

## THEORETICAL INTENSITIES FOR ROTATION-VIBRATION LINES OF WATER USING PARTICLES-ON-A-SPHERE WAVEFUNCTIONS

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Using variational wavefunctions calculated from the particles-on-a-sphere model, and an ab initio electric dipole moment function, we have calculated intensities for the allowed rotation-vibration transitions involving states with  $J=0, 1, 2$  in the pure rotational,  $\nu_2$ , and  $2\nu_2$  bands of water. A comparison of our results with experimental and rigid-rotor intensities suggests that our wavefunctions correctly take into account substantial rotation-bending interactions, but run into difficulties for the  $2\nu_2$  band, where the neglected stretch-bend interactions are important.

### 1. Introduction

The calculation of transition intensities often serves as a much more stringent test of the accuracy of wavefunctions than does the calculation of energy levels. For water, most intensities have been calculated [1-3] using dipole moment functions obtained by fitting experimental intensities. A few calculations of vibrational band intensities have been performed using ab initio electric dipole moment functions [4,5], but these calculations have not included rotational structure. Here we have made such a calculation of intensities for allowed transitions involving states with  $J=0, 1, 2$  in the pure rotational,  $\nu_2$ , and  $2\nu_2$  bands of water.

The variational wavefunctions we employed were calculated using the particles-on-a-sphere method [6,7], which arises naturally from the adiabatic separation of high-frequency stretching modes from bending and rotational modes. As a zero-order approximation, the water molecule is simulated by having the two hydrogens confined to move on a sphere around the oxygen [6]. Various refinements have been made to include excited states of stretching vibrations [7], and work is in progress to include the interaction of stretching and bending motions

into this physical picture. For the present work, however, we consider only the zero-order model and thus concern ourselves only with transitions corresponding to rotational and bending excitations.

### 2. Method of calculation

The particles-on-a-sphere wavefunctions employed here were calculated using the kinetic energy operator described in ref. [6] and the Carney-Curtiss-Langhoff potential [8]. (We found only small changes in our calculated intensities when other potentials were used). These functions are of the form [6]

$$\Psi(\mathbf{R}_1, \mathbf{R}_2) = \mathcal{A}(\mathbf{R}_1 \mathbf{R}_2)^{-1} \Phi(\mathbf{R}_1, \mathbf{R}_2) \times \chi(\theta_1, \varphi_1, \theta_2, \varphi_2), \quad (1)$$

where the variables correspond to the space-fixed spherical polar coordinates of the two H atoms, and  $\mathcal{A}$  is the antisymmetrization operator. The radial localization of the H atoms in the ground stretching state leads to their radial wavefunction being well approximated by

$$\Phi(\mathbf{R}_1, \mathbf{R}_2) = \delta(R_1 - R_c) \delta(R_2 - R_c). \quad (2)$$

The angular wavefunction is

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$$\chi_M^J = \sum_{j_1 j_2} C_{j_1 j_2 J} |j_1 j_2 JM\rangle, \quad (3)$$

where the basis functions are coupled spherical harmonics

$$|j_1 j_2 JM\rangle = \sum_{m_1 m_2} Y_{j_1 m_1}(\theta_1, \varphi_1) Y_{j_2 m_2}(\theta_2, \varphi_2) \times \langle j_1 m_1 j_2 m_2 | JM \rangle. \quad (4)$$

In order to perform the necessary integrals with the dipole moment function in internal coordinates, these basis functions were transformed, using the method and conventions of Hunter and Berry [9], into functions depending on the H-O-H bond angle ( $\theta_{12}$ ) and the Euler angles of the body-fixed bisector frame  $x' y' z'$ :

$$|j_1 j_2 JM\rangle = \sum_K (-1)^{M+K} F_{j_1 j_2}^{JK}(\theta_{12}) \mathcal{D}_{-MK}^J(\alpha\beta\gamma), \quad (5)$$

where

$$F_{j_1 j_2}^{JK}(\theta_{12}) = \sum_{m_1 m_2} Y_{j_1 m_1}(\theta'_1, \varphi'_1) Y_{j_2 m_2}(\theta'_2, \varphi'_2) \langle j_1 m_1 j_2 m_2 | J-K \rangle, \quad (6)$$

and  $(\theta'_i, \varphi'_i)$  are the spherical polar coordinates of hydrogen atom  $i$  in the body-fixed frame. With our choice of this frame, the H-O-H triangle lies in the  $x' z'$  plane with the O at the origin and the  $x'$  axis bisecting  $\theta_{12}$ , such that

$$(\theta'_1, \varphi'_1) = (\frac{1}{2}(\pi - \theta_{12}), 0), \quad (7a)$$

$$(\theta'_2, \varphi'_2) = (\frac{1}{2}(\pi + \theta_{12}), 0). \quad (7b)$$

The coupled spherical harmonics of eq. (4) naturally and implicitly take into account interactions between bending and rotation; this is seen explicitly in the transformed form given in eq. (5).

The ab initio electric dipole moment function we used was that of Rosenberg, Ermler, and Shavitt (RES) [10], who calculated its body-fixed Cartesian components as functions of the deviations of the internal coordinates  $R_1$ ,  $R_2$ , and  $\theta_{12}$  from their equilibrium values. In order to transform  $\mu$  into the space-fixed frame, we rewrite it as a spherical tensor [11] of rank one with components

$$\begin{aligned} \mu_q &= \mu_{z'}, & q=0, \\ &= \mp (1/\sqrt{2})(\mu_{x'} \pm i\mu_{y'}), & q=\pm 1. \end{aligned} \quad (8)$$

This quantity is real since the molecule lies in the  $x' z'$  plane. (Note that the body-fixed axes  $x'$ ,  $y'$ ,  $z'$  of ref. [10] correspond respectively to our  $y'$ ,  $z'$ ,  $x'$ .) Now,

$$\mu_m = \sum_q \mathcal{D}_{mq}^{1*}(\alpha\beta\gamma) \mu_q(R_1, R_2, \theta_{12}), \quad (9)$$

and the matrix element necessary for calculating the line intensity

$$\begin{aligned} &\sum_{M_i, M_f, m} |\langle \Psi_f | \mu_m | \Psi_i \rangle|^2 \\ &= 3 \sum_{M_i, M_f} |\langle \Psi_f | \mu_0 | \Psi_i \rangle|^2. \end{aligned} \quad (10)$$

Since the integrations over both the Euler angles and the radial variables can be effected analytical, we are left with only a one-dimensional integral over  $\theta_{12}$  to perform numerically. The above matrix element corresponds to  $R_A^B$  of Flaud and Camy-Peyret [1], whose formulae we used to convert this quantity into an intensity.

### 3. Results and discussion

Our results for pure rotational transitions are presented in table 1 and compared with those of Flaud et al. [2] and with pure rigid-rotor intensities calculated using experimental values for the rotational constants [12] and dipole moment [13,14], and energy [15] and line strength [16] tables for an asymmetric rigid rotor. The rigid-rotor values are nearly indistinguishable from those of Flaud et al. [2], showing that at least for these low-lying rotational states the rigid-rotor approximation is quite good. Our results also agree well with those of the other two calculations, apart from an overall factor averaging 1.07 which probably results from the inaccuracy of the RES dipole moment function since  $(\mu_{RES}/\mu_{exp})^2 = 1.06$ .

For the  $\nu_2$  band our results are given in table 2 along with other values for comparison. Clearly the values calculated by Camy-Peyret and Flaud [3] agree quite well with the available experimental values [17,18]. The rigid-rotor intensities presented here

Table 1

Intensities for pure rotational transitions in water. Energies, from ref. [2], are in  $\text{cm}^{-1}$ . Intensities are given for a temperature of 296 K. The numbers in parentheses represent powers of ten

$\Delta E$	$J'_{KaKc} \leftarrow J_{KaKc}$	$E_{\text{lower}}$	Intensity ( $\text{cm}^{-1}/\text{molecule cm}^{-2}$ )			$I_3/I_2$
			rigid rotor $I_1$	ref. [2] $I_2$	this work $I_3$	
18.577	$1_{10} \leftarrow 1_{01}$	23.794	5.29(-20)	5.27(-20)	5.61(-20)	1.06
25.085	$2_{11} \leftarrow 2_{02}$	70.091	3.49(-20)	3.48(-20)	3.57(-20)	1.03
32.954	$2_{02} \leftarrow 1_{11}$	37.137	2.53(-20)	2.53(-20)	2.85(-20)	1.13
37.137	$1_{11} \leftarrow 0_{00}$	0.000	5.04(-20)	5.03(-20)	5.35(-20)	1.06
40.988	$2_{20} \leftarrow 2_{11}$	95.176	4.89(-20)	4.82(-20)	5.43(-20)	1.13
55.406	$2_{21} \leftarrow 2_{12}$	79.496	1.85(-19)	1.83(-19)	1.94(-19)	1.06
55.702	$2_{12} \leftarrow 1_{01}$	23.794	4.34(-19)	4.34(-19)	4.62(-19)	1.06
92.530	$2_{21} \leftarrow 1_{10}$	42.372	1.01(-18)	1.01(-18)	1.07(-18)	1.06
99.027	$2_{20} \leftarrow 1_{11}$	37.137	3.24(-19)	3.23(-19)	3.31(-19)	1.03

were calculated with the formula of ref. [19], using interpolated asymmetric rotor line strengths [16] and assuming a total band intensity of  $1.04 \times 10^{-17} \text{ cm}^{-1}/\text{molecule cm}^{-2}$  and a band center of  $1594.747 \text{ cm}^{-1}$  [2]. As seen in the eighth column of table 2, these predicted rigid-rotor intensities vary widely in their agreement with the more accurate values. By

contrast, our variational functions yield quite good *relative* intensities, as seen in the nearly constant value of the ratio of our intensities to those of ref. [3] in the final column of table 2. This suggests that our wavefunctions correctly take into account the interaction of bending and rotation. Our absolute numbers appear to be too large by an average factor

Table 2

Intensities for rovibrational transitions in the  $\nu_2$  band of water

$\Delta E$	$J'_{KaKc} \leftarrow J_{KaKc}$	$E_{\text{lower}}$	Intensity ( $\text{cm}^{-1}/\text{molecule cm}^{-2}$ )				$I_1/I_3$	$I_4/I_3$
			rigid rotor $I_1$	expt. $I_2$	ref. [3] $I_3$	this work $I_4$		
1498.806	$1_{11} \leftarrow 2_{20}$	136.164	3.59(-20)	-	5.09(-20)	6.07(-20)	0.71	1.19
1505.606	$1_{10} \leftarrow 2_{21}$	134.902	1.31(-19)	1.81(-19) <sup>a)</sup>	1.80(-19)	2.22(-19)	0.73	1.23
1539.063	$1_{01} \leftarrow 2_{12}$	79.496	1.76(-19)	-	1.97(-19)	2.52(-19)	0.89	1.28
1542.161	$2_{12} \leftarrow 2_{21}$	134.902	7.47(-20)	-	1.05(-19)	1.27(-19)	0.71	1.21
1557.489	$2_{11} \leftarrow 2_{20}$	136.164	3.78(-20)	-	4.93(-20)	6.30(-20)	0.77	1.28
1557.611	$0_{00} \leftarrow 1_{11}$	37.137	4.86(-20)	-	5.49(-20)	6.98(-20)	0.88	1.27
1564.879	$1_{11} \leftarrow 2_{02}$	70.091	3.14(-20)	2.85(-20) <sup>a)</sup>	3.09(-20)	4.29(-20)	1.02	1.39
1569.795	$2_{02} \leftarrow 2_{11}$	95.176	7.65(-20)	9.17(-20) <sup>a)</sup>	9.31(-20)	1.15(-19)	0.82	1.24
1576.188	$1_{01} \leftarrow 1_{10}$	42.372	2.16(-19)	2.37(-19) <sup>a)</sup>	2.47(-19)	3.11(-19)	0.87	1.26
1616.714	$1_{10} \leftarrow 1_{01}$	23.794	2.42(-19)	2.12(-19) <sup>a)</sup>	2.23(-19)	2.91(-19)	1.09	1.30
1623.562	$2_{11} \leftarrow 2_{02}$	70.091	8.94(-20)	-	7.97(-20)	1.00(-19)	1.12	1.25
1627.834	$2_{02} \leftarrow 1_{11}$	37.137	3.84(-20)	-	4.00(-20)	5.08(-20)	0.96	1.27
1634.970	$1_{11} \leftarrow 0_{00}$	0.000	6.11(-20)	-	5.69(-20)	7.35(-20)	1.07	1.29
1648.316	$2_{20} \leftarrow 2_{11}$	95.176	4.88(-20)	-	3.75(-20)	5.04(-20)	1.30	1.34
1653.268	$2_{12} \leftarrow 1_{01}$	23.794	2.48(-19)	2.56(-19) <sup>b)</sup>	2.33(-19)	2.99(-19)	1.06	1.28
1662.811	$2_{21} \leftarrow 2_{12}$	79.496	1.05(-19)	8.43(-20) <sup>b)</sup>	7.74(-20)	1.03(-19)	1.36	1.32
1699.935	$2_{21} \leftarrow 1_{10}$	42.372	2.33(-19)	1.75(-19) <sup>b)</sup>	1.74(-19)	2.27(-19)	1.34	1.31
1706.355	$2_{20} \leftarrow 1_{11}$	37.137	6.62(-20)	-	4.88(-20)	6.33(-20)	1.36	1.30

<sup>a)</sup> Ref. [17]. <sup>b)</sup> Ref. [18].

of 1.28. This may be due to the RES dipole moment function since another calculation [4] using it gives a total band intensity which is larger than the value of ref. [2] by a factor of 1.45.

We do not present our results for the  $2\nu_2$  band since neither the relative nor absolute intensities we calculated were accurate, the results being too small by a factor ranging from about 3 to 5. This appears to be a consequence of neglect of stretch-bend interactions, which are particularly important for this band because of its near-degeneracy with the  $\nu_1$  and  $\nu_3$  bands. We hope to improve these results and to make accurate calculations possible for the  $\nu_1$  and  $\nu_3$  bands as well by substituting for the function  $\Phi(R_1, R_2)$  in eq. (2) the appropriate solution of the two-dimensional stretching equation [7]. We are also planning to implement a more effective adiabatic separation of motions by solving the two-dimensional stretching equation at different values of the bending angle [20,21].

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