

## Dynamics of Structural Rearrangements in the Water Trimer

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**Abstract:** The internal dynamics of the hydrogen bonding network of the water trimer are investigated by tunable far-infrared laser spectroscopy. New intermolecular vibrations have been measured at 87.1 [(H<sub>2</sub>O)<sub>3</sub>] and 98.1 cm<sup>-1</sup> [(D<sub>2</sub>O)<sub>3</sub>]. Symmetry restrictions produce an exact oblate symmetric rotor pattern in the spectrum, even though theory predicts the trimer structure to be an asymmetric near-planar ring. In addition, each rovibrational transition is split into a quartet. A group theoretical treatment identifies two classes of structural rearrangements to account for these effects.

There is considerable current interest in the spectroscopy and dynamics of small water clusters. Experimental and theoretical investigations of these species are motivated by the quest for a detailed understanding of the intermolecular forces and dynamics of the hydrogen bonding networks that operate in the condensed phases of water and in many biological systems.<sup>1</sup> Numerous spectroscopic,<sup>2</sup> *ab initio*,<sup>3</sup> and empirical studies<sup>4</sup> have addressed the intermolecular dynamics and potential energy surface of the water dimer. A similarly detailed characterization of the water trimer will enable a quantitative comparison with the dimer that could contribute significantly to the understanding of macroscopic systems. For instance, comparison of the water dimer and trimer *ab initio* intermolecular potential energy surfaces (IPS) predicts that non-pairwise additive forces ("three-body" interactions that can occur in the trimer but not the dimer) contribute 10% of the total binding energy of the trimer. Other predicted "three-body" effects are shorter O–O distances and higher average intermolecular vibrational frequencies in the trimer than in the dimer. Similarities in internal dynamics of the dimer and trimer can suggest mechanisms for important processes, such as proton transfer, that occur in the condensed phases of water. Tunable far-infrared laser vibration–rotation–tunneling spectroscopy (FIRVRTS) has emerged as a powerful new tool for addressing such subjects.<sup>1</sup>

Pugliano and Saykally<sup>5</sup> (P&S) recently reported the first detailed experimental study of the cyclic water trimer. In that work, an intermolecular vibration of (D<sub>2</sub>O)<sub>3</sub> was measured near 89.6 cm<sup>-1</sup>. This band displayed a strongly perturbed near-symmetric top rotational pattern with each rovibrational transition split into a quartet. Crude estimates of the O–O distances were made by assuming three point masses of 20 amu and adjusting their separations for optimal agreement with the reported rotational constants. The spectral splittings were interpreted as resulting from isomerization tunneling among 96 identical frameworks (48 pairs of enantiomers) via three pathways: (1) "flipping"

of a single free hydrogen from one side of the ring to the other; (2) a motion that effectively results in a C<sub>2</sub> rotation of a single monomer about its symmetry axis; and (3) a concerted motion that reverses the sense ("clockwise" or "counterclockwise" [cw–ccw], i.e., O<sub>A</sub>–H···O<sub>B</sub>–H···O<sub>C</sub>–H···O<sub>A</sub> or O<sub>A</sub>···H···O<sub>C</sub>–H···O<sub>B</sub>–H···O<sub>A</sub>) of the hydrogen bonding network around the ring.

That work precipitated a number of sophisticated theoretical calculations of the trimer structure, vibrational frequencies, and interconversion tunneling dynamics.<sup>6–11</sup> Of these, the calculations by Fowler and Schaefer<sup>6</sup> are done at the highest level. All high-level *ab initio* calculations agree that the lowest energy structure is that shown in Figure 1, and that the flipping motion is nearly free; moreover, all disagree with the crudely estimated O–O distances. Wales<sup>10</sup> elegant treatment of the tunneling dynamics identified three low-energy reaction paths on the twelve-dimensional IPS and estimated and associated splittings within a high barrier approximation. Schütz *et al.*<sup>11</sup> carried out a detailed treatment of just the three flipping coordinates, giving special attention to the implications of the very low barrier to flipping. The highest-level *ab initio* calculations performed to date are those of Fowler and Schaefer.<sup>6</sup>

In this paper, we report the measurement of two new intermolecular vibrations of FIRVRTS. The Berkeley tunable far infrared spectrometer systems employed in this work have been described in detail elsewhere.<sup>13</sup> A total of 284 VRT transitions rotationally assigned to a c-type band of (H<sub>2</sub>O)<sub>3</sub> and 57 transitions assigned to an a-type band of (D<sub>2</sub>O)<sub>3</sub> were measured. The transitions of each isotopomer were fit to a symmetric top hamiltonian and the determined molecular constants are listed in Table 1. Portions of the (H<sub>2</sub>O)<sub>3</sub> and (D<sub>2</sub>O)<sub>3</sub> data are displayed in Figure 2.

(6) Fowler, J.; Schaefer, H. F., III *J. Am. Chem. Soc.*, submitted for publication.

(7) Xantheas, S. S.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 8774.

(8) van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *Chem. Phys.*, submitted for publication.

(9) M6, O.; Yáñez, M.; Elguero, J. *J. Chem. Phys.* **1992**, *97*, 6628.

(10) Wales, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 11180.

(11) Schütz, M.; Bürgi, T.; Leutwyler, S.; Bürgi, H. B. *J. Chem. Phys.* **1993**, *99*, 5228.

(12) Owicki, J. C.; Shipman, L. L.; Scheraga, H. A. *J. Phys. Chem.* **1975**, *79*, 1794.

(13) Blake, G. A.; Laughlin, K. B.; Cohen, R. C.; Busarow, K. L.; Gwo, D.-H.; Schmittenmaer, C. A.; Steyert, D. W.; Saykally, R. *J. Rev. Sci. Instrum.* **1991**, *62*, 1701.

(14) Bunker, P. R. *Molecular Symmetry and Spectroscopy*; Academic Press: San Diego, 1979.

(15) Coudert, L. H.; Hougen, J. T. *J. Mol. Spectrosc.* **1988**, *130*, 86.

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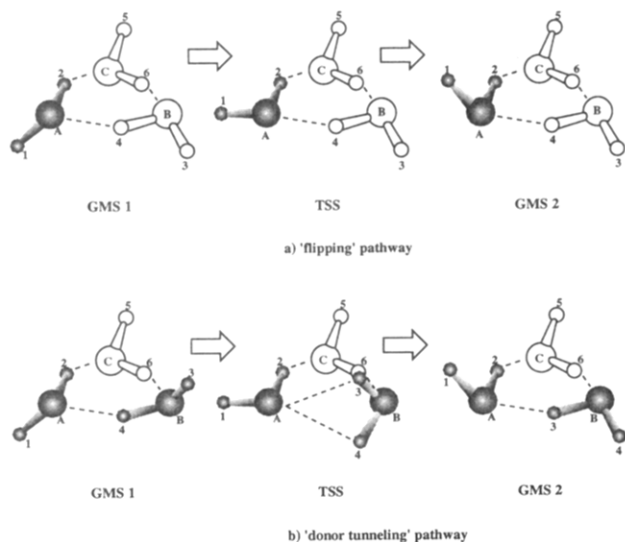
(1) Saykally, R. J.; Blake, G. A. *Science* **1993**, *259*, 1570 and references therein.

(2) Fraser, G. T. *Int. Rev. Phys. Chem.* **1991**, *10*, 189 and references therein.

(3) Smith, B. J.; Swanton, D. J.; Pople, J. A.; Schaefer, H. F., III; Radom, L. *J. Chem. Phys.* **1990**, *92*, 1240. Niesor, U.; Corongin, G.; Clementi, E.; Kneller, G.; Bhattacharaya, D. *J. Phys. Chem.* **1990**, *94*, 7949.

(4) Reimers, J. R.; Watts, R. O.; Klein, M. L. *Chem. Phys.* **1982**, *64*, 95 and references therein. Cieplak, P.; Kollman, P.; Lybrand, T. *J. Chem. Phys.* **1990**, *92*, 6755. Jorgensen, W. L.; Chandrasekhar, J.; Madura, J.; Impey, R.; Klein, M. *J. Chem. Phys.* **1983**, *79*, 926. Townsend, M.; Morse, M.; Rice, S. A. *J. Chem. Phys.* **1983**, *79*, 2496.

(5) Pugliano, N.; Saykally, R. J. *Science* **1992**, *257*, 1937.



**Figure 1.** (a) The structure and proposed flipping pathway for the water trimer. The theoretically predicted equilibrium geometry of the water trimer is a hydrogen-bonded ring in which each water acts as a donor and as an acceptor. Two of the free hydrogens lie above the ring and one below. Flipping, a large-amplitude motion that is mathematically described by the PI operation  $F$ , is accomplished by rotating one water monomer (shaded) about its donated hydrogen bond. This pathway connects a given global minimum structure (GMS 1) to an enantiomeric form (GMS 2). The transition-state structure (TSS) corresponds to two free hydrogens on opposite sides of the ring and the third, in the process flipping, approximately in the plane of the ring. In the early work of Owicki *et al.*<sup>12</sup> this energy barrier was estimated to be very low:  $-0.04$  kcal mol<sup>-1</sup> for (H<sub>2</sub>O)<sub>3</sub> and  $0.12$  kcal mol<sup>-1</sup> for (D<sub>2</sub>O)<sub>3</sub> after the zero-point correction. (b) The proposed "donor tunneling" pathway.<sup>10</sup> This is a mechanism for one of the possible rearrangements that exchange the hydrogen bonded and the free hydrogens on one water monomer, any of which could give rise to the observed quartet splittings in the spectra. Considering only the monomer pair highlighted in the diagram, donor tunneling in the water trimer is analogous to donor tunneling in the water dimer.<sup>15</sup> In the trimer, donor tunneling involves two water units having their free hydrogens on opposite sides of the ring. The free donor hydrogen moves into the bonded hydrogen and the latter moves to the other side of the ring. This exchange is accompanied by flipping of the free acceptor hydrogen. The TSS corresponds to the acceptor molecule in the plane of the ring and the donor molecule perpendicular to and bisected by that plane.

It is clear from the high quality of the new rotational fits that the (H<sub>2</sub>O)<sub>3</sub> and (D<sub>2</sub>O)<sub>3</sub> vibrational states accessed by these new bands are unperturbed. In contrast, the (D<sub>2</sub>O)<sub>3</sub> vibrational states accessed in the band previously discovered by P&S were both highly perturbed so that the rotational constants reported by them are likely to have little physical meaning.

It is tempting to try to extract structural information from the well-determined rotational constants for the two isotopomers studied in this work. As was also inferred by P&S, the oblate top rotational pattern of the VRT spectra confirms that the trimer is a ring, rather than a chain. The large, negative inertial defect ( $I_c - I_b - I_a > 0$ ;  $I_b \sim 1/B$ ), evident in the (D<sub>2</sub>O)<sub>3</sub> rotational constants, suggests that the ring structure is not rigidly planar; either the equilibrium structure is planar and some of the hydrogens make large amplitude excursions above or below the ring, or the equilibrium structure is actually nonplanar. However, for the reasons discussed below, further structural interpretations are likely to be misleading, and we must discount even the crude estimate of the O—O distances made previously by P&S. As in the cases of the more weakly bound van der Waals complexes

**Table 1.** The Molecular Constants of (H<sub>2</sub>O)<sub>3</sub> and (D<sub>2</sub>O)<sub>3</sub> in MHz<sup>a</sup>

		(H <sub>2</sub> O) <sub>3</sub> (c-type)	(D <sub>2</sub> O) <sub>3</sub> (a-type)
ground state	$A'' = B''$	6646.94(2)	5796.19(17)
	$C''$		3088.46(15)
	$D_J''$	0.0414(1)	0.0257(29)
	$D_{JK}''$	-0.0619(6)	-0.0281(27)
excited state	$A' = B'$	6626.16(2)	5786.19(17)
	$C'$		3089.69(16)
	$C' - C''$	0.82(1)	
	$D_J'$	0.0400(2)	0.0243(29)
	$D_{JK}'$	-0.0604(6)	-0.0236(33)
band origin	$\nu_0$	2609774.63(20)	2940935.80(61)
quartet splitting	$\Delta\nu$	289.4(11)	5

<sup>a</sup> A total of 284 VRT transitions were rotationally assigned to a c-type band of (H<sub>2</sub>O)<sub>3</sub> and 57 transitions were assigned to an a-type band of (D<sub>2</sub>O)<sub>3</sub>. The rotational assignment of these regularly spaced transitions was unambiguous. The transitions of each isotopomer were fit to a symmetric top hamiltonian including only the vibrational frequency, rotational constants ( $[A + B]/2$  and  $C$ ) and small (quartic) centrifugal distortion terms ( $D_J$  and  $D_{JK}$ ). The standard deviations in the last digits are listed in parentheses. The residuals of these fits were less than the instrumental resolution of 2 MHz. For (H<sub>2</sub>O)<sub>3</sub>, all four quartet components were fit individually. Only slight differences were found in their rotational constants, which are listed here for only one component. For (D<sub>2</sub>O)<sub>3</sub>, only the most intense component was included in the fit. Note that for the c-type band (the direction of dipole moment change upon vibrational excitation is along the c principal inertial axis) observed for (H<sub>2</sub>O)<sub>3</sub> as well as the (D<sub>2</sub>O)<sub>3</sub> band observed by P&S, only the difference between  $C''$  and  $C'$  can be determined, while for the new (D<sub>2</sub>O)<sub>3</sub> a-type band, these constants can be determined independently for each vibrational state.

studied by FIRVRTS,<sup>1</sup> an experimental determination of the water trimer structure will require a rather complete characterization of the associated IPS. Since all theoretical studies of the trimer agree that the equilibrium structure<sup>6-12</sup> is that shown in Figure 1, we shall assume that structure in the analysis below.

Two immediately obvious features of the water trimer spectra are (1) the rotational constants determined from the new spectra correspond to exact oblate symmetric rotors, even though the theoretically predicted equilibrium trimer structure is asymmetric and (2) each rovibrational transition is split into a quartet. These observations can be explained through the use of permutation inversion (PI) group theory to explore the full dynamical symmetry of the water trimer.

The trimer structure shown in Figure 1 has no symmetry, and therefore is described by the point group  $C_1$ , which contains only the identity operation ( $E$ ). This is the smallest possible molecular symmetry group for the trimer. But, as previously explained by P&S, there are actually 96 structurally equivalent (but differently labeled) global maxima on the 12-dimensional IPS. Therefore, the largest possible molecular symmetry group appropriate for the analysis of water trimer VRT spectra contains 96 permutation-inversion operations. These symmetry operations describe permutations of identical nuclei that are not necessarily located in chemically equivalent positions. The PI group that is actually appropriate for the present analysis will contain only feasible operations and products of feasible operations. By definition, if a feasible PI operation is applied to one labeled structure to obtain a second labeled structure, there exists a low-energy pathway on the IPS that connects the two global minima corresponding to the two labeled structures. The energy barrier (usually the relative energy at a first-order saddle point) in this pathway must be low enough that the associated splitting of the rovibrational energy levels can be resolved by our instrument. These quantum mechanical splittings occur when the vibrational wave functions tunnel through the barriers on the IPS and thereby sample more than one of the 96 equivalent minima at once. The number of minima connected by tunneling is equal to the number of operations in the appropriate molecular symmetry group.

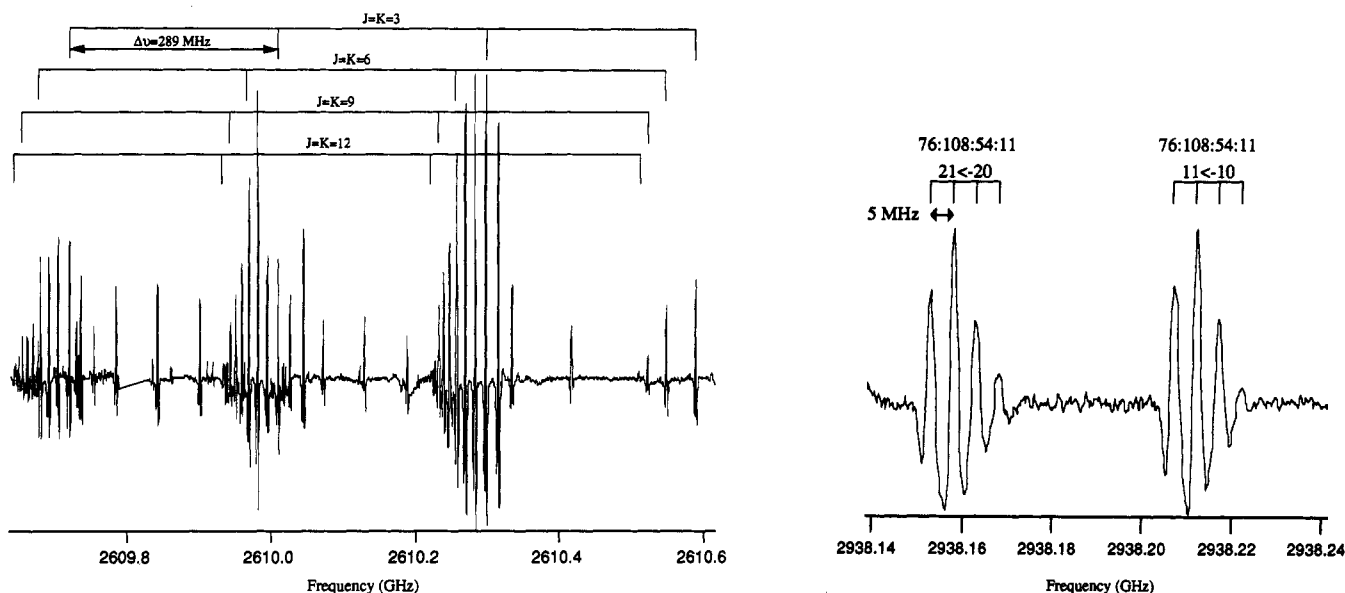
We do not know, *a priori*, which of the 96 PI operations are feasible. We can, however, assume different subgroups of  $G_{96}$

(16) Coudert, L. H.; Hougen, J. T. *J. Mol. Spectrosc.* **1990**, *139*, 259. Zwart, E.; J. ter Meulen, J. J.; Meerts, W. L.; Coudert, L. H. *J. Mol. Spectrosc.* **1991**, *147*, 27.

(17) Zwart, E. Ph.D. Thesis, University of Nijmegen, 1991.

(18) Cruzan, J. D.; Liu, Kun; Saykally, R. J. unpublished results.

(19) Suzuki, S.; Blake, G. A. unpublished data.



**Figure 2.** (a, left) A portion of the FIRVRT spectrum of  $(\text{H}_2\text{O})_3$ . This is the Q branch ( $J'' = J'$ ,  $J' > 1$ ) of the  $J = K_c$  subband. The transitions with  $K_c = 3, 6, 9$ , and  $12$  are labeled. The quartet spacing of 289 MHz is much larger than the 5-MHz spacing in  $(\text{D}_2\text{O})_3$ . The relative intensities of the transitions in each quartet cannot be used to compare with predicted proton spin statistical weights because of the long-term fluctuations in laser power. However, one of the transitions in the quartet is missing when  $K_c \neq 3n$  because its statistical weight is zero. This unmistakable signature shows that the PI group  $G_{48}$  is the appropriate molecular symmetry group for  $(\text{H}_2\text{O})_3$ . The quartet splitting may arise from motion along the pathway shown in Figure 1b. (b, right) Two of the quartets in the new  $(\text{D}_2\text{O})_3$  spectrum. The rotational assignments are  $J_{K_c} = 2_1 \leftarrow 2_0$  on the left and  $1_1 \leftarrow 1_0$  on the right. The relative intensities within each quartet correspond to the nuclear spin statistical weights (76:108:54:11) corresponding to  $A_1$ ,  $F_A$ ,  $F_B$ , and  $B_1$  states classified in the  $G_{48}$  molecular symmetry group. Methods: The Berkeley tunable far infrared spectrometer systems have been described in detail elsewhere.<sup>13</sup> Briefly, tunable far infrared light is generated by mixing light from an optically pumped, line tunable, far infrared laser with continuously tunable microwave radiation in a GaAs Schottky barrier diode. The resulting tunable sidebands ( $\nu_{\text{tunable sidebands}} = \nu_{\text{far infrared}} \pm \nu_{\text{microwave}}$ ) are separated from the far infrared carrier, and then directed into a vacuum chamber where they are multipassed 8–10 times through a planar supersonic jet containing the clusters of interest. Finally, the direct absorption signal is monitored by a liquid helium cooled stressed Ga:Ge photoconductor. For the present experiments, water clusters were produced and cooled to  $\sim 5$  K by bubbling argon through water and expanding the saturated gas in the planar supersonic jet.

as the appropriate molecular symmetry group and predict the associated tunneling splitting patterns in the rovibrational energy levels. Different assumptions lead to qualitative differences in the expected spectra, hence we have been able to experimentally identify the correct molecular symmetry group for the water trimer to be  $G_{48}$ . Given more extensive spectra, we could also determine which PI operations in this group are actually feasible. The recent studies by Wales<sup>10</sup> and Schütz *et al.*<sup>11</sup> approach this problem from the theoretical perspective. Our findings agree well with their results.

One six-element subgroup of  $G_{96}$ , called  $C_{3h}(M)$  by P&S, can be generated from the PI operation (153)(264)(ACB)\*, which we will call F. The PI notation is defined and the effect of F on a labeled configuration of the water trimer is shown in Figure 3a. The PI group  $C_{3h}(M)$  is isomorphic to the point group  $C_{3h}$ , which describes a solid object with a 3-fold axis of symmetry and a reflection plane perpendicular to the symmetry axis. This point group does NOT describe the theoretically predicted equilibrium structure of the water trimer.

It is uniformly found in theoretical studies<sup>6–12</sup> that F is a feasible operation for the water trimer. The proposed tunneling pathway associated with F is illustrated in Figure 1a; it involves the flipping of a single free hydrogen from one side of the ring to the other. A very low barrier is thought to exist along the flipping pathway, so low that it may lie ( $< \sim 0.1$  kcal mol<sup>-1</sup>) below the zero-point vibrational level for the  $(\text{H}_2\text{O})_3$  isotopomer.<sup>10–12</sup>

As F becomes feasible, the rovibrational energy levels of the trimer split into the six tunneling sublevels listed in column (b) of Table 2. Because of two accidental degeneracies, these states appear as a quartet. The nuclear spin statistical weights (which determine the relative intensity pattern) of these tunneling sublevels are also given in Table 2. Comparison of the relative intensities of the observed quartets with these statistical weights

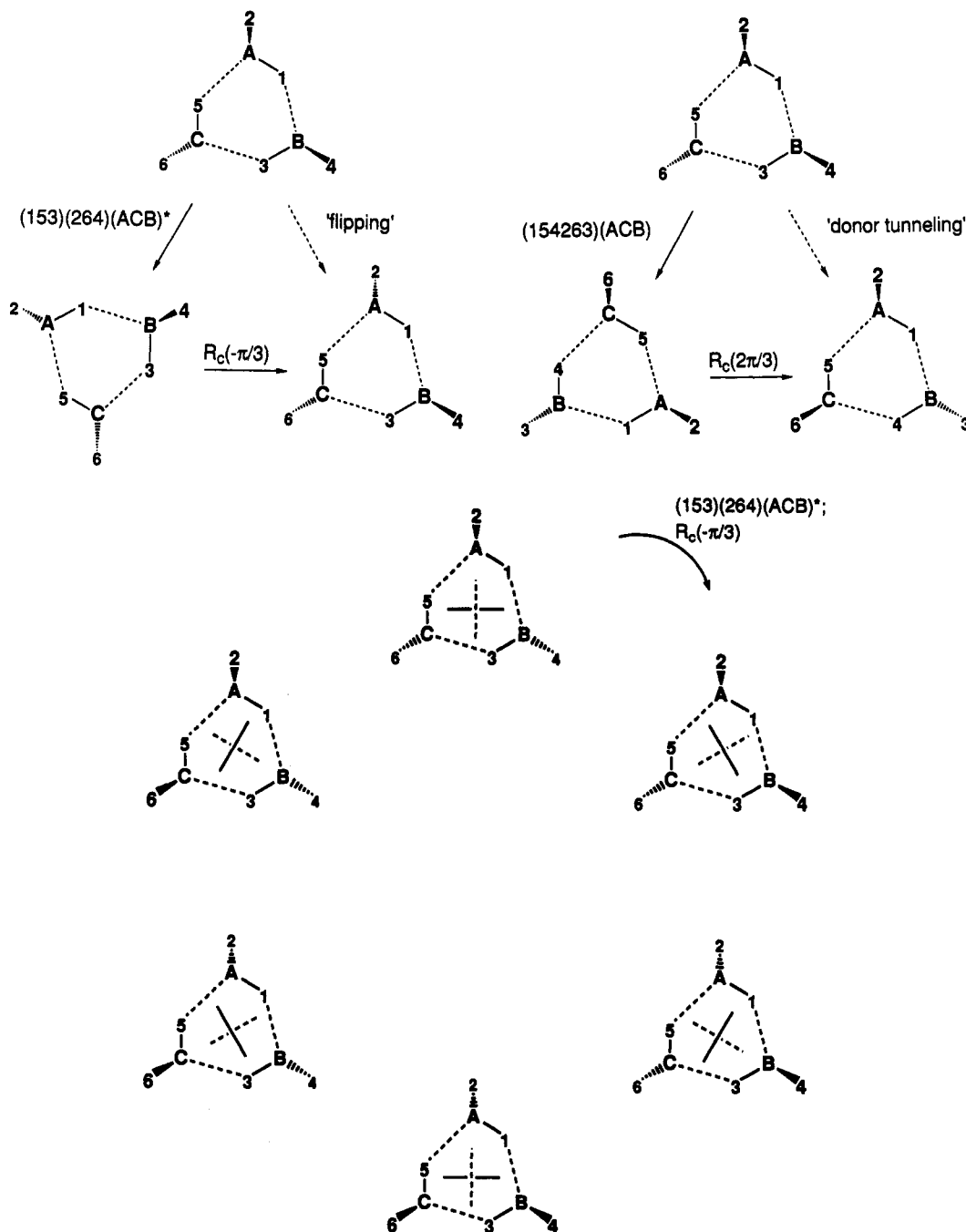
indicates that flipping does not explain the closely spaced quartets in our spectra.

As flipping becomes increasingly facile, the description of this motion as a tunneling process becomes inappropriate. Flipping of a free hydrogen from one side of the ring to the other causes the  $a$  and  $b$  principal axes of inertia to rotate by  $60^\circ$  about the  $c$  axis. When the same flipping operation is repeated six times, a full  $360^\circ$  rotation is completed. This process, diagrammed in Figure 3b, is called pseudorotation,<sup>20</sup> and it is symmetrically indistinguishable from true rotation of the trimer. Pseudorotation in the water trimer has been discussed in detail by Schütz *et al.*,<sup>11</sup> who estimated effective pseudorotational constants ( $A_{\text{pseudo}}$ ) for  $(\text{H}_2\text{O})_3$  and  $(\text{D}_2\text{O})_3$  at 24 and 12 wavenumbers, respectively, using the approach of Harris and co-workers.<sup>21</sup> When the potential energy barrier to flipping is very low, the quartet of tunneling states introduced above is more accurately described as part of a manifold of low-energy pseudorotation states that appear at energies near  $A_{\text{pseudo}}m^2$ . Each vibrational state will have such a manifold of pseudorotation states. The vibrational angular momentum due to pseudorotation can couple to rotational angular momentum and serve to contaminate the  $C$  rotational constant. The closer the spacing of the pseudorotational energy levels is to the spacing of the true rotational levels, the less structural information is contained in  $C$ .

A further consequence of the dynamical  $C_{3h}(M)$  symmetry of the water trimer is that asymmetry doubling of  $|K_c| > 0$  rotational states is not allowed. When asymmetry doubling is forbidden, the actual equilibrium geometry of the water trimer clearly cannot be determined from the measured rotational constants, since they are then required to describe an object with an apparent  $C_{3h}$  point group symmetry. The inability to deduce the geometrical

(20) Harris, D. O.; Harrington, H. W.; Luntz, A. C.; Gwinn, W. D. *J. Chem. Phys.* 1966, 44, 3467.

(21) Ewig, C. S.; Harris, D. O. *J. Chem. Phys.* 1970, 52, 6268.



**Figure 3.** (a, top left) The structural rearrangement that could be physically accomplished by a "flipping" hydrogen 2 (shown in Figure 1a) is mathematically described by applying the PI operation  $F = (153)(264)(ACB)^*$ , followed by the inverse of its equivalent rotation,  $[R_c(\pi/3)]^{-1} = R_c(-\pi/3)$ , to a labeled trimer structure. Here, (ACB) is the cyclic permutation that replaces A by C, C by B, and B by A. The asterisk indicates inversion of all coordinates through the center of mass.<sup>14</sup> F is a generator of the molecular symmetry group  $C_{3h}(M)$ , which contains 6 elements:  $E, F, F^2, E^* = F^3, F^4, F^5$ . (b, top right) When this flipping operation is repeated 6 times in succession, the  $a$  and  $b$  principal axes of inertia (indicated by the dotted lines) complete a full  $360^\circ$  rotation. This process is an example of pseudorotation. (c, bottom) The structural rearrangement that could occur via "donor tunneling" (shown in Figure 1b) is mathematically described by applying the PI operation  $(34)F^4 = (154263)(ACB)$ , followed by the inverse of its equivalent rotation  $[R_c(-2\pi/3)]^{-1} = R_c(2\pi/3)$ , to a labeled structure. F and  $(34)F^4$  are generators of the molecular symmetry group  $G_{48}$ , a group of 48 PI operations. We should note that, in this work, we have not shown that  $(34)F^4$  is a feasible PI operation.  $G_{48}$  can be generated from  $C_{3h}(M)$  if at least one of these PI operations is feasible:  $(34), (34)F, (34)F^2, (34)^*, (34)F^4$ , or  $(34)F^5$ .

structure of the trimer directly from these constants is therefore mandated by the dynamical symmetry.

The spectrum observed previously by P&S appears to be that of an asymmetric rotor. If the symmetry operations of  $C_{3h}(M)$  are indeed feasible for the trimer, we must assign the observed splitting of the  $|K_c| > 0$  states in the data of P&S to some other effect. Ascribing this splitting to strong Coriolis perturbations would be consistent with both the proposed dynamical  $C_{3h}(M)$  symmetry and the observations of P&S.

Since an analysis based on the  $C_{3h}(M)$  molecular symmetry group does not account for the observed quartet structure of the

observed rovibrational transitions, we consider a larger possible molecular symmetry group ( $G_{48}$ ) which contains 48 elements, generated by the PI operations F and (34). By using this group, we are assuming that one or more of the following new symmetry operations are feasible:  $(34), (34)F, (34)F^2, (34)F^3 = (34)^*, (34)F^4, (34)F^5$ . These six operations involve the interchange of the hydrogen-bonded and the free proton on one of the water monomers. The effect of the PI operation  $(34)F^4$  on a labeled configuration of the trimer is diagrammed in Figure 3b. A possible low energy pathway between the two corresponding minima on the trimer IPS is illustrated in Figure 1b. This pathway (donor

**Table 2.** Symmetry Labels for the VRT States for Each of Three Possible Molecular Symmetry Groups for the Water Trimer Followed by the Relative Intensities (statistical weights) for (H<sub>2</sub>O)<sub>3</sub> (in bold type) and (D<sub>2</sub>O)<sub>3</sub> That Should Be Observed in Their Spectra<sup>a</sup>

a) C <sub>1</sub> no structural interconversions	b) C <sub>3h</sub> (M) 'flipping'	c) G <sub>48</sub> 'flipping' and 'donor tunneling'	
		B <sub>1</sub> <sup>-</sup>	11, 11
	A <sub>1</sub> <sup>-</sup>	F <sub>B</sub> <sup>-</sup>	9, 54
	24, 249	F <sub>A</sub> <sup>-</sup>	3, 108
	(m+K <sub>c</sub> =6n+3)	A <sub>1</sub> <sup>-</sup>	1, 76
		B <sub>2</sub> <sup>+</sup> ; B <sub>3</sub> <sup>+</sup>	8, 8; 8, 8
	A <sub>2</sub> <sup>+</sup> ; A <sub>3</sub> <sup>+</sup>	F <sub>B</sub> <sup>+</sup> ; F <sub>B</sub> <sup>+</sup>	9, 54; 9, 54
	20, 240; 20, 240	F <sub>A</sub> <sup>+</sup> ; F <sub>A</sub> <sup>+</sup>	3, 108; 3, 108
	(m+K <sub>c</sub> =6n+2; 6n-2)	A <sub>2</sub> <sup>+</sup> ; A <sub>3</sub> <sup>+</sup>	0, 70; 0, 70
A		B <sub>2</sub> <sup>-</sup> ; B <sub>3</sub> <sup>-</sup>	8, 8; 8, 8
128, 1458	A <sub>2</sub> <sup>-</sup> ; A <sub>3</sub> <sup>-</sup>	F <sub>B</sub> <sup>-</sup> ; F <sub>B</sub> <sup>-</sup>	9, 54; 9, 54
	20, 240; 20, 240	F <sub>A</sub> <sup>-</sup> ; F <sub>A</sub> <sup>-</sup>	3, 108; 3, 108
	(m+K <sub>c</sub> =6n+1; 6n-1)	A <sub>2</sub> <sup>-</sup> ; A <sub>3</sub> <sup>-</sup>	0, 70; 0, 70
		B <sub>1</sub> <sup>+</sup>	11, 11
	A <sub>1</sub> <sup>+</sup>	F <sub>B</sub> <sup>+</sup>	9, 54
	24, 249	F <sub>A</sub> <sup>+</sup>	3, 108
	(m+K <sub>c</sub> =6n)	A <sub>1</sub> <sup>+</sup>	1, 76

<sup>a</sup> If no structural rearrangements occur on the time scale of our experiment, the observed rovibrational transitions will not be split by tunneling. <sup>b</sup> If flipping has a low enough energy barrier to be observable, one rovibrational state splits into six VRT states, which appear as a quartet. These evolve into part of a manifold of pseudorotation states, with  $m = 0, \pm 1, \pm 2, \pm 3 \dots$  etc., as the barrier to flipping becomes very low. VRT transitions from states with  $m + K_c = 3n$  and  $m + K_c \neq 3n$  will have different intensities. Asymmetry doubling of  $K_c \neq 0$  rotational states is forbidden. <sup>c</sup> If donor tunneling (or any motion that exchanges the bound and free hydrogens on one monomer) also has a low enough energy barrier, each pseudorotation state splits into eight VRT states, which also appear as a quartet. The A or B symmetry of each monomer with respect to this interchange is preserved. The A, F<sub>A</sub>, F<sub>B</sub>, and B states are formed from A-A-A, [A-A-B, A-B-A, B-A-A], [A-B-B, B-A-B, B-B-A], and B-B-B monomer states, respectively. <sup>d</sup> G<sub>96</sub> is not shown. If cw-ccw rearrangements were feasible, then each of the G<sub>48</sub> VRT states (except for A<sub>2</sub>, A<sub>3</sub>, B<sub>2</sub>, and B<sub>3</sub> which would become E states) would split into a closely spaced doublet. For (H<sub>2</sub>O)<sub>3</sub>, a G<sub>48</sub> A<sub>1</sub>, F<sub>A</sub>, F<sub>B</sub>, or B<sub>1</sub> state would split into doublets with 1:0, 3:0, 6:3, and 10:1 intensity ratios, respectively. The observable splitting of the F<sub>B</sub> and B<sub>1</sub> states is not seen in our (H<sub>2</sub>O)<sub>3</sub> spectra, nor is the analogous effect observed in any of the (D<sub>2</sub>O)<sub>3</sub> spectra.

tunneling) was proposed by Wales,<sup>10</sup> who estimates a barrier of about 1.9 kcal mol<sup>-1</sup>. The higher level calculations of Fowler and Schaefer<sup>6</sup> indicate a barrier of 1.5 kcal/mol (corrected for zero-point effects) for this motion. It is markedly similar to the donor tunneling found in the water dimer,<sup>15</sup> for which Smith *et al.*<sup>3</sup> calculate a barrier of about 1.7 kcal mol<sup>-1</sup>. In the tunneling sublevels of the ground vibrational state of (H<sub>2</sub>O)<sub>2</sub>, the actual splitting due to donor tunneling is roughly 1.4 GHz,<sup>16</sup> while in (D<sub>2</sub>O)<sub>2</sub>, it is estimated to be 13 MHz.<sup>17</sup>

As donor tunneling becomes feasible, each pseudorotation state of the water trimer splits into eight tunneling sublevels, which appear as a quartet, due to degeneracies. These new tunneling sublevels are listed in columns (c) of Table 2, along with their nuclear spin statistical weights. Two examples of the new (D<sub>2</sub>O)<sub>3</sub> quartets are shown in Figure 2b. Careful relative intensity measurements of all the (D<sub>2</sub>O)<sub>3</sub> quartets, including those first observed by P&S, agree quantitatively with these statistical weights, indicating that G<sub>48</sub> (and not G<sub>96</sub>) is indeed the appropriate molecular symmetry group for the trimer. The (H<sub>2</sub>O)<sub>3</sub> quartets, shown in Figure 2a, are too widely spaced to permit such reliable

relative intensity measurements, but the zero statistical weight of the A states when K<sub>c</sub> is not a multiple of 3 is unmistakable. This confirms that the origin of the (H<sub>2</sub>O)<sub>3</sub> quartet splitting is the same as that for (D<sub>2</sub>O)<sub>3</sub>.

The ordering of the very lowest energy quartet states is always the same, no matter which of the new PI operations is feasible. The A states are lowest, then F<sub>A</sub>, then F<sub>B</sub>, then B. Wales<sup>10</sup> has calculated how this ordering changes in the other flipping levels of the lowest vibrational state, assuming that F and (34)F<sup>4</sup> are feasible, within a high barrier approximation.

The spacing of the transitions in the observed quartets corresponds to the sum or the difference of the donor tunneling splittings between the lower and upper vibrational states. In the (D<sub>2</sub>O)<sub>3</sub> quartets (spaced by 5 MHz) the A states appear at lowest frequency, then the F<sub>A</sub> states, and then the F<sub>B</sub> states, and the B states appear at highest frequency. Therefore, the ordering of these tunneling states must be the same in the lower and upper vibrational states, the tunneling splitting increases upon vibrational excitation, and we have measured the difference in donor tunneling splittings. The transitions in the (H<sub>2</sub>O)<sub>3</sub> quartets appear in the opposite order (spaced by 289 MHz), implying that either (1) the ordering of the tunneling states is reversed, and we have measured the sum of the tunneling splittings, or (2) the tunneling splitting has decreased in the upper vibrational state, and we have measured the difference. The measured spacings of the quartets are of the same order of magnitude as the absolute donor tunneling splittings in the corresponding dimer isotopomers and may establish the time scale for this process in a more general sense.

We now consider the nature of the intermolecular vibrations reported in this work and in the previous work by P&S. A number of theoretical studies<sup>6,7,9-12</sup> include calculations of water trimer intermolecular "normal mode" frequencies and IR intensities in the double harmonic approximation. The lowest frequency modes of (H<sub>2</sub>O)<sub>3</sub> are calculated to lie between 100 and 200 cm<sup>-1</sup>, 50–100% higher in frequency than the (H<sub>2</sub>O)<sub>3</sub> band we report here. However, the crudeness of the double harmonic approximation for calculating intermolecular modes due to their large inherent anharmonicities makes information on the calculated vibrational eigenvectors extremely valuable in (sometimes futile) attempts to match observed intermolecular vibrational bands with calculated normal modes. Only Schütz *et al.*<sup>11</sup> provide such a description of their calculated vibrations. They conclude that of the 12 intermolecular trimer modes, three of the lowest frequency vibrations are combinations of flipping motions (these have the highest IR intensity), and three are mainly intermolecular stretches. They replace their harmonic treatment of the lowest flipping vibration by the more appropriate pseudorotation model discussed above, using the approach of Harris to estimate the pseudorotation constant.<sup>21</sup>

For (H<sub>2</sub>O)<sub>3</sub>, we report a c-type band at 87.1 cm<sup>-1</sup>. For (D<sub>2</sub>O)<sub>3</sub>, we report an a-type band at 98.1 cm<sup>-1</sup> and P&S reported a c-type band at 89.6 cm<sup>-1</sup>. The new spectra of (D<sub>2</sub>O)<sub>3</sub> have no eigenstates in common with those observed by P&S. It has now been experimentally determined that the band observed by P&S is a hot band; that is, the lower state of this band is not the ground state of (D<sub>2</sub>O)<sub>3</sub>.<sup>18</sup> We postulate, then, that this state is the  $m = 1$  pseudorotation level built on the ground state. It is unlikely that the strong perturbations observed by P&S could occur in the ground state of the trimer.

The observed rotational constants in the new (unperturbed) data change very little between lower and upper vibrational states; this makes the assignment of the observed bands to intermolecular stretches (where the vibrationally averaged hydrogen bond lengths are longer, due to anharmonicity) rather unlikely. One possibility suggested by Schütz *et al.*<sup>11</sup> is that the vibration observed by P&S is one of the other two flipping vibrational modes. Since the observed rotational constants are already "flipping-averaged"

in the ground state, it is reasonable to expect that they would not change much in such a vibration. Thus, such an assignment for all three of the bands observed so far seems consistent with our analysis. More data, including a connection between the  $(\text{D}_2\text{O})_3$  states observed by P&S and the states reported here, are needed in order to better characterize this flipping mode.

Finally, we note that Suzuki *et al.*<sup>19</sup> have recently observed a third c-type  $(\text{D}_2\text{O})_3$  band near  $41.1\text{ cm}^{-1}$ . The lower state of this

band is the same as that of the new  $98.1\text{-cm}^{-1}$  band reported here.

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