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### $(\text{H}_2\text{O})_2$ : spectroscopy, structure and dynamics

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## $(\text{H}_2\text{O})_2$ : spectroscopy, structure and dynamics

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Tunnelling in water dimer allows each of the hydrogen atoms to participate in the hydrogen bonding, giving rise to a complicated energy-level scheme and rotational spectrum. As a result of new theoretical and experimental developments, great progress has been made in the analysis and interpretation of this spectrum, yielding detailed information about this hydrogen-bonded interaction. This paper reviews the spectroscopy of this highly non-rigid dimer, which is becoming a prototype system for the study of multidimensional tunnelling problems in weakly bound complexes.

### 1. Introduction

The water dimer is perhaps the most important hydrogen-bonded system in chemistry. An accurate determination of the potential energy surface characterizing this interaction is essential to any complete molecular understanding of solution chemistry, solvation, cloud formation, and a number of biochemical processes. The spectroscopic study of hydrogen-bonded and van der Waals complexes has played an active role in our efforts to understand intermolecular forces. In particular, high-resolution microwave and laser spectroscopies have provided detailed and reliable information about the equilibrium geometries and vibrational-rotational energy-level structure for these species. For a few cases, such as the rare-gas complexes with hydrogen, the hydrogen halides, or the halogens, this has led to accurate intermolecular potentials characterizing the pair interactions. For more complicated systems, such as  $(\text{H}_2\text{O})_2$  or  $(\text{NH}_3)_2$ , the spectroscopic results are not as complete, nor are the theoretical tools yet available to determine accurate experimental potentials. Instead, the experimental results furnish a critical test of the reliability of *ab initio* or semiempirical surfaces, particularly in the vicinity of the absolute minima, and provide a valuable data set for the development of electrostatic and other perturbative theories of intermolecular forces.

For a number of non-rigid complexes, including  $(\text{H}_2\text{O})_2$ , the comparison between theory and experiment is not straightforward due to the complications in the spectroscopy of these species arising from large amplitude motions. In the case of  $(\text{H}_2\text{O})_2$ , there exist eight isoenergetic minima which are accessible at the zero-point level of excitation. Tunnelling between these minima leads to an extremely complex energy-level scheme. One type of tunnelling motion (denoted 'interconversion tunnelling' here) corresponds to the two  $\text{H}_2\text{O}$  subunits interchanging proton-donor and proton-acceptor bonding roles in the complex. This motion is similar to that found by Dyke *et al.* (1972) for  $(\text{HF})_2$ . The other tunnelling motions can be pictured as resulting from twofold rotations of either or both of the water units about their  $C_2$  symmetry axes, as shown in figure 1.

Substantial experimental and theoretical progress has been made in recent years in the analysis of the  $(\text{H}_2\text{O})_2$  rotation-tunnelling spectrum, requiring the cooperative efforts of a number of different laboratories. These results are reviewed and suggestions

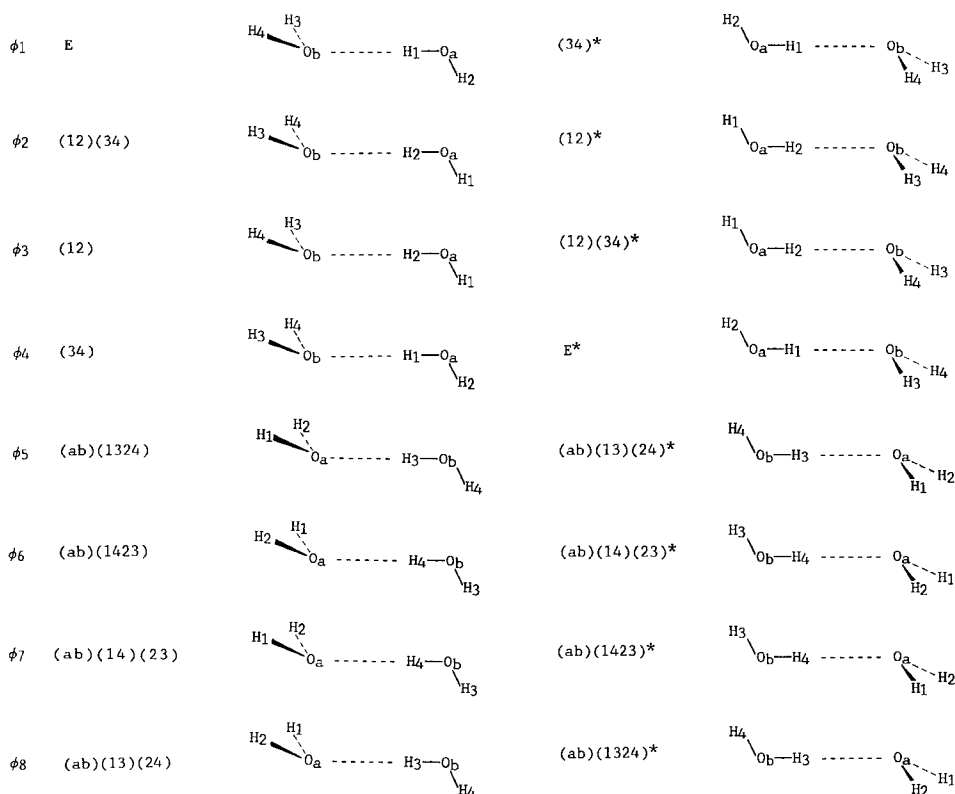


Figure 1. Effect of the permutation-inversion operations of  $G_{16}$  on  $(\text{H}_2\text{O})_2$  (Dyke 1977). The first column of structures (1–8) shows the eight frameworks for  $(\text{H}_2\text{O})_2$  as defined by Hougen (1985). The vibrational wavefunctions associated with these frameworks are designated  $\phi_1$ – $\phi_8$ . The second column of structures (1'–8') differs from the first by a  $180^\circ$  rotation of the complex about the  $b$  inertial axis, which points out of the plane of the paper. The  $a$  inertial axis is nearly coincident with the line connecting the oxygen nuclei.

will be presented where further experimental measurements or theoretical developments are necessary. The review is written assuming that the reader has a familiarity with molecular spectroscopy. The first part of the review will present the theoretical models necessary for the description of the spectroscopy of  $(\text{H}_2\text{O})_2$ . These include the group theoretical treatment of  $(\text{H}_2\text{O})_2$  by Dyke (1977) and the rotational-tunnelling formalism of Hougen (1985) and Coudert and Hougen (1988, 1990) for characterizing multidimensional tunnelling in the dimer. The second part of the review will summarize and discuss the experimental results on  $(\text{H}_2\text{O})_2$ , starting from the initial microwave investigation of Dyke and Muentzer (1974).

## 2. Group theory

A useful starting point for the theory of the spectroscopy of a highly non-rigid complex such as  $(\text{H}_2\text{O})_2$  is the molecular symmetry group of Longuet-Higgins (1963). Dyke *et al.* (1972) used the molecular symmetry group in analysing the effects of interconversion tunnelling on the microwave spectrum of  $(\text{HF})_2$ , and the success of this approach prompted Dyke (1977) to apply this group as a first step to understanding the spectroscopy of  $(\text{H}_2\text{O})_2$ . It has since been employed by Nelson and Klemperer (1987)

and Fraser *et al.* (1988) to interpret the microwave spectra of (NH<sub>3</sub>)<sub>2</sub> and (HCCH)<sub>2</sub>, which also display complications from interconversion tunnelling. The molecular symmetry group consists of all the permutation-inversion operations of the identical nuclei which can result by feasible tunnelling and/or overall rotational motions. An allowable tunnelling motion is one which leads to an energy-level splitting of sufficient magnitude to be observable in the experiment. By this criterion, motions which break covalent bonds are not considered. For the C<sub>s</sub> symmetry (H<sub>2</sub>O)<sub>2</sub>, Dyke (1977) obtained the permutation-inversion operations shown in figure 1. The molecular symmetry group generated by these 16 operations is given in table 1. It is denoted G<sub>16</sub> and is isomorphic to the D<sub>4h</sub> point group. The molecular symmetry group for the planar T-shaped acetylene dimer (Fraser *et al.* 1988) is likewise G<sub>16</sub>.

Of the 16 (H<sub>2</sub>O)<sub>2</sub> structures shown in figure 1, eight are not superimposable on each other, indicating that in G<sub>16</sub> the ground vibrational state of the dimer is eightfold degenerate. Here we will use the convention of Hougen (1985) and designate structure 1 as our initial reference configuration. Structures 2–8 differ from 1 by a tunnelling motion, denoted 1→2, 1→3, ...; structures 1'–8' differ from 1–8 by a 180° rotation about an axis out of the plane of the page. The vibrational wavefunctions for configurations 1–8 and 1'–8' will be denoted φ<sub>1</sub>–φ<sub>8</sub>. The feasible tunnelling motions will split each rigid-molecule (H<sub>2</sub>O)<sub>2</sub> rotational state of the ground vibrational state into at most eight tunnelling sublevels. Dyke (1977) has found that for (H<sub>2</sub>O)<sub>2</sub> rotational states of A' symmetry in C<sub>s</sub>, rotational-tunnelling sublevels of A<sub>1</sub><sup>+</sup>, B<sub>1</sub><sup>+</sup>, E<sup>+</sup>, A<sub>2</sub><sup>-</sup>, B<sub>2</sub><sup>-</sup> and E<sup>-</sup> symmetry result; for rotational states of A'' symmetry, sublevels of A<sub>1</sub><sup>-</sup>, B<sub>1</sub><sup>-</sup>, E<sup>-</sup>, A<sub>2</sub><sup>+</sup>, B<sub>2</sub><sup>+</sup> and E<sup>+</sup> symmetry result. Here the E<sup>+</sup> and E<sup>-</sup> states are doubly degenerate. Since the electric dipole moment operator transforms like A<sub>1</sub><sup>-</sup> in G<sub>16</sub> the overall selection rules are

$$A_1^+ \leftrightarrow A_1^-, \quad B_1^+ \leftrightarrow B_1^-, \quad A_2^+ \leftrightarrow A_2^-, \quad B_2^+ \leftrightarrow B_2^-, \quad E^+ \leftrightarrow E^-. \quad (1)$$

Dyke (1977) has also shown that the products of the four *I* = ½ proton nuclear spin functions of (H<sub>2</sub>O)<sub>2</sub> generate a (2*I* + 1)<sup>4</sup> dimensional representation of G<sub>16</sub> which reduces to 6A<sub>1</sub><sup>+</sup> + 3B<sub>1</sub><sup>+</sup> + B<sub>2</sub><sup>+</sup> + 3E<sup>+</sup>. With the Pauli exclusion principle requiring that the total wavefunction have a symmetry of B<sub>2</sub><sup>+</sup> or B<sub>2</sub><sup>-</sup> in G<sub>16</sub>, Dyke (1977) obtained the following statistical weights for the (H<sub>2</sub>O)<sub>2</sub> rovibronic species:

$$A_1^+, A_1^- \quad 1, \quad B_1^+, B_1^- \quad 0, \quad A_2^+, A_2^- \quad 3, \quad B_2^+, B_2^- \quad 6, \quad E^+, E^- \quad 3. \quad (2)$$

### 3. Tunnelling formalism

Following Coudert and Hougen (1988), we describe each *J, K* rotational state of A' or A'' symmetry for C<sub>s</sub> (H<sub>2</sub>O)<sub>2</sub> by the following Hamiltonian matrix for the rotational-tunnelling problem,

$$\begin{bmatrix} H_{JK} & H_{12} & H_{13} & H_{14} & H_{15} & H_{15} & H_{17} & H_{17} \\ H_{12} & H_{JK} & H_{14} & H_{13} & H_{15} & H_{15} & H_{17} & H_{17} \\ H_{13} & H_{14} & H_{JK} & H_{12} & H_{17} & H_{17} & H_{15} & H_{15} \\ H_{14} & H_{13} & H_{12} & H_{JK} & H_{17} & H_{17} & H_{15} & H_{15} \\ H_{15} & H_{15} & H_{17} & H_{17} & H_{JK} & H_{12} & H_{13} & H_{14} \\ H_{15} & H_{15} & H_{17} & H_{17} & H_{12} & H_{JK} & H_{14} & H_{13} \\ H_{17} & H_{17} & H_{15} & H_{15} & H_{13} & H_{14} & H_{JK} & H_{12} \\ H_{17} & H_{17} & H_{15} & H_{15} & H_{14} & H_{13} & H_{12} & H_{JK} \end{bmatrix}, \quad (3)$$

Table 1. The  $G_{1,6}$  molecular symmetry group for  $(H_2O)_2$  (Dyke 1977).

	(34) (12)	(ab)(13)(24) (ab)(14)(23)	(ab)(1324) (ab)(1423)	(12)(34)	E*	(34)* (12)*	(ab)(13)(24)* (ab)(14)(23)*	(ab)(1324)* (ab)(1423)*	(12)(34)*
$A_1^+$	1	1	1	1	1	1	1	1	1
$A_2^+$	-1	-1	1	1	1	-1	1	1	1
$B_1^+$	1	-1	-1	1	1	1	-1	-1	1
$B_2^+$	-1	1	-1	1	1	-1	1	-1	1
$E^+$	2	0	0	-2	2	0	0	0	-2
$A_1^-$	1	1	1	1	-1	-1	-1	-1	-1
$A_2^-$	-1	-1	1	1	-1	1	1	1	-1
$B_1^-$	1	-1	-1	1	-1	-1	-1	-1	-1
$B_2^-$	-1	1	-1	1	-1	1	1	1	-1
$E^-$	2	0	0	-2	-2	0	0	0	2

where the basis set is  $\phi_{\text{rot}}\phi_i$ ,  $i = 1, 8$ . Here,  $\phi_{\text{rot}}$  is a prolate symmetric-top wavefunction of definite parity and the  $\phi_i$  have been defined above. In this basis,  $H_{JK}$  resembles the standard energy-level expression for a near prolate asymmetric rotor with a large  $A$  rotational constant, and  $H_{ij}$  are tunnelling matrix elements connecting configurations  $i$  and  $j$  in figure 1. We have used symmetry to replace  $H_{23}$  by  $H_{14}$ ,  $H_{34}$  by  $H_{12}$ , and so on. Note that  $H_{23} = H_{14}$  since both  $1 \rightarrow 4$  and  $2 \rightarrow 3$  require interchanging the two protons on the proton-acceptor water unit and the two protons on the proton-donor unit. Similar relationships exist for  $H_{34}$  and  $H_{12}$ , and for a number of the other tunnelling matrix elements.

In general, the angular momentum generated by the  $i \rightarrow j$  tunnelling makes each of the  $H_{ij}$  a function of the  $J$  and  $K$  quantum number labels. Coudert and Hougen (1988, 1990) have developed a procedure for determining these dependencies in the high-tunnelling-barrier limit by using an internal-axis-type method (IAM) for multidimensional tunnelling problems, as developed by Hougen (1985, 1987). They write  $H_{1j} = h_{jv} f_j(J, K, A')$  and  $H_{1j} = h_{jv} f_j(J, K, A'')$  for  $A'$  and  $A''$  rotational states respectively, where  $h_{jv}$  is the true tunnelling frequency for  $C_s$  vibrational state  $v$  and  $f_j$  is the  $J$  and  $K$  dependence of  $H_{1j}$ . In their picture  $h_{jv}$  is related to an overlap integral between the vibrational wavefunctions  $\phi_1$  and  $\phi_j$  and a potential-energy-surface coupling term and the  $f_j$  are Wigner  $D_{K', K}^{(j)}$  functions, depending on tunnelling pathway and geometry of the dimer. For  $J = 0$  and for tunnelling motions that do not generate angular momentum (i.e. inversion in NH<sub>3</sub>) the  $f_j$  are unity. In Hougen's formalism the  $f_j$  are expressed as functions of the Euler angles  $(\phi_j, \theta_j, \chi_j)$ , which specify the rotation of the IAM reference framework required to cancel out the angular momentum generated by  $1 \rightarrow j$ . In some cases the  $(\phi_j, \theta_j, \chi_j)$  are known by symmetry, although typically they, together with the  $h_{jv}$ , are determined from a fit to the spectrum. Although the  $h_{jv}$  and  $(\phi_j, \theta_j, \chi_j)$  are intimately related to the dimer potential surface, techniques are not presently available to use this relationship to test or refine existing potential surfaces.

It should be noted that both  $E^+$  and  $E^-$  symmetry species appear in the  $A'$  and  $A''$  Hamiltonian matrices of expression (3), leading to non-zero matrix elements between the  $A'$  and  $A''$  blocks. In addition, there are off-diagonal matrix elements between different  $K$  blocks of the same  $C_s$  symmetry. For our purposes matrix elements off-diagonal in  $C_s$  symmetry or  $K$  will be ignored; they are discussed in detail by Coudert and Hougen (1990).

The eigenvalues resulting from the diagonalization of the Hamiltonian matrix above are (Coudert and Hougen 1988, Odutola *et al.* 1988),

$$\left. \begin{aligned} E(A_1^\pm) &= H_{JK} + H_{12} + H_{13} + H_{14} + 2H_{15} + 2H_{17}, \\ E(B_1^\pm) &= H_{JK} + H_{12} + H_{13} + H_{14} - 2H_{15} - 2H_{17}, \\ E(A_2^\pm) &= H_{JK} + H_{12} - H_{13} - H_{14} + 2H_{15} - 2H_{17}, \\ E(B_2^\pm) &= H_{JK} + H_{12} - H_{13} - H_{14} - 2H_{15} + 2H_{17}, \end{aligned} \right\} \quad (4)$$

with

$$\left. \begin{aligned} E(E^+) &= H_{JK} - H_{12} - H_{13} + H_{14}, \\ E(E^-) &= H_{JK} - H_{12} + H_{13} - H_{14}, \end{aligned} \right\} \quad (5)$$

for the  $A'$  block, and

$$\left. \begin{aligned} E(E^+) &= H_{JK} - H_{12} + H_{13} - H_{14}, \\ E(E^-) &= H_{JK} - H_{12} - H_{13} + H_{14}, \end{aligned} \right\} \quad (6)$$

for the A" block. In the expressions above, the  $E^\pm$  states do not depend on the matrix elements associated with  $1 \rightarrow 5$  or  $1 \rightarrow 7$  tunnelling, whereas the nondegenerate states have contributions from  $2H_{15} = H_{15} + H_{16}$  and  $2H_{17} = H_{17} + H_{18}$ . For the degenerate  $E^\pm$  states  $H_{15}$  and  $H_{16}$ , and  $H_{17}$  and  $H_{18}$ , interfere destructively. The  $1 \rightarrow 5$  and  $1 \rightarrow 7$  tunnelling motions, which lead to an interchange of bonding roles in the complex for the two  $H_2O$  units (see figure 1), are referred to as the geared and antigeared interconversion tunnelling pathways respectively. They qualitatively resemble the geared and antigeared tunnelling pathways in  $(HF)_2$  (Hougen and Ohashi 1985), for which only the geared motion is found to be important for the ground vibrational state tunnelling splittings.

It is fruitful to consider the  $K=0$  energy-level structure expected from the energy levels of equations (4)–(6) above. From the results of Coudert and Hougen (1988, 1990) and of Odutola *et al.* (1988) we find that for  $K=0$ ,  $J$  even,

$$\left. \begin{aligned} E(A_1^+) &= 2h_{4v} + 2h_{5v} + 2h_{7v} + h_{2v} + E_{vJ0}, \\ E(B_1^+) &= 2h_{4v} - 2h_{5v} - 2h_{7v} + h_{2v} + E_{vJ0}, \\ E(E^+) &= 2h_{4v} - h_{2v} + E_{vJ0}, \\ E(A_2^-) &= -2h_{4v} + 2h_{5v} - 2h_{7v} + h_{2v} + E_{vJ0}, \\ E(B_2^-) &= -2h_{4v} - 2h_{5v} + 2h_{7v} + h_{2v} + E_{vJ0}, \\ E(E^-) &= -2h_{4v} - h_{2v} + E_{vJ0}, \end{aligned} \right\} \quad (7)$$

and for  $K=0$ ,  $J$  odd,

$$\left. \begin{aligned} E(A_1^-) &= 2h_{4v} - 2h_{5v} - 2h_{7v} + h_{2v} + E_{vJ0}, \\ E(B_1^-) &= 2h_{4v} + 2h_{5v} + 2h_{7v} + h_{2v} + E_{vJ0}, \\ E(E^-) &= 2h_{4v} - h_{2v} + E_{vJ0}, \\ E(A_2^+) &= -2h_{4v} - 2h_{5v} + 2h_{7v} + h_{2v} + E_{vJ0}, \\ E(B_2^+) &= -2h_{4v} + 2h_{5v} - 2h_{7v} + h_{2v} + E_{vJ0}, \\ E(E^+) &= -2h_{4v} - h_{2v} + E_{vJ0}, \end{aligned} \right\} \quad (8)$$

where  $E_{vJ0} = (B+C)_v J(J+1) - 4D_v [J(J+1)]^2$ . Here we have ordered the  $h_{iv}$  by decreasing magnitude as found in the experimental measurements to be discussed later (i.e.  $|2h_{4v}| > |2h_{5v}| > |2h_{7v}| \approx |h_{2v}|$  with  $h_{3v} = 0$ ). Also,  $(B+C)_v$  and  $D_v$  are the rotational and distortion constants for vibrational state  $v$ . The results of equations (7) and (8) are summarized in the energy-level diagram of figure 2 where we have taken all the  $h_{iv} < 0$  to be consistent with the totally symmetric  $A_1^+$  state being of lowest energy.

Figure 2 shows that the major tunnelling splitting,  $h_{4v}$ , splits each  $J$  level into a set of '–' states and a set of '+' states, separated by  $4|h_{4v}|$ . For convenience we will designate the E states associated with the  $A_1$  and  $B_1$  states as  $E_1$  and the E states associated with the  $A_2$  and  $B_2$  states as  $E_2$ . The interconversion tunnelling matrix elements  $h_{5v}$  and  $h_{7v}$  split the  $A_1$  and  $B_1$  states symmetrically by  $\pm 2|h_{5v} + h_{7v}|$  from their  $E_1$  partner, and similarly split the  $A_2$  and  $B_2$  states symmetrically by  $\pm 2|h_{5v} - h_{7v}|$  from their  $E_2$  partner. The A and B states then become asymmetrically displaced from their E partner by the  $h_{2v}$  tunnelling matrix element. As discussed by Dyke (1977), the  $\Delta J = 1$ ,  $E_2^+ \leftrightarrow E_2^-$  and  $\Delta J = 1$ ,  $E_1^+ \leftrightarrow E_1^-$  transitions follow a rigid-rotor-like pattern, whereas the  $\Delta J = 1$ ,  $A_2^+ \leftrightarrow A_2^-$ ,  $B_2^+ \leftrightarrow B_2^-$ ,  $B_1^+ \leftrightarrow B_1^-$  and  $A_1^+ \leftrightarrow A_1^-$  transitions are displaced from the rigid-rotor E state lines by either  $4|h_{5v} + h_{7v}|$  or  $4|h_{5v} - h_{7v}|$ . To directly determine  $h_{2v}$  requires the observation of  $\Delta K = 1$  transitions.

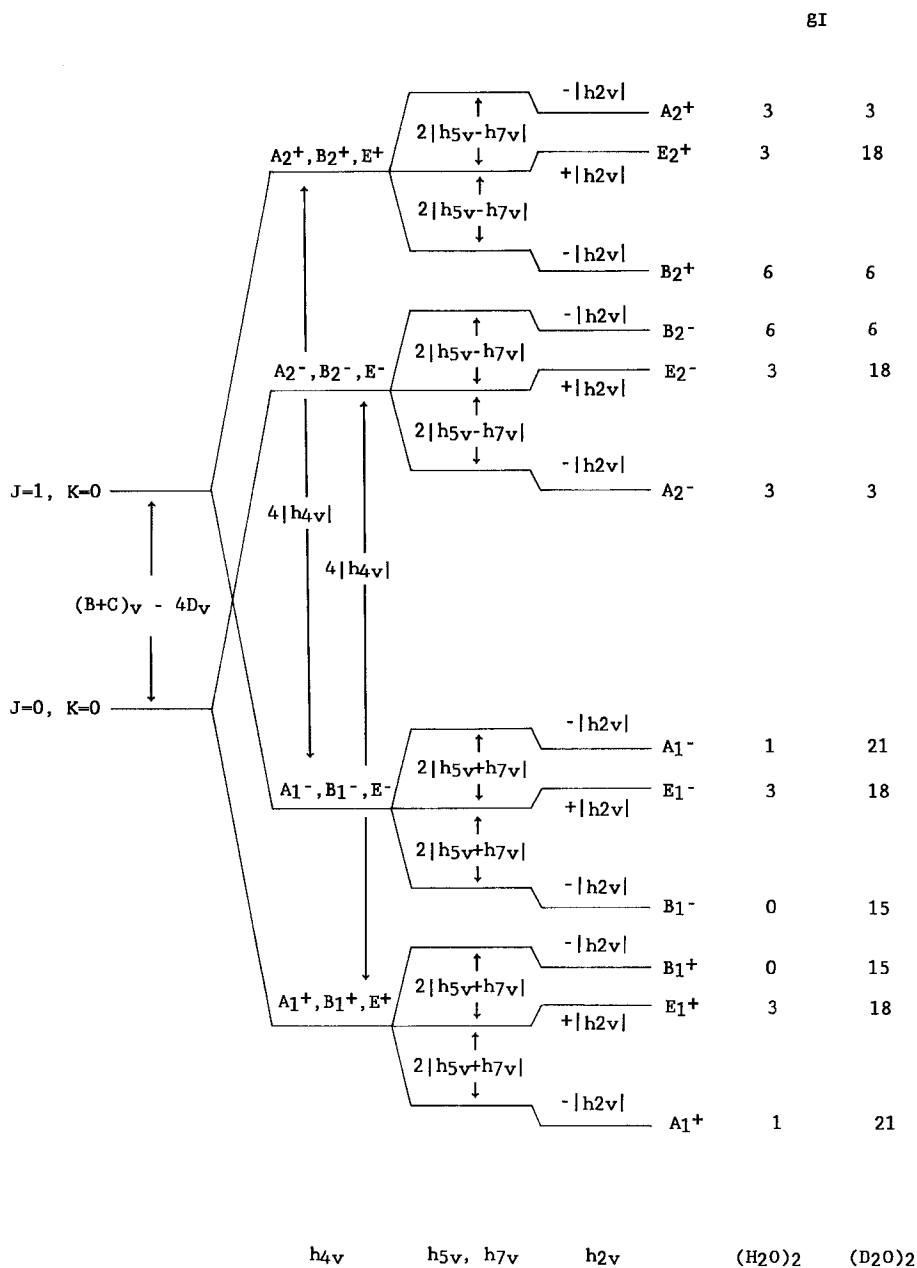


Figure 2. Energy-level diagram showing the effects of the tunnelling matrix elements  $h_{4v}$ ,  $h_{5v}$ ,  $h_{7v}$ , and  $h_{2v}$  on the  $K=0$  rotational levels of the dimer (Coudert and Hougen 1988). Also given are the statistical weights,  $g_I$ , for the protonated and deuterated forms of the dimer.



#### 4. Correlations between monomer and dimer states

As discussed initially by Nelson and co-workers for  $(\text{NH}_3)_2$  and  $(\text{H}_2\text{O})_2$  (Nelson and Klemperer 1987, Nelson *et al.* 1987) and later by Fraser *et al.* (1988) for  $(\text{HCCH})_2$ , insight is gained into the nature of the rovibronic species and energy levels for homogeneous dimers by using the rotational wavefunctions and nuclear-spin functions of the two monomer units as a basis set for the description of the tunnelling-rotational and nuclear-spin states of the dimer. Using these basis sets for  $(\text{H}_2\text{O})_2$  Nelson and Klemperer (1987) obtained the correlation between the monomer and dimer states as shown in table 2. Here we use the conventional asymmetric rotor description for the rotational states of the  $\text{H}_2\text{O}$  units, that is  $K_a + K_c$  is even if the rotational wavefunction of the  $\text{H}_2\text{O}$  unit is symmetric with respect to a  $\pi$  rotation about the  $b$  inertial axis ( $C_2$  symmetry axis) of  $\text{H}_2\text{O}$  and odd if the wavefunction is antisymmetric with respect to this rotation. Qualitatively, interconversion tunnelling (i.e.  $1 \rightarrow 5$ ,  $1 \rightarrow 7$ ) occurs for the A and B states by rotational angular momentum exchange between the two units, driven by the appropriate coupling terms in the intermolecular potential. For the E states this exchange process does not occur since it requires changing a  $K_a + K_c$  even state to a  $K_a + K_c$  odd state. By symmetry, there are no terms in the intermolecular potential which generate these 'selection rules'. In addition, tunnelling for the E states requires a change in nuclear-spin state from  $I_H = 1$  to 0 or *vice versa* for the two  $\text{H}_2\text{O}$  units. This type of event is unlikely since it is driven by spin-spin couplings with matrix elements on the order of 1 kHz or less in magnitude.

Correlation diagrams, such as those shown in table 2, are useful for insight into which states will be populated in a molecular beam experiment where the rotational temperatures can approach 1 K (Fraser *et al.* 1985, Nelson *et al.* 1985a, 1987). For  $\text{H}_2\text{O}$  monomer in a 1 K beam only the lowest energy states associated with the two nuclear spin modifications of  $\text{H}_2\text{O}$  will have substantial population. These are the  $0_{00}$  and  $1_{01}$  rotational states, with resultant proton nuclear spins,  $I_H$ , of 0 and 1 respectively. The  $1_{01}$  state is populated even though it is nearly  $24 \text{ cm}^{-1}$  above the  $0_{00}$  level since it is collisionally ('nuclear-spin') forbidden to relax to the  $0_{00}$  state. With just collisions involving Ar and  $\text{H}_2\text{O}$  units there are no terms in the interaction potentials coupling a  $K_a + K_c$  odd state to a  $K_a + K_c$  even state. Such effects originally seen in molecular beams by Beck *et al.* (1979) for benzene, have now been observed for a number of stable molecules.

In the dimer we expect to populate states correlating to the two different nuclear-spin modifications of  $\text{H}_2\text{O}$ . Thus, even with a substantial energy difference between the  $A_1^\pm/B_1^\pm$  states and  $A_2^\pm/B_2^\pm$  states, we anticipate appreciable population of the higher energy  $A_2^\pm/B_2^\pm$  states. This will not hold if the following exothermic collision process is efficient,

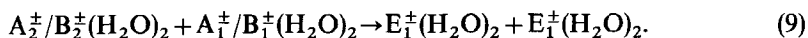
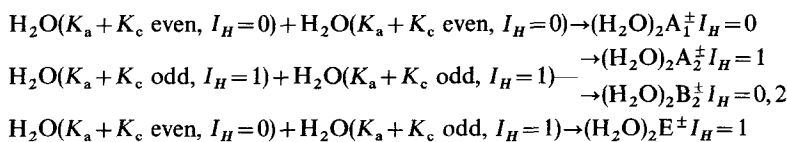
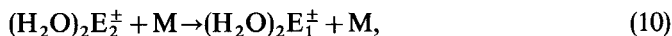


Table 2. Correlation diagram showing the formation of the dimer states from the free-monomer states.  $K_a$  and  $K_c$  are the pseudo-prolate and oblate quantum number labels for  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$  States with  $K_a + K_c$  even are symmetric with respect to a  $\pi$  rotation about the  $C_2$  axis, states with  $K_a + K_c$  odd are antisymmetric.



This relaxation channel corresponds to the exchanging of water units between dimer units. For (H<sub>2</sub>O)<sub>2</sub>, the large population of the A<sub>2</sub><sup>±</sup>/B<sub>2</sub><sup>±</sup> states in 1 K beams (Coudert *et al.* 1987) suggests that this reaction is not important.

The following collision-induced interconversion process does appear to be, though,



since these same 1 K beams give little evidence for the presence of E<sub>2</sub><sup>±</sup> states. Recall that transitions between the E<sub>2</sub><sup>±</sup> and E<sub>1</sub><sup>±</sup> states are not electric-dipole forbidden so that the relaxation channel of equation (10) can be driven by low-order terms in the interaction potential between M and the dimer. Also note in equation (10) that the donor and acceptor water units interchange roles in the complex. Assuming that the *h*<sub>4<sub>u</sub></sub> tunnelling matrix element is the largest, the E<sub>2</sub><sup>±</sup> states corresponds to the I<sub>H</sub> = 1H<sub>2</sub>O unit being the proton acceptor and the I<sub>H</sub> = 0 water unit being the proton donor, and *vice versa* for the E<sub>1</sub><sup>±</sup> states (Nelson and Klemperer 1987, Odutola *et al.* 1988).

### 5. Spectroscopic results

The first microwave spectrum of (H<sub>2</sub>O)<sub>2</sub>, obtained using the molecular beam electric-resonance technique (MBER), was reported in a preliminary communication over 15 years ago by Dyke and Muenter (1974), with a more detailed study (Dyke, *et al.* 1977) published three years later. A complicated and dense spectrum was found, suggesting the presence of hydrogen tunnelling, similar to that observed in (HF)<sub>2</sub> (Dyke *et al.* 1972). A rigid-rotor-like set of J + 1 ↔ J, ΔK = 0 transitions, spaced by about (B + C)(J + 1), where B + C ≅ 12.3 GHz, and a set of ΔJ = 0, ΔK = 0 asymmetry-doublet-type radio-frequency transitions for K = 2 were assigned to the E<sub>2</sub><sup>±</sup> rotational-tunnelling states of the complex, by virtue of their pure rotational selection rules (see figure 2). The rigid-rotor like transitions, together with (D<sub>2</sub>O)<sub>2</sub> data and the μ<sub>a</sub> = 2.6 D dipole moment component from Stark-effect measurements, were interpreted in terms of a hydrogen-bonded structure, similar to that shown in figure 1. The rotational constant, B + C, gives an O...O separation, R<sub>OO</sub>, of 2.98 Å and the centrifugal distortion constant, D, yields a van der Waals stretching frequency, ν<sub>s</sub>, of 150 cm<sup>-1</sup>. For comparison, R<sub>FF</sub> = 2.79 Å and ν<sub>s</sub> ~ 154 cm<sup>-1</sup> for (HF)<sub>2</sub> (Howard *et al.* 1984), and R<sub>NN</sub> = 3.29 Å and ν<sub>s</sub> ~ 106 cm<sup>-1</sup> for (NH<sub>3</sub>)<sub>2</sub> (Nelson *et al.* 1987) with the same approximations. Dyke *et al.* (1977) also observed a number of transitions between 12 and 24 GHz for (H<sub>2</sub>O)<sub>2</sub> which were postulated to be rotational-tunnelling transitions between the A and B states of the complex.

Later, Dyke and co-workers (Dyke 1987, Odutola *et al.* 1988) were able to assign a set of these previously unreported lines to the K = 0, A<sub>2</sub><sup>±</sup> and B<sub>2</sub><sup>±</sup> rotational-tunnelling states with transition frequencies given by approximately (B + C)(J + 1) ± ν<sub>t</sub>. Here ν<sub>t</sub> ~ 19.5 GHz is an interconversion tunnelling frequency similar to that observed in (HF)<sub>2</sub>, where ν<sub>t</sub> ~ 19.7 GHz (Dyke *et al.* 1972). The value found for B + C of 12.2 GHz is nearly identical to that observed for the E<sub>2</sub><sup>±</sup> states. The K assignment for the series was established by the observation of transitions involving J = 0. The assignment of these transitions to the A<sub>1</sub><sup>±</sup>/B<sub>1</sub><sup>±</sup> states was ruled out since the B<sub>2</sub><sup>±</sup> states have zero statistical weight for the totally protonated species, and since high-resolution scans (~ 3 kHz) showed nuclear-spin hyperfine structure, indicating that the resultant proton nuclear spin, I<sub>H</sub>, is non-zero for the observed states. Recall that the A<sub>1</sub><sup>±</sup> states have a statistical weight of unity, corresponding to I<sub>H</sub> = 0. The interconversion tunnelling splitting for the A<sub>2</sub><sup>±</sup>/B<sub>2</sub><sup>±</sup> gives 4|h<sub>5<sub>v</sub></sub> - h<sub>7<sub>v</sub></sub>| = 19.5 GHz, or h<sub>5<sub>v</sub></sub> ~ 4.9 GHz if the geared tunnelling pathway dominates as in (HF)<sub>2</sub>.

Subsequently, Coudert *et al.* (1987), using a pulsed-nozzle Fourier transform microwave spectrometer (Balle and Flygare 1981), reported an additional set of rotational-tunnelling transitions originating within  $K=1$  and giving  $\nu_i=16.2$  GHz, compared to the 19.5 GHz value found by Dyke and co-workers (Dyke 1987, Odutola *et al.* 1988) for  $K=0$ . These results indicate a much weaker  $K$  dependence to the interconversion tunnelling in  $(\text{H}_2\text{O})_2$  than in  $(\text{HF})_2$  (Dyke *et al.* 1972, Howard *et al.* 1984), where  $\nu_i=19.7$  and 31.9 GHz for  $K=0$  and 1 respectively. Again these transitions were assigned to the  $A_2^\pm/B_2^\pm$  states of the dimer since each  $C_s$  rotational state had two tunnelling components associated with it, whereas for the  $A_1^\pm/B_1^\pm$  states the  $B_1^\pm$  component would have zero statistical weight and therefore be missing. The observation that both the  $K=1$  and  $K=0$ ,  $A_2^\pm/B_2^\pm$  states were populated in the 1 K rotational temperature of the molecular beam suggested that the energy separation between these two  $K$  states is small for these symmetry species, on the order of 30 GHz or less.

To aid the interpretation of their microwave Fourier-transform spectrum, Coudert *et al.* (1987) resorted to model calculations (Coudert and Hougen 1988) on the RWK2 (Reimers *et al.* 1982) potential energy surface used by Coker and Watts (1987) in their quantum simulations of the structure and vibrational spectrum of  $(\text{H}_2\text{O})_2$ . The calculations verified the original suggestion of Nelson and Klemperer (1987) that the largest tunnelling-splitting should arise from the interchange of the hydrogens on the proton-acceptor unit (i.e. 1 $\rightarrow$ 4 of figure 1). The modelling also indicated that the most likely tunnelling pathway for 1 $\rightarrow$ 4 consists of a wag of the  $\text{H}_2\text{O}$  acceptor unit through planarity with a concomitant 180° rotation of the other  $\text{H}_2\text{O}$  unit about the  $\text{O}\cdots\text{H}-\text{O}$  bond, leading Coudert and Hougen (1988) to suggest the analogy to internal-rotation-inversion tunnelling in methylamine (Tsuboi *et al.* 1964). The calculated barriers to pure internal rotation of the proton-acceptor and proton-donor  $\text{H}_2\text{O}$  units about their  $C_2$  axes for this potential are substantial, being about 1070 and 2670  $\text{cm}^{-1}$  respectively, with the later barrier being of the order of the well depth of 2060  $\text{cm}^{-1}$  since the hydrogen bond is completely broken and reformed during this tunnelling motion. For this reason, pure internal rotations of the  $\text{H}_2\text{O}$  units about their  $C_2$  axes are not expected to contribute significantly to the 1 $\rightarrow$ 4 or 1 $\rightarrow$ 3 tunnelling processes.

The model calculations suggesting that  $h_{4v}$  is the largest tunnelling matrix element, together with the observation that both  $K=0$  and  $K=1$ ,  $A_2^\pm/B_2^\pm$  states are populated at 1 K, and that the interconversion tunnelling-splittings are 19.5 and 16.2 GHz for the  $K=0$  and 1 states, led Coudert *et al.* (1987) to suggest the energy-level diagram pictured in figure 3 for the dimer. Additionally, since they did not observe  $K=1$ ,  $E^\pm$  states, but just the original  $K=0$ ,  $E^\pm$  series of Dyke *et al.* (1977), Coudert *et al.* (1987) assigned the Dyke *et al.* series to the  $E_1^\pm$  states. In their picture, the  $K=0$  and 1,  $E_2^\pm$  states are collisionally relaxed in the molecular beam to the lower energy  $K=0$ ,  $E_1^\pm$  states.

Further verification of the  $E_1^\pm$  states assignment came from the work of Martinache *et al.* (1988) who employed microwave-microwave double-resonance in a pulsed-nozzle Fourier transform microwave spectrometer to observe the  $K=0$ ,  $J=2-1$   $E_2^\pm$  transition for the first time. Here they used He as a carrier gas instead of the Ar used previously, resulting in a substantially warmer rotational temperature in the molecular-beam expansion so that the higher energy  $E_2^\pm$  states were more populated. In argon they were not able to see either the  $J=1-0$  or  $J=2-1$ ,  $K=0$ ,  $E_2^\pm$  transitions. Whereas the  $J=2-1$  and  $1-0$ ,  $K=0$ ,  $E_1^\pm$  series are almost perfectly harmonically related, with a centrifugal distortion constant  $D=49$  kHz, the  $K=0$ ,  $E_2^\pm$  series requires a large negative  $D=-780$  kHz. As first pointed out by Hu and Dyke (1990), and later

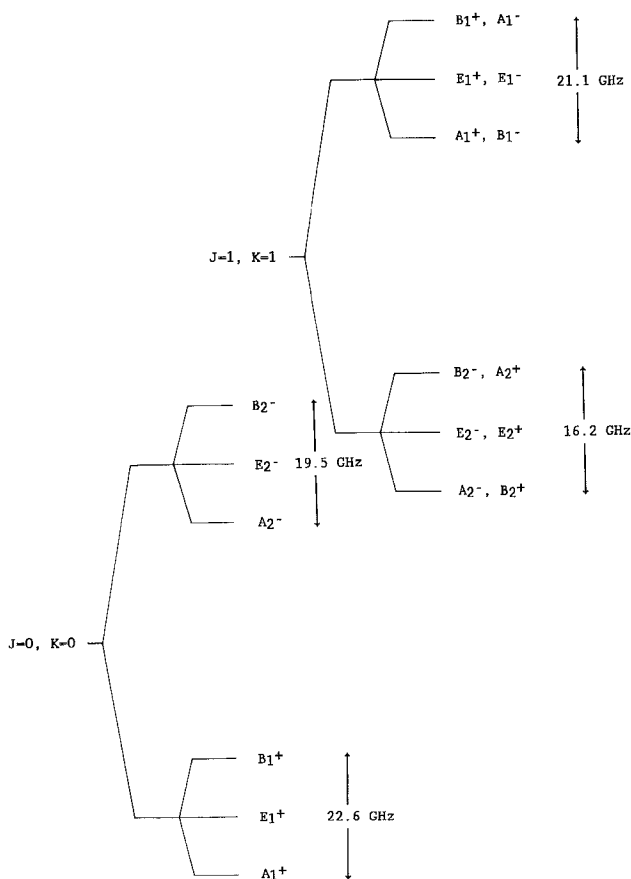


Figure 3. Energy-level diagram initially proposed by Coudert *et al.* (1987) for the  $J=K$  states of  $(H_2O)_2$ . The asymmetry splitting of the  $K=1$  levels is not shown. The  $K=0$  and  $K=1A_2^\pm/B_2^\pm/E_2^\pm$  levels are nearly degenerate, being split by approximately 27 GHz (Fraser *et al.* 1989a, b). The measured interconversion tunnelling-splittings are also given.

verified by Fraser *et al.* (1989a) for the  $A_2^\pm/B_2^\pm$  states, this is the result of a large perpendicular Coriolis interaction between the nearly overlapping  $K=0$  and 1 levels for the  $E_2^\pm$ ,  $A_2^\pm$  and  $B_2^\pm$  species.

Further progress on the energy-level structure for  $(H_2O)_2$  was the result of the far-infrared experiments of Busarow *et al.* (1989) on a perpendicular band of the complex, and the near-infrared spectrum of Huang and Miller (1988, 1989) of the O–H stretches of the dimer. In their far-infrared investigation, Busarow *et al.* (1989) used the direct absorption of tunable far-infrared laser radiation by a continuous slit-shaped molecular beam of  $H_2O$  in Ar to obtain the spectrum of the  $K=2-1$  subband for the  $A_2^\pm$  and  $B_2^\pm$  states of the complex. The results determined the  $K=2-1$  separation to be  $22\text{ cm}^{-1}$  and the interconversion tunnelling splitting for the  $K=2$ ,  $A_2^\pm/B_2^\pm$  states to be 11 GHz. The lack of observation of the  $E_2^\pm$  states is consistent with the results of Coudert *et al.* (1987) and Martinache *et al.* (1988), who showed efficient collisional relaxation of the  $E_2^\pm$  states in an Ar expansion.

Huang and Miller (1988, 1989) obtained high-resolution spectra of the O–H stretching bands of the dimer using optothermal detection (Gough *et al.* 1977) of the absorption of colour-centre laser radiation by a molecular beam of H<sub>2</sub>O in He. Their work was an extension of previous lower resolution molecular-beam experiments by Coker *et al.* (1985) and Lee and co-workers (Vernon *et al.* 1982, Lee and Shen 1980, Page *et al.* 1984). In the Huang and Miller investigation, spectra were recorded for the four O–H stretching bands of the complex, with origins at 3530, 3600, 3730, and 3745 cm<sup>-1</sup>, for the proton-donor bound O–H stretch, the proton-acceptor symmetric stretch, the proton-donor free O–H stretch, and the proton-acceptor asymmetric stretch respectively. For the acceptor asymmetric stretch the vibrational predissociation broadening is minimal, allowing individual rotational lines to be resolved in the P, Q, and R branches, leading to a definitive rotational assignments. The observed nuclear-spin statistical weights and ground-state combination differences identified the transitions as originating from the  $K=0$  and 1,  $A_2^\pm/B_2^\pm/E_2^\pm$  states characterized in the previous microwave investigations. However, the statistical weight results required a flipping of the previous (Coudert *et al.* 1987)  $A_2^\pm$  assignments to  $B_2^\pm$ , and *vice versa*. No transitions were observed from the  $A_1^\pm$  or  $E_1^\pm$  states, possibly due to decreased sensitivity for these states from pre-dissociation broadening. For the proton-acceptor asymmetric stretch the pre-dissociation linewidths were found to vary by more than an order of magnitude between  $K$  and tunnelling states. Similar effects have been seen in the pre-dissociation linewidths of the HF stretches in (HF)<sub>2</sub> (Pine and Fraser 1988).

The infrared measurements also show a dramatic decrease in the interconversion tunnelling splittings in the excited O–H stretches, from  $\sim 19.5$ – $\sim 1.8$  GHz for the proton-acceptor asymmetric stretch. Such large vibrational dependencies in the interconversion tunnelling-splittings are also seen for the hydrogenic stretches in the (HF)<sub>2</sub> (Pine *et al.* 1984), (HCl)<sub>2</sub> (Schuder *et al.* 1989, Ohashi and Pine 1984, Moazzen-Ahmadi *et al.* 1988, Blake *et al.* 1988, Blake and Bumgarner 1989) and (HCCH)<sub>2</sub> (Fraser *et al.* 1988) dimers. For (HF)<sub>2</sub>, it was suggested (Pine *et al.* 1984) that the origin of this large decrease is due to the difficulty of exchanging the vibrational excitation between the two units in order for tunnelling to occur. This has been discussed more formally by Mills (1984) as arising from a breakdown of the Born–Oppenheimer separation of the high-frequency H–F stretches from the low-frequency tunnelling mode. Fraser (1989) has discussed infrared transition dipole coupling as a mechanism for the vibrational exchange, and has presented a method which allows one to calculate this vibrational dependence, and its effect on the tunnelling-state selection rules for the infrared transition. This model gives good results for (HF)<sub>2</sub> and (HCCH)<sub>2</sub>, but has not yet been applied to H<sub>2</sub>O dimer, mainly due to the complicated tunnelling paths involved.

In the above microwave studies no evidence was obtained for the  $A_1^\pm$  states, suggesting that the values of the  $|h_{5v} - h_{7v}|$  and  $|h_{5v} + h_{7v}|$  terms differ appreciably, presumably due to a significant contribution of the anti-gated tunnelling pathway ( $1 \rightarrow 7$ ) to the interconversion tunnelling splittings. A large  $h_{7v}$  matrix element could push the  $A_1^\pm$  microwave transitions outside the spectral windows searched previously. In addition, the assignment of the  $A_1^\pm$  transitions is made difficult because the  $A_1^\pm$  states have the smallest non-zero statistical weight and their  $B_1^\pm$  partner states have zero statistical weight. Fraser *et al.* (1989a), using their newly developed electric-resonance optothermal spectrometer (EROS), which allows broad spectral coverage with high sensitivity in the microwave region, have done extensive searches on the (H<sub>2</sub>O)<sub>2</sub> system in the 14–110 GHz region of the spectrum. These studies enabled them to observe the

$K=0$ ,  $\Delta J = \pm 1$ ,  $A_1^\pm$  series, giving an interconversion tunnelling-splitting of 22.6 GHz for the  $A_1^\pm$  states. From this value it was concluded that the antigeared tunnelling motion contributes approximately  $\pm 1.5$  GHz to the  $K=0$  interconversion tunnelling-splittings with  $h_{5v} \sim -5.26$  GHz and  $h_{7v} \sim -0.38$  GHz. Hu and Dyke (1989) later verified the singlet nature of the resultant proton nuclear spin function of the  $A_1^\pm$  state of Fraser *et al.*, by examining a Stark transition within the  $J=4$ ,  $K=0$  state at high resolution ( $\sim 3$  kHz).

A large contribution of the anti-geared tunnelling pathway to the interconversion tunnelling-splitting in  $(\text{H}_2\text{O})_2$  is surprising, however, since for  $(\text{HF})_2$  only the geared tunnelling pathway appears significant, the anti-geared barrier being much higher because of steric hindrance. For  $(\text{H}_2\text{O})_2$ , one possibility is that the geared tunnelling-splitting is weakly dependent on the degree of 'excitation' of the  $1 \rightarrow 4$  motion. This effect is ignored in the high barrier model, but is not unexpected since it is well known that tunnelling-splittings exhibit a significant dependence on vibrational excitation in other coordinates. For instance, in  $\text{NH}_3$  the inversion splittings are 29.7 and 10.7 GHz for the two N–H stretching vibrations (Angstl *et al.* 1985), compared to the ground state value of 23.8 GHz.

The Fraser *et al.* (1989a) study, discussed above, also led to the observation of the c-type  $K=1-0$  band for the  $A_2^\pm/B_2^\pm$  states, verifying that the energy separation between the  $K=1$  and  $0$ ,  $A_2^\pm/B_2^\pm$  states is indeed small (about 27 GHz), as originally postulated by Coudert *et al.* (1987), and giving an estimate for  $A + 4h_{4v}$  ( $h_{4v} < 0$ ), where  $A$  is a rotational constant. The c-type spectrum is extremely weak, consistent with the observations of Busarow *et al.* who noted that their  $K=2 \leftarrow 1$  far-infrared band was also weak. The  $K=1-0$  Coriolis coupling, originally postulated by Hu and Dyke (1989), was found to be b-type, with an interaction constant of 1.6 GHz, or approximately 25% of the  $B$  rotational constant, indicating a largely unquenched vibrational angular momentum from tunnelling. Hu and Dyke (1989) have similarly analysed the  $E_2^\pm$   $K=1$  and  $0$  data and find a nearly identical interaction constant.

In their initial study, Fraser *et al.* (1989a) were unable to find c-type  $E_2^\pm$  lines due to a combination of the small c-type dipole moment component as well as the lower population of the  $E_2^\pm$  states relative to the  $A_2^\pm/B_2^\pm$  states. With the addition of a microwave amplifier and microwave–microwave double-resonance capabilities these transition were later observed and analysed (Fraser *et al.* 1989b), yielding information about  $h_{2v}$ , the tunnelling matrix element giving the displacement of the  $E_2^\pm$  states from the midpoint of their  $A_2^\pm/B_2^\pm$  partners. The  $h_{2v}$  matrix element was found to be about  $-740$  MHz, indicating that the  $E_2^\pm$  levels are displaced by  $|2h_{2v}| \cong 1.5$  GHz from the centre of their associated  $A_2^\pm/B_2^\pm$  states.

Using their model, Coudert and Hougen (1990) have recently carried out a detailed fit of the  $(\text{H}_2\text{O})_2$  dimer spectrum, including all the microwave and far-infrared data, except for the most recent measurements of Zwart *et al.* (1990). Their analysis determined standard prolate asymmetrical top rotational constants ( $A, B, C$ ), tunnelling matrix elements  $h_{2v}, h_{4v}, h_{5v}, h_{7v}$ , Eulerian angles ( $\phi_i, \theta_i, \chi_i$ ) for the tunnelling pathway  $1 \rightarrow i$ , and centrifugal distortion contributions to the rotational constants, the  $h_{iv}$ , and the Eulerian angles.

The fit of the 173 far-infrared and microwave transitions is almost to within experimental precision, but requires a substantial number of parameters (29) to characterize the data. These include a large  $K^2$ -dependent centrifugal distortion term to  $h_{5v}$  of 1095 MHz, or approximately 10% of  $|h_{5v}|$ , as well as five distortion terms associated with the  $1 \rightarrow 4$  tunnelling. In addition, as commented on by Coudert and

Hougen (1990), the predictions from the model were poor for the later measured far-infrared spectrum of Zwart *et al.* (1990). It may be that the  $(\text{H}_2\text{O})_2$  dimer system is not the most appropriate complex for application of this model since the model assumes a tunnelling barrier near the high barrier limit, where the tunnelling-splittings are a small fraction of the vibrational spacings. Here the  $1 \rightarrow 4$  motion, which leads to splittings on the order of several wavenumbers, may not qualify.

The large  $K$ -dependent centrifugal distortion to the interconversion tunnelling splittings seen in  $(\text{H}_2\text{O})_2$  is also seen in  $(\text{HF})_2$  (Howard *et al.* 1984, Pine *et al.* 1984), and less so in  $(\text{HCCH})_2$  (Fraser *et al.* 1988) and  $(\text{D}_2\text{O})_2$  (Suenram *et al.* 1989). For  $(\text{HF})_2$  (Pine *et al.* 1984, Bunker *et al.* 1989) and  $(\text{HCCH})_2$  (Fraser *et al.* 1988) it has been suggested that this effect arises from centrifugal forces associated with rotation about the  $a$ -inertial axis increasing or decreasing the barrier to interconversion tunnelling. Stated differently, it is the result of the coupling of the  $A$  rotational and the tunnelling potential through their mutual dependence on the tunnelling coordinate. The  $A$  rotational constant is most strongly coupled to the tunnelling coordinate in these systems since its value changes dramatically with tunnelling coordinate, whereas the  $B+C$  rotational constant has an inherent inertial stability resulting from the large centre-of-mass separation between the two binding partners. The  $K$ -dependence is not well characterized by adding centrifugal distortion terms to the tunnelling-splitting or to the  $A$  rotational constant. The  $K$ -dependence in  $(\text{H}_2\text{O})_2$  could also have this origin, and it would be interesting to consider this possibility in the tunnelling formalism. It should also be noted that  $B-C$  is likewise strongly coupled to the tunnelling coordinate and this may, in part, be the basis for the flipping of the effective sign of the asymmetry splitting (Zwart *et al.* 1990) between the  $K=1$   $E_1^\pm$  and  $E_2^\pm$  states.

Guided by the theoretical analysis of Coudert and Hougen (1990) summarized above, Zwart *et al.* (1990) were able to observe the far-infrared spectrum of the  $K=1-0$ ,  $A_1^\pm/E_1^\pm$  band, the origin ( $14.3 \text{ cm}^{-1}$ ) of which specifies  $\sim A - 4h_{4v}$  (recall  $h_{4v} < 0$ ). Their results also force a reassignment of the  $+/-$  labels on the previously characterized  $K=1$ ,  $E_1^\pm$  states. In addition, they determine the interconversion tunnelling splitting for the  $K=1$ ,  $A_1^\pm$  states to be  $21.1 \text{ GHz}$ . Their band origin, together with  $K=1-0$  and  $K=2-1$ ,  $A_2^\pm/B_2^\pm/E_2^\pm$  origins of Fraser *et al.* (1989) and Busarow *et al.* (1989) will allow a more precise determination of  $A$  and  $h_{4v}$  to be made.

## 6. $(\text{D}_2\text{O})_2$

For  $(\text{D}_2\text{O})_2$  the tunnelling-splittings are substantially reduced, suggesting that the formalism of Coudert and Hougen may be more appropriate. Unfortunately, there is much less data available for this system to properly test the model. The initial MBER work of Odutola *et al.* identified an  $a$ -type  $K=0$  series for an  $A$ ,  $B$  and  $E$  state of the dimer, and these same series were further characterized by Coudert *et al.* using pulsed-nozzle Fourier-transform microwave spectroscopy. Later, Suenram *et al.* using a combination of EROS and Fourier transform microwave spectroscopy found another  $K=0$ ,  $A/B$  series as well as two sets of  $K=1$   $A/B$  series. From relative intensity measurements in the EROS and Fourier transform experiments, the assignments to the  $A_1^\pm/B_1^\pm/E_1^\pm$  and  $A_2^\pm/B_2^\pm/E_2^\pm$  states were made. For the  $(\text{D}_2\text{O})_2$  the statistical weights are 21, 3, 15, 6, 18 for the  $A_1^\pm$ ,  $A_2^\pm$ ,  $B_1^\pm$ ,  $B_2^\pm$ , and  $E^\pm$  rovibronic species. Note in particular that the  $B_1^\pm$  states no longer have a zero weight. Also the statistical weights for the  $A_2^\pm/B_2^\pm$  species are the same for the protonated and deuterated species since in both cases these states correlate to monomer states with resultant proton/deuteron nuclear spins of one (i.e.  $I_H=1$  and  $I_D=1$ ).

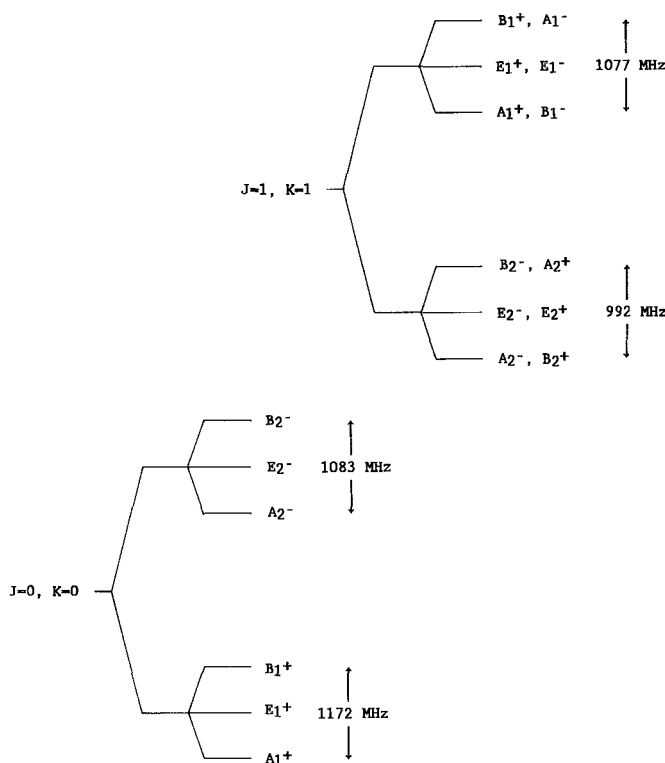


Figure 4. Energy-level diagram for the  $J = K$  states of  $(D_2O)_2$  (Suenram *et al.* 1989) showing the measured interconversion tunnelling-splittings.

The tunnelling-splittings determined for the observed  $(D_2O)_2$  states are summarized in the energy level diagram of figure 4. As seen in the figure, the interconversion tunnelling-splittings are about a factor of 20 less than those found in the protonated species. At present no data exist for perpendicular bands of the complex which would allow a determination of the  $A$  rotational constant and the  $h_{4v}$  and  $h_{2v}$  tunnelling matrix elements.

There have also been isotopic studies on a number of partially deuterated dimers, but these studies (Odutola and Dyke 1980, Coudert *et al.* 1987) are still incomplete and will not be reviewed here. It should be noted that these species are classified using subgroups of the  $G_{16}$  molecular symmetry group used for the totally protonated or deuterated forms.

### 7. Discussion

The spectroscopy of  $(H_2O)_2$  is presently well characterized for the ground vibrational state. A phenomenological Hamiltonian has been proposed and shown to fit the microwave and far-infrared data to near experimental uncertainty. The next steps toward characterizing the  $H_2O-H_2O$  interaction include the observation and analysis of the excited van der Waals vibrational states and the development of theoretical models to use the experimentally determined spectroscopic constants ( $A, B, C, h_{iv}, (\phi_i, \theta_i, \chi_i)$ , and so on) to obtain information about the potential energy surface.



These constants together with vibrational data should allow the determination of tunnelling barriers and pathways, harmonic and anharmonic force constants, and the equilibrium geometry of the complex, which can be used to test or refine existing  $(\text{H}_2\text{O})_2$  potentials. For the related  $(\text{HF})_2$  a large effort is presently underway in this direction with a number of *ab initio* or empirical potentials proposed (see the review by Truhlar (1990)), and with methods being developed to calculate rotation-vibration-tunnelling spectra from these potentials to compare with experiment (Bunker *et al.* 1989, Barton and Howard 1982).

For  $(\text{H}_2\text{O})_2$  the problem is compounded due to the additional degrees of freedom which must be included. This together with the relatively large anisotropy of the interaction makes a free-rotor treatment of the bending functions of the complex undesirable. In a free-rotor basis a large number of angular functions are required to both localize the vibration near equilibrium, as well as to give it sufficient leakage into the classical forbidden regions to allow tunnelling. Perhaps procedures based on collocation (Peet and Yang 1989) or discrete variable representation (Choi and Light 1990) methods will be more appropriate in handling this calculation problem.

In addition to  $(\text{H}_2\text{O})_2$ , there are a number of other complexes which display interconversion tunnelling-splittings. These include the homogenous dimers of  $\text{SO}_2$  (Nelson *et al.* 1985b),  $\text{HCl}$  (Schuder *et al.* 1989, Ohashi and Pine 1984, Moazzen-Ahmadi *et al.* 1988, Blake *et al.* 1988, Blake and Bumgarner 1989),  $\text{HF}$  (Dyke *et al.* 1972),  $\text{HCCH}$  (Fraser *et al.* 1988),  $\text{H}_2\text{CO}$  (Lovas *et al.* 1990), and  $\text{NH}_3$  (Nelson and Klemperer 1987, Havenith *et al.* 1990), with tunnelling-splittings ranging from 65 kHz for  $(\text{SO}_2)_2$  to  $15\text{ cm}^{-1}$  for  $(\text{HCl})_2$ . For  $(\text{HCCH})_2$ ,  $(\text{H}_2\text{CO})_2$ ,  $(\text{SO}_2)_2$  and  $(\text{NH}_3)_2$  multiple minima and tunnelling pathways are involved. Like  $(\text{H}_2\text{O})_2$ , the rotational-tunnelling states of  $(\text{SO}_2)_2$ ,  $(\text{HCCH})_2$ , and  $(\text{H}_2\text{CO})_2$  are all classified in  $G_{16}$ , whereas  $(\text{NH}_3)_2$  is classified in  $G_{36}$  (Nelson and Klemperer 1987). For  $(\text{SO}_2)_2$ , which consists totally of spin-zero nuclei, only the  $A_1^\pm$  species are allowed, giving rise to an extremely sparse spectrum for such a non-rigid molecule. At present, only the spectroscopy of the dimers of  $\text{HF}$ ,  $\text{HCl}$  and  $\text{HCCH}$  are well understood, although it is anticipated that the present success on  $(\text{H}_2\text{O})_2$  will motivate a more complete understanding of tunnelling in these systems, as well as in other complexes displaying multiple minima. For  $(\text{NH}_3)_2$  this is particularly important due to the disagreement between the theoretical predictions and the experimental geometry (Nelson *et al.* 1987) proposed for this system.

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### References

- ANGSTL, T., FINSTERHÖZL, H., FRUNDER, H., ILLIG, D., PAPOUŠEK, D., PRANCNA, P., RAO, K. N., SCHRÖTTER, H. W., and URBAN, Š., 1985, *J. molec. Spectrosc.*, **114**, 454.  
 BALLE, T. J., and FLYGARE, W. H., 1981, *Rev. Scient. Instrum.*, **52**, 33.  
 BARTON, A. E., and HOWARD, B. J., 1982, *Faraday Discuss. Chem. Soc.*, **73**, 45.  
 BECK, S. M., LIVERMAN, M. G., MONTS, D. L., and SMALLEY, R. E., 1979, *J. chem. Phys.*, **70**, 232.  
 BLAKE, G. A., BUSAROW, K. L., COHEN, R. C., LAUGHLIN, K. B., LEE, Y. T., and SAYKALLY, R. J., 1988, *J. chem. Phys.*, **89**, 6577.  
 BLAKE, G. A., and BUMGARNER, R. E., 1989, *J. chem. Phys.*, **91**, 4418.

- BUNKER, P. R., CARRINGTON, JR., T., GOMEZ, P. C., MARSHALL, M. D., KOFRANEK, M., LISCHKA, H., and KARPEN, A., 1989, *J. chem. Phys.*, **91**, 5154.
- BUSAROW, K. L., COHEN, R. C., BLAKE, G. A., LAUGHLIN, K. B., LEE, Y. T., and SAYKALLY, R. J., 1989, *J. chem. Phys.*, **90**, 3937.
- CHOI, S. E., and LIGHT, J. C., 1990, *J. chem. Phys.*, **92**, 2129.
- COKER, D. F., MILLER, R. E., and WATTS, R. O., 1985, *J. chem. Phys.*, **82**, 3554.
- COKER, D. F., and WATTS, R. O., 1987, *J. phys. Chem.*, **91**, 2513.
- COUDERT, L. H., LOVAS, F. J., SUENRAM, R. D., and HOUGEN, J. T., 1987, *J. chem. Phys.*, **87**, 6290.
- COUDERT, L. H., and HOUGEN, J. T., 1988, *J. molec. Spectrosc.*, **130**, 86.
- COUDERT, L. H., and HOUGEN, J. T., 1990, *J. molec. Spectrosc.*, **139**, 259.
- DYKE, D. R., HOWARD, B. J., and KLEMPERER, W., 1972, *J. chem. Phys.*, **56**, 2442.
- DYKE, D. R., and MUENTER, J. S., 1974, *J. chem. Phys.*, **60**, 2929.
- DYKE, D. R., 1977, *J. chem. Phys.*, **66**, 492.
- DYKE, D. R., MACK, K. M., and MUENTER, J. S., 1977, *J. chem. Phys.*, **66**, 498.
- DYKE, D. R., 1987, *Structure and Dynamics of Weakly Bound Molecular Complexes*, edited by A. Weber (Boston: Reidel), pp. 43–56.
- FRASER, G. T., NELSON, D. D., JR., GERFEN, G. J., and KLEMPERER, W., 1985, *J. chem. Phys.*, **83**, 5442.
- FRASER, G. T., SUENRAM, R. D., LOVAS, F. J., PINE, A. S., HOUGEN, J. T., LAFFERTY, W. J., and MUENTER, J. S., 1988, *J. chem. Phys.*, **89**, 6028.
- FRASER, G. T., 1989, *J. chem. Phys.*, **90**, 2097.
- FRASER, G. T., SUENRAM, R. D., and COUDERT, L. H., 1989a, *J. chem. Phys.*, **90**, 6077.
- FRASER, G. T., SUENRAM, R. D., COUDERT, L. H., and FRYE, R. S., 1989b, *J. molec. Spectrosc.*, **130**, 244.
- GOUGH, T. E., MILLER, R. E., and SCOLES, G., 1977, *Appl. Phys. Lett.*, **30**, 338.
- HAVENITH, M., GWO, D.-H., COHEN, R. C., BUSAROW, K. L., LEE, Y. T., and SAYKALLY, R. J., 1990, *J. chem. Phys.* (in preparation).
- HOUGEN, J. T., 1985, *J. molec. Spectrosc.*, **114**, 395.
- HOUGEN, J. T., and OHASHI, N., 1985, *J. molec. Spectrosc.*, **109**, 134.
- HOUGEN, J. T., 1987, *Structure and Dynamics of Weakly Bound Molecular Complexes*, edited by A. Weber (Boston: Reidel), pp. 191–199.
- HOWARD, B. J., DYKE, T. R., and KLEMPERER, W., 1984, *J. chem. Phys.*, **81**, 5417.
- HU, T. A., and DYKE, T. R., 1990, *J. chem. Phys.*, **91**, 7348.
- HUANG, Z. S., and MILLER, R. E., 1988, *J. chem. Phys.*, **88**, 8008.
- HUANG, Z. S., and MILLER, R. E., 1989, *J. chem. Phys.*, **91**, 6613.
- LEE, Y. T., and SHEN, Y. R., 1980, *Phys. Today*, **33**, 52.
- LOVAS, F. J., SUENRAM, R. D., COUDERT, L. H., BLAKE, T. A., GRANT, K. J., and NOVICK, S. E., 1990, *J. chem. Phys.*, **92**, 891.
- LONGUET-HIGGINS, H. C., 1963, *Molec. Phys.*, **6**, 445.
- MARTINACHE, L., JANS-BURLI, S., VOGELSANGER, B., and BAUDER, A., 1988, *Chem. Phys. Lett.*, **149**, 424.
- MILLS, I. M., 1984, *J. phys. Chem.*, **88**, 532.
- MOAZZEN-AHMADI, N., MCKELLAR, A. R. W., and JOHNS, J. W. C., 1988, *Chem. Phys. Lett.*, **151**, 318.
- NELSON, D. D., JR., FRASER, G. T., and KLEMPERER, W., 1985a, *J. chem. Phys.*, **83**, 6201.
- NELSON, D. D., JR., FRASER, G. T., and KLEMPERER, W., 1985b, *J. chem. Phys.*, **83**, 945.
- NELSON, D. D., JR., KLEMPERER, W., FRASER, G. T., LOVAS, F. J., and SUENRAM, R. D., 1987, *J. chem. Phys.*, **87**, 6364.
- NELSON, D. D., JR., and KLEMPERER, W., 1987, *J. chem. Phys.*, **87**, 139.
- ODUTOLA, J. A., and DYKE, T. R., 1980, *J. chem. Phys.*, **72**, 5062.
- ODUTOLA, J. A., HU, T. A., PRINSLOW, D., O'DELL, S. E., and DYKE, T. R., 1988, *J. chem. Phys.*, **88**, 5352.
- OHASHI, N., and PINE, A. S., 1984, *J. chem. Phys.*, **81**, 73.
- PAGE, R. H., FREY, J. G., SHEN, Y. R., and LEE, Y. T., 1984, *Chem. Phys. Lett.*, **106**, 373.
- PEET, A. C., and YANG, W., 1989, *J. chem. Phys.*, **91**, 6598.
- PINE, A. S., LAFFERTY, W. J., and HOWARD, B. J., 1984, *J. chem. Phys.*, **81**, 2939.
- PINE, A. S., and FRASER, G. T., 1988, *J. chem. Phys.*, **89**, 6636.
- REIMERS, J. R., WATTS, R. O., and KLEIN, M. L., *Chem. Phys.*, **64**, 95.
- SCHUDER, M. D., LOVEJOY, C. M., NELSON, D. D., JR., and NESBITT, D. J., 1989, *J. chem. Phys.*, **91**, 4418.

- SUENRAM, R. D., FRASER, G. T., and LOVAS, F. J., *J. molec. Spectrosc.*, **138**, 440.
- TRUHLAR, D. G., 1990, *Dynamics of Polyatomic van der Waals Clusters*, edited by K. C. Janda and N. Halberstadt (NATO ASI).
- TSUBOI, M., HIRAKAWA, A. Y., INO, T., SASAKI, T., and TAMAGAKE, K., 1964, *J. chem. Phys.*, **41**, 2721.
- VERNON, M. F., KRAJNOVICH, D. J., KWOK, H. S., LISY, J. M., SHEN, Y. R., and LEE, Y. T., 1982, *J. chem. Phys.*, **77**, 47.
- ZWART, E., TER MEULEN, J. J., and MEERTS, W. L., 1990, *Chem. Phys. Lett.*, **166**, 500.