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# Quantum scattering studies of inelastic collisions of $\text{NH}(A^3\Pi)$ with helium: Fine-structure and $\Lambda$ -doublet propensities

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The results of full close-coupled calculations of state-to-state cross sections for rotationally inelastic collisions of  $\text{NH}$  in its  $A^3\Pi$  electronic state with helium, based on the recently calculated *ab initio* potential energy surfaces of Jonas and Staemmler [Z. Phys. D **14**, 143 (1989)], are presented. The calculated  $\Lambda$ -doublet resolved cross sections have been compared with predictions based on formal analyses of the scattering equations both in the Hund's case (a) and (b) limits. For transitions involving low  $J$  levels, a strong propensity toward conservation of the  $e/f$  label was found, as expected in the case (a) limit. For higher  $J$ , the cross sections connecting related pairs of  $\Lambda$ -doublet levels were found to be unequal, reflecting a quantum mechanical interference between the two potential energy surfaces arising from the interaction of a molecule in a  $\Lambda > 0$  state with a perturber. For transitions connected by even  $l$  terms in the expansion of the potentials, a simple analysis, based on the relative strengths of the  $l = 2$  coupling matrix elements of the electrostatic potential, was found capable of explaining the relative ordering of the cross sections in most cases. A similar success for predicting transitions coupled by odd  $l$  terms in the potential was not found; this reflects the fact that the  $l = 3$  terms are relatively small for the  $\text{NH}(A^3\Pi)$ -He interaction. The calculated cross sections for large  $J$  also exhibit a propensity for conservation of the fine-structure label, as expected in the case (b) limit. As an indication of the reliability of the calculated interaction potential and our treatment of the collision dynamics, appropriately summed calculated cross sections reproduce well the experimental rates for transitions from selected  $f$  levels into all  $e$  levels, as measured by Stuhl and co-workers.

## I. INTRODUCTION

In recent years there have been a considerable number of studies of inelastic collisions of open-shell molecules. These have included both formal and computational theoretical, as well as state-resolved experimental, investigations; the latter have principally employed molecular beam or laser double resonance techniques. The overwhelming bulk of these studies have dealt with molecules in  $^2\Sigma^+$ ,  $^1\Pi$ , and  $^2\Pi$  electronic states, including  $\text{CaCl}(X^2\Sigma^+)$ ,<sup>1</sup>  $\text{OH}(A^2\Sigma^+)$ ,<sup>2-4</sup>  $\text{Na}_2(B^1\Pi_u)$ ,<sup>5-8</sup>  $\text{Li}_2(B^1\Pi_u)$ ,<sup>9,10</sup>  $\text{CaF}(A^2\Pi)$ ,<sup>11,12</sup>  $\text{OH}(X^2\Pi)$ ,<sup>13-18</sup>  $\text{NO}(X^2\Pi)$ ,<sup>19,20</sup>  $\text{CH}(X^2\Pi)$ ,<sup>21</sup>  $\text{CN}(X^2\Sigma^+)$ ,<sup>22,23</sup>  $\text{N}_2^+(X^2\Sigma_g^+)$ ,<sup>24</sup>  $\text{CdH}(A^2\Pi)$ ,<sup>25</sup> and  $\text{ZnH}(A^2\Pi)$ .<sup>26</sup> From this body of work, considerable insight into the dynamics of such inelastic collisions, for example, the origin of spin state and  $\Lambda$ -doublet propensities, has been obtained. A qualitative analysis,<sup>27</sup> based on first-order perturbation theory, was shown to be very useful in predicting which transitions between specific initial and final  $\Lambda$ -doublet levels would be favored in collisions of  $^2\Pi$  molecules following Hund's case (b), or intermediate case, coupling.

By contrast, considerably less attention has been paid to collisions of molecules in electronic states of triplet spin mul-

tiplicity. Formal analyses of inelastic collisions of molecules in  $^3\Sigma$  electronic states have been carried out.<sup>28,29</sup> In addition, there have been computational or experimental determinations of inelastic cross sections for collisions of  $\text{O}_2(X^3\Sigma_g^-)$ ,<sup>30,31</sup>  $\text{NH}(X^3\Sigma^-)$ ,<sup>32</sup>  $\text{S}_2(B^3\Sigma_u^-)$ .<sup>33</sup> The close-coupling equations which describe inelastic collisions of molecules in  $^3\Pi$  electronic states have been presented.<sup>34,35</sup> The structure of the coupling matrix elements of the electrostatic potential, which are formally identical to the structure of the  $S$ -matrix elements in the energy sudden limit,<sup>36</sup> were then used to derive<sup>34</sup> several propensity rules valid for collisions involving  $^3\Pi$  molecules whose electronic wave function could be well described in Hund's case (a).<sup>37,38</sup> To date there have been no quantum calculations of inelastic cross sections for molecules in  $^3\Pi$  electronic states. A state-resolved laser double resonance investigation of  $\text{N}_2(B^3\Pi_g)$ -Ar collisions has been carried out by Ali and Dagdigan.<sup>39</sup> These workers also considered how the transition to case (b) coupling in a  $^3\Pi$  state would alter the predicted propensities. Recently, Stuhl and, independently, Anderson and their co-workers<sup>40,41</sup> have been investigating inelastic collisions of  $\text{NH}(A^3\Pi)$  by laser excitation and spectral resolution of the resulting fluorescence.

In this paper, we present quantum calculations of inelas-

tic cross sections for collisions of NH( $A^3\Pi$ ) with helium. These cross sections will be compared with the information which can be obtained from the experiments<sup>40</sup> in Stuhl's laboratory. In addition, we also use these calculated cross sections to investigate fine-structure and  $\Lambda$ -doublet propensities in collisions of this  $^3\Pi$  electronic state. This will provide a quantitative measure of the propensities predicted from analysis of the close-coupling equations.

As we have shown previously for  $^2\Pi$  electronic states,<sup>27</sup> the  $\Lambda$ -doublet propensities which are expected for a state which follows Hund's case (b), or intermediate case, coupling, are different from those expected for a state which follows Hund's case (a) coupling. In the latter situation one expects to find<sup>34,42</sup> a propensity for conservation of the  $e/f$  symmetry label.<sup>43</sup> In collisions of a molecule in a  $^2\Pi$  electronic state in the intermediate coupling or case (b) limit, one expects<sup>27</sup> to see propensities toward population of either symmetric [ $\Pi(A')$ ] metric [ $\Pi(A'')$ ]  $\Lambda$ -doublet levels,<sup>44</sup> regardless of the initial  $\Lambda$ -doublet level. These propensities were shown to arise from a quantum mechanical interference, reflecting the fact that two potential energy surfaces are required to describe the interaction between a molecule in a  $\Pi$  electronic state and a closed shell partner.<sup>35</sup> The NH  $A$  state is an example of a  $^3\Pi$  state which goes over to case (b) coupling at fairly low values of  $J$ . As a result, one would expect to see changing  $\Lambda$ -doublet propensities which reflect this transition from case (a) to case (b). In the case (b) limit, we shall interpret the observed propensities in a treatment similar to that which we employed previously to understand similar propensities in  $^2\Pi$  electronic states.<sup>27</sup>

## II. QUANTUM FORMULATION OF THE COLLISION DYNAMICS

The quantum collision dynamics for rotationally inelastic collisions involving molecules in  $^3\Pi$  electronic states has been considered previously, both in Hund's case (a) (Refs. 34 and 35) and intermediate case<sup>39</sup> coupling. We review these results here, as they pertain to the calculation of NH( $A^3\Pi$ )-He inelastic cross sections.

The electronic-rotational wave functions of the NH molecule in the  $A^3\Pi$  electronic state will be expressed in an intermediate coupling case basis as<sup>37,45,46</sup>

$$|JMF_i\epsilon\rangle = \sum_{\Omega=0}^2 C_{JF_i\epsilon}^{\Omega} |JM\Omega\epsilon\rangle, \quad (1)$$

where the symmetry index  $\epsilon = \pm 1$  and the symmetrized case (a) basis functions are given by

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

The total angular momentum  $J$  (excluding nuclear spin) of the molecule has projections  $M$  and  $\Omega$  along the space-fixed and molecule-fixed  $z$  axes, respectively;  $\Lambda$  and  $\Sigma$  are the projections along the molecule-fixed  $z$  axis of the electronic orbital and spin angular momenta, respectively, with  $\Omega = \Lambda + \Sigma$ . The molecular eigenfunctions [Eq. (1)] are labeled  $F_1, F_2, F_3$  in order of increasing energy.<sup>38</sup> The total

parity<sup>47</sup> of these wave functions is  $\epsilon(-1)^{J-1}$ . Levels with  $\epsilon = -1$  are labeled in modern spectroscopic notation<sup>43</sup> as  $e$ , and  $\epsilon = +1$  as  $f$ . In Eq. (2),  $|\Lambda\Sigma\rangle$  designates the electronic wave function; the electronic spin angular momentum [not included explicitly in Eq. (2)] is denoted as  $S$ .

The rotational part of the unsymmetrized case (a) wave functions is given by<sup>37,45,46</sup>

$$|JM\Omega\rangle = [(2J+1)/4\pi]^{1/2} D_{M\Omega}^{J*}(\alpha\beta, \gamma=0), \quad (3)$$

where  $D_{M\Omega}^J$  is a rotation matrix element.<sup>48</sup> As in our previous papers,<sup>16,20,35,49</sup> the arbitrary third Euler angle is set equal to zero. The expansion coefficients in Eq. (1) can be obtained for NH( $A^3\Pi$ ) by diagonalization of the Hamiltonian derived by Brazier, Ram, and Bernath<sup>50</sup> from a spectroscopic analysis of the NH  $A^3\Pi$ - $X^3\Sigma^-$  band system. Since the NH( $A^3\Pi$ ) state rapidly approaches Hund's case (b) coupling<sup>38</sup> with increasing  $J$ , it is convenient to label the energy levels with the angular momentum  $N = J - S$ . We have  $J = N + 1$ ,  $N$ , and  $N - 1$  for the  $F_1, F_2$ , and  $F_3$  fine-structure levels, respectively. For reference in the succeeding discussion, Fig. 1 shows the labeling and relative energies of the lower fine-structure levels of NH( $A^3\Pi$ ) with  $N \leq 6$ .

It is convenient to solve the close-coupled scattering equations<sup>9,14-16,20,23,31,51</sup> in a basis  $|JF_i\epsilon L J_i M_i\rangle$ , where  $L$  is the orbital angular momentum of the relative motion of the collision partners and  $J_i$  and  $M_i$  are the total angular momentum and its projection on the space-fixed  $z$  axis. In this basis, the matrix elements of the interaction potential  $V$  can be written as<sup>39</sup>

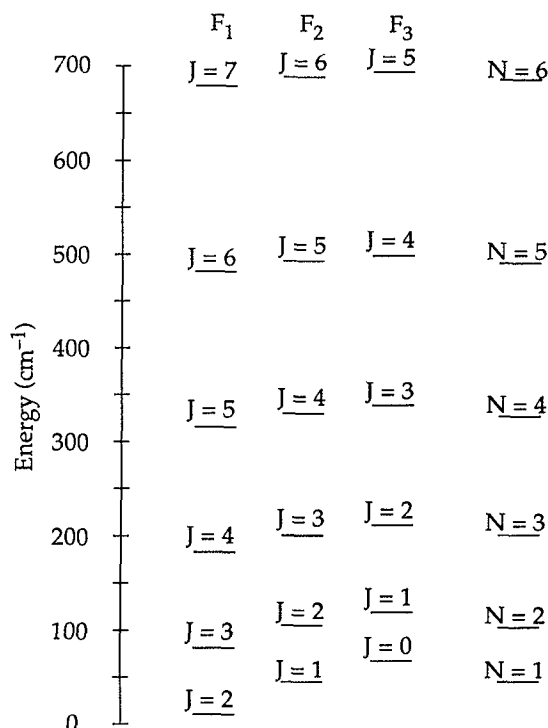


FIG. 1. Labeling and relative energies of the lower multiplet levels of NH( $A^3\Pi$ ) as determined using the spectroscopic constants of Brazier *et al.* (Ref. 50). Each line represents a closely spaced  $\Lambda$ -doublet.

$$\begin{aligned}
& \langle J'F_i' \epsilon' L' J_i M_i | V | JF_i \epsilon L J_i M_i \rangle \\
& = (-1)^{J+J'+J_i} \\
& \quad \times [(2L+1)(2L'+1)(2J+1)(2J'+1)]^{1/2} \\
& \quad \times \sum_l \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J' & L' & J_i \\ L & J & l \end{Bmatrix} F_{J'F_i',J\epsilon}^l \\
& \quad \times [A_{J'F_i',JF_i\epsilon}^l V_{10}(R) + B_{J'F_i',JF_i\epsilon}^l V_{12}(R)], \quad (4)
\end{aligned}$$

where

$$F_{J'F_i',J\epsilon}^l = \frac{1}{2} [1 + \epsilon \epsilon' (-1)^{J+J'+l}], \quad (5)$$

$$\begin{aligned}
& A_{J'F_i',JF_i\epsilon}^l \\
& = \sum_{\Omega=0}^2 (-1)^{\Omega} C_{J'F_i'\epsilon}^{\Omega} C_{JF_i\epsilon}^{\Omega} \begin{pmatrix} J' & l & J \\ -\Omega & 0 & \Omega \end{pmatrix}, \quad (6)
\end{aligned}$$

$$\begin{aligned}
& B_{J'F_i',JF_i\epsilon}^l \\
& = \epsilon \sum_{\Omega=0}^2 (-1)^{\Omega} C_{J'F_i'\epsilon}^{\Omega-2} C_{JF_i\epsilon}^{\Omega} \begin{pmatrix} J' & l & J \\ \Omega-2 & 2 & -\Omega \end{pmatrix}. \quad (7)
\end{aligned}$$

The radial terms  $V_{10}(R)$  and  $V_{12}(R)$  are coefficients in the expansion of the sum  $V_{\text{sum}}$  and difference  $V_{\text{diff}}$ , respectively, of the symmetric ( $A'$ ) and antisymmetric ( $A''$ ) potential energy surfaces<sup>35</sup> arising from the interaction of the helium target with the doubly degenerate NH( $A^3\Pi$ ) electronic state. These terms are given by<sup>35</sup>

$$\sum_{l=0}^{l_{\max}} P_l(\cos \theta) V_{10}(R) = [V_{A'}(R, \theta) + V_{A''}(R, \theta)]/2, \quad (8)$$

$$\begin{aligned}
& \sum_{l=2}^{l_{\max}} \left[ \frac{(l-2)!}{(l+2)!} \right]^{1/2} P_l^2(\cos \theta) V_{12}(R) \\
& = [V_{A'}(R, \theta) - V_{A''}(R, \theta)]/2. \quad (9)
\end{aligned}$$

Here,  $R$  and  $\theta$  are, respectively, the separation between the

centers of mass of the collision partners and the angle between the diatomic axis and the body frame  $z$  axis.

Integral cross sections for inelastic transitions are calculated from the  $S$  matrices which are determined by matching the solution of the close-coupled equations to the usual scattering boundary conditions.<sup>51</sup> We have

$$\begin{aligned}
& \sigma(J, F_i, \epsilon \rightarrow J', F_i', \epsilon') \\
& = \frac{\pi}{(2J+1)k_{JF_i}^2} \\
& \quad \times \sum_{J'', l', l} (2J+1) |S^J(J, F_i, \epsilon, l | J', F_i', \epsilon', l')|^2, \quad (10)
\end{aligned}$$

where  $k_{JF_i}$  is the wave vector in the initial channel and  $l$  and  $l'$  designate the initial and final values of the nuclear orbital angular momentum of the NH-He pair.<sup>42,52</sup>

### III. SCATTERING CALCULATIONS

The interaction potentials employed in the present computation of inelastic cross sections were taken from the work of Jonas and Staemmler,<sup>53</sup> who carried out coupled electron pair approximation (CEPA) calculations of the NHHe  $1^3A'$  and  $2^3A''$  states, which correlate asymptotically with NH( $A^3\Pi$ ) + He. In addition, for each value of  $R$  used in the *ab initio* calculations (4, 4.25, 4.5, 5, and 6 bohr), they fitted their calculated energies as a function of  $\theta$  to obtain the terms  $V_{10}(R)$  and  $V_{12}(R)$  in Eqs. (8) and (9) including all terms up to order  $l_{\max} = 5$ . Since they defined the difference potential as the inverse of ours [see Eq. (9)], their terms  $V_{12}(R)$  were multiplied by  $-1$ . We fit their tabulated radial terms to flexible functional forms to determine the potential at any desired value of  $R$ . The  $V_{10}$ ,  $V_{40}$ ,  $V_{50}$ ,  $V_{32}$ , and  $V_{42}$  terms were fit to the following expansion:

$$\begin{aligned}
V_i(R) = & [C_1 \exp(-\lambda_1 R) \\
& + (C_2 + C_3 R) \exp(-\lambda_2 R)] D(R), \quad (11)
\end{aligned}$$

with

$$D(R) = -0.5 \{ \tanh[1.5(R-7)] - 1 \}, \quad (12)$$

and with the coefficients in Eq. (11) given in Table I. The

TABLE I. Parameters in fit to *ab initio*  $V_i(R)$  expansions for the NH( $A^3\Pi$ ) + He system.<sup>a</sup>

Term <sup>b</sup>	$\lambda_1$	$\lambda_2$	$C_1$	$C_2$	$C_3$
$V_{10}$	2.068 73	0.758 610	-5.744 88(+6)	8.012 07(+2)	0
$V_{40}$	1.117 82	0.755 176	1.897 43(+5)	-7.062 48(+4)	8.103 11(+3)
$V_{50}$	1.581 25	0.381 250	1.069 77(+3)	8.012 07(+2)	-1.580 06(+2)
$V_{32}$	1.267 42	0.339 203	-5.119 97(+4)	5.584 73(+1)	0
$V_{42}$	1.300 00	0.500 000	2.586 28(+4)	-7.187 41(+1)	0
		$\lambda$	$C_1$	$C_2$	$C_3$
$V_{00}$		2.964 19	2.800 56(+9)	-1.576 88(+9)	2.402 29(+8)
$V_{20}$		1.104 58	4.815 36(+5)	-1.791 00(+5)	1.573 50(+4)
$V_{30}$		2.228 91	4.741 52(+7)	-2.500 61(+7)	2.987 76(+6)
$V_{22}$		1.325 83	6.208 86(+5)	-6.956 08(+4)	2.740 68(+2)
$V_{52}$		1.466 61	-1.826 59(+4)	-6.307 87(+1)	0

<sup>a</sup>Distances in units of bohr, energies in units of  $\text{cm}^{-1}$ . Powers of ten in parentheses.

<sup>b</sup> $V_{10}$ ,  $V_{40}$ ,  $V_{50}$ ,  $V_{32}$ , and  $V_{42}$  fit to Eq. (11);  $V_{00}$ ,  $V_{20}$ ,  $V_{30}$ ,  $V_{22}$ , and  $V_{52}$  fit to Eq. (13).

$V_{00}$ ,  $V_{20}$ ,  $V_{30}$ ,  $V_{22}$ , and  $V_{32}$  terms were fit to the following expression:

$$V_i(R) = \exp(-\lambda R)(C_1 + C_2 R + C_3 R^2)D(R), \quad (13)$$

with  $D(R)$  given by Eq. (12) and the coefficients given in Table I. The relative rms error in the fit to the tabulated *ab initio* energies parameters was  $< 1\%$ . A contour plot of the *ab initio*  $A'$  and  $A''$   $\text{NHHe}$  potentials is given in Fig. 2. In Fig. 3 we show plots of the  $V_{10}$ ,  $V_{10}$ ,  $V_{20}$ ,  $V_{22}$ ,  $V_{30}$ , and  $V_{32}$  expansion coefficients as a function of  $R$ .

The nominal electronic configuration of the  $A^3\Pi$  state of  $\text{NH}$  is  $1\sigma^2 2\sigma^2 3\sigma 1\pi^3$ . Thus, we expect the  $A''$  surface, in which two of the  $\pi$  electrons are in the triatomic plane and the third, perpendicular to the plane, to be more repulsive than the  $A'$  surface, in which two  $\pi$  electrons are perpendicular to the plane. This is clearly apparent in Fig. 2, in which  $V_{22}$  is seen to be positive. Of course, for collinear geometry, both  $\Pi$  states are degenerate, so that the two potentials become identical for  $\theta = 0^\circ$  and  $180^\circ$ .

Jonas and Staemmler<sup>53</sup> used a coordinate system with origin on the N atom, whereas in the Jacobi coordinate system used in the quantum treatment of the collision dynamics,<sup>34,35,39</sup> the origin is fixed at the center-of-mass of the  $\text{NH}$  molecule. The shift in the origin is small (0.12 bohr), but not negligible. The most satisfactory way to correct for this would mean refitting the original *ab initio* points in the Jacobi coordinate system. This was not done here. Consequently, we shall assume that fit defined in Eqs. (11)–(13) does indeed refer to the Jacobi coordinate system in which the collision dynamics are treated.

The close-coupled equations were solved using the HIBRIDON code.<sup>54</sup> To ensure convergence in the calculated inelastic cross sections it was necessary to include in the

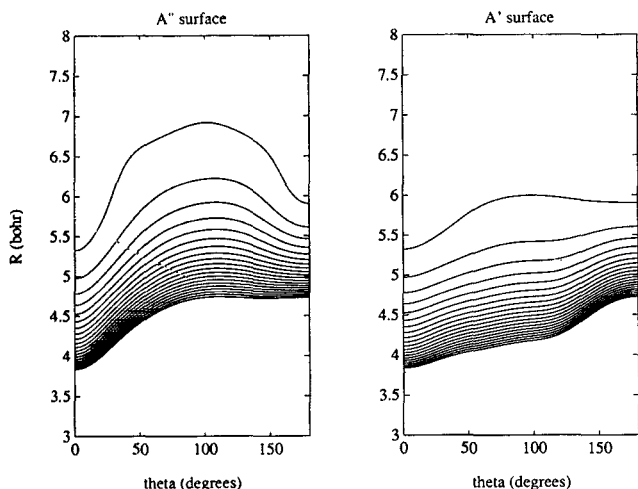


FIG. 2. Contour plot of the CEPA  $\text{NH}(A^3\Pi) + \text{He}$  potential energy surfaces of Jonas and Staemmler (Ref. 53) corresponding to a wave function of  $A''$  (left panel) and  $A'$  (right panel) symmetry. An angle of  $\theta = 0$  corresponds to a linear  $\text{HNHe}$  geometry. Displayed are 20 equally spaced contours ranging from 10 to  $1000 \text{ cm}^{-1}$ .

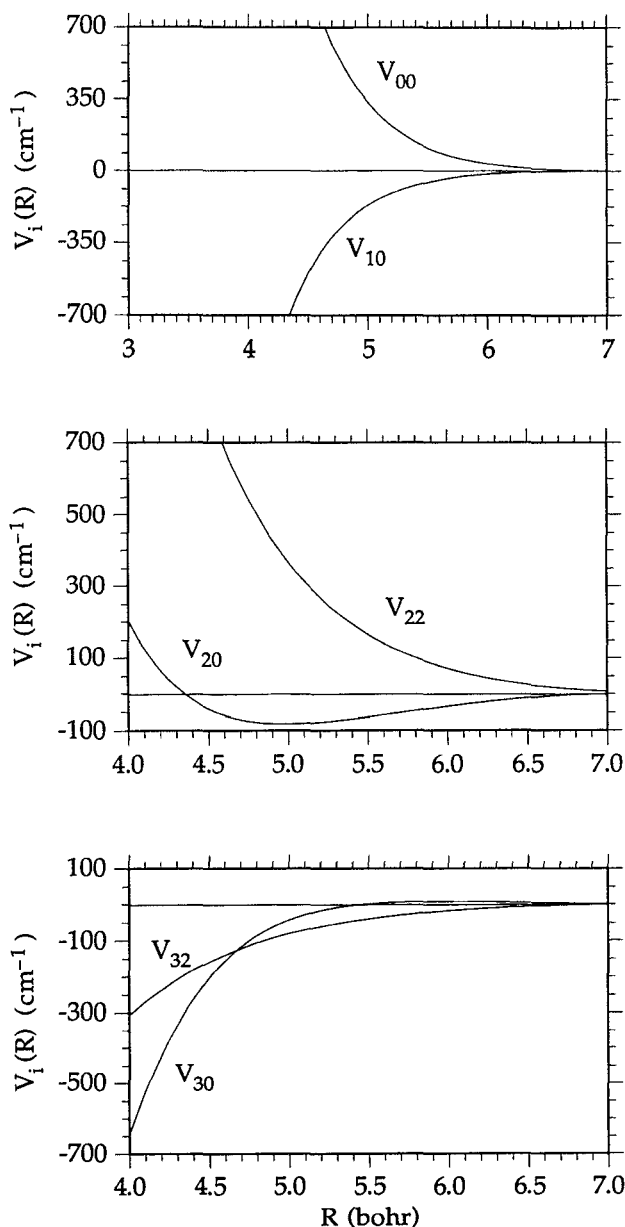


FIG. 3. (Upper panel) Comparison of various terms in the expansion of the  $\text{NH}(A^3\Pi) + \text{He}$  potential energy surfaces [Eqs. (8) and (9)] as a function of the interparticle distance. (Upper panel)  $V_{00}(R)$  and  $V_{10}(R)$  terms; (middle panel)  $V_{20}(R)$  and  $V_{22}(R)$  terms; (lower panel)  $V_{30}(R)$  and  $V_{32}(R)$  terms.

channel basis all energetically accessible electronic-rotational levels plus low-lying energetically forbidden (closed) levels. At the highest energy considered here ( $E = 1400 \text{ cm}^{-1}$ ), the calculations involved 358 coupled channels. With this basis, the determination of inelastic cross sections at one energy involved a total of 46 partial waves and required 70 h of CPU time on a DECStation 5000.

## IV. RESULTS

### A. A-doublet propensities

Pouilly and Alexander<sup>34</sup> have shown that for a  $^3\Pi$  molecule in the Hund's case (a) limit, there will exist a propen-

sity in inelastic collisions between a given  $J, \Omega$  initial fine-structure level and a  $J', \Omega'$  final level to *preserve* the  $e/f$  symmetry label. To verify whether this propensity rule applies to collisions of  $\text{NH}(\Lambda^3\Pi)$  with He, we present in Table II cross sections for transitions out of the  $J = 0, 1$  levels of  $\text{NH}$  (Fig. 1) into the  $J = 0, 1$ , and 2 levels. For transitions within the  $\Omega = 0(F_1)$  spin-orbit manifold, the propensity toward  $e/f$  conservation will apply at all values of  $J$ , but for transitions involving levels in the other ( $\Omega = 1$  and 2) spin-orbit manifolds, the propensity is expected to become increasingly strong as  $J$  increases. Despite this caveat, we see in Table II that for transitions involving just the  $J = 0$  and 1 levels, which are those for which the  $\Lambda^3\Pi$  state of  $\text{NH}$  lies closest to a case (a) limit, the propensity toward conservation of the  $e/f$  index is obeyed without exception. A breakdown of this propensity does occur for transitions into the  $J = 2$  (and, presumably, higher) levels, where the final state can no longer be well described in case (a).

For transitions between levels which are well described in case (b) coupling, we can determine propensities using the approach we developed earlier in the study of collisions of hydrides in  $^2\Pi$  electronic states (e.g., OH, CH).<sup>27</sup> For a given  $J\epsilon \rightarrow J'\epsilon'$  transition, the phase factor  $F'_{J'\epsilon', J\epsilon}$  in Eq. (5) implies that only even or only odd values of  $l$  will contribute to the sum in Eq. (4). The same set of  $l$  values also contribute to the corresponding  $J, -\epsilon \rightarrow J', -\epsilon'$  transition. In the case (a) limit, the  $J\epsilon \rightarrow J'\epsilon'$  and  $J, -\epsilon \rightarrow J', -\epsilon'$  transitions will have cross sections of the same magnitude, so that the final state will possess equal  $\Lambda$ -doublet populations if the initial state has equal  $\Lambda$ -doublet populations, as would be produced in a supersonic beam.<sup>13,18,19,21</sup> By contrast, for levels following case (b) or intermediate case coupling, quantum interference, reflected in the constructive or destructive addition of the two terms in square brackets in Eq. (4), will give rise to propensities toward production of a given final  $\Lambda$ -doublet level. Furthermore, unequal final state  $\Lambda$ -doublet popula-

tions will be expected in general when a single initial  $\Lambda$ -doublet level is prepared, for example by electronic excitation on an isolated rotational line, as for example in Stuhl's experiments,<sup>40</sup> since different  $l$  values couple the  $J\epsilon \rightarrow J'\epsilon'$  and  $J, -\epsilon \rightarrow J', -\epsilon'$  transitions.

This interference will take place only for  $l \geq 2$ , since the  $B'$  terms exist only for  $l \geq 2$ . Let us assume that the lowest values of  $l$  (which correspond to the lowest order anisotropies) will make the largest contribution to the coupling matrix element in Eq. (4). Thus, the relative strength of a particular transition between individual  $\Lambda$ -doublet levels might be predicted by comparison of the relative signs of the  $A'$  and  $B'$  coefficients for either  $l = 2$  or 3, multiplied, of course, by the two expansion terms in the potential which appear in Eq. (4), namely,  $V_{10}(R)$  and  $V_{12}(R)$ , for either  $l = 2$  or 3. For the potential of Jonas and Staemmler,<sup>53</sup> at collision energies sampled in thermal experiments, the classical turning point occurs at a  $\text{NH-He}$  distance  $R$  of 4.5–5 bohr. As can be seen in Fig. 3, at this range of interparticle separations,  $V_{20}(R)$  and  $V_{22}(R)$  are of *opposite* sign while  $V_{30}(R)$  and  $V_{32}(R)$  are of the *same* sign. Thus, for transitions which are coupled by even  $l$  terms, we predict the largest cross sections for transitions for which the  $A'$  and  $B'$  coefficients are of *opposite* sign, while for transitions which are coupled by odd  $l$  terms, we predict the largest cross sections for transitions for which the  $A'$  and  $B'$  coefficients are of the *same* sign.

In our previous article on collisions of the  $^2\Pi$  hydrides,<sup>27</sup> we presented numerical tables of  $A'$  and  $B'$  coefficients. Rather than doing so here, we shall report in tabular form only the predicted  $\Lambda$ -doublet propensities obtained from considering the relative signs of the  $A'$  and  $B'$  coefficients. As stated above, for a given  $J\epsilon \rightarrow J'\epsilon'$  transition only  $l$  even or  $l$  odd will contribute. Values of  $l$  of the same parity will contribute to the  $J, -\epsilon \rightarrow J', -\epsilon'$  transition, while values of  $l$  of the opposite parity will contribute to the  $J, \epsilon \rightarrow J', -\epsilon$  and  $J, -\epsilon \rightarrow J'\epsilon'$  transitions. With these consid-

TABLE II. Cross sections ( $\text{\AA}^2$ ) for scattering out of the  $J = 0$  and 1 levels.

Final state	Initial state					
	$J=0 F_3 e$ $E_{\text{col}}^a = 251$	$J=0 F_3 f$ 248	$J=1 F_3 e$ 251	$J=1 F_3 f$ 249	$J=1 F_2 e$ 250	$J=1 F_2 f$ 250
$J=0 F_3 e$	3.93(+1)	0.00	2.58(-1)	2.26(-2)	3.90(-1)	1.44(-1)
$F_3 f$	0.00	3.93(+1)	1.26(-1)	8.12(-1)	3.53(-2)	4.20(-1)
$J=1 F_3 e$	4.74(-1)	2.45(-1)	4.06(+1)	3.09(-1)	4.21	6.97(-2)
$F_3 f$	3.93(-2)	2.05	3.07(-1)	4.21(+1)	4.93(-1)	4.83(-1)
$F_2 e$	1.33	1.24(-1)	5.34	7.21(-1)	4.48(+1)	1.16
$F_2 f$	5.08(-1)	1.39	1.74(-1)	7.75(-1)	1.16	4.62(+1)
$J=2 F_3 e$	8.39(-1)	4.78(-3)	2.97(-1)	2.56	3.40(-1)	3.00(-1)
$F_3 f$	8.55(-3)	5.05(-1)	2.68(-1)	1.59	6.08(-2)	1.22(-1)
$F_2 e$	4.99(-1)	2.28(-2)	1.40	3.49	1.91	1.62
$F_2 f$	2.99(-2)	1.03(+1)	5.19	1.06	2.01(-1)	1.34
$F_1 e$	1.69(+1)	2.13(-2)	2.34	2.46	1.03	7.72
$F_1 f$	1.08(-1)	7.26	3.25	8.72(-1)	3.50	7.13(-1)

<sup>a</sup> Collision energy in initial state in  $\text{cm}^{-1}$ .

erations in mind, we present in Table III, the predicted  $\Lambda$ -doublet propensities for transitions out of the  $N = 6$  levels. We would expect these predictions to be valid whenever the relative magnitude of the four  $\Lambda$ -doublet resolved cross sections for a given  $J \rightarrow J'$  transition can be well predicted from the relative magnitude of the coupling matrix elements.

Table IV presents calculated cross sections for transitions out of  $N = 6$  with  $\Delta N = \pm 1$  and  $\Delta N = -2$ . We observe that for transitions with  $\Delta N = \pm 1$ , all the predictions contained in Table III which are based on the consideration of the coupling induced by the  $l = 2$  terms in the expansion are obeyed. However, for the same  $\Delta N = \pm 1$  transitions nearly all the predictions contained in Table III which are based on the consideration of the coupling induced by the  $l = 3$  terms in the expansion are *violated*. We believe that this is a consequence of the relative sizes of the  $V_{30}$  and  $V_{32}$  terms in the potential. As can be seen in Fig. 3, at the classical turning point for collisions at thermal energies, these terms are three to five times smaller than the  $V_{10}$  and  $V_{22}$  terms. Consequently, transitions which are directly coupled by the  $V_{30}$  and  $V_{32}$  terms can also be coupled effectively by second and higher order virtual transitions involving the  $V_{10}$  and  $V_{22}$  terms. It is thus difficult to make predictions by examining the relative sizes of just the  $V_{30}$  and  $V_{32}$  terms. The contribution of second and higher order virtual transitions seems also to provide a reasonable explanation why the  $\Lambda$ -doublet propensities of Table III do no seem to apply well to the  $\Delta N = -2$  transitions.

For the downward transitions ( $N = 6 \rightarrow N = 5$ ), we observe an overall propensity toward population of the  $\Pi(A')$   $\Lambda$ -doublet levels, in which the electronic wave function is symmetric with respect to reflection of the electronic coordinates in the plane of rotation.<sup>44</sup> For the upward transitions ( $N = 6 \rightarrow N = 7$ ), we see that although the relative magnitude of the calculated cross sections is fully consistent with our qualitative predictions based on consideration of the relative signs of the appropriate  $A'$  and  $B'$  coefficients for  $l = 2$ , no overall propensity is found, either toward conservation of the  $e/f$  label or toward population of either  $\Pi(A'')$  or  $\Pi(A')$  levels.

So far we have considered transitions out of the  $J = 0$  and 1 levels of  $\text{NH}(A^3\Pi)$ , which are closest to the Hund's case (a) limit, and transitions out of  $N = 6$ , which approached the case (b) limit. We now consider transitions out of  $N = 2$ , which corresponds to a coupling scheme intermediate between case (a) and case (b). Similarly to the case of transitions out of  $N = 6$ , we can make predictions of  $\Lambda$ -doublet propensities from consideration of the relative magnitude of the  $A'$  and  $B'$  coefficients in Eq. (4). These predictions, for the  $\Delta N = \pm 1$  transitions, are contained in Table V, and the calculated cross sections, in Table VI. We observe that the predictions based on consideration of the relative signs of the appropriate  $A'$  and  $B'$  coefficients for  $l = 2$  are obeyed without exception for the  $\Delta N = +1$  transitions, and, in many cases, also for the downward  $\Delta N = -1$  transitions.

TABLE III. Predicted propensities for scattering out of the  $N = 6$  levels.

Final state	Initial state ( $N = 6$ )		
	$F_3$	$F_2$	$F_1$
	$l = 2$		
$N = 4 F_3$	$e \rightarrow e > f \rightarrow f$	... <sup>a</sup>	... <sup>a</sup>
$N = 4 F_2$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$	... <sup>a</sup>
$N = 4 F_1$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$
$N = 5 F_3$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$	... <sup>a</sup>
$N = 5 F_2$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$
$N = 5 F_1$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$	$e \rightarrow f > f \rightarrow e$
$N = 7 F_3$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$
$N = 7 F_2$	$f \rightarrow f > e \rightarrow e$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$
$N = 7 F_1$	... <sup>a</sup>	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$
	$l = 3$		
$N = 4 F_3$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$	... <sup>a</sup>
$N = 4 F_2$	$f \rightarrow f > e \rightarrow e$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$
$N = 4 F_1$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$
$N = 5 F_3$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$
$N = 5 F_2$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$	$e \rightarrow f > f \rightarrow e$
$N = 5 F_1$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$
$N = 7 F_3$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$
$N = 7 F_2$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$	$e \rightarrow f > f \rightarrow e$
$N = 7 F_1$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$

<sup>a</sup>Transition not coupled by this  $l$  expansion term.

TABLE IV. Cross sections (in  $\text{\AA}^2$ ) for scattering out of the  $N = 6$  levels.\*

Final state	Initial state ( $N = 6$ )					
	$F_3 e(A'')$ $E_{\text{col}}^a = 717$	$F_3 f(A')$ 717	$F_2 e(A')$ 724	$F_2 f(A'')$ 724	$F_1 e(A'')$ 731	$F_1 f(A')$ 732
$N = 4 F_3 e(A'')$	7.82(−1)	3.58(−1)	1.45(−1)	6.76(−2)	2.85(−2)	1.78(−2)
$f(A')$	9.42(−1)	6.67(−1)	9.23(−2)	5.24(−1)	2.76(−2)	3.09(−2)
$N = 4 F_2 e(A')$	4.32(−1)	2.93(−1)	6.22(−1)	6.30(−1)	5.05(−1)	9.67(−2)
$f(A'')$	1.98(−1)	4.59(−1)	2.23(−1)	6.04(−1)	8.48(−2)	1.47(−1)
$N = 4 F_1 e(A'')$	5.04(−2)	8.92(−2)	4.73(−1)	1.68(−1)	6.46(−1)	4.80(−1)
$f(A')$	7.98(−2)	8.00(−2)	3.26(−1)	3.74(−1)	9.79(−1)	9.90(−1)
$N = 5 F_3 e(A'')$	1.70	9.76(−1)	2.00(−1)	2.69(−1)	4.48(−2)	2.49(−2)
$f(A')$	3.60	2.01	4.56(−1)	9.33(−1)	4.01(−2)	6.66(−2)
$N = 5 F_2 e(A')$	1.42	6.95(−1)	1.73	2.65	9.20(−1)	4.61(−1)
$f(A'')$	2.13(−1)	6.51(−1)	7.28(−1)	1.49	3.30(−1)	1.93(−1)
$N = 5 F_1 e(A'')$	4.07(−2)	8.79(−2)	6.61(−1)	2.35(−1)	1.68	1.15
$f(A')$	1.65(−1)	1.21(−1)	6.89(−1)	1.37	3.63	2.51
$N = 6 F_3 e(A'')$	4.63(+1)	6.24(−1)	1.92(−1)	1.35	8.08(−2)	3.85(−2)
$f(A')$	6.24(−1)	4.37(+1)	1.39	1.82(−1)	4.53(−2)	1.14(−1)
$N = 6 F_2 e(A')$	2.29(−1)	1.66	4.25(+1)	5.22(−1)	1.83(−1)	1.30
$f(A'')$	1.60	2.17(−1)	5.20(−1)	4.51(+1)	1.53	1.90(−1)
$N = 6 F_1 e(A'')$	1.13(−1)	6.31(−2)	2.13(−1)	1.79	4.68(+1)	7.40(−1)
$f(A')$	5.37(−2)	1.59(−1)	1.52	2.23(−1)	7.41(−1)	4.38(+1)
$N = 7 F_3 e(A'')$	1.15	3.34	8.63(−1)	8.86(−2)	1.21(−2)	7.08(−2)
$f(A')$	8.86(−1)	1.84	4.63(−1)	4.17(−1)	3.66(−2)	5.13(−2)
$N = 7 F_2 e(A')$	1.90(−1)	4.51(−1)	1.58	6.27(−1)	4.14(−1)	4.89(−1)
$f(A'')$	1.56(−1)	8.28(−1)	2.47	1.02	9.29(−2)	8.13(−1)
$N = 7 F_1 e(A'')$	2.33(−2)	4.26(−2)	7.95(−1)	1.80(−1)	1.08	3.10
$f(A')$	1.86(−2)	5.35(−2)	4.65(−1)	1.74(−1)	8.81(−1)	2.21

\* Collision energy in initial state in  $\text{cm}^{-1}$ . Powers of ten in parentheses. The pairs of cross sections whose relative magnitudes are correctly predicted by the  $l = 2$  propensities reported in Table III are italicized.

## B. Fine-structure state propensities

Pouilly and Alexander<sup>34</sup> have demonstrated that cross sections from the  $(\Omega = 0)F_1$  and  $(\Omega = 2)F_3$  spin-orbit manifolds into rotational levels of the  $(\Omega = 1)F_2$  manifold will be rigorously zero if the  $^3\Pi$  molecule can be well de-

scribed in case (a). This occurs because the electronic wave functions for the  $F_1$  and  $F_3$  manifolds involve [Eq. (2)] a linear combination of electronic states with spin projections  $\Sigma = \pm 1$ , while the electronic wave functions for the  $F_2$  manifold involve only spin states  $\Sigma = 0$ . Since the electrostatic potential between NH and He cannot effect the elec-

TABLE V. Predicted propensities for scattering out of the  $N = 2$  levels.

Final state	Initial state ( $N = 2$ )		
	$F_3$	$F_2$	$F_1$
$N = 1 F_3$	... <sup>a</sup>	$f \rightarrow f > e \rightarrow e$	... <sup>a</sup>
$N = 1 F_2$	$e \rightarrow e > f \rightarrow f$	$e \rightarrow f > f \rightarrow e$	$e \rightarrow e > f \rightarrow f$
$N = 1 F_1$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$	$e \rightarrow f > f \rightarrow e$
$N = 3 F_3$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$
$N = 3 F_2$	$f \rightarrow f > e \rightarrow e$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$
$N = 3 F_1$	... <sup>a</sup>	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$
$l = 3$			
$N = 1 F_3$	... <sup>a</sup>	... <sup>a</sup>	$f \rightarrow f > e \rightarrow e$
$N = 1 F_2$	... <sup>a</sup>	$f \rightarrow f > e \rightarrow e$	$f \rightarrow e > e \rightarrow f$
$N = 1 F_1$	$f \rightarrow f > e \rightarrow e$	$e \rightarrow f > f \rightarrow e$	$f \rightarrow f > e \rightarrow e$
$N = 3 F_3$	$e \rightarrow e > f \rightarrow f$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$
$N = 3 F_2$	$e \rightarrow f > f \rightarrow e$	$e \rightarrow e > f \rightarrow f$	$e \rightarrow f > f \rightarrow e$
$N = 3 F_1$	$f \rightarrow f > e \rightarrow e$	$f \rightarrow e > e \rightarrow f$	$e \rightarrow e > f \rightarrow f$

\* Transition not coupled by this  $l$  expansion term.



TABLE VI. Cross sections (in  $\text{\AA}^2$ ) for scattering out of the  $N = 2$  levels.<sup>a</sup>

Final state	Initial state ( $N = 2$ )					
	$F_3 e(A'')$ $E_{\text{col}}^a = 591$	$F_3 f(A')$ 589	$F_2 e(A')$ 605	$F_2 f(A'')$ 603	$F_1 e(A'')$ 628	$F_1 f(A')$ 628
$N = 1 F_3 e(A'')$	4.12(−1)	1.24(−1)	2.12(−1)	6.87(−2)	7.30(−1)	6.72(−3)
$f(A')$	1.99(−1)	6.71(−1)	2.82(−2)	1.21	8.29(−3)	1.67(−1)
$N = 1 F_2 e(A')$	3.44	5.39(−1)	1.22	5.12(−1)	1.21	3.02(−1)
$f(A'')$	3.90(−1)	1.03	8.90(−1)	1.51	1.04	5.13(−1)
$N = 1 F_1 e(A'')$	2.07	1.88	2.15	1.17	1.13	1.78
$f(A')$	2.52	6.90(−1)	7.42(−1)	2.74	1.98	1.56
$N = 2 F_3 e(A'')$	3.85(+1)	6.20(−1)	7.84(−1)	1.92	1.00	1.33(−1)
$f(A')$	6.18(−1)	3.94(+1)	1.46	4.90(−1)	9.44(−2)	4.55(−1)
$N = 2 F_2 e(A')$	1.34	2.50	3.74(+1)	9.92(−1)	2.26(−1)	1.68
$f(A'')$	3.27	8.37(−1)	9.90(−1)	3.75(+1)	3.21	3.74(−1)
$N = 2 F_1 e(A'')$	2.48	2.35(−1)	3.28(−1)	4.68	4.16(+1)	1.86
$f(A')$	3.29(−1)	1.13	2.44	5.46(−1)	1.86	4.09(+1)
$N = 3 F_3 e(A'')$	9.32(−1)	2.34	2.82	5.06(−1)	5.17(−1)	6.12(−1)
$f(A')$	3.89(−1)	1.78	5.93(−1)	1.11	3.42(−1)	2.72(−1)
$N = 3 F_2 e(A')$	7.11(−1)	5.53(−1)	1.49	2.95(−1)	1.42	6.53(−1)
$f(A'')$	1.16	3.54	9.25(−1)	9.87(−1)	9.51(−1)	2.27
$N = 3 F_1 e(A'')$	1.68	1.19(−1)	2.35	2.04	1.18	2.60
$f(A')$	4.91(−2)	5.92(−1)	6.74(−1)	6.41(−1)	1.24	2.14

<sup>a</sup> Collision energy in initial state in  $\text{cm}^{-1}$ . Powers of ten in parentheses. The pairs of cross sections whose relative magnitudes are correctly predicted by the  $l = 2$  propensities reported in Table III are italicized.

tronic spin, collisions will not lead to transitions in which  $\Sigma$  goes from  $\pm 1$  to 0. We see from Table II that this selection rule is not well obeyed here. This is because for NH even for  $J = 1$  and 2 the case (a) (definite  $\Omega$ ) wave functions are significantly mixed even for  $J = 1$  and 2.

At high  $J$ , however, the electronic spin uncouples from the sum of the nuclear rotational and electronic orbital angular momenta ( $N$ ) so that, for a given  $N$ , the three  $F_i$  states correspond to the three possible ways of coupling  $S$  with  $N$  (in a space-fixed frame). As before, the electrostatic potential will not affect  $S$ , which will remain a spectator during the collision. For a situation in which most collisions are glancing encounters, in which the magnitude, but not the orientation, of  $N$  is affected, then the relative angle between  $S$  and  $N$  will not be significantly altered. Thus, exactly as in the case of collisions involving molecules in  $^2\Sigma$  states,<sup>1,2,4,55</sup> we would expect a propensity for  $\Delta F_i = 0$ . Similarly, since a change from  $F_{i=1,3}$  to  $F_{i=3,1}$  involves a greater reorientation of  $N$  with respect to  $S$  than transitions from  $F_{i=1,3}$  to  $F_{i=2}$ , we would expect the cross sections for the latter process to be larger than for the former.

To ascertain the existence of spin-orbit propensities, we list in Table VII cross sections for transitions out of the three  $N = 2$  fine structure levels, averaged over the initial  $\Lambda$ -doublet and summed over the final  $\Lambda$ -doublet levels. There is some evidence for conservation of the initial  $F_i$  index, although not pronounced, and not without exceptions. Table VIII presents similar cross sections, averaged over the initial  $\Lambda$ -doublet and summed over the final  $\Lambda$ -doublet, but for transitions out of the  $N = 6$  level. Here, for an initial state which is well described in Hund's case (b), we see clear

evidence of a strong tendency for conservation of the  $F_i$  label, and, secondarily, of a tendency for the cross sections with  $\Delta F_i = \pm 1$  to be greater than those for  $\Delta F_i = \pm 2$ . These propensities are not as apparent for transitions with large  $\Delta N$ . These strongly inelastic cross sections are induced primarily by collisions at smaller impact parameter, which would tend to reorient  $N$  more strongly than those at larger impact parameter.

TABLE VII. Cross sections ( $\text{\AA}^2$ ) for scattering out of the  $N = 2$  levels, averaged over the  $\Lambda$ -doublet levels of the initial state and summed over the  $\Lambda$ -doublet levels of the final state.

Final state	Initial state ( $N = 2$ )		
	$F_3$ $E_{\text{col}}^a = 590$	$F_2$ 604	$F_1$ 628
$N = 1 F_3$	1.41	1.52	0.91
$N = 1 F_2$	5.40	4.13	3.07
$N = 1 F_1$	7.16	6.80	6.45
$N = 2 F_3$	79.14	4.65	1.68
$N = 2 F_2$	7.95	76.88	5.49
$N = 2 F_1$	4.17	7.99	86.22
$N = 3 F_3$	5.44	5.03	1.74
$N = 3 F_2$	5.96	3.70	5.29
$N = 3 F_1$	2.44	5.70	7.16
$N = 4 F_3$	2.48	1.92	0.65
$N = 4 F_2$	2.06	1.46	1.68
$N = 4 F_1$	0.48	1.57	2.31

<sup>a</sup> Collision energy in initial state in  $\text{cm}^{-1}$ .

TABLE VIII. Cross sections (in  $\text{\AA}^2$ ) for scattering out of the  $N = 6$  levels, averaged over the  $\Lambda$ -doublet levels of the initial state and summed over the  $\Lambda$ -doublet levels of the final state;  $E_{\text{col}} = 250 \text{ cm}^{-1}$ .

Final state	Initial state ( $N = 6$ )		
	$F_3$	$F_2$	$F_1$
$N = 1 F_3$	4.72(−3)	7.00(−3)	2.39(−3)
$N = 1 F_2$	1.96(−2)	8.27(−3)	1.36(−2)
$N = 1 F_1$	2.27(−2)	2.53(−2)	1.40(−2)
$N = 2 F_3$	6.79(−2)	2.64(−2)	6.38(−3)
$N = 2 F_2$	4.93(−2)	5.91(−2)	3.08(−2)
$N = 2 F_1$	1.52(−2)	4.23(−2)	8.01(−2)
$N = 3 F_3$	2.30(−1)	4.01(−2)	8.38(−3)
$N = 3 F_2$	1.01(−1)	2.12(−1)	4.06(−2)
$N = 3 F_1$	2.77(−2)	9.28(−2)	2.64(−1)
$N = 4 F_3$	7.47(−1)	2.30(−1)	2.60(−2)
$N = 4 F_2$	4.18(−1)	5.51(−1)	2.26(−1)
$N = 4 F_1$	8.70(−2)	3.98(−1)	8.44(−1)
$N = 5 F_3$	3.87	1.00	9.18(−2)
$N = 5 F_2$	1.60	2.90	1.04
$N = 5 F_1$	2.22(−1)	1.59	4.15
$N = 6 F_3$	5.55(+1)	2.32	1.81(−1)
$N = 6 F_2$	2.81	5.37(+1)	2.46
$N = 6 F_1$	2.62(−1)	2.94	5.61(+1)
$N = 7 F_3$	1.21(−1)	3.62(−2)	4.21(−3)
$N = 7 F_2$	3.85(−2)	1.17(−1)	3.83(−2)
$N = 7 F_1$	5.92(−3)	4.79(−2)	1.88(−1)

## V. COMPARISON WITH EXPERIMENT

In the experiments of Stuhl and Kaes<sup>40</sup> for collisions of  $\text{NH}(A^3\Pi)$  with He, it was possible to determine only the total inelastic thermal rate constant for scattering out of individual  $\Pi(A'')$   $N, F_i$  levels into all  $\Pi(A')$  states. This rate constant can be written as

$$k(N, F_i, \epsilon; T) = \langle v \sigma(N, F_i, \epsilon; v) \rangle, \quad (14)$$

where  $v$  is the relative collision velocity and the angle brackets indicate an average over an assumed Maxwellian velocity distribution. In this equation the cross section is defined by

$$\sigma(N, F_i, \epsilon; v) = \sum_{N', F'_i} \sigma(N, F_i, \epsilon \rightarrow N', F'_i, \epsilon'; v). \quad (15)$$

The thermal average in Eq. (14) can be written as

$$k(N, F_i, \epsilon; T) = N(T) \int E \sigma(N, F_i, \epsilon; E) \times \exp(-E/kT) dE, \quad (16)$$

where we have used the relative translational energy, rather than the relative velocity, as the independent variable. In Eq. (16),  $N(T)$  is the appropriate normalization factor. To evaluate Eq. (16) we first computed the underlying cross sections at  $\sim 15$  values of the relative energy which span the range sampled by the Boltzmann weighting  $E \exp(-E/kT)$  and then used spline interpolation to evaluate the integral numerically.

TABLE IX. Rate constants (in units of  $10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ) for scattering out of selected  $\Pi(A'')$   $\Lambda$ -doublets into all energetically accessible  $\Pi(A')$  final states.

Initial state	Theory <sup>a</sup>	Experiment <sup>b</sup>
$N = 3 F_1 e$	1.23	$1.3 \pm 0.1$
$N = 4 F_3 e$	1.36	$1.0 \pm 0.2$
$N = 5 F_3 e$	1.20	$0.9 \pm 0.1$
$N = 6 F_2 f$	1.00	$1.1 \pm 0.1$

<sup>a</sup> See Eq. (16).

<sup>b</sup> Experimental data from Ref. 40.

In Table IX we compare the calculated  $k(N, F_i, \epsilon; T)$  rate constants with the available experimental data [Eq. (14)], as reported by Stuhl and Kaes.<sup>40</sup> The agreement between the absolute magnitude of the calculated and experimental rate constants is excellent (virtually within the experimental error bars). Nevertheless, there are some differences in the relative magnitudes of the cross sections.

## VI. CONCLUSION

We have presented the results of full close-coupled calculations of state-to-state cross sections for rotationally inelastic collisions of  $\text{NH}$  in its  $A^3\Pi$  electronic state with helium. These computations were based on recently calculated *ab initio* potential energy surfaces of Jonas and Staemmler.<sup>53</sup> The calculated cross sections have been compared with predictions based on formal analyses of the scattering equations both in the Hund's case (a) (Refs. 34 and 35) and (b) (Ref. 39) limits. For transitions between low  $J$  levels, where  $\text{NH}(A)$  is closest to Hund's case (a) coupling, we observed a strong tendency toward conservation of the  $e/f$  label, as predicted initially by Pouilly and Alexander.<sup>34</sup> At higher  $J$ , where the rotational levels of  $\text{NH}(A)$  are better described in intermediate, and, eventually in Hund's case (b), coupling, the unequal cross sections for  $J\epsilon \rightarrow J'\epsilon$  vs  $J, -\epsilon \rightarrow J', -\epsilon$  transitions reveal the effect of quantum interference between the two potential energy surfaces which arise when the orbital degeneracy of  $\text{NH}(A^3\Pi)$  is raised by the approach of a collision partner. When  $\Delta N = \pm 1$ , for the pair of  $JF_i\epsilon \rightarrow J'F'_i\epsilon'$  transitions which are coupled by the  $l = 2$  (quadrupole-like) terms in the expansion of the potentials, the dominant transition can be predicted reliably by an examination of the relative strength of the relevant coupling matrix elements of the electrostatic potential. In contrast, however, to our earlier investigation<sup>27</sup> of collisions involving hydrides in  $^2\Pi$  electronic states [ $\text{CH}(X^2\Pi)$  and  $\text{OH}(X^2\Pi)$ ], similar predictions cannot be made successfully for transitions which are coupled by the weaker  $l = 3$  terms. This reflects the contribution of higher order virtual processes toward the transition in question.

We have also investigated the existence of fine-structure propensities in  $\text{NH}(^3\Pi)$ -He inelastic cross sections averaged and summed over the initial and final  $\Lambda$ -doublet levels,

respectively. For transitions out of the  $N = 6$  manifold, for which the wave functions are well described in case (b) coupling, a definite preference for conservation of the  $F_i$  label was found, particularly for small  $\Delta N$ . This propensity arises because the electronic spin  $S$  is not affected by the purely electrostatic forces operative in a collision and, furthermore, in most encounters it is the *magnitude* of the angular momentum  $N$ , and not the angle between  $N$  and  $S$ , which is altered.<sup>39</sup> By contrast, this propensity is much less pronounced for transitions out of the  $N = 2$  manifold.

The present study shows that a simple analysis is capable of understanding the relative ordering of most state-to-state cross sections for inelastic scattering of a molecule in a  $^3\Pi$  state. For such states, there are six levels for each value of  $J$ , resulting in a large number of possible fine-structure-resolved transitions. The major inadequacy of our analysis was its inability of explaining the relative magnitudes of  $\Lambda$ -doublet resolved transitions coupled by odd  $l$  terms in the potential. This mainly reflects the fact that for the lowest  $l$  value, namely  $l = 3$ , the  $V_{10}$  and  $V_{12}$  terms in the  $\text{NH}(^3\Pi)$ -He potential are relatively small so that a simple analysis based on first-order perturbation theory fails.

For collisions of  $\text{NH}(A^3\Pi)$  with He, the only experimentally reported inelastic cross sections are for transitions out of selected fine-structure/ $\Lambda$ -doublet levels of  $\Pi(A'')$  symmetry into all other accessible levels of *opposite*  $\Pi(A')$  symmetry.<sup>40</sup> The appropriately summed calculated rates agree with the reported experimental values virtually to within the reported experimental error. Although this is satisfying, the reader should remember that the potential surface used here, although based on an *ab initio* calculation, was expanded<sup>53</sup> in a coordinate system slightly displaced from that in which the collision dynamics were formulated. Although this will likely have little impact on the *qualitative* collisional propensities which are the primary subject of this paper, the magnitude of the ensuing error in the calculated cross sections might shift these to poorer agreement with the experimentally measured quantities. A more stringent test of the accuracy of the *ab initio* potential surface would involve an eventual comparison between calculated cross sections based on an expansion in the correct Jacobi coordinate system and more highly resolved experimental data.

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