neq 0$ , $\Delta J = 0$ TRANSITIONS

The discussion surrounding Eq. (23) can be used to show that it is not possible to use the asymptotic limits of the  $3j$  symbols in Eq. (13) to extract a large- $J$  propensity rule valid for all  $JK \rightarrow J'K'$  transitions. However, the approach developed in the preceding section can be applied successfully to the case of transitions which are inelastic in  $K$  but *elastic* in  $J$ . In this case, we use the asymptotic relation<sup>28</sup>

$$\begin{aligned} \lim_{J \gg L} \begin{pmatrix} J & L & J \\ \pm K' & M^\mp & -K \end{pmatrix} &= (-1)^{K-J} (2J+1)^{-1/2} d_{M^\mp,0}^L(\beta) \\ &= (-1)^{K-J} (2J+1)^{-1/2} \left[ \frac{(L-K \pm K')!}{(L+K \mp K')!} \right]^{1/2} P_L^{K \mp K'}(x), \end{aligned} \quad (24)$$

where  $x = \cos(\beta) = \mp K'/J$ , to reduce Eq. (13) to the following expression:

$$\begin{aligned} \lim_{J \text{ large}} \sigma_{J K \epsilon \rightarrow J' K' \epsilon'} &= N_K^2 N_{K'}^2 \sum_L \frac{1}{2} [1 + \epsilon' P(L)] \left\{ \frac{(L-K+K')!}{(L+K-K')!} [P_L^{K-K'}(x)]^2 Q(L, M^-, M^-) \right. \\ &\quad + 2\epsilon' \left[ \frac{(L-K+K')!(L-K-K')!}{(L+K-K')!(L+K+K')!} \right]^{1/2} P_L^{K-K'}(x) P_L^{K+K'}(x) \text{Re}[Q(L, M^-, M^-)] \\ &\quad \left. + \frac{(L-K-K')!}{(L+K+K')!} [P_L^{K+K'}(x)]^2 Q(L, M^+, M^+) \right\}. \end{aligned} \quad (25)$$

In the limit as  $J \rightarrow \infty$ , the argument of the associated Legendre polynomials in Eq. (25) will go to zero. From Eq. (18), we see that this implies that each term in the summation in Eq. (25) will vanish unless

$$(-1)^{L-K+K'} = (-1)^{L-K-K'} = +1. \quad (26)$$

Whenever this condition is satisfied, the parity factor  $[1 + \epsilon \epsilon' P(L)]$  will vanish unless the initial and final parity indices are identical. Thus, we see that the propensity toward conservation of the parity index is also valid for transitions which are inelastic in  $K$  but elastic in  $J$ .

As in Sec. III, it is possible to estimate, for each  $K, K'$  pair, the minimum value of  $J$  for which this propensity rule can be expected to become valid by consideration of the ratio of the cross sections for the  $JK\epsilon - JK'\epsilon'$ ,  $-\epsilon$  and the  $JK\epsilon - JK'\epsilon'$  transitions. In line with the discussion in the last paragraph of Sec. III, we expect the largest contribution to come from the smallest value of  $L$ , which, from the restrictions imposed by the parity factor, will be  $L = M^-$  (or  $M^+$ ) for the  $\epsilon - \epsilon$  transition and  $L = M^- + 1$  (or  $M^+ + 1$ ) for the  $\epsilon - -\epsilon$  transition. For a particular choice of  $K$  and  $K'$ , the determination of whether the  $M^+$  or  $M^-$  term (or both) in Eq. (25) will make a contribution depends on  $n$ . Following the discussion leading to Eq. (19), we can estimate the cross-section ratio for transitions in which the parity index changes to those in which the parity index is conserved as

$$\sigma_{JK\epsilon - JK'\epsilon', -\epsilon} / \sigma_{JK\epsilon - JK'\epsilon'} \approx R_J^{\pm}(K, K') \\ = \left( \begin{array}{ccc} J & M^{\pm} + 1 & J \\ \pm K' & M^{\pm} & -K \end{array} \right)^2 / \left( \begin{array}{ccc} J & M^{\pm} & J \\ \pm K' & M^{\pm} & -K \end{array} \right)^2. \quad (27)$$

Table II presents, for various  $K, K'$  pairs, the minimum value of  $J$  such that the ratio  $R_J^{\pm}(K, K')$  is less than  $\delta = 0.5$ . For transitions (and particular systems) in which both the  $M^+$  and  $M^-$  terms contribute, the larger of the values of  $J_{\min}$  would be the conservative estimate of the onset of the propensity toward conservation of the parity index. It is clear from Table II that this onset will occur at higher values of  $J$  as the initial value of  $K$  increases and as the magnitude of the change in  $K$  increases.

## V. PROPENSITY RULES IN THE BORN LIMIT

The propensity rules developed in the preceding two sections were derived within a sudden formulation of the collision dynamics. It is worthwhile to investigate whether the propensity toward conservation of the parity index remains valid under conditions where the sudden approximation is completely inappropriate, as for example in the weak coupling limit where one might use

TABLE II. Minimum rotational quantum numbers for onset of propensity toward conservation of the parity index; transitions elastic in  $J$  but inelastic in  $K$ .<sup>a</sup>

K	$J_{\min}$					
	$\Delta K = 1$		$\Delta K = 2$		$\Delta K = 3$	
	$M^+$	$M^-$	$M^+$	$M^-$	$M^+$	$M^-$
0	2	2	3	3	6	6
1	4	3	6	5	10	8
2	6	4	10	6	13	9
3	9	5	13	7	17	11
4	11	6	16	8	21	12
5	14	7	19	10	24	13
6	16	8	22	11	28	14
7	18	9	25	12	32	15
8	21	10	29	13	36	17
9	23	11	32	14	39	18

<sup>a</sup>Indicated are values of  $J_{\min}$  such that the estimated cross section ratio  $R_J^{\pm}(K, K + \Delta K)$  [Eq. (27)] will be less than  $\delta = 0.5$  for  $J \geq J_{\min}$ . The two columns under each  $\Delta K$  entry correspond to both choices of the  $\pm$  sign in Eq. (27).

the Born approximation.<sup>26</sup> Within the quantum Born approximation, the cross section is given by<sup>38</sup>

$$\sigma_{JK\epsilon - J'K'\epsilon'}^B = \frac{\pi}{(2J+1)k_{JK\epsilon}^2} \sum_{\mathcal{J}} (2\mathcal{J}+1) \sum_{L, L'} |T_{JL, K\epsilon, J'L', K'\epsilon'}^{\mathcal{J}}|^2, \quad (28)$$

where  $k_{JK\epsilon}$  is the wave vector for the initial channel,  $\mathcal{J}$  and  $L$  are, respectively, the total and orbital angular momenta of the atom-symmetric top system, and the Born  $T$ -matrix element is given by<sup>38</sup>

$$T_{JL, K\epsilon, J'L', K'\epsilon'}^{\mathcal{J}} = 4im_e \hbar^{-2} (k_{JK\epsilon} k_{J'K'\epsilon'})^{1/2} \\ \times \int_0^{\infty} \langle J'L'K'\epsilon' | \mathcal{J} \mathcal{M} | V | JLK\epsilon \mathcal{J} \mathcal{M} \rangle \\ \times j_{L'}(k_{J'K'\epsilon'} R) j_L(k_{JK\epsilon} R) R^2 dR. \quad (29)$$

Here,  $j_L(x)$  is a spherical Bessel function and  $m_e$  is the collision reduced mass.

In the integrand appears the matrix element of the interaction potential between states in the coupled angular momentum basis, defined by<sup>7</sup>

$$|JLK\epsilon \mathcal{J} \mathcal{M}\rangle = \sum_{M, L} (JMLM_L | J\mathcal{J} \mathcal{M}) |JMK\epsilon\rangle |LM_L\rangle, \quad (30)$$

where  $(\dots | \dots)$  is a Clebsch-Gordan coefficient,  $|LM_L\rangle$  is a spherical harmonic, and the  $|JMK\epsilon\rangle$  functions are defined by Eq. (1). Following Green,<sup>7</sup> the matrix element of the potential can be written as

$$\langle J'K'L'\epsilon' \mathcal{J} \mathcal{M} | V | JKL\epsilon \mathcal{J} \mathcal{M} \rangle = N_K N_{K'} (-1)^{J'+J'+K'-\mathcal{J}} [(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2} \sum_{\lambda \mu} [(2\lambda+1)/4\pi]^{1/2} \\ \times v_{\lambda \mu}(R)^{1/2} [1 + \epsilon \epsilon' (-1)^{J'+J'+\lambda+\mu}] \begin{pmatrix} L & L' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J' & L' & \mathcal{J} \\ L & J & \lambda \end{Bmatrix} \\ \times \left[ \omega \begin{pmatrix} J' & \lambda & J \\ -K' & \pm \mu & K \end{pmatrix} + \epsilon \begin{pmatrix} J' & \lambda & J \\ -K' & \mu & -K \end{pmatrix} \right], \quad (31)$$

where  $\{\cdot\cdot\cdot\}$  is a  $6j$  symbol and where  $v_{\lambda\mu}(R)$  is a particular coefficient in the expansion of the potential. There will be a contribution from the first term in large square brackets only if  $\pm\mu = K' - K$ , in which case<sup>7</sup>

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

There will be a contribution from the second term only if  $\mu = K' + K$ .

Consider first the case where  $K' = K$ . Then, the summation in Eq. (31) is restricted to the  $\mu = 0$  and  $\mu = 2K$  terms. If  $2K$  is not an integer multiple of  $n$ , then only the first term contributes, so that the summation becomes

$$\sum_{\lambda} [(2\lambda + 1)/4\pi]^{1/2} v_{\lambda 0}(R) \frac{1}{2} [1 + \epsilon \epsilon' (-1)^{J+J'+\lambda}] \\ \times \begin{pmatrix} L & L' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J' & L' & J \\ L & J & \lambda \end{Bmatrix} \begin{pmatrix} J' & \lambda & J \\ -K & 0 & K \end{pmatrix}. \quad (32)$$

The parity factor and the last  $3j$  symbol are the same as those present in Eq. (15). Thus, the discussion surrounding Eqs. (16)–(18) can be applied directly here to demonstrate that in the large  $J$  limit the summation in Eq. (32), and, from Eq. (29), the  $T$ -matrix element itself, will vanish if  $\epsilon \neq \epsilon'$ .

Thus, the propensity toward conservation of the parity index for transitions within a  $K$  stack is equally valid within both the Born and sudden limits. A similar argument can be used to demonstrate from Eq. (31) that the propensity toward conservation of the parity index for transitions which are elastic in  $J$  but inelastic in  $K$  is also valid within the Born limit.

## VI. COMPARISON WITH THEORETICAL CALCULATIONS

Recently, Green<sup>9</sup> has published an extensive table of inelastic rate constants for the  $p$ -NH<sub>3</sub> + He system, determined within the accurate coupled-states treatment of the collision dynamics. The rate constants are defined in terms of the inelastic cross sections as<sup>39</sup>

$$k_{J K \epsilon \rightarrow J' K' \epsilon'}(T) = \left[ \frac{8}{\pi m_c (kT)^3} \right]^{1/2} \int_0^\infty \sigma_{J K \epsilon \rightarrow J' K' \epsilon'}(E) E \\ \times \exp(-E/kT) dE, \quad (33)$$

where  $k$  is Boltzmann's constant and  $T$  is the assumed translational temperature which describes the distribution of relative velocities of the He–NH<sub>3</sub> system. Obviously, if the underlying cross sections exhibit a strong propensity toward conservation of the parity index, then a sufficient condition for a similar propensity to be manifest in the resulting rate constants is that the significant contributions to the integrand in Eq. (33) arise from a range of translational energies within which either a Born or sudden treatment of the dynamics is valid. This is not a necessary condition; it is entirely possible that the propensity toward conservation of the parity index holds outside of both of these dynamical limits.

TABLE III. Ratio of rate constants for transitions where the parity index changes to rate constants for transitions where the parity index is conserved; NH<sub>3</sub>–He collisions.<sup>a</sup>

J	K	Ratio <sup>b</sup>			
		T = 15 K	30 K	100 K	300 K
ΔK = 0 ΔJ = 1					
1	1 <sup>c</sup>	0.17	0.18	0.17	0.18
2	1	0.086	0.086	0.076	0.081
3	1	0.062	0.061	0.056	0.057
2	2 <sup>c</sup>	0.16	0.18	0.17	0.19
3	2	0.14	0.14	0.13	0.12
ΔK = 0 ΔJ = 2					
2	1 <sup>c</sup>	1.8	2.1	2.6	3.0
ΔK = 1 ΔJ = 0					
3	1	0.098	0.11	0.16	0.25
4	1	0.058	0.058	0.069	0.089
ΔK = 2 ΔJ = 0					
4	2 <sup>c</sup>	0.85	0.89	1.09	1.22

<sup>a</sup>Rate constants taken from Ref. 9.

<sup>b</sup> $k_{J K \epsilon \rightarrow J' K' \epsilon'}/k_{J K \epsilon \rightarrow J' K' \epsilon'}$ , where the rate constants are defined by Eq. (33) and the value of  $\epsilon$  is taken to be +1. The ratios for  $\epsilon = -1$  are virtually identical.

<sup>c</sup>The value of  $J$  is too small to satisfy the criterion for validity of the propensity rule toward conservation of the parity index. See Secs. III and IV and Tables I and II.

Table III presents the ratio of the rate constants for NH<sub>3</sub>–He transitions, elastic in either  $K$  or  $J$ , and with a change in parity index, to the rate constant for the same  $J, K$  transition, but where the parity index is conserved. Independent of the temperature the propensity toward conservation of the parity index is clearly evident for all the transitions for which rate constants were reported by Green and for which the initial value of  $J$  is at least equal to the minimum value for onset of the propensity rule (Tables I and II). Indeed, the propensity is also apparently obeyed for several transitions involving initial rotational quantum numbers which are less than the appropriate values in Tables I and II. We note that for given values of  $K$  and  $\Delta K$ , the ratios decrease as  $J$  increases. This is to be expected, since as  $J \rightarrow \infty$  the propensity rules become rigorous selection rules.

Table IV displays similar ratios for the H<sub>2</sub>CO–He system determined for all the  $J \rightarrow J'$ ,  $\Delta K = 0$ , and  $K - K'$ ,  $\Delta J = 0$  rate constants tabulated by Green, Garrison, Lester, and Miller.<sup>6</sup> It is worthwhile to consider first the transitions elastic in  $K$ . Since H<sub>2</sub>CO has a twofold axis of rotation, all three terms in curly brackets in Eq. (14) will contribute, so that the development of the propensity rule, which proceeds through Eq. (15) by neglect of the second and third terms in Eq. (14), is no longer rigorous. Despite this fact, the propensity toward conservation of the parity index is remarkably well satisfied, with very few exceptions. The contribution of the second term in Eq. (14), which will add to the two others either constructively or destructively depending

TABLE IV. Ratio of cross sections for transitions where the parity index changes to rate constants for transitions where the parity index is conserved;  $\text{H}_2\text{CO}-\text{He}$  collisions.<sup>a</sup>

		Ratio <sup>b</sup>			
		$\epsilon = -1^{\circ}$		$\epsilon = +1^{\circ}$	
J	K <sup>c</sup>	T=30 K	80 K	T=30 K	80 K
$\Delta K=0, \Delta J=1$					
1	1 <sup>d</sup>	0.57	0.76	1.02	1.10
2	1	0.27	0.36	0.61	0.60
3	1	0.20	0.28	0.48	0.43
4	1	0.20	0.24	0.30	0.29
5	1	0.21	0.23	0.27	0.28
6	1	0.18	0.22	0.27	0.22
7	1	0.18	0.21	0.25	0.24
3	2 <sup>d</sup>	0.29	0.37	0.29	0.39
$\Delta K=0, \Delta J=2$					
2	1 <sup>d</sup>	0.31	0.35	1.42	0.87
3	1	0.41	0.38	1.06	0.81
4	1	0.47	0.33	0.87	0.74
5	1	0.44	0.37	0.85	0.65
6	1	0.51	0.38	0.78	0.66
$\Delta K=0, \Delta J=3$					
3	1	0.44	0.45	1.04	0.78
4	1	0.56	0.61	1.00	0.67
5	1	0.55	0.50	1.00	0.77
$\Delta K=0, \Delta J=4$					
3	1	0.32	0.44	3.2	2.1
4	1	0.52	0.50	3.0	2.3
$\Delta J=0, \Delta K=2$					
3	0	e	e	0.77	0.80
4	0	e	e	0.86	0.81
4	1 <sup>f</sup>	2.0	1.7	1.0	1.2
5	1 <sup>f</sup>	3.9	3.5	0.80	1.1

<sup>a</sup>Rate constants taken from Ref. 6.<sup>b</sup> $k_{JK\epsilon-J+\Delta J, K+\Delta K, -\epsilon}/k_{JK\epsilon-J+\Delta J, K+\Delta K, \epsilon}$ , where rate constants are defined by Eq. (33).<sup>c</sup>In conventional notation the levels are designated  $J_{KK'}$ , where  $K'$  is the projection quantum number in the oblate limit. See Ref. 33 and Eq. (6).<sup>d</sup>The value of  $J$  is too small to satisfy the criterion for validity of the propensity rule for conservation of the parity index. See Secs. III and IV and Tables I and II.<sup>e</sup>Only  $\epsilon = +1$  levels exist for  $K=0$ .<sup>f</sup>For these two transitions  $M=2$ , so that the values of  $J$  are too small to satisfy the criterion for validity of the propensity rule (see Table II and the discussion at the end of Sec. VI).

on the sign of  $\epsilon'$ , is responsible for the large variation in the rate constant ratios for the  $\epsilon = -1 \rightarrow \epsilon = \pm 1$  and  $\epsilon = +1 \rightarrow \epsilon = \pm 1$  cases.

For the transitions which are elastic in  $J$  but inelastic in  $K$ , both the  $M^-$  and  $M^+$  terms in Eq. (25) will contribute, again because  $\text{H}_2\text{CO}$  has only a twofold axis of rotation. For the  $K=1-3$  transitions in Table IV,  $M^-$  is 2 so that  $J_{\min}$  (Table II) is 6, which probably explains why the propensity rule is not satisfied.

## VII. COMPARISON WITH DOUBLE RESONANCE DATA

In the double resonance experiments on  $\text{NH}_3$  carried out by Oka, Shimizu, and their co-workers,<sup>13-15,18-21</sup>

a strong cw microwave or infrared source is used to alter the relative population of the two levels of a particular  $JK$  inversion doublet in  $\text{NH}_3$ , called the pump doublet, and then the relative change in intensity  $\Delta I/I$  is observed in the absorption of a weak cw probe signal tuned to another inversion doublet, called the signal doublet. An analysis of the competing rate processes in this four-level system indicates<sup>15</sup> that the sign of  $\Delta I/I$  is determined by the relative size of the collisional rate constant between the lower levels of the pump and probe doublets as compared to the rate constant between the lower level of the pump doublet and the upper level of the probe doublet. For the microwave-microwave double resonance experiments<sup>13-15</sup> on finds<sup>9,10,15</sup>

$$\text{sign}(\Delta I/I) = \text{sign}(k_{lu} - k_{ll}) . \quad (34)$$

In these experiments, the pump acts to increase the population of the upper level of the pump doublet relative to the population in the lower level. By contrast, in the infrared-microwave double resonance experiments by Shimizu and co-workers,<sup>18,19</sup> the pump acts to decrease the population in the upper level of the pump doublet. This difference implies that a steady-state analysis of Shimizu's experiments will lead to a relationship opposite to Eq. (34), namely,

$$\text{sign}(\Delta I/I) = \text{sign}(k_{ll} - k_{lu}) . \quad (35)$$

As demonstrated in the preceding three sections, in the large  $J$  limit, we expect a strong propensity toward conservation of the parity index for both the  $\Delta J=0$ ,  $\Delta K$ , and  $\Delta K=0$ ,  $\Delta J$  transitions. From Eq. (2), we observe that within a given  $K$  stack the parity indices of the upper and lower inversion levels alternate with  $J$ . Thus, for the  $\Delta K=0$ ,  $\Delta J$  transitions, we anticipate that the lower-upper transition rate will be greater than the lower-lower rate when  $\Delta J$  is odd and vice versa when  $\Delta J$  is even. From Eq. (34), we predict for Oka's experiments,<sup>13-15</sup>  $\Delta I/I > 0$  for  $\Delta K=0$ ,  $\Delta J=\text{odd}$  and  $\Delta I/I < 0$  for  $\Delta K=0$ ,  $\Delta J=\text{even}$ . The predicted signs of  $\Delta I/I$  will be inverted for the experiment of Shimizu and co-workers, as is clear from Eq. (35). Similarly, from Eq. (2), we see that for a given value of  $J$  the assignment of the parity indices to the upper and lower inversion levels is independent of  $K$ . Thus, for the  $\Delta J=0$ ,  $\Delta K$  transitions, we anticipate that at high  $J$  the lower-lower rate will be greater than the lower-upper rate, so that the sign of  $\Delta I/I$  is predicted to be negative in the experiments of Oka<sup>13-15</sup> and positive in those of Shimizu.<sup>18,19</sup>

Table V compares these predictions with the actual experimental values of  $\Delta I/I$  for collisions of  $\text{NH}_3$  with He, Ar, and Xe, as well as with  $\text{H}_2$ . It might be reasonable to treat  $\text{H}_2$  as a structureless collision partner, since the molecule is nonpolar and has large rotational spacings.<sup>40</sup> We have included in Table V all the available experimental data for both  $\Delta K=0$ ,  $\Delta J$ , and  $\Delta J=0$ ,  $\Delta K$  transitions which satisfy the criteria for onset of the propensity toward conservation of the parity index (Tables I and II) and some data for  $J$  values just slightly below the values of  $J_{\min}$  in Tables I and II. For the  $\Delta K=0$ ,  $\Delta J=1$  transitions at large  $K$ , the values of  $J$  were considerably smaller than the appropriate values of  $J_{\min}$ , but the  $\Delta I/I$  data was included nevertheless. The



TABLE V. Change in intensity of absorption in four-level double resonance experiments on  $\text{NH}_3$ +noble gas mixtures.<sup>a</sup> Comparison is made with predictions based on conservation of the parity index.<sup>b</sup>

Pump		Signal		$\Delta I/I(\%)$				
<i>J</i>	<i>K</i>	<i>J</i>	<i>K</i>	H <sub>2</sub>	He	Ar	Xe	Predicted sign
$\Delta K=0, \Delta J=1$								
2	1	1	1 <sup>c</sup>	+5.2 <sup>d</sup>	<u>-3.5<sup>d,e</sup></u>	+5.8	+6.3	+
3	1	2	1		+2.5	+5.6	+5.6	+
4	1	3	1		+4.4	+6.3	+5.6	+
3	2	2	2 <sup>c</sup>	+2.3 <sup>d</sup>	<u>-4.2<sup>d,e</sup></u>			+
4	2	3	2		0.0	+6.9	+2.3	+
5	3	4	3 <sup>c</sup>		0.0	+4.7	+1.3	+
5	4	4	4 <sup>c</sup>		0.0	+2.2	+1.5	+
6	5	5	5 <sup>c</sup>		+1.1	+1.1	+0.9	+
7	6	6	6 <sup>c</sup>		+1.0	+0.9	+0.6	+
8	7	7	7 <sup>c</sup>		+0.8	0.0	0.0	+
8	7	7	7 <sup>c</sup>		-1.8 <sup>f</sup>			- <sup>g</sup>
8	7	9	7 <sup>c</sup>		-6.1 <sup>f</sup>			- <sup>g</sup>
9	8	8	8 <sup>c</sup>		+1.3	0.0	0.0	+
$\Delta K=0, \Delta J=2$								
4	1	2	1 <sup>c</sup>		-2.2	0.0	-0.9	-
4	2	2	2 <sup>c</sup>		0.0	<u>+0.6<sup>e</sup></u>	-0.3	-
8	7	10	7 <sup>c</sup>		+0.3 <sup>f</sup>			+ <sup>g</sup>
$\Delta K=1, \Delta J=0$								
2	1	2	2 <sup>c</sup>		-3.0	<u>+0.6<sup>e</sup></u>	<u>+2.3<sup>e</sup></u>	-
3	1	3	2		-2.5	-2.5	-0.9	-
4	1	4	2		-5.0	-4.1	-2.5	-
8	7	8	8 <sup>c</sup>		<u>-0.2<sup>e,f</sup></u>			+ <sup>g</sup>
$\Delta K=2, \Delta J=0$								
4	2	4	4		0.0	0.0	0.0	-
8	7	8	5 <sup>c</sup>		<u>-0.2<sup>e,f</sup></u>			+ <sup>g</sup>

<sup>a</sup>See Ref. 15 for a description of the experiments. All data are taken from Ref. 13 unless otherwise indicated. The quoted uncertainty in the experiments of Oka (Refs. 13 and 14) is  $\pm 0.5\% - \pm 1.0\%$  (Ref. 13).

<sup>b</sup>See Sec. VII of the text.

<sup>c</sup>Either  $J_{\text{pump}}$  or  $J_{\text{signal}}$  (or both) are too small to justify the criterion for validity of the propensity rule for conservation of the parity index. See Secs. III and IV and Tables I and II.

<sup>d</sup>Experimental data from Ref. 14.

<sup>e</sup>The experimental values which differ from the theoretical predictions are underlined.

<sup>f</sup>Values from infrared-microwave double resonance experiments. See Ref. 19.

<sup>g</sup>For the infrared-microwave double resonance experiments the predicted value of  $\Delta I/I$  is opposite in sign to the prediction for the microwave-microwave double resonance experiments. See Sec. VII.

agreement between the signs of the experimental values of  $\Delta I/I$  and the predictions is perfect in the case of transitions where  $\min(J_{\text{pump}}, J_{\text{signal}})$  satisfies the criteria contained in Tables I or II, and even excellent for most of the other transitions. The reader should note that any disagreement is statistically significant only when the magnitude of the values of  $\Delta I/I$  exceeds the quoted<sup>13</sup> experimental uncertainty of  $\pm 0.5\% - \pm 1.0\%$ . Notable discrepancies in Table V are the 21-11 and 32-22 pairs for  $\text{NH}_3$ -He collisions, where the signs of the experimental values of  $\Delta I/I$  also disagree with the predictions

of accurate scattering calculations based on reasonable potential surfaces.<sup>9,10</sup>

## VIII. PROPENSITY RULES FOR ROTATIONAL TRANSITIONS IN LINEAR POLYATOMIC MOLECULES

We consider now inelastic collisions involving linear polyatomic molecules. The coupling of the rotational motion with degenerate bending vibrations results in a doubling of the rotational levels, denoted as  $l$  doubling.<sup>41</sup> The rotational motion is formally equivalent to that of a slightly asymmetric top, and can be described by the wave function of Eq. (4), where the quantum number  $K$  is equal to the number of vibrational quanta in the bending mode.<sup>42</sup> For  $K=1$ , which is the usual situation at low temperature, the  $\epsilon=-1$  level lies lower in energy, for all  $J$ .<sup>43</sup> Because of the equivalency with the rotational motion of an asymmetric top, the discussion contained in Secs. II and III can be applied directly to demonstrate that the propensity toward conservation of the parity index will apply also to rotationally inelastic collisions of  $l$ -doubled linear molecules with structureless atoms. The relation between  $\epsilon$  and the ordering of the  $l$  doublets, discussed above, then indicates that collisional mixing of the upper and lower of the  $l$ -doublet ladders will be much less probable than transfer within one of these ladders.

By means of a time-dependent four-level microwave double-resonance technique,<sup>16,17</sup> Cohen and Wilson<sup>17</sup> have studied rotational energy transfer in collisions of HCN with noble gases. The  $J=10$   $l$  doublet of the  $v=1$  bending level was pumped and the  $J=11, 12$ , and  $13$  doublets were observed. Cohen and Wilson were able to extract from their experimental results relative values of the rate constants for transfer from the  $J=10$  to the  $J=11, 12$ , and  $13$  levels for the two parity index conserving transitions ( $\epsilon=1 \rightarrow 1$ ,  $\epsilon=-1 \rightarrow -1$ ; both treated as equivalent) and for the two parity index changing transitions ( $\epsilon=\pm 1 \rightarrow \mp 1$ ; both treated as equivalent). In their notation, these rates are labeled  $k_{\Delta J, a}$  and  $k_{\Delta J, n}$ , respectively. A propensity toward conservation of the parity index would predict for all  $J$ ,

$$k_{\Delta J, a} > k_{\Delta J, n}. \quad (36)$$

Since the rotational quantum numbers are much larger than  $J_{\text{min}}$  for  $K=1$  (Table I), we expect the propensity rule to be well satisfied.

For the set of rates which best satisfy<sup>44</sup> the HCN-Ar, Xe data of Cohen and Wilson,<sup>17</sup> Eq. (36) is indeed satisfied for  $\Delta J=1, 2$ , and  $3$ , since, in fact, all of the  $\epsilon$  changing rates are found to be negligibly small. For collisions of HCN with He, it was not possible to select a unique set of rates from the double resonance experiments alone. Nevertheless, in all three sets of rate constants presented by Cohen and Wilson,<sup>17</sup> Eq. (36) is satisfied for  $\Delta J=2$  and  $3$ . For  $\Delta J=1$ , Eq. (36) is strongly satisfied for one set of rates, and only slightly violated for the other two. Thus, within the degree of nonuniqueness which characterizes the analysis of the HCN-He experiments, we conclude that the data of Cohen and Wilson<sup>17</sup> does confirm the propensity toward conservation of the parity index.

## IX. SEMICLASSICAL INTERPRETATION

The propensity rules developed in Secs. III and IV arise from taking symmetry adapted linear combinations of the  $|JMK\rangle$  and  $|JM, -K\rangle$  functions [Eqs. (1) and (4)]. Since this type of symmetrization accompanies, in a natural way, the quantum treatment of the collision dynamics, one is led to wonder if the large- $J$  propensity toward conservation of the parity index is a purely quantum mechanical effect which would not arise if the rotationally inelastic collision dynamics was treated by a standard classical trajectory approach,<sup>45-50</sup> as, for example, the propensity toward parity conservation seen in collisions of near homonuclear diatomics.<sup>49-51</sup> An analogous quantum effect, similar to the observed “ $\Delta j$  asymmetry” in collisions of diatomic molecules in  $^1\Pi$  states,<sup>52,53</sup> has been predicted by Poppe<sup>53</sup> for collisions of symmetric top molecules.

To examine this question, we first observe that an alternative, but still fully quantum, description equally valid in the sudden limit, would involve expressing the  $S$ -matrix elements between  $|JMK\rangle$  states as linear combinations of  $S$ -matrix elements between the primitive  $|JMK\rangle$  states.<sup>7,37</sup> In the coupled angular momentum representation,<sup>54</sup> we would have<sup>55</sup>

$$S_{JLK\epsilon, J'L'K'\epsilon'}^g = N_K N_{K'} (S_{JLK, J'L'K'}^g + \epsilon \epsilon' S_{JL-K, J'L'-K'}^g + \epsilon S_{JL-K, J'L'K'}^g + \epsilon' S_{JLK, J'L'-K'}^g) . \quad (37)$$

Since the integral cross section can be expressed as a sum over squares of the  $S_{JLK\epsilon, J'L'K'\epsilon'}^g$  matrix elements [equivalent to Eq. (28)], it is clear that the cross section for a particular  $JK\epsilon \rightarrow J'K'\epsilon'$  transition will vanish only if the individual  $S$ -matrix elements themselves vanish. From Eq. (37), this implies that a sufficient condition for the validity of the large- $J$  limits developed in Secs. III and IV is that the following relations hold within the sudden limit:

$$\lim_{J, J' \rightarrow \infty} S_{JLK, J'L'K'}^g = S_{JL-K, J'L'-K}^g , \quad (38)$$

$$\lim_{J, J' \rightarrow \infty} S_{JLK, J'L'-K}^g = S_{JL-K, J'L'K}^g , \quad (39)$$

$$\lim_{J \rightarrow \infty} S_{JLK, JL'K'}^g = S_{JL-K, JL'-K'}^g , \quad (40)$$

and

$$\lim_{J \rightarrow \infty} S_{JLK, JL'-K'}^g = S_{JL-K, JL'K'}^g . \quad (41)$$

The implication of these equations is that for transitions which are either elastic in  $J$  or elastic in  $K$ , in the large  $J$  limit the scattering is independent of the initial direction of rotation of the top with respect to the symmetry axis.

Miller has shown<sup>4,51,56</sup> how the semiclassical analogues to  $S$ -matrix elements like those in Eqs. (37)–(41) can be written, in primitive<sup>4,56</sup> form, as

$$S_{JLK, J'L'K'}^g = \sum_i [P_{JLK, J'L'K'}^g(q_i)]^{1/2} \exp[i\phi_{JLK, J'L'K'}^g(q_i)] . \quad (42)$$

Here, the sum is over all classical paths (trajectories) which connect the particular initial ( $JLK$ ) and final ( $J'L'K'$ ) final states; the coordinates  $q_i$  denote the

initial values of the coordinates, conjugate to the momenta  $J, L, K$ , which characterize these trajectories; the quantity  $P_{JLK, J'L'K'}^g$  is the purely classical transition probability for this trajectory  $i$ , which can be expressed as a Jacobian of the final momenta ( $J'L'K'$ ) with respect to the initial coordinates<sup>4,56</sup>; and  $\phi_{JLK, J'L'K'}^g$  is the semiclassical phase shift accumulated along the classical path. A purely classical treatment of the dynamics would involve the neglect of all the phase factors in Eq. (42). It is obvious that if the classical transition probabilities in Eq. (42) obey the symmetry relations (38)–(41), then the propensity toward conservation of the parity index will be not lost by neglect of the quantum phases of the individual trajectories. If this is true, then for molecules where the degeneracy of the  $JK\epsilon$  doublets is lifted, as would occur if inversion,  $K$ , or  $l$  doubling were present, then a purely classical calculation could reveal the relative dominance of one type of transition (lower  $\rightarrow$  lower, upper  $\rightarrow$  upper) as against the other type (lower  $\rightarrow$  upper or vice versa).

Augustin and Miller<sup>4</sup> have reported calculations of the energy dependence of the cross sections for the  $JK\epsilon = 11 \pm 1 - 21 \pm 1$  levels in  $\text{H}_2\text{CO}$  (in conventional spectroscopic notation  $1_{11}, 1_{10} - 2_{12}, 2_{11}$ <sup>57</sup>), determined with and without inclusion of the phases in Eq. (42). Although numerical values are not given, it is clear from Fig. 2 of Ref. 4 that, except perhaps in the threshold region, the ratios of the cross sections for the transitions which conserve the parity index ( $1_{11} - 2_{12}$  and  $1_{10} - 2_{11}$ ) to the cross sections for the corresponding transitions where the value of  $\epsilon$  changes ( $1_{11} - 2_{11}$  and  $1_{10} - 2_{12}$ ) are comparable to the ratios determined from the quantum cross sections of Green *et al.*<sup>6</sup> (Table IV). Although the initial value of  $J$  is less than the value of  $J_{\text{min}}$  from Table I, so that we might not expect the propensity toward conservation of the parity index to be satisfied strongly (Table IV), nevertheless, the good agreement between the quantum and classical ratios suggests that classical calculations will be able to reproduce the expected propensity rule. This gives support to the work of Townes and Cheung,<sup>12</sup> where a classical impulsive model was used to explain the anomalous collisional cooling of formaldehyde.

## X. CONCLUSION

In this article, we have used the infinite-order-sudden formulation of atom-symmetric top collisions given by Green<sup>8</sup> to show that, for processes which are either elastic in  $K$  but inelastic in  $J$ , or elastic in  $J$  but inelastic in  $K$ , a propensity toward conservation of the parity index of the rotational wave function will arise and become increasingly apparent as the total angular momentum increases. This propensity rule appears to apply whenever the molecular system is formally analogous to a symmetric top, as, for example, an  $l$ -doubled linear polyatomic (discussed in Sec. VIII), or a diatomic molecule in an electronic state with nonzero spin or orbital angular momentum (discussed in two previous articles<sup>22</sup>). For low values of  $K$ , we have demonstrated that the propensity toward conservation of the parity index can be expected to be apparent even at low values of the total angular momentum. We fur-

ther showed how the identical propensity rule would characterize collisions in the weak coupling limit, where a Born rather than sudden treatment of the dynamics would be appropriate. It is important to observe that the propensity rules developed here are independent of the description of the interaction potential, and thus are far more general than similar rules<sup>13,15,17</sup> derived from an assumed dominance of certain terms in the expansion of the potential.

A comparison with available cross sections for the  $\text{NH}_3\text{-He}$  and  $\text{H}_2\text{CO-He}$  systems demonstrated the accuracy of the propensity rule developed here, even for many transitions where the initial or final values of  $J$  lay outside the estimated region of validity. The analysis of four-level microwave or infrared-microwave double resonance experiments, both cw<sup>13-15,18,19</sup> and pulsed,<sup>16,17</sup> indicates that both the signs and magnitudes of observed intensity changes depend critically on the differences between the rates for transitions which conserve the parity index and for those in which the parity index changes. We have seen that the available experimental data for collisions of  $\text{NH}_3$  and  $\text{HCN}$  with noble gases is in excellent agreement with predictions based on the propensity rule developed here, again even for many transitions which lie outside the expected region of validity. In passing, we note that propensities will obviously not be seen in experiments where the inversion,  $K$ , or  $l$  doublings are not resolved.

Finally, we discussed how the propensity toward conservation of the parity index, which was uncovered within a quantum treatment of the collision dynamics, could persist in a purely classical treatment, provided the scattering were virtually independent of the initial direction of the internal rotation of the symmetric top. Outside of the study by Augustin and Miller, where numerical results were obtained only for a few transitions between low- $J$  levels in  $\text{H}_2\text{CO}$ , there do not exist, to our knowledge, any other classical trajectory studies of atom-symmetric top collisions. Other such studies are needed, to ascertain whether the conservation of the parity index is indeed classically observable.

The propensity rules developed here apply only to collisions which are elastic either in  $J$  or  $K$ . It is intriguing to speculate whether analogous propensity rules apply to the other possible inelastic transitions. From the discussion at the beginning of Sec. IV, we realize that a different approach will be necessary. Also, the present article deals only with atom-molecule collisions. It would be worthwhile to extend the present analysis to collisions involving two molecular tops, for which much double resonance data already exists.<sup>15,16,18,20,21</sup> Further work aimed at revealing the subtle propensities of inelastic scattering will certainly provide a clearer and more intellectually satisfying way of analyzing the apparent complexity of highly state resolved data on rotational energy transfer.

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## APPENDIX

From Eq. (16), we have

$$\lim_{J, J' \rightarrow \infty} R(J, J'; K) = \{ (2J' - 2J)! [P_{\Delta J+1}^{\Delta J}(x)]^2 \} / \{ (2J' - 2J + 1)! [P_{\Delta J}^{\Delta J}(x)]^2 \}, \quad (\text{A1})$$

where  $R(J, J'; K)$  is defined by Eq. (19), where  $x = K/J'$ , and where  $\Delta J = J' - J$  and is assumed positive. The limit of the associated Legendre polynomial in the denominator can be evaluated by means of Eq. (18) to give

$$\lim_{x \rightarrow 0} [P_{\Delta J}^{\Delta J}(x)]^2 = [1 \cdot 3 \cdot 5 \cdots (2\Delta J - 1)]^2. \quad (\text{A2})$$

The limit of the associated Legendre polynomial in the numerator can be evaluated by expansion as a power series

$$P_{\Delta J+1}^{\Delta J}(x) = P_{\Delta J+1}^{\Delta J}(0) + dP_{\Delta J+1}^{\Delta J}(x)/dx|_{x=0}x + \cdots \quad (\text{A3})$$

Here, Eq. (18) can be used to show that the first term vanishes. The second term can be evaluated from the known formula<sup>36</sup>

$$dP_l^m(x)/dx|_{x=0} = 2^{m+1} \pi^{-1/2} \sin[\frac{1}{2}\pi(l+m)] \times \Gamma[\frac{1}{2}(l+m+2)] / \Gamma[\frac{1}{2}(l-m+1)]. \quad (\text{A4})$$

Thus,

$$\lim_{x \rightarrow 0} [P_{\Delta J+1}^{\Delta J}(x)]^2 = x^2 [1 \cdot 3 \cdot 5 \cdots (2\Delta J - 1)(2\Delta J + 1)]^2. \quad (\text{A5})$$

Substitution of Eqs. (A5) and (A2) into Eq. (A1) yields Eq. (20).

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