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ROTATIONAL EXCITATION OF SYMMETRIC TOP MOLECULES  
BY COLLISIONS WITH ATOMS:  
CLOSE COUPLING, COUPLED STATES, AND EFFECTIVE POTENTIAL  
CALCULATIONS FOR NH<sub>3</sub>-He.\*

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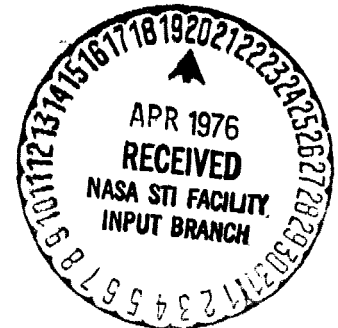
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## ABSTRACT

The formalism for describing rotational excitation in collisions between symmetric top rigid rotors and spherical atoms is presented both within the accurate quantum close coupling framework and also the coupled states approximation of McGuire and Kouri and the effective potential approximation of Rabitz. Calculations are reported for thermal energy  $\text{NH}_3$ -He collisions, treating  $\text{NH}_3$  as a rigid rotor and employing a uniform electron gas (Gordon-Kim) approximation for the intermolecular potential. Coupled states is found to be in nearly quantitative agreement with close coupling results while the effective potential method is found to be at least qualitatively correct. Modifications necessary to treat the inversion motion in  $\text{NH}_3$  are discussed briefly.

## I. Introduction

Recent advances in numerical techniques and computational capabilities have made it possible to study energy transfer in molecular collisions - at least for some simple systems - by obtaining essentially exact numerical solutions to the quantum close coupling (CC) scattering equations for molecules interacting via realistic, e.g., ab initio, intermolecular potentials. Unfortunately, the expense of CC calculations increases rapidly with the number of energetically accessible molecular quantum levels, due, in large part, to the  $2j+1$  degenerate sublevels which must be included for each rotational level,  $j$ . Therefore most calculations to date have been limited to the simplest case, collisions of linear molecules with atoms, and to energies where only a handful of the lowest molecular rotational levels are accessible.<sup>1</sup> The hydrogen molecule with its small moment of inertia has only a few rotational levels below the threshold for vibrational excitation, and calculations have been performed for vibrational-rotational excitation of  $H_2$  by collisions with atoms.<sup>2</sup> Only one calculation for rotational excitation of a linear molecule by another linear molecule ( $H_2-H_2$ ) has been reported;<sup>3</sup> and there has also been one calculation for rotational excitation of an asymmetric top rotor by an atom ( $H_2CO-He$ ).<sup>4</sup>

Because much of the computational effort in CC calculations is due to the degenerate rotational sublevels and because many collisional phenomena are sensitive only to the average over these degeneracies, it seems reasonable to sacrifice some information about these sublevels in order to simplify the calculation. This notion is the basis for the effective potential<sup>5</sup> (EP) approximation of Rabitz and the coupled states<sup>6</sup>

(CS) approximation of McGuire and Kouri. Both of these methods have now been tested by comparison with available CC results for degeneracy-averaged (i.e., state-to-state) integral cross sections,  $\sigma(i \rightarrow f)$ , in linear molecule collisions.<sup>5-7</sup> The CS approximation appears to be quite reliable except, perhaps, when there is strong, long-range anisotropy in the potential. Accuracy of the EP approximation appears to be more sensitive to the strength of the anisotropy in the potential, being better for weaker angle-dependence; however, considering that it is much cheaper than CS, it is probably still accurate enough to be useful for many molecular systems. If these approximations can be shown to remain accurate, they will be invaluable for understanding energy transfer in other, more complicated systems where CC calculations will not be possible.

In this paper we consider scattering of a rigid symmetric top rotor by a closed-shell,  $^1S$  atom. As an example, collisions of  $NH_3$  with He are considered, using a theoretical electron gas approximation to the interaction potential, and treating collision dynamics within the accurate CC framework as well as the CS and EP approximations.

The ammonia molecule is a typical symmetric top, having a three-fold axis of symmetry through the nitrogen. It is not, however, an ideal example of a rigid rotor because it undergoes rapid inversion - a large amplitude vibration of the nitrogen through the plane of the hydrogens. This inversion motion splits the normally degenerate symmetric top k-doublets. Transitions between the inversion doublets are readily observed at microwave frequencies making  $NH_3$  amenable to studies of collisional energy transfer using the microwave double resonance techniques of Oka,<sup>8</sup> and a fair amount of rotational relaxation data is

therefore available for this system.

For the purposes of this study the inversion doubling has been ignored, and  $\text{NH}_3$  treated as a rigid symmetric top. Typical splittings between inversion doublets are 20 - 25 GHz which corresponds, classically, to a vibrational period of about 50 ns. Since the duration of a thermal energy  $\text{NH}_3$ -He collision is  $\leq 1$  ns, the rigid rotor approximation may not be unreasonable. Nonetheless, until this effect is considered in more detail, results from these calculations should be viewed as modelistic, and comparisons with the experimental data should be treated with caution.

Rather, this study was undertaken for the following reasons. There has been no previous study of collisions between symmetric tops and atoms, especially those systems dominated by short-range forces, where the accuracy of the intermolecular potential and scattering approximations could be well documented. Thus, despite a moderate amount of double resonance data, energy transfer in such systems is still not well understood, and "a quantitative theoretical treatment of the transition probability will be needed".<sup>8b</sup> For example, even the typical size and shape of the short-range anisotropy are not known. (It should be recalled in this context that the anisotropy in linear molecule-atom collisions was recently found to be much larger than anticipated.<sup>1c</sup>) Also essentially unknown are the relative magnitudes of different  $\Delta j$  and  $\Delta k$  transitions, and the cause of the observed parity "selection rules". As indicated above it is rapidly becoming possible to examine such questions by accurate scattering calculations on ab initio intermolecular surfaces. Because of its low moment of inertia and hence widely spaced rotational

levels, and also because of ortho-para separation, it is feasible to treat collision dynamics for  $\text{NH}_3$ , at least for the lower rotational levels and thermal collision energies, within the accurate CC framework. These calculations can then be used to test the accuracy of cheaper approximations, such as CS and EP, which might then be used to study collision dynamics for this and similar systems in more detail.

The CC, CS, and EP scattering formalisms for symmetric top-atom collisions are reviewed in Section II since this does not appear to be conveniently available in the literature. The numerical calculations for  $\text{NH}_3$ -He are presented in Section III. Section IV summarizes the major conclusions of these calculations and indicates briefly the modifications necessary to treat the inversion motion.

## II. Scattering Formalism

The total Hamiltonian for collisions of a rigid rotor and an atom, in space-fixed coordinates located at the center of mass of the system can be written as

$$H = H_{\text{rot}}(\hat{\Omega}) + T(\underline{R}) + V(\hat{\Omega}, \underline{R}) \quad (1a)$$

where the kinetic energy of collision,

$$T(\underline{R}) = -(\hbar^2/2\mu) \nabla_{\underline{R}}^2 = -(\hbar^2/2\mu) \left( \frac{d^2}{dR^2} - \underline{l}^2 \right), \quad (1b)$$

can be separated into radial and orbital angular momentum contributions as indicated. The rotor orientation is specified by  $\hat{\Omega}=(\alpha\beta\gamma)$ , the Euler angles<sup>9</sup> that rotate space-fixed axes into the body-fixed, principal moment of inertia axes of the molecule; the collision coordinate from rotor center of mass to the atom is conveniently expressed in polar coordinates as  $\underline{R}=(R,\theta,\phi)$ ;  $\mu$  is the reduced mass for the collision; and  $\hbar$  is Planck's constant divided by  $2\pi$ . The scattering wavefunction is obtained by expanding in the rotor eigenfunctions, which are complete in  $\hat{\Omega}$ ; spherical harmonics (partial waves) complete in  $\hat{R}=(\theta,\phi)$ ; and radial functions  $u(R)$ . Substituting this expansion into the Schrodinger equation leads to coupled second-order differential equations for  $u(R)$ . The usual CC method is obtained by transforming these equations to a total angular momentum representation in the space-fixed coordinates; the CS and EP approximations are obtained by ignoring or averaging over some of the coupling terms. Details of these scattering formalisms will be presented after discussing the rotor functions and the form of the intermolecular potential.

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### A. Rotor wavefunctions.

The general rigid rotor Hamiltonian can be written

$$H_{\text{rot}} = (2I_1)^{-1} \mathcal{J}_{x'}^2 + (2I_2)^{-1} \mathcal{J}_{y'}^2 + (2I_3)^{-1} \mathcal{J}_{z'}^2 \quad (2)$$

where  $I_1$ ,  $I_2$ , and  $I_3$  are moments of inertia about the (molecule-fixed) principal axes of inertia  $x'$ ,  $y'$ , and  $z'$ , respectively. (Primes will be used to denote rotating, body-fixed coordinates.)

For a symmetric top molecule, two of the moments of inertia are equal -  $I_1 = I_2$ , i.e.,  $z'$  is chosen as the symmetry axis - so that Eq. (2) becomes

$$H_{\text{st}} = (2I_1)^{-1} \mathcal{J}^2 + [(2I_3)^{-1} - (2I_1)^{-1}] \mathcal{J}_{z'}^2 \quad (3)$$

where  $\mathcal{J}^2 = \mathcal{J}_{x'}^2 + \mathcal{J}_{y'}^2 + \mathcal{J}_{z'}^2$  is the total angular momentum of the rotor.

Eigenfunctions of  $H_{\text{st}}$  can be labeled by  $j$ ,  $k$ , and  $m$ , the total rotor momentum and its projection on the body-fixed  $z'$ -axis and on the space-fixed  $z$ -axis, respectively. Then

$$\mathcal{J}^2 | jkm \rangle = j(j+1) \hbar^2 | jkm \rangle, \quad (4)$$

$$\mathcal{J}_{z'} | jkm \rangle = k \hbar | jkm \rangle, \quad (5)$$

and  $\mathcal{J}_z | jkm \rangle = m \hbar | jkm \rangle. \quad (6)$

Comparing with Eq. (3) one finds that

$$H_{\text{st}} | jkm \rangle = E_{jk} | jkm \rangle \quad (7)$$

with

$$E_{jk} = \hbar^2 \{ (2I_1)^{-1} j(j+1) + [(2I_3)^{-1} - (2I_1)^{-1}] k^2 \}. \quad (8)$$

The symmetric top eigenfunctions can be identified with matrix elements of the rotation operator,

$$| jkm \rangle = [(2j+1)/(8\pi^2)]^{\frac{1}{2}} \mathcal{D}_{km}^j(\alpha\beta\gamma) \quad (9)$$

where, for historical reasons, we follow the convention of Thaddeus<sup>10</sup>

that

$$D_{km}^j(\alpha\beta\gamma) = e^{im\alpha} e^{ik\gamma} d_{km}^j(\beta) \quad (10)$$

with  $d_{km}^j$  as defined by Edmonds.<sup>9</sup> The total angular momentum quantum number  $j$  may take any non-negative integer value;  $k$  and  $m$ , being projections of  $j$ , are restricted to positive or negative integers whose absolute value is less than or equal to  $j$ .

For future reference, the only non-zero matrix elements of the general (asymmetric top) rigid rotor Hamiltonian, Eq. (2), in this basis are

$$\langle jkm | H_{rot} | jkm \rangle = \hbar^2 \{ [(2I_1)^{-1} + (2I_2)^{-1}] [j(j+1) - k^2] / 2 + (2I_3)^{-1} k^2 \} \quad (11a)$$

and

$$\begin{aligned} \langle j, k+2, m | H_{rot} | jkm \rangle &= \langle jkm | H_{rot} | j, k+2, m \rangle = \\ &(\hbar^2/4) [(2I_1)^{-1} - (2I_2)^{-1}] \{ [j(j+1) - k(k+1)] [j(j+1) - (k+1)(k+2)] \}^{1/2}. \end{aligned} \quad (11b)$$

For the symmetric top, it can be seen from Eq. (8) that  $|jkm\rangle$  and  $|j-km\rangle$  are degenerate so that any linear combination will also be a valid eigenfunction with the same energy. Proper symmetric top wavefunctions must also be eigenfunctions of the inversion operator, and the correct linear combinations are

$$|jkm\epsilon\rangle = [2(1+\delta_{k0})]^{-1/2} ( |jkm\rangle + \epsilon |j-km\rangle ) \quad (12)$$

where now  $k \geq 0$ , and  $\epsilon = \pm 1$  except for  $k=0$  when only  $\epsilon=+1$  is allowed.

Because the  $|jkm\rangle$  are a complete set in the angles of orientation,  $\hat{\Omega}$ , wavefunctions for the general, asymmetric top can also be expanded in this set. It is found, c.f. Eq. (11), that the asymmetric top Hamiltonian will not mix states with different  $j, m$  but only different values of  $k$ . Thus, asymmetric top wavefunctions can be written as

$$|jmr\rangle = \sum_k a_{rk} |jkm\rangle. \quad (13)$$

It is convenient to develop the scattering formalism for "primitive" symmetric top functions,  $|jkm\rangle$ . Because  $k$  plays the role of a "spectator" in the angular momentum coupling, and because the Schrödinger equation is linear, it will then be straightforward to take the appropriate combinations, Eq. (12) or Eq. (13), to obtain the correct formulation for symmetric top or asymmetric top rotors. CC, CS, and EP scattering formalisms will be developed in Sections IIC, IID, and IIE, respectively. Correct symmetrization for symmetric tops will be considered in more detail in Section IIF. Extension to asymmetric tops is straightforward and has been discussed by Garrison.<sup>4</sup>

#### B. Intermolecular potential.

The interaction potential,  $V(\hat{\Omega}, \underline{R})$  in Eq. (1) is a function only of the relative orientation of the projectile with respect to the rotor. Thus,  $V(\hat{\Omega}, \underline{R}) = V(\underline{R}') = V(R', \Theta', \Phi')$  where  $\underline{R}'$  is the position of the projectile with respect to (body-fixed) axes along the principal moments of inertia of the rotor. It is convenient to expand the angular dependence here in spherical harmonics,

$$V(R', \Theta', \Phi') = \sum_{\lambda\mu} v_{\lambda\mu}(R') Y_{\lambda\mu}(\Theta', \Phi'). \quad (14)$$

One can then use the transformation properties of the spherical harmonics to relate body-fixed and space-fixed coordinates.<sup>9</sup>

$$\begin{aligned} V(\hat{\Omega}, \underline{R}) &= D^{-1}(\hat{\Omega}) V(\underline{R}') \\ &= \sum_{\lambda\mu} v_{\lambda\mu}(R') \sum_{\nu} [D^{-1}(\hat{\Omega})]_{\nu\mu}^{\lambda} Y_{\lambda\nu}(\hat{R}) \\ &= \sum_{\lambda\mu\nu} v_{\lambda\mu}(R) D_{\mu\nu}^{\lambda}(\hat{\Omega})^* Y_{\lambda\mu}(\hat{R}), \end{aligned} \quad (15)$$

where the fact that  $R=R'$  has been used.

The phase convention for spherical harmonics,

$$Y_{\lambda, -\mu}(R) = (-)^{\mu} Y_{\lambda\mu}(R)^* , \quad (16)$$

plus the fact that the interaction potential is real imply that

$$v_{\lambda, -\mu}(R) = (-)^{\mu} v_{\lambda\mu}(R)^* . \quad (17)$$

For most systems it will also be possible to choose the principal moment of inertia axes so that the  $v_{\lambda\mu}(R)$  are real. This requires only that the  $x'z'$ -plane be a (reflection) plane of symmetry so that

$$V(R', \Theta', \Phi') = V(R', \Theta', -\Phi') \quad (18)$$

which will always be possible for molecules that are symmetric tops due to an  $n$ -fold axis of symmetry along  $z'$ . The interaction potential can then be written as

$$\begin{aligned} V(R', \Theta', \Phi') &= \sum_{\lambda \geq \mu \geq 0} v_{\lambda\mu}(R') [Y_{\lambda\mu}(R') + (-)^{\mu} Y_{\lambda, -\mu}(R')] \\ &\quad \times (1 + \delta_{\mu 0})^{-1} \\ &= \sum_{\lambda \geq \mu \geq 0} v_{\lambda\mu}(R') (2 - \delta_{\mu 0}) P_{\lambda\mu}(\cos \Theta') \cos_{\mu} \Phi' , \end{aligned} \quad (19)$$

with  $P_{\lambda\mu}$  an associated Legendre polynomial.

It is important to emphasize that the body-fixed coordinate system used to expand the potential must correspond to the principal moment of inertia axes ( $x', y', z'$ ) used to define the rotor wavefunctions.

### C. Close Coupling.

The development of the close coupling equations for symmetric top-atom collisions follows the development for linear molecule-atoms of Arthurs and Dalgarno<sup>11</sup> very closely, so that it will only be outlined below. One can form coupled, total angular momentum functions

$$|JMjk\rangle = \sum_m \langle j_1 m_1 j_2 m_2 | JM \rangle | j_1 m_1 j_2 m_2 \rangle \quad (20)$$

where  $| j_1 m_1 j_2 m_2 \rangle$  are given by Eq. (9), the "partial wave" functions are

$$| \ell m \rangle = Y_{\ell m}(\theta, \phi), \quad (21)$$

and  $\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle$  is a Clebsch-Gordan vector-coupling coefficient.<sup>9</sup>

The scattering wavefunction with total momentum J and projection M on the space-fixed z-axis, and appropriate to the entrance channel jkℓ satisfies a Schrodinger equation

$$[H_{st} - (\hbar^2/2\mu) \nabla_R^2 + V - E - E_{jk}] \Psi_{jk\ell}^{JM} = 0 \quad (22)$$

where E is the relative kinetic energy and  $E_{jk}$  is given by Eq. (8).

Expanding  $\Psi_{jk\ell}^{JM}$

$$\Psi_{jk\ell}^{JM} = \sum_{j'k'\ell'} R^{-1} u_{j'k'\ell'}^{JMjk\ell}(R) | JMj'k'\ell' \rangle \quad (23)$$

and substituting into the Schrodinger equation gives the usual coupled equations for the radial functions:

$$\left[ \frac{d^2}{dR^2} - \frac{\ell(\ell+1)}{R^2} + \kappa_{j'k'jk}^2 \right] u_{j'k'\ell'}^{JMjk\ell}(R) = (2\mu/\hbar^2) \sum_{j''k''\ell''} \langle JMj''k''\ell'' | V | JMj'k'\ell' \rangle u_{j''k''\ell''}^{JMjk\ell}(R) \quad (24)$$

where the wavenumber is given by

$$\kappa_{j'k'jk}^2 = (2\mu/\hbar^2) (E + E_{jk} - E_{j'k'}) \quad (25)$$

and the coupling matrix element is

$$\langle JMjk\ell | \sum_{\lambda\mu} v_{\lambda\mu}(R) Y_{\lambda\mu}(\hat{R}) | JMj'k'\ell' \rangle = \sum_{\lambda\mu} v_{\lambda\mu}(R) (-)^{j+j'+k-J} \left[ \frac{(2j+1)(2j'+1)(2\ell+1)(2\ell'+1)(2\lambda+1)}{4\pi} \right]^{\frac{1}{2}}$$

$$\begin{pmatrix} \ell & \ell' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j' & \lambda \\ k & -k' & \mu \end{pmatrix} \left\{ \begin{matrix} j & \ell' & J \\ \ell & j & \lambda \end{matrix} \right\},$$

with  $(:::)$  a 3-j symbol and  $\{:::\}$  a 6-j symbol.<sup>9</sup> There is no coupling between different JM, and the matrix element is independent of M which

will subsequently be dropped from the notation. It is readily shown that

$$\langle Jjk\ell | Y_{\lambda\mu} | Jj'k'\ell' \rangle = \langle Jj'k'\ell' | (-)^{\mu} Y_{\lambda, -\mu} | Jjk\ell \rangle \quad (27)$$

which, together with Eq. (17) ensures that the coupling matrix is Hermitian. Note that different values of  $k$  are connected only by terms in the potential such that  $\mu = k' - k$ . The following property of the coupling matrix elements will also be useful:

$$\langle Jj-k\ell | Y_{\lambda\mu} | Jj'-k'\ell' \rangle = (-)^{j+j'+\lambda} \langle Jjk\ell | Y_{\lambda, -\mu} | Jj'k'\ell' \rangle. \quad (28)$$

Comparing the asymptotic form of  $u(R)$  with the interactionless solutions defines the scattering  $\underline{S}$ -matrix in the usual way:

$$u_{j'k'\ell'}^{jkk\ell}(R) \sim \delta_{jj'} \delta_{kk'} \delta_{\ell\ell'} \exp[-i(\kappa_{jkk} R - \ell\pi/2)] - (\kappa_{jkk}/\kappa_{j'k'j})^{1/2} \langle jk\ell | S^J | j'k'\ell' \rangle \exp[i(\kappa_{j'k'j} R - \ell'\pi/2)]. \quad (29)$$

State-to-state integral cross sections, summed over final and averaged over initial degeneracies, can be obtained from the  $\underline{S}$ -matrix as

$$\sigma(jk \rightarrow j'k') = \pi \kappa_{jkk}^{-2} (2j+1)^{-1} \sum_{J\ell\ell'} (2J+1) |\delta_{jj'} \delta_{kk'} \delta_{\ell\ell'} - \langle jk\ell | S^J | j'k'\ell' \rangle|^2. \quad (30)$$

It should be noted that the  $k$  quantum number plays a "spectator" role in the angular momentum coupling. Therefore, one can immediately write down formulas, in terms of  $\underline{S}$ -matrix elements, for differential cross sections,<sup>11</sup> pressure broadening,<sup>1a</sup> etc., by merely adding a  $k$  label to the formulas for linear molecules. Furthermore, if the rotor wavefunctions are linear combinations among  $k$  values, as is the case for symmetric top functions of proper symmetry and also for asymmetric tops, it is necessary only to transform the coupling matrix, Eq. (26), into this new basis and replace the  $k$  label with the appropriate new label (i.e.  $k_c$  for symmetric tops, c.f. Eq. (12); or  $\tau$  for asymmetric tops, c.f. Eq. (13)).

#### D. Coupled States.

It is possible to write the CC scattering equations in a body-fixed, i.e., rotating, coordinate system rather than in the space-fixed system of Arthurs and Dalgarno. (See, e.g., the helicity formulation of Jacob and Wick.<sup>12</sup>) The CS approximation is derived in the "R-helicity" coordinates in which the z'-axis lies along the collision coordinate  $\underline{R}$ . Then  $\bar{m}_\ell$ , the projection of the orbital angular momentum on  $\underline{R}$ , is zero by definition so that the total angular momentum expansion basis, analogous to Eq. (20), can be labeled by  $|JMj\bar{m}\rangle$  where  $\bar{m}$  is the projection of  $j$  on  $\underline{R}$ . This basis is related to the space-fixed basis, Eq. (20), by a unitary transformation, as discussed, e.g., by Child<sup>13</sup> and Walker and Light.<sup>14</sup> In the body-fixed system, the interaction potential matrix is diagonal in  $\bar{m}$  and independent of  $\ell$ . However,  $\ell^2$  is no longer diagonal as it is in the space-fixed system, but connects states with different  $\bar{m}$ , corresponding to "Coriolis forces" in the rotating frame.

The coupled states approximation introduced by McGuire and Kouri<sup>6a</sup> consists of neglecting the off-diagonal matrix elements of  $\ell^2$  in the body-fixed frame and further approximating the diagonal ones by

$$\langle JMj\bar{m} | \ell^2 | JMj'k'\bar{m}' \rangle = \hbar^2 J(J+1) \delta_{\bar{m}\bar{m}'} \delta_{jj'} \delta_{kk'} . \quad (31)$$

This approximation and some related variants have been extensively discussed by McGuire and Kouri and co-workers.<sup>6</sup> Therefore, only the modifications to the potential matrix elements necessary for symmetric tops will be presented here. The potential matrix in the body-fixed frame is given by

$$\langle JMj\bar{k}\bar{m} | \sum_{\lambda\mu} v_{\lambda\mu}(R') Y_{\lambda\mu}(\hat{R}') | JMj'k'\bar{m}' \rangle = \sum_{\lambda\mu} v_{\lambda\mu}(R) (-)^{-k'\bar{m}} \quad (32)$$

$$\left[ \frac{(2j+1)(2j'+1)(2\lambda+1)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} j & \lambda & j' \\ -k & \mu & k' \end{pmatrix} \begin{pmatrix} j & \lambda & j' \\ -\bar{m} & 0 & \bar{m}' \end{pmatrix}$$

which is readily derived using the fact that

$$Y_{\lambda\mu}(\beta\gamma) = (-)^{\mu} [(2\lambda+1)/(4\pi)]^{\frac{1}{2}} D_{\mu 0}^{\lambda}(\alpha\beta\gamma). \quad (33)$$

Note that Eq. (32) implies no coupling unless  $\bar{m}=\bar{m}'$ , and also that different values of  $k$  are coupled only by terms in the potential such that  $\mu=k-k'$ . Again, matrix elements are independent of  $M$  which is subsequently dropped from the notation.

As in the CC method, the potential matrix is Hermitean since, c.f. Eq. (27),

$$\langle Jj\bar{k}\bar{m} | Y_{\lambda\mu} | Jj'k'\bar{m}' \rangle = \langle Jj'k'\bar{m}' | (-)^{\mu} Y_{\lambda, -\mu} | Jj\bar{k}\bar{m} \rangle. \quad (34)$$

The following properties of the potential matrix elements will also be useful:

$$\langle Jj\bar{k}-\bar{m} | Y_{\lambda\mu} | Jj'k'\bar{m}' \rangle = (-)^{j+j'+\lambda} \langle Jj\bar{k}\bar{m} | Y_{\lambda\mu} | Jj'k'\bar{m}' \rangle, \quad (35)$$

and

$$\langle Jj-k\bar{m} | Y_{\lambda\mu} | Jj'-k'\bar{m}' \rangle = (-)^{j+j'+\lambda} \langle Jj\bar{k}\bar{m} | Y_{\lambda, -\mu} | Jj'k'\bar{m}' \rangle. \quad (36)$$

The coupled differential equations for the CS approximation are identical in form to those for CC (c.f. Eq. (24)) except that  $\ell=J$  and the channels are labeled by  $Jj\bar{k}\bar{m}$  rather than  $Jjk\ell$ . There is no coupling between channels with different  $\bar{m}$ , and separate sets of equations must be solved for  $\bar{m}=0, \pm 1, \pm 2, \dots, \pm j^*$ , where  $j^*$  is the maximum rotor  $j$ -value of interest. The asymptotic form of the radial functions defines a scattering matrix  $\langle j\bar{k}\bar{m} | S^J | j'k'\bar{m}' \rangle$  exactly as in the CC method (c.f. Eq. (29)) from which the degeneracy averaged cross sections are obtained



(c.f. Eq. (30)) as

$$\sigma(jk \rightarrow j'k') = \pi \kappa_{jkjk}^{-2} (2j+1)^{-1} \sum_{\bar{m}} (2J+1) \quad (37)$$

$$| \delta_{jj'} \delta_{kk'} - \langle jk\bar{m} | S^J | j'k'\bar{m} \rangle |^2$$

### E. Effective potential.

The effective potential approximation was obtained by Rabitz<sup>5a</sup> by taking a particular average of the potential matrix elements over degenerate rotational sublevels in an uncoupled, space-fixed representation. This approach can alternatively be considered to be an expansion of the total scattering wavefunction with "effective rotational states" which are non-degenerate and which do not couple to the (partial wave) orbital angular momentum. This leads to coupled equations identical in form to CC (c.f. Eq. (24)) except that, since  $J$  and  $\ell$  are now identical, the channels can be labeled by  $Jjk$  rather than  $Jjk\ell$ .

The EP matrix elements for symmetric top systems have been derived by Tarr and Rabitz.<sup>5d</sup> For a symmetric top-atom collision the potential matrix is given by

$$\langle Jjk | \sum_{\lambda\mu} v_{\lambda\mu}(R') Y_{\lambda\mu}(R') | Jj'k' \rangle = \sum_{\lambda\mu} v_{\lambda\mu}(R) (-)^{\mu-k} \quad (38)$$

$$\exp[i\pi(|j'-j| + j'+j)/2] (4\pi)^{-\frac{1}{2}} [(2j+1)(2j'+1)]^{\frac{1}{4}}$$

$$\begin{pmatrix} j & \lambda & j' \\ -k & -\mu & k' \end{pmatrix} .$$

The potential matrix is seen to be independent of  $J$ . Coupling between  $k$  levels is due to terms in the potential such that  $\mu = k' - k$ . Hermiticity of the coupling matrix is ensured since, as in CC and CS,

$$\langle Jj'k' | Y_{\lambda\mu} | Jjk \rangle = \langle Jjk | (-)^{\mu} Y_{\lambda, -\mu} | Jj'k' \rangle . \quad (39)$$

The following property will also be useful:

$$\langle Jj-k | Y_{\lambda\mu} | Jj'-k' \rangle = (-)^{j+j'+\lambda} \langle Jjk | Y_{\lambda,-\mu} | Jj'k' \rangle. \quad (40)$$

The asymptotic form of the radial equations defines a scattering matrix  $\langle jk | S^J | j'k' \rangle$  exactly as in CC (c.f. Eq. (29)) from which degeneracy-averaged cross sections are obtained as (c.f. Eq. (30))

$$\sigma(jk \rightarrow j'k') = \pi \kappa_{jkjk}^{-2} / g(j, j') \sum_J (2J+1) |\delta_{jj'} \delta_{kk'} - \langle jk | S^J | j'k' \rangle|^2. \quad (41)$$

The "counting-of-states" correction,  $g(j, j')$ , was introduced by Zarur and Rabitz<sup>5c</sup> to ensure proper detailed balance,

$$(2j+1) \kappa_j^2 \sigma(j \rightarrow j') = (2j'+1) \kappa_{j'}^2 \sigma(j' \rightarrow j), \quad (42)$$

which doesn't arise naturally in EP due to the use of "effective rotational states" that lack the normal  $2j+1$  degeneracy. Zarur and Rabitz suggested for linear molecule-atom collisions the most symmetrical form,

$$g(j, j') = [(2j+1)/(2j'+1)]^{\frac{1}{2}}. \quad (43)$$

However, it appears that a better choice might be<sup>7</sup>

$$g(j, j') = \begin{cases} 1, & j \leq j' \\ (2j+1)/(2j'+1), & j > j' \end{cases}. \quad (44)$$

In either case, the counting-of-states factor is the same for symmetric tops and linear molecules.

#### F. Symmetric top functions of proper parity.

As indicated in Section IIA, symmetric top eigenfunctions with proper parity are, Eq. (12),

$$| jkmc \rangle = [2(1+\delta_{k0})]^{-\frac{1}{2}} ( | jkm \rangle + \epsilon | j-km \rangle )$$

where  $k \geq 0$  and  $\epsilon = \pm 1$  except that only  $\epsilon = +1$  is allowed for  $k=0$ . By consi-

dering this linear combination along with the symmetry properties of the interaction potential, Eq. (19), the final working equations are derived for CC, CS, and EP scattering of a symmetric top molecule by an atom.

In the CC method, one must consider matrix elements of the interaction potential of the form

$$v_{\lambda\mu} \langle Jjk\ell | [Y_{\lambda\mu} + (-)^{\mu} Y_{\lambda-\mu}] / (1+\delta_{\mu 0}) | Jj'k'e'\ell' \rangle = \quad (45)$$

$$v_{\lambda\mu} [2(1+\delta_{\mu 0})]^{-1} [(1+\delta_{k0})(1+\delta_{k'0})]^{-\frac{1}{2}}$$

$$[\langle Jjk\ell | Y_{\lambda\mu} + (-)^{\mu} Y_{\lambda-\mu} | Jj'k'\ell' \rangle + \epsilon \langle Jj-k\ell | Y_{\lambda\mu} + (-)^{\mu} Y_{\lambda-\mu} | Jj'k'\ell' \rangle$$

$$+ \epsilon' \langle Jjk\ell | Y_{\lambda\mu} + (-)^{\mu} Y_{\lambda-\mu} | Jj'-k'\ell' \rangle + \epsilon\epsilon' \langle Jj-k\ell | Y_{\lambda\mu} + (-)^{\mu} Y_{\lambda-\mu} | Jj'-k'\ell' \rangle].$$

Note that  $\mu$ ,  $k$ , and  $k'$  are non-negative here. Recalling that a matrix element vanishes unless  $\mu=k'-k$  and using Eq. (28) to reverse the sign of  $k$  and  $k'$  in the third and fourth terms, one obtains

$$v_{\lambda\mu} \langle Jjk\ell | [Y_{\lambda\mu} + (-)^{\mu} Y_{\lambda-\mu}] / (1+\delta_{\mu 0}) | Jj'k'e'\ell' \rangle = \quad (46)$$

$$v_{\lambda\mu} \vartheta [(1+\delta_{k0})(1+\delta_{k'0})]^{-\frac{1}{2}}$$

$$(\omega \langle Jjk\ell | Y_{\lambda\mu} | Jj'k'\ell' \rangle + \epsilon \langle Jj-k\ell | Y_{\lambda\mu} | Jj'k'\ell' \rangle)$$

where

$$\vartheta = [1 + \epsilon\epsilon' (-)^{j+j'+\lambda+\mu}] / 2. \quad (47)$$

There will be a contribution from the first term in Eq. (46) only if  $\mu=k'-k$ , and it will enter with parity

$$\omega = \begin{cases} 1, & k'-k \geq 0 \\ (-)^{\mu}, & k'-k < 0 \end{cases}. \quad (48)$$

There will be a contribution from the second term only if  $\mu=k'+k$ . Only one of these terms will contribute unless  $k=0$  and/or  $k'=0$ .

It can be verified that the potential matrix elements vanish identically unless

$$\epsilon(-)^{j+k+l} = \epsilon'(-)^{j'+k'+l'} \quad (49)$$

The CC equations can therefore be split into two non-interacting parity blocks for each J, leading to a reduction in computational effort.

The analysis for the EP approximation follows identically that for CC. The final equation is

$$\begin{aligned} v_{\lambda\mu} \langle Jjk\epsilon | [Y_{\lambda\mu} + (-)^{\mu} Y_{\lambda-\mu}] / (1+\delta_{\mu 0}) | Jj'k'\epsilon' \rangle = & \quad (50) \\ v_{\lambda\mu} \vartheta [(1+\delta_{k0})(1+\delta_{k'0})]^{-\frac{1}{2}} & \\ (\omega \langle Jjk | Y_{\lambda+\mu} | Jj'k' \rangle + \epsilon \langle Jj-k | Y_{\lambda\mu} | Jj'k' \rangle) & \end{aligned}$$

with  $\vartheta$  and  $\omega$  as defined by Eqs. (47) and (48).

The analysis for the CS approximation is similar except that the role of  $k$  and  $k'$  is interchanged:

$$\begin{aligned} v_{\lambda\mu} \langle Jjk\bar{m}\epsilon | [Y_{\lambda\mu} + (-)^{\mu} Y_{\lambda-\mu}] / (1+\delta_{\mu 0}) | Jj'k'\bar{m}'\epsilon' \rangle = & \quad (51) \\ v_{\lambda\mu} \vartheta [(1+\delta_{k0})(1+\delta_{k'0})]^{-\frac{1}{2}} & \\ (\bar{\omega} \langle Jjk\bar{m} | Y_{\lambda+\mu} | Jj'k'\bar{m}' \rangle + \epsilon' \langle Jj\bar{k}\bar{m} | Y_{\lambda\mu} | Jj'-k'\bar{m}' \rangle) & \end{aligned}$$

where

$$\bar{\omega} = \begin{cases} 1, & k-k' \geq 0 \\ (-)^{\mu}, & k-k' < 0 \end{cases} \quad (52)$$

and  $\vartheta$  is given by Eq. (47).

### III. Calculations for $\text{NH}_3\text{-He}$

#### A. Intermolecular potential.

The intermolecular potential was obtained as a function of the position of He relative to the ammonia center of mass,  $(R', \theta', \phi')$ , in body-fixed, principal moment of inertia coordinates (c.f. Eq. (14)). The geometry of the ammonia molecule can be described by the (cartesian) coordinates of the nuclei in this same system -  $\text{N}(0., 0., 0.127)$ ,  $\text{H}_1(1.771, 0., -0.5928)$ ,  $\text{H}_2(-0.8855, 1.5337, -0.5928)$ ,  $\text{H}_3(-0.8855, -1.5337, -0.5928)$  with all distances in bohr ( $1 a_0 = 0.52918 \times 10^{-8}$  cm) - which is close to the equilibrium structure inferred from microwave spectra. The interaction potential was computed via the electron gas model of Gordon and Kim,<sup>15</sup> using the computer program of Green and Gordon.<sup>16</sup> From comparisons with more rigorous quantum calculations for other systems it appears that this method provides a semi-quantitative estimate of the distance and angle dependence of the short-range repulsive interaction.<sup>17</sup> It also appears to give a reasonable estimate of the position of the van der Waals minimum. It does not, however, correctly reproduce the long-range induction and dispersion energies, but falls to zero too rapidly. In previous work we have supplemented the electron gas approximation by smoothly joining it to the asymptotically correct long-range electrostatic interaction. Because the cross sections here are not expected to be very sensitive to the long-range interaction, and because this study is designed more as a model calculation than an attempt to obtain detailed cross sections for this system, the electron gas interaction has been used without further

modification.

The electron charge densities necessary for the Gordon-Kim method were obtained from Hartree-Fock functions. The  $\text{NH}_3$  function was obtained using a Gaussian basis of approximately "triple zeta" quality plus p polarization functions on the hydrogens.<sup>18</sup> For He, the accurate Slater basis function of Clementi<sup>19</sup> was used. The interaction potential was computed for  $R'/a_0 = 3.0$  (0.5) 9.5,  $\Theta' = 0$  (30)  $180^\circ$ , and  $\Phi' = 0$  (15)  $60^\circ$ . For each  $R'$  value, the angular dependence was expanded in spherical harmonics, Eq. (19), by minimizing the root-mean-square average error. Because of the three-fold axis of symmetry, only  $Y_{\lambda\mu}$  with  $\mu=3n$  are allowed in the expansion. A twelve term fit, which reproduced all computed points to a few percent, was adopted for the scattering calculations; this is presented in table 1. Smooth radial functions and derivatives were obtained from the tabulated points by fifth-order Lagrange interpolation plus exponential extrapolation at short-range and inverse power extrapolation at long-range.<sup>1c</sup>

By examining semi-logarithmic plots of the  $v_{\lambda\mu}(R')$  for the short-range repulsive interaction, i.e.  $R' \leq 5a_0$ , one finds approximate exponential behavior

$$v_{\lambda\mu} \approx a_{\lambda\mu} \exp(-b_{\lambda\mu} R') \quad (53)$$

Furthermore, the slopes of the dominant terms are quite similar so that

$$v_{\lambda\mu} \approx \alpha_{\lambda\mu} a_{00} \exp(-b_{00} R') \quad (54)$$

The strength of the anisotropy is then reflected in the size of the various  $\alpha_{\lambda\mu}$ , from which it is seen that the interaction here is only weakly anisotropic, i.e.,  $\alpha_{\lambda\mu} \ll 1$ .

## B. Scattering calculations.

Using the intermolecular potential described in the previous section CC, CS, and EP calculations have been performed. The coupled differential equations were solved using the piecewise analytic algorithm of Gordon<sup>20</sup> as implemented in the MOLSCAT<sup>21</sup> computer programs. Tolerances were set to obtain 2-3 significant figure accuracy in the final cross sections.

Because of permutational symmetry among the identical hydrogen nuclei in ammonia, the rotational levels can be divided into two sets which are associated with different nuclear spin states and which interconvert at a negligible rate in thermal energy collisions. Levels with  $k=3n$  are designated ortho-NH<sub>3</sub> and levels with  $k=3n+1$  are designated para-NH<sub>3</sub>. That the scattering calculations predict no interconversion of ortho- and para-NH<sub>3</sub> can be seen as follows: Molecular symmetry ensures that the expansion of the intermolecular potential, Eq. (19), will contain only terms with  $\mu=3n$ . The coupling matrix elements in the scattering formalism vanish unless  $\Delta k=\mu$ . Therefore, there will never be coupling between ortho- and para-levels and hence zero probability for collisional interconversion. Since ortho- and para-NH<sub>3</sub> are totally decoupled, scattering calculations can be done separately for the two species. (This situation is entirely analogous to the more familiar ortho-para distinction in H<sub>2</sub>.)

For para-NH<sub>3</sub> the scattering equations are invariant to simultaneous change of parity in the incoming and outgoing channels. Thus  $\sigma(jk\epsilon \rightarrow j'k'\epsilon')$  is equal to  $\sigma(jk\bar{\epsilon} \rightarrow j'k'\bar{\epsilon}')$  where  $\bar{\epsilon}$  denotes the opposite parity from  $\epsilon$ , and only one of these cross sections will be reported subsequently. Note,

nonetheless, that both parities must be included in the scattering calculations. This symmetry does not obtain for ortho-NH<sub>3</sub> because the k=0 levels exist in only one parity. Also, any energy splitting of the k-doublets, such as that caused by inversion motion, would destroy the perfect symmetry found here for para-NH<sub>3</sub>.

The major approximation in the CC method is retention of only a finite subset of the molecular rotational levels in the expansion of the total wavefunction. Therefore, a number of calculations have been done to examine convergence of the cross sections as the expansion basis is increased. Results of such tests are presented in table 3 for ortho-NH<sub>3</sub> and in table 4 for para-NH<sub>3</sub>. The difficulty in using larger basis sets can be appreciated by noting that the B15 calculation for ortho-NH<sub>3</sub> required solving 61 and 68 coupled equations for the two parities at each J, and the B20 calculation for para-NH<sub>3</sub> required solving two sets of 76 coupled equations for each J. It is apparent that converged cross sections are obtained by including all open (i.e. energetically accessible) channels plus, perhaps, a few of the lowest closed channels. This rapid convergence can be attributed in part to the small anisotropy and widely-spaced energy levels in this system which minimize the effect of indirect (higher order) coupling. If the interaction were more anisotropic, or if the potential well were deeper compared to the energy splittings (leading to Feshbach resonances), one might expect poorer basis set convergence. The basis set convergence in CS and EP calculations was found to be similar to that presented for the CC calculations.



An examination of the CC cross sections begins to reveal interesting "propensity" rules for different  $\Delta j$ ,  $\Delta k$ , and parity transitions, the existence of which had been previously inferred from double resonance data. To systematically study these, however, requires cross sections among more levels than have been included here, so that apparent trends have some statistical validity. Since it is not currently feasible to extend the CC calculations to many more levels, it is important to document the validity of cheaper approximations. Toward this end, CS and EP cross sections are compared with CC values in tables 5 and 6. The EP cross sections are given both with (Eq. (43)) and without (Eq. (44)) the "counting-of-states" correction suggested by Zarur and Rabitz.<sup>5c</sup> The CS approximation is seen to give integral cross sections in semi-quantitative agreement with CC. Although significant differences exist for a few isolated transitions, CS appears to be generally quite reliable for predicting the magnitude and relative size of different cross sections for this system. The cheaper EP approximation is in somewhat poorer quantitative agreement with CC but is still generally reliable for estimating the magnitude and relative size of cross sections. Experience with linear molecule-atom collisions would lead one to attribute the accuracy of EP here to the small anisotropy in this system. Also, following previous experience, for most transitions EP without the "counting-of-states" correction gives better agreement with CC.

The integral cross sections considered above are only one measure of the overall collision dynamics - albeit a very important one since they determine the rate of collisional energy transfer - and it is

important to determine whether CS and EP provide a reliable description of other details of the collision dynamics as well.<sup>1f,22</sup> In this paper only the partial opacities - the contribution to the cross section from different total J or partial waves - will be considered. It is found that the CS partial opacities agree very well with CC values for inelastic processes, the largest discrepancies, if any, being in the lowest few partial waves. For elastic cross sections, however, the agreement is not so good, with the exception of  $\sigma^J(00+00+)$ ; for other elastic transitions CS values tend to oscillate about the CC results. Fig. 1 shows typical examples of both cases. The behavior of EP partial opacities was found to be quite similar to that of CS. Although detailed calculations have not yet been performed, one can anticipate<sup>22</sup> from the behavior of the CS and EP elastic partial opacities that these approximations may not be adequate to describe other collisional phenomena, in particular, differential cross sections and collision induced spectral pressure broadening, for this system.

#### IV. Conclusions

The formalism for describing collisions of a symmetric top rotor with a spherical atom has been presented both within the accurate close coupling framework and also the coupled states and effective potential approximations. Calculations have been performed for a model of the  $\text{NH}_3\text{-He}$  system which demonstrate the feasibility of CC when only a few of the lowest rotational levels are of interest. These begin to show interesting "propensity rules" for parity changes, the existence of which had been previously inferred from microwave double resonance experiments.<sup>8</sup> Unfortunately, a proper study to compare with available data requires more rotational levels than can be handled by CC with present computational techniques.

On the other hand, it was found that the CS approximation gave results in nearly quantitative agreement with CC and that the FP approximation was at least qualitatively correct. These methods are also cheap enough to allow a proper study of collisional energy transfer in ammonia. To compare with experimental data, however, such a study must also account for the inversion motion which has been ignored here. To conclude this paper a brief discussion will be given of the necessary modifications.

To a first approximation, inversion can be described<sup>23</sup> as one-dimensional motion of the nitrogen nucleus along the  $z'$ -axis (with corresponding motion of the hydrogens in the opposite direction to preserve the center of mass at the origin). If this coordinate is labeled  $h$ , then the rigid rotor configuration described in Section III.A

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corresponds to  $h=h_e$ , the equilibrium position. From symmetry, the vibrational potential energy is unchanged on taking  $h \rightarrow -h$  so that there is a corresponding minimum at  $h=-h_e$ , and a potential barrier between these with maximum at  $h=0$ . The lowest vibrational mode in this potential is symmetric with respect to  $h \rightarrow -h$ , and the first excited mode is anti-symmetric. To achieve proper symmetry of the total wavefunctions for ammonia (electronic-vibrational-rotational-nuclear spin) the symmetric (anti-symmetric) inversion function can combine only with one of the two  $|jk_{\pm m}\rangle$  symmetric top functions; the lower (upper) inversion doublet then corresponds to the lowest (first excited) vibrational mode plus the appropriate rotational parity function. For  $k=0$  only one of the rotational parity states exists and only the corresponding even or odd vibrational state is then allowed. (See Ref. 23 for a more detailed discussion.) It is thus seen that each of the parity rotor basis functions used in this study corresponds to a specific upper or lower member of a doublet.

It is also necessary to consider the effect of the inversion motion on the interaction potential and its matrix elements. For the projectile at  $(R', \Theta', \Phi')$  in the molecule-fixed axes it is apparent that the interaction depends parametrically on the inversion coordinate,  $h$ , the potential given in Section III.A corresponding to  $h=h_e$ . From simple geometry considerations one has the useful fact that the coordinate change  $h \rightarrow -h$  is equivalent to  $\Theta' \rightarrow \pi - \Theta'$ . The potential matrix elements must be averaged over the inversion motion. In principle, the interaction must be obtained as a function of  $R', \Theta', \Phi'$ , and  $h$  and averaged over the vibrational functions which depend on  $h$ . It can be noted, however, that the

lowest and first excited vibrational functions for ammonia peak rather sharply near the two equilibrium positions  $h=\pm h_e$ . To a good approximation then, it is seen that vibrational matrix elements between levels with the same parity are given by

$$\begin{aligned} \langle \pm | V | \pm \rangle &\approx \frac{1}{2}[V(R', \Theta', \Phi'; h_e) + V(R', \Theta', \Phi'; -h_e)] \\ &\approx \frac{1}{2}[V(R', \Theta', \Phi'; h_e) + V(R', \pi - \Theta', \Phi'; h_e)], \end{aligned} \quad (55)$$

and between levels of different parity by

$$\langle \mp | V | \pm \rangle \approx \frac{1}{2}[V(R', \Theta', \Phi'; h_e) - V(R', \pi - \Theta', \Phi'; h_e)]. \quad (56)$$

Thus, the computational techniques now appear to be in hand for studying energy transfer in ammonia-rare gas collisions. The experimental results of Oka<sup>8</sup> will then provide a stringent test of these theoretical methods. Besides the double resonance data, collisional excitation of ammonia is also of current astrophysical interest for interpreting the observed non-thermal excitation of interstellar  $\text{NH}_3$ .<sup>24</sup> For these reasons we hope to undertake a more complete study of this system in the near future.

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Table 1

Interaction potential between  $\text{NH}_3$  and He analyzed into spherical harmonics, c.f. Eq. (19).<sup>a</sup>

$R, a_0$	$V_{00}$	$V_{10}$	$V_{20}$	$V_{30}$	$V_{33}$	$V_{40}$	$V_{43}$	$V_{50}$	$V_{53}$	$V_{60}$	$V_{63}$	$V_{66}$
3.0	69800.0	-10700.0	-12100.0	13200.0	-16000.0	633.0	7550.0	-3010.0	432.0	707.0	-1570.0	2160.0
3.5	26200.0	-4020.0	-3900.0	4740.0	-5680.0	141.0	2510.0	-903.0	74.6	203.0	-417.0	551.0
4.0	9070.0	-1450.0	-1150.0	1640.0	-1960.0	2.4	834.0	-269.0	1.0	62.1	-111.0	146.0
4.5	2740.0	-482.0	-288.0	522.0	-627.0	-20.9	265.0	-76.3	-8.5	19.5	-28.9	38.9
5.0	574.0	-141.0	-48.8	140.0	-173.0	-16.0	75.3	-18.2	-6.3	5.9	-6.7	10.3
5.5	-54.7	-31.1	0.0	25.7	-35.4	-9.1	18.5	-2.6	-2.9	2.3	-2.9	3.7
6.0	-168.0	-2.8	-0.4	1.1	-2.3	-3.5	3.0	0.1	-1.8	0.9	-0.7	1.2
6.5	-140.0	2.9	-5.8	-1.2	2.1	-0.2	-0.1	0.2	-0.6	0.3	-0.2	0.5
7.0	-91.0	3.1	-7.6	0.3	0.8	1.1	-0.2	-0.1	-0.1	0.1	-0.1	0.3
7.5	-53.0	2.4	-6.4	1.1	-0.2	1.3	0.0	-0.3	0.2	-0.0	-0.1	0.1
8.0	-30.0	1.8	-4.3	1.0	-0.4	1.1	0.0	-0.2	0.2	-0.1	0.0	0.0
8.5	-15.5	1.3	-2.5	0.6	-0.3	0.8	-0.1	-0.1	0.2	-0.1	0.0	0.0
9.0	-8.1	0.9	-1.3	0.3	-0.1	0.5	-0.1	-0.1	0.1	-0.1	0.0	0.0
9.5	-4.1	0.6	-0.6	0.1	0.0	0.3	-0.1	0.0	0.1	0.0	0.0	0.0

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

Table 2

Rotational levels of ortho- and para-ammonia included in the scattering calculations.

ortho			para		
<u>level</u>	<u>j</u> <u>k</u> <u>ε</u>	<u>E<sub>j k ε</sub>, cm<sup>-1</sup></u>	<u>level</u>	<u>j</u> <u>k</u> <u>ε</u>	<u>E<sub>j k ε</sub>, cm<sup>-1</sup></u>
1	0 0 +	0.	1	1 1 +	16.2446
2	1 0 +	19.8305	2	1 1 -	16.2446
3	2 0 +	59.6414	3	2 1 +	56.0055
4	3 0 +	119.2828	4	2 1 -	56.0055
5	3 3 +	86.5601	5	2 2 +	45.0980
6	3 3 -	86.5601	6	2 2 -	45.0980
7	4 0 +	198.8046	7	3 1 +	115.6469
8	4 3 +	166.0819	8	3 1 -	115.6469
9	4 3 -	166.0819	9	3 2 +	104.7393
10	5 0 +	298.2068	10	3 2 -	104.7393
11	5 3 +	265.4841	11	4 1 +	195.1687
12	5 3 -	265.4841	12	4 1 -	195.1687
13	6 0 +	417.4895	13	4 2 +	184.2612
14	6 3 +	384.7668	14	4 2 -	184.2612
15	6 3 -	384.7668	15	4 4 +	140.6310
16	6 6 +	286.5989	16	4 4 -	140.6310
17	6 6 -	286.5989	17	5 1 +	294.5708
			18	5 1 -	294.5708
			19	5 2 +	283.6631
			20	5 2 -	283.6631

Table 3

Basis set convergence of cross sections for collisions of ortho-NH<sub>3</sub> with He at a total energy of 100. cm<sup>-1</sup>. Basis designated B<sub>n</sub> includes the first n levels of ortho-NH<sub>3</sub> listed in table 2.

		$\sigma(jk\epsilon \rightarrow j'k'\epsilon'), \text{ \AA}^2$			
<u>j k <math>\epsilon</math></u>	<u>j' k' <math>\epsilon'</math></u>	<u>B6</u>	<u>B9</u>	<u>B12</u>	<u>B15</u>
0 0 +	0 0 +	156.	156.	156.	156.
	1 0 +	1.22	1.18	1.18	1.18
	2 0 +	0.46	0.57	0.61	0.67
	3 3 +	0.067	0.092	0.11	0.12
	3 3 -	0.91	0.90	0.94	0.93
1 0 +	1 0 +	162.	162.	162.	162.
	2 0 +	0.99	0.99	1.02	1.03
	3 3 +	0.95	0.95	0.93	0.94
	3 3 -	0.041	0.045	0.047	0.049
2 0 +	2 0 +	158.	158.	158.	158.
	3 3 +	0.27	0.31	0.33	0.36
	3 3 -	0.75	0.77	0.80	0.81
3 3 +	3 3 +	85.5	85.2	84.8	85.1
	3 3 -	0.41	0.41	0.43	0.43
3 3 -	3 3 -	86.0	85.6	85.4	85.6

Table 4

Basis set convergence of cross sections for collisions of para-NH<sub>3</sub> with He at a total energy of 100 cm<sup>-1</sup>. Basis designated B<sub>n</sub> includes the first n levels of para-NH<sub>3</sub> listed in table 2.

$$\sigma(jk\epsilon \rightarrow j'k'\epsilon'), \text{ \AA}^2$$

<u>j k <math>\epsilon</math></u>	<u>j'k'<math>\epsilon'</math></u>	<u>B6</u>	<u>B10</u>	<u>B16</u>	<u>B20</u>
1 1 +	1 1 +	161.	161.	161.	161.
	1 1 -	0.72	0.67	0.60	0.60
	2 1 +	0.67	0.66	0.61	0.61
	2 1 -	0.16	0.16	0.16	0.17
	2 2 +	0.0035	0.012	0.011	0.011
	2 2 -	1.07	1.01	1.03	1.03
2 1 +	2 1 +	163.	162.	161.	161.
	2 1 -	0.49	0.46	0.38	0.37
	2 2 +	0.81	0.74	0.74	0.74
	2 2 -	0.11	0.13	0.12	0.12
2 2 +	2 2 +	165.	165.	165.	165.
	2 2 -	0.74	0.74	0.72	0.71

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Table 5

Comparison of close coupling, coupled states, and effective potential cross sections for excitation of ortho-NH<sub>3</sub>.

Energy, cm <sup>-1</sup>	j k e	j'k'e'	$\sigma(jke \rightarrow j'k'e'), \text{\AA}^2$				
			CC/B15	CS/B15	EP/B15	(corrected) <sup>a</sup>	
100.	0 0 +	0 0 +	156.	156.	157.	157.	
		1 0 +	1.18	1.05	0.97	1.68	
		2 0 +	0.67	0.29	0.12	0.27	
		3 3 +	0.12	0.0	0.029	0.076	
		3 3 -	0.93	1.13	0.52	1.37	
	1 0 +	1 0 +	162.	163.	158.	158.	
		2 0 +	1.03	1.15	2.23	2.89	
		3 3 +	0.94	0.94	0.74	1.14	
		3 3 -	0.049	0.036	0.20	0.30	
	2 0 +	2 0 +	158.	156.	146.	146.	
		3 3 +	0.36	0.29	1.04	1.24	
		3 3 -	0.81	0.81	1.38	1.63	
	3 3 +	3 3 +	85.	86.	77.	77.	
		3 3 -	0.43	0.45	0.43	0.43	
	3 3 -	3 3 -	86.	86.	75.	75.	
	190.	0 0 +	0 0 +	124.	125.	125.	125.
			1 0 +	1.42	1.38	1.24	2.16
			2 0 +	0.25	0.14	0.24	0.54
			3 0 +	0.45	0.46	0.30	0.80
			3 3 +	0.0017	0.0	0.022	0.058
			3 3 -	2.65	2.71	1.63	4.32
			4 3 +	0.0003	0.0	0.0025	0.0075
			4 3 -	0.18	0.17	0.14	0.43
1 0 +		1 0 +	130.	130.	123.	123.	
		2 0 +	1.30	1.30	2.90	3.75	
		3 0 +	0.12	0.15	0.21	0.32	
		3 3 +	2.24	2.30	2.07	3.16	
		3 3 -	0.10	0.11	0.47	0.71	
		4 3 +	0.10	0.11	0.15	0.27	
		4 3 -	0.35	0.33	0.20	0.36	

Table 5, continued

<u>Energy, cm<sup>-1</sup></u>	<u>j k e</u>	<u>j'k'e'</u>	<u>CC/B15</u>	<u>CS/B15</u>	<u>EP/B15</u>	<u>(corrected)</u>
190.	2 0 +	2 0 +	143.	143.	134.	134.
		3 0 +	0.89	0.90	2.17	2.57
		3 3 +	0.22	0.24	0.80	0.95
		3 3 -	1.49	1.56	1.76	2.08
		4 3 +	0.84	0.84	0.64	0.86
		4 3 -	0.018	0.028	0.077	0.095
	3 0 +	3 0 +	162.	162.	155.	155.
		3 3 +	0.77	0.80	1.10	1.10
		3 3 -	0.27	0.30	0.47	0.47
		4 3 +	0.051	0.064	0.24	0.27
		4 3 -	0.97	1.01	0.82	0.93
	3 3 +	3 3 +	153.	153.	153.	153.
		3 3 -	1.13	1.19	0.52	0.52
		4 3 +	0.48	0.49	0.0073	0.0083
		4 3 -	0.096	0.11	0.081	0.091
	3 3 -	3 3 -	153.	153.	153.	153.
		4 3 +	0.11	0.12	0.032	0.036
		4 3 -	0.47	0.48	0.0095	0.011
	4 3 +	4 3 +	150.	146. <sup>b</sup>	149.	149.
		4 3 -	0.38	1.37 <sup>b</sup>	1.05	1.05
4 3 -	4 3 -	150.	146. <sup>b</sup>	150.	150.	

<sup>a</sup> Values corrected for "counting of states" obtained via Eq. (43); uncorrected values obtained via Eq. (44).

<sup>b</sup> From a CS/B17 calculation.

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Table 6

Comparison of close coupling, coupled states, and effective potential cross sections for excitation of para-NH<sub>3</sub> at a total energy of 250 cm<sup>-1</sup>.

		$\sigma(jk\epsilon-j'k'\epsilon')$ , Å <sup>2</sup>			
<u>j k ε</u>	<u>j'k'ε'</u>	<u>CC/B20</u>	<u>CS/B20</u>	<u>EP/B20</u>	<u>(corrected)<sup>a</sup></u>
1 1 +	1 1 +	113.	113.	110.	110.
	1 1 -	0.81	0.89	0.41	0.41
	2 1 +	1.00	1.00	0.28	0.36
	2 1 -	0.21	0.15	1.00	1.29
	2 2 +	0.0006	0.0005	0.11	0.14
	2 2 -	1.56	1.47	5.88	7.59
	3 1 +	0.069	0.14	0.052	0.080
	3 1 -	0.36	0.36	0.68	1.04
	3 2 +	0.41	0.42	1.20	1.83
	3 2 -	0.22	0.49	0.69	1.05
	4 1 +	0.12	0.15	0.049	0.085
	4 1 -	0.0076	0.0050	0.12	0.21
	4 2 +	0.053	0.053	0.13	0.22
	4 2 -	0.033	0.048	0.11	0.19
	4 4 +	0.044	0.045	0.015	0.026
	4 4 -	1.24	1.15	0.94	1.63
2 1 +	2 1 +	122.	122.	116.	116.
	2 1 -	0.62	0.65	1.22	1.22
	2 2 +	0.87	0.89	2.54	2.54
	2 2 -	0.16	0.23	0.57	0.57
	3 1 +	0.85	0.94	1.15	1.36
	3 1 -	0.070	0.053	0.058	0.069
	3 2 +	0.018	0.019	0.033	0.039
	3 2 -	0.81	0.85	1.61	1.90
	4 1 +	0.019	0.055	0.026	0.035
	4 1 -	0.085	0.089	0.16	0.21
	4 2 +	0.20	0.20	0.38	0.51
	4 2 -	0.075	0.13	0.14	0.19
	4 4 +	0.91	0.94	1.08	1.45
	4 4 -	0.14	0.13	0.13	0.18



Table 6, continued

<u>j k ε</u>	<u>j'k'e'</u>	<u>CC/B20</u>	<u>CS/B20</u>	<u>EP/B20</u>	<u>(corrected)<sup>a</sup></u>
2 2 +	2 2 +	120.	119.	117.	117.
	2 2 -	1.33	1.35	0.69	0.69
	3 1 +	0.15	0.15	0.24	0.28
	3 1 -	0.29	0.28	0.69	0.82
	3 2 +	0.91	0.82	0.14	0.16
	3 2 -	0.12	0.05 <sup>4</sup>	0.48	0.57
	4 1 +	0.038	0.038	0.067	0.090
	4 1 -	0.039	0.070	0.13	0.17
	4 2 +	0.015	0.13	0.022	0.030
	4 2 -	0.21	0.22	0.22	0.30
	4 4 +	0.068	0.066	0.048	0.064
	4 4 -	0.0006	0.0007	0.0039	0.0052
3 1 +	3 1 +	141.	141. <sup>b</sup>	134.	134.
	3 1 -	0.30	0.34 <sup>b</sup>	0.76	0.76
	3 2 +	0.77	0.82 <sup>b</sup>	1.24	1.24
	3 2 -	0.041	0.047 <sup>b</sup>	0.16	0.16
	4 1 +	0.72	0.73 <sup>b</sup>	0.97	1.10
	4 1 -	0.023	0.030 <sup>b</sup>	0.043	0.049
	4 2 +	0.018	0.022 <sup>b</sup>	0.023	0.026
	4 2 -	0.48	0.51 <sup>b</sup>	0.56	0.63
	4 4 +	0.17	0.19 <sup>b</sup>	0.24	0.27
	4 4 -	0.51	0.52 <sup>b</sup>	0.68	0.77

<sup>a</sup> Values corrected for "counting of states" obtained via Eq. (43); uncorrected values obtained via Eq. (44).

<sup>b</sup> From a CS/B16 calculation.

