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# Infinite order sudden calculation of Raman $Q$ -branch linewidths for $\text{H}_2\text{O} + \text{H}_2\text{O}$

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The infinite order sudden (IOS) approximation is extended to calculate rate constants for rotationally inelastic scattering between two  $\text{H}_2\text{O}$  molecules. A modified version of the breathing sphere (BS) approximation, which has previously been shown to work reasonably well for  $\text{N}_2 + \text{N}_2$  rotationally inelastic scattering, is also extended to  $\text{H}_2\text{O} + \text{H}_2\text{O}$  scattering. The rate constants obtained using both approximations are used to determine Raman  $Q$ -branch spectral linewidths. In order to calculate such linewidths, it is necessary to sum the rate constants for any initial rotational level over all final inelastic rotational levels. While the IOS linewidths are in reasonable agreement with experiment over a range of temperatures, the IOS-BS linewidths are much too small.

## I. INTRODUCTION

In a previous paper<sup>1</sup> results of calculations on the  $\text{N}_2$ - $\text{N}_2$  collision system were reported. Those calculations involved the use of the infinite order sudden (IOS) approximation to determine rotationally inelastic state-to-state rate constants, and the subsequent use of these rate constants to predict Raman  $Q$ -branch spectral linewidths. A simpler approximation, a modified version of the breathing sphere (BS) approximation which involved restricting the perturbing molecule to a fixed rotational state during the collision, was also introduced. The IOS approximation was then used to determine rate constants for the rotational transitions in the perturbed molecule. This approximation, termed the IOS-BS approximation, reduced the necessary computational time by an order of magnitude and gave results that compared well both with those calculated using the IOS approximation and with experiment.

As explained in the previous paper,<sup>1</sup> the  $\text{N}_2$ - $\text{N}_2$  collision system was chosen as  $\text{N}_2$  is abundant in combustion chambers, and a knowledge of state-to-state rotationally inelastic rate coefficients allows the inversion of temperatures from spectra obtained by coherent anti-Stokes-Raman spectroscopy (CARS)<sup>2-7</sup> at high temperature and pressure. Given the accuracy of the theoretical Raman  $Q$ -branch linewidths calculated for  $\text{N}_2$ , it would seem timely to extend the quantum mechanical approximations used in that work to the rotationally inelastic scattering of two nonlinear polyatomic molecules. The  $\text{H}_2\text{O}$  molecule is also abundant in a combustion chamber, and, since there are now experimental Raman  $Q$ -branch linewidths with which to compare,<sup>8</sup> the  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  scattering system would seem to be a suitable choice. As far as we are aware, no quantum mechanical calculations of this type have previously been undertaken on such a scattering system, presumably because it has been regarded as being too complex, and because the necessary calculations would put too much strain on computational facilities.

In Sec. II, the IOS formula for integral cross sections in  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  rotationally inelastic scattering is derived. In Sec. III, the IOS-BS method is presented. Both IOS and IOS-

BS predictions of Raman  $Q$ -branch spectral linewidths are compared with experimental data for a range of collision energies in Sec. IV and conclusions are given in Sec. V. The reasonable agreement between theoretical and experimental Raman  $Q$ -branch linewidths presented in this paper displays the possibilities which are now open in this area of molecular collision theory involving polyatomic molecules.

## II. APPLICATION OF THE IOS APPROXIMATION TO ASYMMETRIC TOP-ASYMMETRIC TOP SCATTERING

### A. Asymmetric top wave functions

Before considering the problem of asymmetric top-asymmetric top scattering, it is useful to discuss the properties of the asymmetric top molecular wave functions.<sup>9,10</sup>

The coordinate system used in this work for  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  scattering is shown in Fig. 1. Two sets of axes are represented; first, *body-fixed* (BF) axes in which the  $Z$  axis is placed along the vector  $\mathbf{R}$  joining the centers of mass of the two molecules; and second, two sets of *molecule-fixed* (MF) axes  $(x_1, y_1, z_1)$ , denoted by  $\omega_1$ , and  $(x_2, y_2, z_2)$ , denoted by  $\omega_2$ , which are defined to be coincident with the principal axes of the individual molecules. The Euler angles which rotate the BF axes onto the two sets of MF axes are then  $(\phi, \theta, \chi)$  for the first molecule and  $(\alpha, \beta, \gamma)$  for the second molecule.

An asymmetric top molecule is characterized by its possession of three different principal moments of inertia. If  $I_i$  ( $i = x, y, z$ ) are the principal moments of inertia of the molecule, then the rotational constants of the molecule are given by

$$A = \frac{1}{2I_y}, \quad (1a)$$

$$B = \frac{1}{2I_z}, \quad (1b)$$

and

$$C = \frac{1}{2I_x}. \quad (1c)$$

These definitions of the rotational constants comply

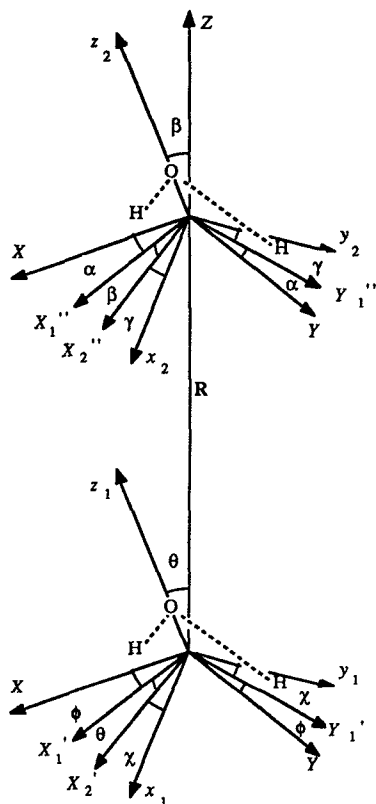


FIG. 1. Euler angles ( $\phi, \theta, \chi$ ) and ( $\alpha, \beta, \gamma$ ) rotating BF axes ( $X, Y, Z$ ) onto MF axes ( $x_1, y_1, z_1$ ) and ( $x_2, y_2, z_2$ ), respectively, for H<sub>2</sub>O–H<sub>2</sub>O rotationally inelastic scattering. Euler angles are defined as follows: First, transform the BF axes to positions ( $X_1, Y_1, Z$ ) by rotating through an angle  $\phi/\alpha$  about the  $Z$  axis. Next, rotate through an angle  $\theta/\beta$  about the  $Y_1$  axis to positions ( $X_2, Y_1, z$ ), and finally, rotate through an angle  $\chi/\gamma$  about the  $z$  axis to final positions ( $x, y, z$ ). The intermediate axes of the Euler rotations are marked with single and double primes for the first and second molecule, respectively. The collision vector  $R$  lies along the BF  $Z$  axis.

with the usual convention for asymmetric top molecules that  $A > B > C$ . The values of  $A$ ,  $B$ , and  $C$  for the H<sub>2</sub>O molecule are given in Table I.<sup>11</sup>

In the MF coordinate system, the rotational Hamiltonian of the top is

$$H_{\text{rot}} = \frac{1}{2} \left( \frac{j_x^2}{I_x} + \frac{j_y^2}{I_y} + \frac{j_z^2}{I_z} \right), \quad (2)$$

or

$$H_{\text{rot}} = Cj_x^2 + Aj_y^2 + Bj_z^2, \quad (3)$$

where  $j_i$  ( $i = x, y, z$ ) are the components of  $\mathbf{j}$ , the rotational angular momentum of the molecule, along the MF axes.

Using the fact that

$$\mathbf{j}^2 = j_x^2 + j_y^2 + j_z^2, \quad (4)$$

Eq. (3) becomes

$$H_{\text{rot}} = \left( \frac{A+C}{2} \right) \mathbf{j}^2 + \left( B - \frac{A+C}{2} \right) j_z^2 + \left( \frac{C-A}{4} \right) (j_+^2 + j_-^2), \quad (5)$$

where  $j_{\pm}$  are the shift operators  $j_x \pm ij_y$ .

The Schrödinger equation for this rotational Hamiltonian is then

$$H_{\text{rot}} \psi_{\tau}^{m_j}(\phi, \theta, \chi) = E_{\text{rot}} \psi_{\tau}^{m_j}(\phi, \theta, \chi), \quad (6)$$

where  $E_{\text{rot}}$  represents the rotational energy levels of the molecule and  $\psi_{\tau}^{m_j}(\phi, \theta, \chi)$  is the wave function of the asymmetric top molecule;  $m_j$  is the projection of  $j$  along the BF  $Z$  axis, and the label  $\tau$  is defined below.

TABLE I. Rotational constants for the H<sub>2</sub>O molecule.

$A(\text{cm}^{-1})$	27.33
$B(\text{cm}^{-1})$	14.57
$C(\text{cm}^{-1})$	9.49

In order to solve the Schrödinger equation (6) it is convenient to expand the asymmetric top wave function in a basis set of symmetric top wave functions  $\Psi_{jm,k}(\phi, \theta, \chi)$ . (A symmetric top is characterized by its possession of two equal moments of inertia.)

$$\psi_{\tau}^{m_j}(\phi, \theta, \chi) = \sum_{k=-j}^j a_{k\tau}^j \Psi_{jm,k}(\phi, \theta, \chi), \quad (7)$$

where<sup>12</sup>

$$\Psi_{jm,k}(\phi, \theta, \chi) = \left( \frac{2j+1}{8\pi^2} \right)^{1/2} D_{m,k}^{j*}(\phi, \theta, \chi). \quad (8)$$

Here,  $D_{m,k}^{j*}(\phi, \theta, \chi)$  is an element of the matrix (known as the Wigner rotation matrix) which rotates the BF coordinate system into the MF system as described earlier;  $j(j+1)$ ,  $m_j$  ( $|m_j| \leq j$ ) and  $k$  ( $|k| \leq j$ ) are the eigenvalues of  $\mathbf{j}^2$ ,  $j_z$  (BF projection) and  $j_z$  (MF projection), respectively. It should be noted that  $\mathbf{j}^2$  and  $j_z$  are conserved for both symmetric and asymmetric tops, while  $j_z$  is conserved only for a symmetric top, and, consequently, for given values of  $j$  and  $m_j$ , mixing of the  $(2j+1)$  values of  $k$  occurs to form  $(2j+1)$  states of the asymmetric top. These asymmetric top states are labeled by the index  $\tau$  in Eqs. (6) and (7). An asymmetric top molecule will exist in a rotational state  $(j, \tau)$ , where  $\tau$  may either be odd (*ortho* state) or even (*para* state). It is interesting to note that in the H<sub>2</sub>O molecule, with  $C_{2v}$  symmetry, *ortho* and *para* states are not interconnected during rotationally inelastic collisions.

The Schrödinger equation (6) then becomes

$$\sum_k a_{k\tau}^j H_{\text{rot}} \Psi_{jm,k}(\phi, \theta, \chi) = \sum_k a_{k\tau}^j E_{\text{rot}} \Psi_{jm,k}(\phi, \theta, \chi). \quad (9)$$

If both sides of Eq. (9) are multiplied on the left by  $\Psi_{jm,k}^*(\phi, \theta, \chi)$  and integrated over the full solid angle, then on rearrangement

$$\sum_k a_{k\tau}^j \{ \langle \Psi_{jm,k}^*(\phi, \theta, \chi) | H_{\text{rot}} | \Psi_{jm,k}(\phi, \theta, \chi) \rangle - E_{\text{rot}} \delta_{k\tau} \} = 0, \quad (10)$$

for the  $(2j+1)$  values of  $\tau$ .

The nonzero matrix elements of the symmetric top basic functions with  $H_{\text{rot}}$  for rigid rotors are<sup>11</sup>

$$\langle \Psi_{jm,k}(\phi, \theta, \chi) | H_{\text{rot}} | \Psi_{jm,k}(\phi, \theta, \chi) \rangle = \left( \frac{A+C}{2} \right) j(j+1) + \left( B - \frac{A+C}{2} \right) k^2, \quad (11)$$

and

$$\begin{aligned} \langle \Psi_{jm,k}(\phi, \theta, \chi) | H_{\text{rot}} | \Psi_{jm,k \pm 2}(\phi, \theta, \chi) \rangle \\ = \left( \frac{C-A}{4} \right) \{ [j(j+1) - (k \pm 2)(k \pm 1)] \\ \times [j(j+1) - (k \pm 1)k] \}^{1/2}. \end{aligned} \quad (12)$$

The set of equations (10) can then be solved by standard techniques in linear algebra to yield the eigenvalues  $E_{\text{rot}}$  and expansion coefficients  $a_{kr}^j$  of the asymmetric top. The rotational energy levels of the H<sub>2</sub>O molecule are presented in Table II for values of  $j$  from 0 to 7.

## B. Potential expansion

A third coordinate system, the *space-fixed* (SF) system, may be defined in which the orientations of  $\mathbf{R}$ ,  $\hat{\omega}_1$  and  $\hat{\omega}_2$  are represented by  $\hat{R}$ ,  $\hat{\omega}_1$ , and  $\hat{\omega}_2$ , respectively. The intermolecular potential then depends on  $R$ ,  $\hat{R}$ ,  $\hat{\omega}_1$ , and  $\hat{\omega}_2$  according to<sup>13</sup>

$$V(R, \hat{R}, \hat{\omega}_1, \hat{\omega}_2) = \sum_{L_1 K_1 L_2 K_2 L} v_{L_1 K_1 L_2 K_2 L}(R) \times \sum_M D_{0M}^{L*}(\hat{R}) \mathcal{D}_{L_1 K_1 L_2 K_2}^{LM*}(\hat{\omega}_1, \hat{\omega}_2), \quad (13)$$

where

$$\mathcal{D}_{L_1 K_1 L_2 K_2}^{LM*}(\hat{\omega}_1, \hat{\omega}_2) = 8\pi^2 \sum_{M_1 M_2} \langle L_1 M_1 L_2 M_2 | LM \rangle \left( \frac{2L_1 + 1}{8\pi^2} \right)^{1/2} \times D_{M_1 K_1}^{L_1*}(\hat{\omega}_1) \left( \frac{2L_2 + 1}{8\pi^2} \right)^{1/2} D_{M_2 K_2}^{L_2*}(\hat{\omega}_2). \quad (14)$$

The SF functions are related to the BF functions by<sup>13</sup>

$$D_{0M}^{L*}(\hat{R}) \mathcal{D}_{L_1 K_1 L_2 K_2}^{LM*}(\hat{\omega}_1, \hat{\omega}_2) = \sum_{\lambda} D_{0M}^{L*}(\hat{R}) D_{\lambda M}^L(\hat{R}) \mathcal{D}_{L_1 K_1 L_2 K_2}^{L\lambda*}(\phi, \theta, \chi, \alpha, \beta, \gamma). \quad (15)$$

The sum over  $M$  in Eq. (13) is performed by use of the unitary property of the Wigner rotation matrices, namely,

$$\sum_M D_{\lambda'M}^{L*}(\hat{R}) D_{\lambda M}^L(\hat{R}) = \delta_{\lambda\lambda'}, \quad (16)$$

and since, in (15),  $\lambda'$  is zero,

$$\sum_M D_{0M}^{L*}(\hat{R}) \mathcal{D}_{L_1 K_1 L_2 K_2}^{LM*}(\hat{\omega}_1, \hat{\omega}_2) = \mathcal{D}_{L_1 K_1 L_2 K_2}^{L0*}(\phi, \theta, \chi, \alpha, \beta, \gamma). \quad (17)$$

The expansion of the intermolecular potential (13) therefore becomes

$$V(R, \hat{R}, \hat{\omega}_1, \hat{\omega}_2) = \sum_{L_1 K_1 L_2 K_2 L} v_{L_1 K_1 L_2 K_2 L}(R) \mathcal{D}_{L_1 K_1 L_2 K_2}^{L0*}(\phi, \theta, \chi, \alpha, \beta, \gamma) = V(R, \phi, \theta, \chi, \alpha, \beta, \gamma). \quad (18)$$

The potential may be expanded as a function of five angles,  $\theta$ ,  $\chi$ ,  $\alpha'$ ,  $\beta$ , and  $\gamma$ , where  $\alpha' = \phi - \alpha$ , but for convenience it will be written as a function of six angles.

## C. The Hamiltonian

In the BF coordinate system the Hamiltonian for the complete asymmetric top-asymmetric top scattering system may be written as<sup>13</sup>

$$H = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hbar^2}{2\mu R^2} |\mathbf{J} - \mathbf{j}|^2 + H_{\text{rot}}^{(1)} + H_{\text{rot}}^{(2)} + V(R, \phi, \theta, \chi, \alpha, \beta, \gamma), \quad (19)$$

where  $\mu$  is the molecule-molecule reduced mass,  $\mathbf{J}$  is the

TABLE II. Rotational energy levels of H<sub>2</sub>O.

Para-H <sub>2</sub> O levels			Ortho-H <sub>2</sub> O levels		
$j$	$\tau$	Energy (cm <sup>-1</sup> )	$j$	$\tau$	Energy (cm <sup>-1</sup> )
0	0	0.00	1	-1	24.06
1	0	36.82	1	1	41.90
2	-2	70.94	2	-1	79.86
2	0	95.10	2	1	133.38
2	2	134.62	3	-3	138.58
3	-2	143.72	3	-1	174.00
3	0	205.56	3	1	211.34
4	-4	225.28	4	-3	227.80
4	-2	277.28	3	3	282.96
3	2	282.76	4	-1	300.82
4	0	316.11	5	-5	330.48
5	-4	331.58	4	1	381.00
4	2	382.32	5	-3	402.88
5	-2	418.38	5	-1	448.57
6	-6	454.27	6	-5	454.72
4	4	486.40	4	3	486.38
5	0	503.92	5	1	508.83
6	-4	548.47	6	-3	557.38
7	-6	597.00	7	-7	596.83
6	-2	602.29	5	3	609.64
5	2	609.42	6	-1	651.09
6	0	663.99	7	-5	712.48
7	-4	717.00	5	5	744.60
5	4	744.59			

total angular momentum of the system,  $\mathbf{j}$  is the vector sum of the rotational angular momenta of the individual molecules,

$$\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2, \quad (20)$$

and  $H_{\text{rot}}^{(n)}$  is given by

$$H_{\text{rot}}^{(n)} = \frac{1}{2} \left( \frac{j_{nx}^2}{I_{nx}} + \frac{j_{ny}^2}{I_{ny}} + \frac{j_{nz}^2}{I_{nz}} \right), \quad n = 1, 2, \quad (21)$$

where the principal moments of inertia of the  $n$ th molecule,  $I_{ni}$  ( $i = x, y, z$ ) are related to the rotational constants of that molecule by Eq. (1).

The Schrödinger equation for the system may be written as

$$H\psi^J = E\psi^J, \quad (22)$$

where  $\psi^J$  represents the molecular wave function for fixed  $J$  and  $E$  represents the energy of the system. The exact solution of this equation using the Hamiltonian of Eq. (19) via the close-coupling equations would be too costly, and hence two approximations are introduced.

First, the centrifugal sudden (CS) approximation<sup>14</sup> (also known as the coupled states approximation<sup>15</sup>) is applied, which results in the neglect of the coupling between different  $\Omega$  states, where  $\Omega$  is the projection of  $\mathbf{J}$  and  $\mathbf{j}$  on the BF  $Z$  axis, and the resultant Hamiltonian (19) is

$$H = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hbar^2}{2\mu R^2} [J(J+1) + j(j+1) - 2\Omega^2] + H_{\text{rot}}^{(1)} + H_{\text{rot}}^{(2)} + V(R, \phi, \theta, \chi, \alpha, \beta, \gamma). \quad (23)$$

Second, the energy sudden (ES) approximation<sup>16,17</sup> is applied, which results in the neglect of all terms in the Hamiltonian which are dependent on either  $\mathbf{j}_1$  or  $\mathbf{j}_2$ , since the rotational constants of both molecules are set to zero. This combined application of the CS and ES approximations gives the infinite order sudden (IOS) approximation,<sup>18-20</sup> and the resultant IOS Hamiltonian is

$$H = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hbar^2}{2\mu R^2} J(J+1) + V(R, \phi, \theta, \chi, \alpha, \beta, \gamma). \quad (24)$$

## D. Solutions to the Schrödinger equation

The solutions  $f^J(R; \phi, \theta, \chi, \alpha, \beta, \gamma)$  to the Schrödinger equation (22) are subjected to the following boundary conditions:

$$f^J(0; \phi, \theta, \chi, \alpha, \beta, \gamma) = 0, \quad (25a)$$

and

$$\lim_{R \rightarrow \infty} f^J(R; \phi, \theta, \chi, \alpha, \beta, \gamma) = \kappa^{-1/2} \left\{ \exp \left[ -i \left( \kappa R - J \frac{\pi}{2} \right) \right] - S^J(\phi, \theta, \chi, \alpha, \beta, \gamma) \exp \left[ i \left( \kappa R - J \frac{\pi}{2} \right) \right] \right\}, \quad (25b)$$

where  $\kappa$  is the collision wave number and is related to the relative kinetic energy  $E$  of the scattering bodies by

$$\kappa^2 = \frac{2\mu E}{\hbar^2}. \quad (26)$$

Such a definition of  $\kappa$  neglects the rotational energy spacing of the molecules, which is consistent with the ES approximation in which the rotational energy spacing is considered to be negligible relative to the collision energy. The asymptotic boundary condition (25b) defines the  $S$ -matrix elements  $S^J(\phi, \theta, \chi, \alpha, \beta, \gamma)$ , which are complex functions of the phase shift,  $\eta^J(\phi, \theta, \chi, \alpha, \beta, \gamma)$ ,

$$S^J(\phi, \theta, \chi, \alpha, \beta, \gamma) = \exp[2i\eta^J(\phi, \theta, \chi, \alpha, \beta, \gamma)]. \quad (27)$$

In this work the phase shifts are calculated using the common Jeffries-Kramers-Wentzel-Brillouin JKWB approximation.<sup>14</sup>

Equivalent to the result for diatom-diatom scattering,<sup>21</sup> the approximation to the CS  $S$  matrix is

$$S_{j_1 \tau_1 j_1' \tau_1' j_2 \tau_2 j_2' \tau_2' \Omega \Omega'}^J = \langle \psi_{\tau_1 \tau_2}^{j_1 j_2 \Omega}(\phi, \theta, \chi, \alpha, \beta, \gamma) | S^J(\phi, \theta, \chi, \alpha, \beta, \gamma) | \psi_{\tau_1' \tau_2'}^{j_1' j_2' \Omega'}(\phi, \theta, \chi, \alpha, \beta, \gamma) \rangle, \quad (28)$$

where

$$\psi_{\tau_1 \tau_2}^{j_1 j_2 \Omega}(\phi, \theta, \chi, \alpha, \beta, \gamma) = \sum_{m_1 m_2} \langle j_1 m_1 j_2 m_2 | j \Omega \rangle \psi_{\tau_1}^{j_1 m_1}(\phi, \theta, \chi) \times \psi_{\tau_2}^{j_2 m_2}(\alpha, \beta, \gamma). \quad (29)$$

## E. IOS degeneracy-averaged cross sections

The IOS approximation to the degeneracy-averaged integral cross section for the simultaneous transitions between rotational levels  $(j_1, \tau_1)$  and  $(j_1', \tau_1')$  in the first molecule and  $(j_2, \tau_2)$  and  $(j_2', \tau_2')$  in the second molecule is<sup>22</sup>

$$\begin{aligned} \sigma(j_1' \tau_1' j_2' \tau_2' \leftarrow j_1 \tau_1 j_2 \tau_2) &= \frac{\pi}{\kappa^2 (2j_1 + 1)(2j_2 + 1)} \sum_{j_{\text{B}} \Omega \Omega'} (2J + 1) |S_{j_1 \tau_1 j_1' \tau_1' j_2 \tau_2 j_2' \tau_2' \Omega \Omega'}^J|^2 \\ &= \frac{\pi}{\kappa^2 (2j_1 + 1)(2j_2 + 1)} \sum_{j_{\text{B}} \Omega \Omega'} (2J + 1) \\ &\quad \times |\langle \psi_{\tau_1 \tau_2}^{j_1 j_2 \Omega}(\phi, \theta, \chi, \alpha, \beta, \gamma) | S^J(\phi, \theta, \chi, \alpha, \beta, \gamma) | \psi_{\tau_1' \tau_2'}^{j_1' j_2' \Omega'}(\phi, \theta, \chi, \alpha, \beta, \gamma) \rangle|^2. \end{aligned} \quad (30)$$

Using the expansion of the asymmetric top wave functions in a basis set of symmetric top wave functions of Eq. (7), this becomes

$$\begin{aligned} \sigma(j_1' \tau_1' j_2' \tau_2' \leftarrow j_1 \tau_1 j_2 \tau_2) &= \frac{\pi}{\kappa^2 (2j_1 + 1)(2j_2 + 1)} \sum_{j_{\text{B}} \Omega \Omega'} (2J + 1) \left| \sum_{k_1 k_2 k_1' k_2' m_1 m_2 m_1' m_2'} d_{k_1 \tau_1}^{j_1} d_{k_1' \tau_1'}^{j_1'} d_{k_2 \tau_2}^{j_2} d_{k_2' \tau_2'}^{j_2'} \langle j_1 m_1 j_2 m_2 | j \Omega \rangle \langle j_1' m_1' j_2' m_2' | j' \Omega' \rangle \right. \\ &\quad \times \langle \Psi_{j_1 m_1 k_1}(\phi, \theta, \chi) \Psi_{j_2 m_2 k_2}(\alpha, \beta, \gamma) | S^J(\phi, \theta, \chi, \alpha, \beta, \gamma) | \Psi_{j_1' m_1' k_1'}(\phi, \theta, \chi) \Psi_{j_2' m_2' k_2'}(\alpha, \beta, \gamma) \rangle \left. \right|^2. \end{aligned} \quad (31)$$

It is convenient to expand the  $S$ -matrix elements in the same fashion as the intermolecular potential (18), namely,

$$S^J(\phi, \theta, \chi, \alpha, \beta, \gamma) = \sum_{L_1 K_1 L_2 K_2 L} S_{L_1 K_1 L_2 K_2 L}^J \mathcal{D}_{L_1 K_1 L_2 K_2}^{L 0*}(\phi, \theta, \chi, \alpha, \beta, \gamma), \quad (32)$$

where

$$S_{L_1 K_1 L_2 K_2 L}^J = \left(\frac{1}{8\pi^2}\right)^2 \int_0^{2\pi} d\phi \int_{-1}^{+1} d(\cos \theta) \int_0^{2\pi} d\chi \int_0^{2\pi} d\alpha \int_{-1}^{+1} d(\cos \beta) \int_0^{2\pi} d\gamma \\ \times \mathcal{D}_{L_1 K_1 L_2 K_2}^{L 0}(\phi, \theta, \chi, \alpha, \beta, \gamma) S^J(\phi, \theta, \chi, \alpha, \beta, \gamma). \quad (33)$$

The integrals over  $\phi$ ,  $\chi$ ,  $\alpha$ , and  $\gamma$  may be evaluated numerically using equal-spacing quadrature, while those over  $\theta$  and  $\beta$  may be evaluated using Gauss–Legendre quadrature.

If the expansion for  $S$ -matrix elements (32) is substituted into the matrix elements in Eq. (31), then

$$\langle \Psi_{j_1 m_1 k_1}(\phi, \theta, \chi) \Psi_{j_2 m_2 k_2}(\alpha, \beta, \gamma) | S^J(\phi, \theta, \chi, \alpha, \beta, \gamma) | \Psi_{j'_1 m'_1 k'_1}(\phi, \theta, \chi) \Psi_{j'_2 m'_2 k'_2}(\alpha, \beta, \gamma) \rangle \\ = \sum_{L_1 K_1 L_2 K_2 L} S_{L_1 K_1 L_2 K_2 L}^J \langle \Psi_{j_1 m_1 k_1}(\phi, \theta, \chi) \Psi_{j_2 m_2 k_2}(\alpha, \beta, \gamma) | \\ \times \mathcal{D}_{L_1 K_1 L_2 K_2}^{L 0*}(\phi, \theta, \chi, \alpha, \beta, \gamma) | \Psi_{j'_1 m'_1 k'_1}(\phi, \theta, \chi) \Psi_{j'_2 m'_2 k'_2}(\alpha, \beta, \gamma) \rangle \\ = \sum_{L_1 K_1 L_2 K_2 L} S_{L_1 K_1 L_2 K_2 L}^J (2L_1 + 1)^{1/2} (2L_2 + 1)^{1/2} \sum_{M_1} \langle L_1 M_1 L_2, -M_1 | L 0 \rangle \\ \times \langle \Psi_{j_1 m_1 k_1}(\phi, \theta, \chi) \Psi_{j_2 m_2 k_2}(\alpha, \beta, \gamma) | D_{M_1 K_1}^{L_1*}(\phi, \theta, \chi) D_{-M_1 K_2}^{L_2*}(\alpha, \beta, \gamma) \\ \times | \Psi_{j'_1 m'_1 k'_1}(\phi, \theta, \chi) \Psi_{j'_2 m'_2 k'_2}(\alpha, \beta, \gamma) \rangle. \quad (34)$$

The relationship between the symmetric top wave function and the Wigner rotation matrix (8) leads to

$$\langle \Psi_{j_1 m_1 k_1}(\phi, \theta, \chi) \Psi_{j_2 m_2 k_2}(\alpha, \beta, \gamma) | S^J(\phi, \theta, \chi, \alpha, \beta, \gamma) | \Psi_{j'_1 m'_1 k'_1}(\phi, \theta, \chi) \Psi_{j'_2 m'_2 k'_2}(\alpha, \beta, \gamma) \rangle \\ = \left(\frac{2j_1 + 1}{8\pi^2}\right)^{1/2} \left(\frac{2j_2 + 1}{8\pi^2}\right)^{1/2} \left(\frac{2j'_1 + 1}{8\pi^2}\right)^{1/2} \left(\frac{2j'_2 + 1}{8\pi^2}\right)^{1/2} \sum_{L_1 K_1 L_2 K_2 L} S_{L_1 K_1 L_2 K_2 L}^J \\ \times (2L_1 + 1)^{1/2} (2L_2 + 1)^{1/2} \sum_{M_1} \langle L_1 M_1 L_2, -M_1 | L 0 \rangle \\ \times \langle D_{m_1 k_1}^{j_1*}(\phi, \theta, \chi) D_{m_2 k_2}^{j_2*}(\alpha, \beta, \gamma) | D_{M_1 K_1}^{L_1*}(\phi, \theta, \chi) D_{-M_1 K_2}^{L_2*}(\alpha, \beta, \gamma) \\ \times | D_{m'_1 k'_1}^{j'_1*}(\phi, \theta, \chi) D_{m'_2 k'_2}^{j'_2*}(\alpha, \beta, \gamma) \rangle. \quad (35)$$

Use of the Clebsch–Gordan series then leads to the following equation for degeneracy-averaged integral cross sections:

$$\sigma(j'_1 \tau'_1 j'_2 \tau'_2 \leftarrow j_1 \tau_1 j_2 \tau_2) \\ = \frac{\pi}{\kappa^2 (2j_1 + 1)(2j_2 + 1)} \sum_{J \text{ even}} (2J + 1) \left| \sum_{L_1 L_2 L} (2L_1 + 1)^{1/2} (2L_2 + 1)^{1/2} \sum_{k_1 k'_1 k_2 k'_2} d_{k_1 \tau_1}^{j_1} d_{k'_1 \tau'_1}^{j'_1} d_{k_2 \tau_2}^{j_2} d_{k'_2 \tau'_2}^{j'_2} \right. \\ \times \sum_{m_1 m'_1 m'_2 M_1} \langle j_1 m_1 j_2 m_2 | j \Omega \rangle \langle j'_1 m'_1 j'_2 m'_2 | j' \Omega' \rangle \langle L_1 M_1 L_2, -M_1 | L 0 \rangle \\ \times \left(\frac{2j_1 + 1}{8\pi^2}\right)^{1/2} \left(\frac{2j_2 + 1}{8\pi^2}\right)^{1/2} \left(\frac{2j'_1 + 1}{8\pi^2}\right)^{1/2} \left(\frac{2j'_2 + 1}{8\pi^2}\right)^{1/2} S_{L_1 K_1 L_2 K_2 L}^J \\ \times \frac{8\pi^2}{2j_1 + 1} \langle j'_1 k'_1 L_1 K_1 | j_1 k_1 \rangle \langle j'_1 m'_1 L_1 M_1 | j_1 m_1 \rangle \\ \times \left. \frac{8\pi^2}{2j_2 + 1} \langle j'_2 k'_2 L_2 K_2 | j_2 k_2 \rangle \langle j'_2 m'_2 L_2, -M_1 | j_2 m_2 \rangle \right|^2, \quad (36)$$

with  $K_1$  and  $K_2$  defined by

$$K_n = k_n - k'_n, \quad n = 1, 2. \quad (37)$$

If the square modulus is replaced by a double summation, then introducing subscripts  $a$  and  $b$  which refer to different spectroscopic levels, and using the invariance of the Wigner 3- $j$  symbol under cyclic permutation of its columns, together with use of the orthogonality of the Clebsch–Gordan coefficients, we obtain

$$\sigma(j'_1 \tau'_1 j'_2 \tau'_2 \leftarrow j_1 \tau_1 j_2 \tau_2) = \sum_{L_1 L_2 L} F(j'_1 \tau'_1 j'_2 \tau'_2 | j_1 \tau_1 j_2 \tau_2 | L_1 L_2) Q^s(L_1 K_{1a} K_{1b} L_2 K_{2a} K_{2b} L), \quad (38)$$

where all information concerning the spectroscopic levels is contained in the coefficient

$$\begin{aligned} & F(j'_1 \tau'_1 j'_2 \tau'_2 | j_1 \tau_1 j_2 \tau_2 | L_1 L_2) \\ &= (2j'_1 + 1)(2j'_2 + 1) \sum_{\substack{k_{1a} k'_{1a} k_{1b} k'_{1b} \\ k_{2a} k'_{2a} k_{2b} k'_{2b}}} a_{k_{1a} \tau_1}^{j'_1} a_{k'_{1a} \tau_1}^{j_1} a_{k_{1b} \tau_1}^{j'_1} a_{k'_{1b} \tau_1}^{j_1} a_{k_{2a} \tau_2}^{j'_2} a_{k'_{2a} \tau_2}^{j_2} a_{k_{2b} \tau_2}^{j'_2} a_{k'_{2b} \tau_2}^{j_2} (-)^{k'_{1a} + k'_{1b} + k'_{2a} + k'_{2b}} \\ & \times \begin{pmatrix} j'_1 & L_1 & j_1 \\ k'_{1a} & K_{1a} & -k_{1a} \end{pmatrix} \begin{pmatrix} j'_1 & L_1 & j_1 \\ k'_{1b} & K_{1b} & -k_{1b} \end{pmatrix} \begin{pmatrix} j'_2 & L_2 & j_2 \\ k'_{2a} & K_{2a} & -k_{2a} \end{pmatrix} \begin{pmatrix} j'_2 & L_2 & j_2 \\ k'_{2b} & K_{2b} & -k_{2b} \end{pmatrix}, \end{aligned} \quad (39)$$

and all information concerning the collision dynamics is contained in the factor

$$Q^s(L_1 K_{1a} K_{1b} L_2 K_{2a} K_{2b} L) = \frac{\pi}{K^2} \sum_J (2J + 1) S_{L_1 K_{1a} L_2 K_{2a} L}^J S_{L_1 K_{1b} L_2 K_{2b} L}^{J*}. \quad (40)$$

## F. IOS rate constants

The individual cross sections,  $\sigma(j'_1 \tau'_1 \leftarrow j_1 \tau_1)$ , for the first, perturbed molecule are calculated by a Boltzmann-weighted summation over the rotational states of the second, perturbing molecule. That is,

$$\sigma(j'_1 \tau'_1 \leftarrow j_1 \tau_1) = \sum_{j_2 \tau_2} \rho_{j_2 \tau_2} \sigma(j'_1 \tau'_1 j'_2 \tau'_2 \leftarrow j_1 \tau_1 j_2 \tau_2), \quad (41)$$

where  $\rho_{j_2 \tau_2}$  is the Boltzmann probability of the perturbing molecule existing in the initial rotational level  $(j_2, \tau_2)$ ,

$$\rho_{j_2 \tau_2} = \frac{(2j_2 + 1) X_{j_2 \tau_2}}{\sum_{j_2 \tau_2} (2j_2 + 1) X_{j_2 \tau_2}}, \quad (42a)$$

with

$$X_{j_2 \tau_2} = \exp\left(\frac{-E_{j_2 \tau_2}}{k_B T}\right). \quad (42b)$$

Here  $E_{j_2 \tau_2}$  is the rotational energy of the perturbing molecule, and  $k_B$  is the Boltzmann constant.

Individual rate constants,  $\gamma_{j'_1 \tau'_1 j_1 \tau_1}$ , for rotational transitions in the perturbed molecule are then given by

$$\gamma_{j'_1 \tau'_1 j_1 \tau_1} = v_{\text{rel}} \sigma(j'_1 \tau'_1 \leftarrow j_1 \tau_1), \quad (43)$$

where  $v_{\text{rel}}$  is the relative collision velocity, defined by

$$v_{\text{rel}} = \left(\frac{2E}{\mu}\right)^{1/2}. \quad (44)$$

The rate constants are multiplied by the factor  $\exp[-(\Delta E/2k_B T)]$ ,<sup>23</sup> where  $\Delta E$  is the collisional inelasticity for upward rotational transitions.

Raman  $Q$ -branch linewidths  $\Gamma_{j_1 \tau_1}$  are calculated simply by summing the IOS inelastic rate constants over all final rotational levels and multiplying by two<sup>6</sup>

$$\Gamma_{j_1 \tau_1} = 2 \sum_{j'_1 \tau'_1 (\neq j_1 \tau_1)} \gamma_{j'_1 \tau'_1 j_1 \tau_1}. \quad (45)$$

## III. APPLICATION OF THE IOS-BS APPROXIMATION TO ASYMMETRIC TOP-ASYMMETRIC TOP SCATTERING

### A. The BS intermolecular potential

As described in the previous paper,<sup>1</sup> where the modified BS approximation was applied to diatom–diatom scattering, the BS intermolecular potential for asymmetric top–asymmetric top scattering is formed by averaging the angle-dependent intermolecular potential over the wave function of the perturbing molecule, which is held in a fixed rotational level. That is,

$$\begin{aligned} \bar{V}_{j_2 \tau_2}(R, \phi, \theta, \chi) &= \langle \psi_{j_2 \tau_2}^{j_2 m_j}(\alpha, \beta, \gamma) \\ &\times |V(R, \phi, \theta, \chi, \alpha, \beta, \gamma)| \psi_{j_2 \tau_2}^{j_2 m_j}(\alpha, \beta, \gamma) \rangle, \end{aligned} \quad (46)$$

where the subscripts  $j_2 \tau_2$  label the fixed rotational level.

It is most straightforward to fix the perturbing molecule in the ground rotational level ( $j_2, \tau_2 = 0, 0$ ), and given the definition of the asymmetric top wave function [Eqs. (7) and (8)] the ground rotational wave function is

$$\psi_0^0(\alpha, \beta, \gamma) = \left(\frac{1}{8\pi^2}\right)^{1/2}. \quad (47)$$

The BS intermolecular potential is then given by

$$\bar{V}_{00}(R, \phi, \theta, \chi) = \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_{-1}^{+1} d(\cos \beta) \times \int_0^{2\pi} d\gamma V(R, \phi, \theta, \chi, \alpha, \beta, \gamma). \quad (48)$$

On averaging the intermolecular potential in this way, the perturbing H<sub>2</sub>O molecule may be considered to be a structureless spherical particle and the scattering system is equivalent to an atom-asymmetric top scattering system. The BS intermolecular potential may be more simply defined in terms of just two Euler angles  $\theta$  and  $\chi$  with the third angle  $\phi$  being effectively redundant. Consistent with Sec. however,  $\phi$  will be retained when dealing with the molecular wave functions.

## B. The Hamiltonian

With the rotation of the perturbing molecule treated using the BS approximation, the rotational transitions in the perturbed molecule are treated using the IOS approximation. In the BF coordinate system, the Hamiltonian for the complete scattering system is written as

$$H = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hbar^2}{2\mu R^2} J(J+1) + \bar{V}_{j_2\tau_2}(R, \theta, \chi), \quad (49)$$

where the CS and ES approximations are applied as in Sec. II.

The solutions,  $f_{j_2\tau_2}^J(R; \theta, \chi)$ , to the Schrödinger equation are subjected to the boundary conditions given in Eqs. (25a) and (25b), the latter being the asymptotic boundary condition which defines the  $S$ -matrix elements  $S_{j_2\tau_2}^J(\theta, \chi)$ . These are complex functions of the phase shift  $\eta_{j_2\tau_2}^J(\theta, \chi)$ ,

$$S_{j_2\tau_2}^J(\theta, \chi) = \exp[2i\eta_{j_2\tau_2}^J(\theta, \chi)]. \quad (50)$$

The IOS-BS approximation to the CS  $S$  matrix is

$$S_{j_1\tau_1 j_2\tau_2}^{Jm_j} = \langle \psi_{\tau_1}^{j_1 m_j}(\phi, \theta, \chi) | S_{j_2\tau_2}^J(\theta, \chi) | \psi_{\tau_1}^{j_1 m_j}(\phi, \theta, \chi) \rangle. \quad (51)$$

## C. IOS-BS degeneracy-averaged cross sections

The IOS-BS approximation to the degeneracy-averaged integral cross section for the transition between rotational levels ( $j_1, \tau_1$ ) and ( $j_1', \tau_1'$ ) in the perturbed molecule is

$$\begin{aligned} \sigma_{j_2\tau_2}(j_1' \tau_1' \leftarrow j_1 \tau_1) &= \frac{\pi}{k^2(2j_1+1)} \sum_{m_j} (2J+1) |S_{j_1\tau_1 j_2\tau_2}^{Jm_j}|^2 \\ &= \frac{\pi}{k^2(2j_1+1)} \sum_{m_j} (2J+1) |\langle \psi_{\tau_1}^{j_1 m_j}(\phi, \theta, \chi) | \\ &\quad \times S_{j_2\tau_2}^J(\theta, \chi) | \psi_{\tau_1'}^{j_1' m_j}(\phi, \theta, \chi) \rangle|^2. \end{aligned} \quad (52)$$

Using the expansion of the asymmetric top wave functions in a basis set of symmetric top wave functions, Eq. (7) this becomes

$$\begin{aligned} \sigma_{j_2\tau_2}(j_1' \tau_1' \leftarrow j_1 \tau_1) &= \frac{\pi}{k^2(2j_1+1)} \sum_{m_j} (2J+1) \\ &\quad \times \left| \sum_{k_1 k_1'} d_{k_1 \tau_1}^{j_1} d_{k_1' \tau_1'}^{j_1'} \langle \Psi_{j_1 m_j k_1}(\phi, \theta, \chi) | \right. \\ &\quad \times S_{j_2\tau_2}^J(\theta, \chi) | \Psi_{j_1' m_j k_1'}(\phi, \theta, \chi) \rangle \left. \right|^2. \end{aligned} \quad (53)$$

It is convenient to expand the  $S$ -matrix elements as a sum of spherical harmonic functions,

$$S_{j_2\tau_2}^J(\theta, \chi) = (4\pi)^{1/2} \sum_{L_1 K_1} S_{L_1 K_1 j_2\tau_2}^J Y_{L_1}^{K_1}(\theta, \chi), \quad (54)$$

where

$$\begin{aligned} S_{L_1 K_1 j_2\tau_2}^J &= \left(\frac{1}{4\pi}\right)^{1/2} \int_0^{2\pi} d\chi \int_{-1}^{+1} d(\cos \theta) \\ &\quad \times Y_{L_1}^{K_1*}(\theta, \chi) S_{j_2\tau_2}^J(\theta, \chi). \end{aligned} \quad (55)$$

The integral over  $\chi$  may be evaluated numerically using equal-spacing quadrature, while that over  $\theta$  may be evaluated using Gauss-Legendre quadrature.

If the expansion for the  $S$ -matrix elements (54) is substituted into the matrix elements in Eq. (53), then

$$\begin{aligned} \langle \Psi_{j_1 m_j k_1}(\phi, \theta, \chi) | S_{j_2\tau_2}^J(\theta, \chi) | \Psi_{j_1' m_j k_1'}(\phi, \theta, \chi) \rangle \\ = (4\pi)^{1/2} \sum_{L_1 K_1} S_{L_1 K_1 j_2\tau_2}^J \langle \Psi_{j_1 m_j k_1}(\phi, \theta, \chi) | Y_{L_1}^{K_1}(\theta, \chi) | \\ \times \Psi_{j_1' m_j k_1'}(\phi, \theta, \chi) \rangle. \end{aligned} \quad (56)$$

The relationship between the spherical harmonic function and the Wigner rotation matrix,

$$Y_L^K(\theta, \chi) = (-)^K \left(\frac{2L+1}{4\pi}\right)^{1/2} D_{0K}^{L*}(\phi, \theta, \chi), \quad (57)$$

together with that between the symmetric top wave function and the Wigner rotation matrix (8), leads to

$$\begin{aligned} \langle \Psi_{j_1 m_j k_1}(\phi, \theta, \chi) | S_{j_2\tau_2}^J(\theta, \chi) | \Psi_{j_1' m_j k_1'}(\phi, \theta, \chi) \rangle \\ = \sum_{L_1 K_1} S_{L_1 K_1 j_2\tau_2}^J (-)^{K_1} \left(\frac{2j_1+1}{8\pi^2}\right)^{1/2} \left(\frac{2j_1'+1}{8\pi^2}\right)^{1/2} \\ \times (2L_1+1)^{1/2} \langle D_{m_j k_1}^{j_1*}(\phi, \theta, \chi) | \\ \times D_{0K_1}^{L_1*}(\phi, \theta, \chi) | D_{m_j k_1'}^{j_1'}(\phi, \theta, \chi) \rangle. \end{aligned} \quad (58)$$

Use of the Clebsch-Gordan series then leads to the following equation for degeneracy-averaged integral cross sections:



$$\sigma_{j_2\tau_2}(j'_1\tau'_1 \leftarrow j_1\tau_1) = \frac{\pi}{\kappa^2(2j_1+1)} \sum_{Jm_j} (2J+1) \left| \sum_{k_1k'_1} a_{k_1\tau_1}^{j_1} a_{k'_1\tau'_1}^{j'_1} \sum_{L_1} S_{L_1K_1j_2\tau_2}^J \right. \\ \left. \times (-)^{k_1} \left( \frac{2j_1+1}{8\pi^2} \right)^{1/2} \left( \frac{2j'_1+1}{8\pi^2} \right)^{1/2} (2L_1+1)^{1/2} \frac{8\pi^2}{2j_1+1} \langle j'_1 k'_1 L_1 K_1 | j_1 k_1 \rangle \langle j'_1 m_j L_1 0 | j_1 m_j \rangle \right|^2. \quad (59)$$

If the square modulus is replaced by a double summation, then, introducing subscripts *a* and *b* which refer to different spectroscopic levels,

$$\sigma_{j_2\tau_2}(j'_1\tau'_1 \leftarrow j_1\tau_1) = \frac{\pi}{\kappa^2} (2j'_1+1) \sum_{Jm_j} (2J+1) \sum_{k_{1a}k'_{1a}k_{2a}k'_{2a}} a_{k_{1a}\tau_1}^{j_1} a_{k'_{1a}\tau'_1}^{j'_1} a_{k_{1b}\tau_1}^{j_1} a_{k'_{1b}\tau'_1}^{j'_1} \\ \times \sum_{L_1L_2} S_{L_1K_{1a}j_2\tau_2}^J S_{L_2K_{1b}j_2\tau_2}^{J*} (2L_1+1)^{1/2} (2L_2+1)^{1/2} (-)^{k'_{1a}+k'_{1b}} \\ \times \begin{pmatrix} j'_1 & L_1 & j_1 \\ k'_{1a} & K_{1a} & -k_{1a} \end{pmatrix} \begin{pmatrix} j'_1 & L_2 & j_1 \\ k'_{1b} & K_{1b} & -k_{1b} \end{pmatrix} \begin{pmatrix} j'_1 & L_1 & j_1 \\ m_j & 0 & -m_j \end{pmatrix} \begin{pmatrix} j'_1 & L_2 & j_1 \\ m_j & 0 & -m_j \end{pmatrix}. \quad (60)$$

The invariance of the Wigner 3-*j* symbol under cyclic permutation of its columns, together with use of the orthogonality of the Clebsch–Gordan coefficients leads to

$$\sigma_{j_2\tau_2}(j'_1\tau'_1 \leftarrow j_1\tau_1) = \sum_{L_1} F(j'_1\tau'_1 | j_1\tau_1 | L_1) Q_{j_2\tau_2}^s(L_1 K_{1a} K_{1b}), \quad (61)$$

where all information concerning the spectroscopic levels is contained in the coefficient

$$F(j'_1\tau'_1 | j_1\tau_1 | L_1) = (2j'_1+1) \sum_{k_{1a}k'_{1a}k_{2a}k'_{2a}} a_{k_{1a}\tau_1}^{j_1} a_{k'_{1a}\tau'_1}^{j'_1} a_{k_{1b}\tau_1}^{j_1} a_{k'_{1b}\tau'_1}^{j'_1} \\ \times (-)^{k'_{1a}+k'_{1b}} \begin{pmatrix} j'_1 & L_1 & j_1 \\ k'_{1a} & K_{1a} & -k_{1a} \end{pmatrix} \\ \times \begin{pmatrix} j'_1 & L_1 & j_1 \\ k'_{1b} & K_{1b} & -k_{1b} \end{pmatrix}, \quad (62)$$

and all information concerning the collision dynamics is contained in the factors

$$Q_{j_2\tau_2}^s(L_1 K_{1a} K_{1b}) = \frac{\pi}{\kappa^2} \sum_J (2J+1) S_{L_1K_{1a}j_2\tau_2}^J S_{L_1K_{1b}j_2\tau_2}^{J*}. \quad (63)$$

Note that this formula is very similar to the IOS formula for atom–asymmetric top scattering.<sup>24</sup>

#### D. IOS-BS rate constants

IOS-BS rate constants  $\gamma_{j'_1\tau'_1j_1\tau_1}^{j_2\tau_2}$  are given by

$$\gamma_{j'_1\tau'_1j_1\tau_1}^{j_2\tau_2} = v_{\text{rel}} \sigma_{j_2\tau_2}(j'_1\tau'_1 \leftarrow j_1\tau_1), \quad (64)$$

where  $v_{\text{rel}}$  is the relative velocity of collision as defined in Eq. (44).

The IOS-BS rate constants may be Boltzmann averaged over  $j_2$  as for the IOS rate constants in Sec. II, but they are quite insensitive to varying  $j_2$ ,  $\tau_2$  and the calculations in this work are performed with  $j_2$ ,  $\tau_2 = 0,0$ .

As in the IOS approximation, the IOS-BS rate constants were multiplied by the correction factor  $\exp[-(\Delta E/2k_B T)]$ .

As before, Raman *Q*-branch linewidths  $\Gamma_{j_1\tau_1}^{j_2\tau_2}$  are calculated by summing the IOS-BS inelastic rate constants over all final rotational states of the perturbed molecule, and multiplying by two,

$$\Gamma_{j_1\tau_1}^{j_2\tau_2} = 2 \sum_{j'_1\tau'_1 (\neq j_1\tau_1)} \gamma_{j'_1\tau'_1j_1\tau_1}^{j_2\tau_2}. \quad (65)$$

#### E. Intermolecular potential

The potential surface used in this work for the interaction of two H<sub>2</sub>O molecules was that (RWK2) derived by Reimers *et al.*<sup>25</sup> Corrections to typographical errors in this reference were reported by Coker and Watts.<sup>26</sup> This is a semiempirical potential, derived to model various physical properties of water in the solid, liquid, and gas phases.

#### IV. RESULTS AND DISCUSSION

IOS rate constants have been calculated for rotational transitions in the H<sub>2</sub>O molecule resulting from collision with another H<sub>2</sub>O molecule, as described in Sec. II, and the IOS-BS approximation as described in Sec. III. In this section the results of these calculations are presented in such a way as to allow a direct comparison of the two theoretical methods, and to assess their relative accuracy when compared with experimental Raman *Q*-branch linewidths.<sup>8</sup> Since the Raman *Q*-branch linewidths are obtained from experiments involving vibrational excitation of one of the H<sub>2</sub>O molecules, it is not necessary to consider the exchange symmetry of the two H<sub>2</sub>O molecules in the formulation.

Individual rate constants have been calculated using both theoretical methods for thermal collision energies ranging from 300 up to 1200 K, these being the temperatures for which experimental Raman *Q*-branch linewidths have been measured. The amount of computational time required to

TABLE III. Values of  $Q^i(L_1 K_{1a} K_{1b} L_2 K_{2a} K_{2b} L)$  ( $a_0^2$ ). ( $K_{1a} = K_{1b} = K_{2a} = K_{2b} = 0$ ).

(a)	$L_1$	$L_2$	$L$	$T =$	300(K)	404(K)	601(K)	802(K)	1200(K)
	0	1	1		0.194	0.191	0.136	0.135	0.106
	1	1	0		43.0	38.8	29.9	26.6	20.8
	1	1	2		2135.9	1812.9	1451.6	1230.6	970.9
	0	2	2		73.7	62.4	51.7	44.2	36.0
	2	2	0		2.77	2.47	1.91	1.72	1.34
	2	2	2		74.4	61.7	50.5	42.3	33.4
	2	2	4		362.9	311.4	254.2	218.7	177.5

(b) Values of  $Q_{00}^i(L_1 K_{1a} K_{1b})$  ( $a_0^2$ ).

	$L$	$K_a$	$K_b$	$T =$	300(K)	404(K)	601(K)	802(K)	1200(K)
	1	0	0		15.90	14.73	13.39	12.48	11.05
	2	0	0		3.03	2.48	1.87	1.50	0.81

calculate a complete set of IOS rate constants for H<sub>2</sub>O–H<sub>2</sub>O scattering is intractably large. For this reason, it has proved very useful to investigate the contributions of the different values of  $L_1$ ,  $L_2$ , and  $L$  to the overall inelastic cross section (38). A comparison is made between the values of  $Q^i(L_1 K_{1a} K_{1b} L_2 K_{2a} K_{2b} L)$  (40) and  $Q_{00}^i(L_1 K_{1a} K_{1b})$  (63) in the IOS and IOS-BS approximations, respectively. The results of this comparison are presented in Table III. In this table, the dominant contributions to the IOS cross sections are included for values of  $L_1$  and  $L_2$  up to 2. For this reason, only those contributions with  $K_{1a} = K_{1b} = K_{2a} = K_{2b} = 0$  are included, as those with nonzero values of these quantum labels are relatively negligible.

The comparison presented in Table III shows quite clearly that the dominant contribution to the IOS inelastic cross section is that with  $L_1 = L_2 = 1$  and  $L = 2$ . The term with  $L_1 = L_2 = 2$  and  $L = 4$  contributes of the order of 10% to the cross section and a reasonable estimate of the cross section may be obtained by ignoring this contribution. These contributions are those associated with the dipole–dipole and quadrupole–quadrupole interactions, respectively. In other words, the cross section for rotationally inelastic collisions is dominated to the order of some 90% by the interaction of the dipole moments of the two molecules. In these calculations, the Raman  $Q$ -branch linewidths were calculated using only the contribution of the term with  $L_1 = L_2 = 1$  and  $L = 2$ . This means that only those general transitions with  $|\Delta j_1| \leq 1$  and  $|\Delta j_2| \leq 1$  are included in the calculations of the Raman  $Q$ -branch linewidths. It was also found that it was only necessary to calculate transitions with  $|\Delta \tau_1| \leq 2$  and  $|\Delta \tau_2| \leq 2$ , other transitions having negligible contributions to the  $Q$ -branch linewidths.

In the IOS-BS approximation, the effect of restricting the perturbing molecule to the ground rotational level and spherically averaging the angle-dependent intermolecular potential is to average out the contributions of the angle-dependent dipole–dipole and quadrupole–quadrupole interactions to the overall cross section. The results show that this averaging causes a drastic reduction in the cross sections.

Raman  $Q$ -branch linewidths have been calculated using both the IOS and IOS-BS theories and these are presented in Table IV. Experimental linewidths exist for these temperatures<sup>8</sup> and they are also presented for comparison. The results are presented graphically in Fig. 2. (It should be noted that the quantities presented in Table IV and Fig. 2 are actually halfwidths, i.e.,  $\Gamma_{ji\tau_1}/2$ ). The factor  $f$  converting the units of the dynamical rate constants ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) to those of the spectral linewidths ( $\text{cm}^{-1} \text{ atm}^{-1}$ ) is given by<sup>27</sup>

$$f = \left( \frac{D}{2\pi c} \right) (273/T), \quad (66)$$

where  $D$  is the density number at STP ( $D = 2.69 \times 10^{19} \text{ molecule cm}^{-3}$ ) and  $c$  is the speed of light (in  $\text{cm s}^{-1}$ ).

The results show very clearly that, even including just the  $\Delta j_1 \leq 1$  rotational transitions, the IOS calculations tend to overestimate Raman  $Q$ -branch linewidths. The degree of overestimation of the theoretical linewidths is only of the order of two to three times experiment for all the temperatures, and this is not an unreasonable discrepancy. We consider that such a discrepancy is unlikely to arise solely as a result of the use of the IOS approximation, as the IOS works well for He + H<sub>2</sub>O collisions<sup>28</sup> when rate constants are compared with more accurate CS rate constants.<sup>29</sup> The discrepancy could also result from inaccuracies in the intermolecular potential. This hypothesis is strengthened by the fact that the discrepancy between the IOS and the experimental linewidths does not increase markedly at lower temperatures, this being the phenomenon shown by the results in the previous paper<sup>1</sup> for N<sub>2</sub>–N<sub>2</sub> scattering. In that case, the discrepancy was principally due to the fact that large rotational transitions were being overestimated by the IOS approximation at lower collision energies as the rotational spacing was not negligible relative to the collision energy. In this case, only the smallest rotational transitions are being included in the calculation of Raman  $Q$ -branch linewidths, and hence the IOS approximation is likely to be reasonably accurate. However, it would be useful to have more accurate rate con-

TABLE IV. Comparison of IOS ( $\Gamma_{j_1\tau_1}/2$ ), IOS-BS ( $\Gamma_{j_1\tau_1}^{\text{BS}}/2$ ), and experimental (Ref. 8) Raman  $Q$ -branch halfwidths ( $\text{cm}^{-1} \text{atm}^{-1}$ ) for  $\text{H}_2\text{O}-\text{H}_2\text{O}$  rotationally inelastic scattering.

$T = 1200 \text{ K}$	$j_1, \tau_1$	IOS	IOS-BS	Expt.	$T = 601 \text{ K}$	$j_1, \tau_1$	IOS	IOS-BS	Expt.
	0,0	0.287	0.0165	...		3,0	0.559	0.0206	0.224
	1, -1	0.287	0.0158	0.103		3,1	0.554	0.0206	0.211
	1,0	0.282	0.0158	0.136		3,2	0.541	0.0195	0.208
	1,1	0.283	0.0160	0.098		3,3	0.530	0.0195	0.200
	2, -2	0.283	0.0159	0.112		4, -4	0.559	0.0200	0.240
	2, -1	0.280	0.0158	0.112		4, -3	0.555	0.0197	0.219
	2,0	0.284	0.0159	0.120		4, -2	0.570	0.0204	0.218
	2,1	0.274	0.0158	...		4, -1	0.548	0.0203	...
	2,2	0.269	0.0158	...		4,0	0.561	0.0204	...
	3, -3	0.278	0.0158	0.111		4,1	0.540	0.0200	0.212
	3, -2	0.275	0.0158	0.117		4,2	0.525	0.0200	0.242
	3, -1	0.282	0.0157	0.123		4,3	0.525	0.0185	...
	3,0	0.274	0.0161	0.114		4,4	0.517	0.0185	...
	3,1	0.272	0.0159	0.116					
	3,2	0.266	0.0155	...	$T = 404 \text{ K}$	$j_1, \tau_1$	IOS	IOS-BS	Expt.
	3,3	0.260	0.0155	0.120		0,0	0.780	0.0257	0.241
	4, -4	0.274	0.0157	0.121		1, -1	0.780	0.0246	0.260
	4, -3	0.273	0.0156	0.117		1,0	0.769	0.0247	0.414
	4, -2	0.279	0.0157	0.114		1,1	0.771	0.0246	0.260
	4, -1	0.268	0.0160	...		2, -2	0.773	0.0246	0.256
	4,0	0.275	0.0158	...		2, -1	0.765	0.0239	0.294
	4,1	0.265	0.0158	0.132		2,0	0.771	0.0250	0.252
	4,2	0.257	0.0158	0.156		2,1	0.746	0.0239	0.292
	4,3	0.257	0.0150	...		2,2	0.733	0.0239	...
	4,4	0.254	0.0150	...		3, -3	0.759	0.0242	0.311
						3, -2	0.748	0.0235	0.293
						3, -1	0.767	0.0246	0.290
$T = 802 \text{ K}$	$j_1, \tau_1$	IOS	IOS-BS	Expt.		3,0	0.746	0.0244	0.331
	0,0	0.453	0.0187	...		3,1	0.739	0.0243	0.299
	1, -1	0.453	0.0180	0.144		3,2	0.722	0.0228	0.262
	1,0	0.447	0.0183	0.164		3,3	0.707	0.0227	0.273
	1,1	0.449	0.0180	0.146		4, -4	0.746	0.0236	0.297
	2, -2	0.450	0.0180	0.146		4, -3	0.741	0.0232	0.291
	2, -1	0.444	0.0177	0.159		4, -2	0.760	0.0242	0.293
	2,0	0.449	0.0183	0.161		4, -1	0.730	0.0239	...
	2,1	0.433	0.0178	0.163		4,0	0.748	0.0240	...
	2,2	0.426	0.0177	...		4,1	0.720	0.0231	0.274
	3, -3	0.441	0.0177	0.157		4,2	0.700	0.0230	0.265
	3, -2	0.435	0.0175	0.172		4,3	0.700	0.0210	...
	3, -1	0.446	0.0181	0.153		4,4	0.690	0.0209	...
	3,0	0.433	0.0181	0.236					
	3,1	0.430	0.0181	0.164	$T = 300 \text{ K}$	$j_1, \tau_1$	IOS	IOS-BS	Expt.
	3,2	0.420	0.0172	0.170		0,0	1.141	0.0293	0.329
	3,3	0.411	0.0172	0.163		1, -1	1.141	0.0281	0.355
	4, -4	0.433	0.0175	0.178		1,0	1.126	0.0280	0.385
	4, -3	0.431	0.0173	0.177		1,1	1.129	0.0279	0.336
	4, -2	0.442	0.0179	0.165		2, -2	1.132	0.0281	0.341
	4, -1	0.425	0.0180	...		2, -1	1.119	0.0269	0.394
	4,0	0.435	0.0180	...		2,0	1.129	0.0284	0.360
	4,1	0.419	0.0177	0.178		2,1	1.091	0.0270	...
	4,2	0.408	0.0177	0.199		2,2	1.073	0.0269	...
	4,3	0.408	0.0166	...		3, -3	1.110	0.0275	0.428
	4,4	0.401	0.0166	0.168		3, -2	1.095	0.0265	0.379
						3, -1	1.122	0.0279	0.403
$T = 601 \text{ K}$	$j_1, \tau_1$	IOS	IOS-BS	Expt.		3,0	1.091	0.0273	0.372
	0,0	0.584	0.0214	0.197		3,1	1.082	0.0273	0.394
	1, -1	0.584	0.0205	0.183		3,2	1.057	0.0253	...
	1,0	0.576	0.0209	0.255		3,3	1.035	0.0251	...
	1,1	0.578	0.0205	0.186		4, -4	1.091	0.0266	0.431
	2, -2	0.580	0.0206	0.192		4, -3	1.085	0.0259	0.416
	2, -1	0.573	0.0202	0.210		4, -2	1.113	0.0274	0.449
	2,0	0.578	0.0210	0.195		4, -1	1.069	0.0266	...
	2,1	0.559	0.0202	0.192		4,0	1.095	0.0269	...
	2,2	0.549	0.0202	...		4,1	1.054	0.0254	0.325
	3, -3	0.568	0.0202	0.216		4,2	1.025	0.0252	0.262
	3, -2	0.561	0.0199	0.231		4,3	1.025	0.0225	...
	3, -1	0.574	0.0207	0.203		4,4	1.010	0.0225	...

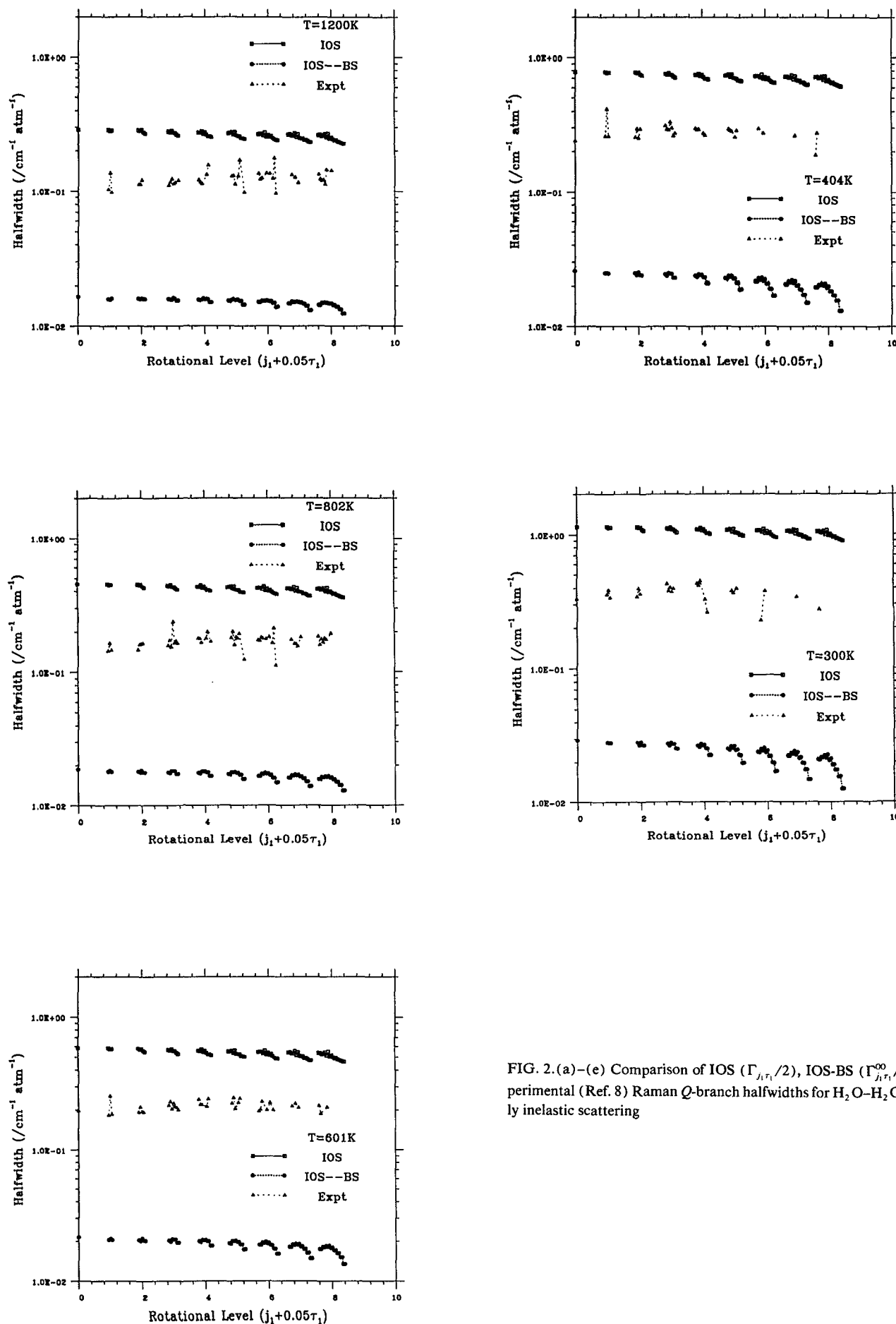


FIG. 2.(a)–(e) Comparison of IOS ( $\Gamma_{j_1\tau_1}/2$ ), IOS-BS ( $\Gamma_{j_1\tau_1}^{\infty}/2$ ), and experimental (Ref. 8) Raman Q-branch halfwidths for  $\text{H}_2\text{O}-\text{H}_2\text{O}$  rotationally inelastic scattering

stants, such as coupled states, to examine this point in more detail.

Of interest also is the  $(j, \tau)$  dependence of the linewidths. As can be seen from Fig. 2, the calculated linewidths are almost insensitive to  $j_1$  and decrease slightly as  $\tau_1$  is increased for each  $j$ . This is also the finding in the experiments, particularly at higher temperatures.<sup>8</sup> Furthermore, our finding that transitions with  $|\Delta j_1|, |\Delta j_2| \leq 1$  are dominant, as expected from the strong dipole-dipole interaction, suggests that only a very small set of rate constants might be needed in the inversion of CARS spectra to produce temperatures for  $\text{H}_2\text{O}$  in high-pressure combustion chambers. The IOS approximation is clearly a useful method for providing these rate constants.

## V. CONCLUSIONS

Both the IOS and IOS-BS approximations have been used to calculate rotationally inelastic rate constants in  $\text{H}_2\text{O} + \text{H}_2\text{O}$  scattering. As far as we are aware, this is the first time such quantum mechanical methods have been used to perform calculations in collisions between two nonlinear polyatomic molecules. This work has shown that quantum mechanical approximations may be used with some success to predict Raman spectral linewidths even for polyatomic collision systems. The results suggest that such calculations might also be useful for providing the rotationally inelastic rate constants that are needed for thermometry in combustion chambers.

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