Fluxionality and low-lying transition structures of the water trimer

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The minimum energy structure of the cyclic water trimer, its stationary points, and rearrangement processes at energies < 1 kcal/mol above the global minimum are examined by \textit{ab initio} molecular orbital theory. Structures corresponding to stationary points are fully optimized at the Hartree–Fock and second-order Møller–Plesset levels, using the 6-311++G(d,p) basis; each stationary point is characterized by harmonic vibrational analyses. The lowest energy conformation has two free O–H bonds on one and the third O–H bond on the other side of an approximately equilateral hydrogen-bonded O···O···O (O3) triangle. The lowest energy rearrangement pathway corresponds to the flipping of one of the two free O–H bonds which are on the same side of the plane across this plane via a transition structure with this O–H bond almost within the O3 plane. Six distinguishable, but isometric transition structures of this type connect six isometric minimum energy structures along a cyclic vibrational-tunneling path; neighboring minima correspond to enantiomers. The potential energy along this path has $C_6$ symmetry and a very low barrier $V_6=0.1 \pm 0.1$ kcal/mol. This implies nearly free pseudorotational interconversion of the six equilibrium structures. The corresponding anharmonic level structure was modeled using an internal rotation Hamiltonian. Two further low-energy saddle points on the surface are of second and third order; they correspond to crown-type and planar geometries with $C_3$ and $C_{3v}$ symmetries, respectively. Interconversion tunneling vibrations via these stationary points are also important for the water trimer dynamics. A unified and symmetry-adapted description of the intermolecular potential energy surface is given in terms of the three flipping coordinates of the O–H bonds. Implications of these results for the interpretation of spectroscopic data are discussed.

I. INTRODUCTION

Water clusters are the subject of intense research because of their importance for understanding hydrogen bonding, for interpreting the many special features of the structure, dynamics and energetics of bulk solid and liquid water, and because hydrogen bonding to water molecules is of general importance in many biological, chemical, and physical systems. Large-amplitude motions of hydrogen-bonded species are of interest in understanding the nature and relevant reaction coordinates of proton transfer in small hydrogen-bonded clusters containing water molecules.

Theoretical investigations of the water trimer have focused mainly on the role of collective effects in H bonding. In a series of pioneering papers, Clementi and co-workers investigated cyclic water clusters by \textit{ab initio} calculations and developed analytical H2O–H2O two-body potentials. More recently, successively refined approximations for the three-body and four-body interactions were presented by this and other groups. Vibrational shifts induced by H bonding in the water trimer were also studied by \textit{ab initio} calculations. Yoon et al. and Chalasinski et al. reported \textit{ab initio} calculations of water trimers using large basis sets; their focus was also on nonadditivity effects and they investigated only selected geometries without full structural optimization. Very recently, Mó \textit{et al.} studied a large part of the intermolecular potential energy surface (PES) of (H2O)$_3$ by \textit{ab initio} methods, and found a total of 14 stationary points, including three minima. Although their study was very systematic, at least three energetically low-lying (<0.6 kcal/mol) stationary points were not described. It is precisely these low-barrier transition structures that are most important for the understanding of structural interconversions, fluxionality, and low-frequency intermolecular vibrations of this molecular cluster and that we address in this work.

All \textit{ab initio} calculations agree that the lowest energy minimum on the 12-dimensional intermolecular potential energy surface is a cyclic structure with three “bent” hydrogen bonds, and three “free” O–H bonds, two of which lie on one and the third on the other side of the O···O···O (O3) plane. As first discussed by Owicki \textit{et al.}, the intermolecular potential energy surface exhibits 96 isoeNERGETIC minima, corresponding to isometric cyclic trimers which differ in the positions of the protons relative to the O3 triangle taken in a fixed orientation. There are three isomers with two free protons above and one below the O3 plane, and three isomers with two protons below and one above. They can interconvert by flipping one of the two protons which are on the same side to the other side. For each of the three water molecules, the free and the bonded proton may be interchanged about the molecular C2 axis (C2 tunneling), giving $2 \cdot 2 \cdot 2 = 8$ sets of six isomers. Fi-
nally, the triangle of H-bonded protons can adopt two enantiomeric positions relative to the O₃ triangle (clockwise/counterclockwise tunneling), corresponding to a further doubling of the number of isomers. The group theoretical aspects and nuclear spin statistics of nonrigid (H₂O)₃ and (D₂O)₃ have been analyzed conclusively by Balasubramanian and Dyke.²⁰

Here, the subspace of the intermolecular PES which depends on the three flipping coordinates only is investigated. The subgroup of the full molecular symmetry group G₉₆ which is relevant for this subspace is the molecular symmetry group C₃h(M),²⁰,²¹ isomorphic to S₆ and C₆. Thus, only one of the 16 sets of six distinguishable isomers needs to be considered.

Direct observation of an intermolecular vibrational transition of (D₂O)₃ in a molecular beam was recently reported by Pugliano and Saykally.²¹ Rotationally resolved far-infrared absorption spectra at 89.3 cm⁻¹ were interpreted in terms of a vibrational-tunneling band and furnished rotational constants. Band splittings in the 10 MHz range were interpreted as being due to hydrogen interchange tunneling via rotation of monomers around their molecular C₂ axes. This important work draws attention to the question of fluxionality and structural interconversions in the water trimer. The high-frequency intramolecular vibrations of (H₂O)₃ have also been investigated by IR and coherent anti-Stokes Raman spectroscopy (CARS).²²,²³

As will be shown, several isomerization pathways of (H₂O)₃ along the flipping coordinates have very low barriers. In order to visualize the minima, transition structures (saddle points), interconversion pathways, and vibrations in three dimensions and from a unified point of view, we have chosen to represent the intermolecular PES in a symmetry-adapted coordinate system based on the flipping coordinates (Sec. II). Several features of this representation are analogous to that used for the mapping of the conformations of cycloalkanes.²⁴ Specifically, the potential-energy hypersurface of cyclohexane has been treated both qualitatively and quantitatively in an analogous representation.²⁴-²⁶ In Sec. III, the energetics of the stationary points and rearrangement pathways are explored by ab initio molecular orbital theory. Section IV presents both harmonic (normal coordinate) and anharmonic vibrational analyses of (H₂O)₃ and (D₂O)₃, and Sec. V discusses the experimental data in light of our results.

II. ISOMERS, TRANSITION STRUCTURES, AND ISOMERIZATION PATHS

The internal coordinate system adopted here is shown in Fig. 1(a). Its origin is chosen to correspond not to the "chair"-type minimum energy structure, but to the planar C₃h structure, which is a low-energy stationary point on the intermolecular PES. The basis vectors are the flipping coordinates Δαᵢ (i=1,2,3) of each individual H₂O molecule, as indicated in Fig. 1(a). Positive coordinate values correspond to H atom positions above the O₃ plane (up=υν), negative Δαᵢ to positions below this plane (down=νd). Positions in or very close to the O₃ plane are designated "planar" (=p). As will be shown in Sec. III, four types of stationary points were found in this subspace—a set {udd} of six isometric equilibrium structures whose members are designated by the permutations of (udd) and (udd); a set {udp} of six first-order transition structures labeled by the six permutations of (udp); a set {uuu} of two higher-order C₃ symmetric "crown"-type transition structures, which includes (uuu) and (dd); and another higher-order C₃h symmetric planar transition structure (ppp).

In the 3-space of the flipping coordinates, the six chair structures {udd} correspond, very approximately, to six of the eight corners of a cube centered on the origin [which corresponds to the (ppp) structure] and with edges parallel to the Δαᵢ coordinate axes (Fig. 1). The six {udp} transition structures are located close to the centers of the edges interconnecting these six corners. The {uuu} and {dd} transition structures lie close to the remaining two corners of the cube (Fig. 1). From the three flipping internal coordinates Δαᵢ, i=1···3, three symmetry adapted linear combinations (SALCs) φᵢ can be formed, where φᵢ transforms as αᵢ and φ₂,₃ together as the e' representation in

![FIG. 1. A definition of the flipping coordinate system. (a) The three flipping coordinates Δαᵢ (i=1,2,3) for torsion of each water molecule around the hydrogen-bonded O-H bond are employed as a basis for a three-dimensional orthogonal coordinate system. The planar (ppp) structure is chosen as the origin. The H-bonded O-H···O-H···O-H cycle is symbolized by a triangle (thin line), the free O-H bonds by bold lines if coplanar with the O₃ plane or as filled triangles otherwise. (b) Based on this coordinate system, the six isometric (uuu) structures lie at six corners of a cube connected by full edges. The (uuu) and (dd) structures lie at the two remaining vertices and are connected to the six other corners by dashed edges.](image-url)
FIG. 2. The cube and coordinate systems shown in Fig. 1(b) are rotated so that the SALC $\phi_1$ (see the text) forms the vertical axis. The (uuu), (ddd), and (uud) structures are placed at the $\Delta\alpha_i$ coordinate positions calculated at the HF level (cf. Table II). The polyhedron connecting the stationary points is seen to be compressed along the vertical axis, yielding $C_{3v}$.

Therefore, enantiomerization takes place without the trimer ever passing through a structure of higher symmetry. In contrast, enantiomerization via the body diagonals proceeds via the $C_{3v}$ symmetric ($ppp$) transition structure. Note also that the arrangement both of the six (uud) and of the six (udp) points in the space of flipping coordinates show $S_6$ symmetry, isomorphic to the relevant molecular symmetry group $C_{3v}(M)$.

III. ENERGETICS AND STRUCTURES OF STATIONARY AND SPECIAL POINTS

The structures, energies, force constants, vibrational modes, and frequencies of all of the stationary points of the (H$_2$O)$_3$ intermolecular PES as a function of $\alpha_i$ were explored by ab initio calculations at the Hartree–Fock (HF) and second-order Möller–Plesset (MP2) levels. Structures and energies were also calculated for the {upd} and {uuu} geometries which are not stationary points. All ab initio calculations in this work were performed with GAUSSIAN 92.

Full structural optimizations were performed at both levels using the 6-311+ +G(d,p) basis set, which has sufficient flexibility and was shown previously to give reliable results for (H$_2$O)$_2$ and (H$_2$O)$_3$. SCF convergence was assumed when the rms difference between the density matrix elements in consecutive SCF cycles was $<1E-10$. For structural optimizations, the largest component of the nuclear gradient vector in internal coordinates was converged to $<1E-6$ hartree/bohr (or hartree/rd). For some points, only single point MP2 calculations at the corresponding HF geometries were made.

The basis set superposition error (BSSE) was computed using the full counterpoise (CP) procedure. At the HF level, the CP corrections amount to 0.7–1.1 kcal/mol (see below), i.e., 5%–8% of the HF binding energy, and vary according to geometry. As expected, the BSSE is much larger at the MP2 level, being 55%–70% of the MP2 contribution to the binding energy $\Delta E$(MP2); the geometry dependence is substantial and cannot be neglected. Thus, CP uncorrected MP2 stabilization energies are not meaningful for the basis set size used in this study. On the other hand, the CP uncorrected HF calculations generally provide quite close predictions for the fully CP corrected HF+MP2 binding energies, due to fortuitous cancellation of the MP2 stabilization contribution with the sum of the HF and MP2 BSSEs; we find that $\Delta E$(HF) and $\Delta E$(MP2,CP) differ by only 1%–3%. Similar behavior was found in our recent study on phenol·H$_2$O.

Table I collects the binding energy and BSSE contributions obtained at the HF and the MP2 levels for both HF-optimized and MP2-optimized structures at the four configurations which are stationary points on the intermolecular PES. The set of six {uud} chair structures consti-
TABLE I. Calculated binding energy contributions $\Delta E$ (kcal/mol) for the equilibrium structure and several transition structures of $\left(\text{H}_2\text{O}\right)_3$ optimized at the HF and MP2 levels.

<table>
<thead>
<tr>
<th>Structure Optimization level</th>
<th>{uud}</th>
<th>{uuu}</th>
<th>{PPP}</th>
<th>{ud}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\Delta E(HF)</td>
<td>13.70</td>
<td>13.09</td>
<td>13.13</td>
<td>13.64</td>
</tr>
<tr>
<td>\Delta E(MP2)\textsuperscript{b}</td>
<td>3.60</td>
<td>4.69</td>
<td>2.60</td>
<td>3.45</td>
</tr>
<tr>
<td>\Delta E(MP2)\textsuperscript{c}</td>
<td>3.13</td>
<td>4.46</td>
<td>2.93</td>
<td></td>
</tr>
<tr>
<td>\Delta E(MP2)\textsuperscript{d}</td>
<td>-0.87</td>
<td>-0.78</td>
<td>-0.69</td>
<td>-0.98</td>
</tr>
<tr>
<td>\Delta E(MP2)\textsuperscript{e}</td>
<td>-2.03</td>
<td>-2.90</td>
<td>-1.52</td>
<td>-2.32</td>
</tr>
<tr>
<td>\Delta E(MP2)\textsuperscript{f}</td>
<td>-2.90</td>
<td>-3.68</td>
<td>-2.21</td>
<td>-3.29</td>
</tr>
<tr>
<td>\Delta E(HF) + \Delta E(MP2)</td>
<td>13.78</td>
<td>13.91</td>
<td>13.52</td>
<td>13.80</td>
</tr>
</tbody>
</table>

\textsuperscript{a}HF optimized structure only.

\textsuperscript{b}MP2 contribution; frozen-core approximation employed.

\textsuperscript{c}Counterpoise correction at the HF level.

\textsuperscript{d}Counterpoise correction at the MP2 level.

tute the global minima. These are interconnected by six first-order saddle points which are close to the midpoints of the equatorial cube edges, i.e., to \{ud\} configurations. The calculated \{ud\} barrier height amounts to only 20 cm\textsuperscript{-1} at the HF level, and for the counterpoise corrected HF+MP2 calculation, the barrier height decreases to $-5$ cm\textsuperscript{-1} (see Table II), i.e., transition states and minima are reversed. In both cases, the modulation of the potential energy is so low that quasifree pseudorotation of the trimer along the equatorial pathway must occur (see Sec. IV).

The \{uuu\} and \{PPP\} structures were optimized under the respective C\textsubscript{3v} and C\textsubscript{3h} symmetry constraints. At the CP corrected HF level, the \{uuu\} transition structure is 121 cm\textsuperscript{-1} and the \{PPP\} transition structure 90 cm\textsuperscript{-1} above the global minimum. At the CP corrected MP2 level, both barrier heights increase, but the ordering remains the same. However, at the CP uncorrected HF level, the relative order is inverted. Independent of the level of the calculation, the lower-energy transition structure is a second-order saddle point and the higher-energy structure a third-order saddle point on the PES. We conclude that the \{uuu\} and \{PPP\} structures are transition structures of very low energy, but their relative ordering will have to be studied at higher levels of theory. In any case, inversion tunneling of the water trimer by simultaneous flipping of all three free O-H bonds \{ud\} $\leftrightarrow$ \{du\} constitutes an additional important set of motions on the intermolecular PES.

Two further sets of configurations which are not stationary points were also characterized—the \{ud\} and \{PPP\} structures correspond approximately to the midpoints of the dashed cube edges and the cube faces, respectively. Despite extensive searches, no first-order saddle points were found in these regions of the PES. Along the dashed edges, the potential energy increases monotonically from the \{ud\} minima through the \{ud\} configurations at 140 cm\textsuperscript{-1} to the \{uuu\} crown isomers at 172 cm\textsuperscript{-1} (HF energies relative to minimum). Also, the direct paths connecting the three chair configurations of the same handed-
ness along the face diagonals presumably cross a potential energy ridge, not a saddle.

Table II compiles energies relative to the \{uud\} configuration and important structural parameters. Some structural attributes are quite general. At the HF level, the O···O distances are approximately equal and close to 2.90 Å for all stationary and "special" points, about 0.1 Å shorter than in the water dimer.\(^{30,31}\) The deviation of the hydrogen bonds from linearity are 22°-24° for all structures. The "free" O–H bond lengths are all 0.941 Å and the H bonded O–H bonds are 0.948–0.949 Å.

The flipping coordinates are \(\approx 20°\) if all three free O–H bonds are on the same side of the O\(_3\) plane (\{uuu\}), about 31°-33° if two O–H bonds are on the same side (\{uud\}, \{uup\}), and about 41°-44° for one O–H bond on a given side (\{uud\}, \{udp\} and \{upp\}). This trend can be rationalized on the basis of electrostatic repulsion of the H atoms.

At the optimized 6-311+G(d,p) MP2 geometries, the O···O bond distances are significantly shorter, by about 0.1 Å. This is qualitatively in accord with the increase in calculated bond energy and also with the results on water dimer and other hydrogen-bonded complexes (for recent overviews, see Refs. 29–33). Also the calculated flip angles \(\Delta \alpha_{1,2,3}\) are slightly larger, increasing by 2° to 14°. The deviations of the H bonds from linearity are similar to those at the HF minimum. The "free" O–H bond lengths are all close to 0.959 Å, while the H-bonded O–H bond lengths are 0.970–0.971 Å.

The radial distances \(D\) of the configurations from the center of the cube in internal coordinates calculated as \(D = (\Delta \alpha_1^2 + \Delta \alpha_2^2 + \Delta \alpha_3^2)^{1/2}\) are also given. The radial distance of the \{udp\} transition structures is close to that of the \{uud\} configurations, implying that both sets lie approximately on a sphere. In contrast, the radial distance \(D\) of the crown isomers from the center of the cube is only about half of that of the chair isomer (cf. Table II). Thus the cube represented in Fig. 1(b) is actually strongly compressed along one space diagonal, yielding a rhombohedron. A more accurate rendering of the calculated stationary points in \(\alpha_1\) space is given in Fig. 2.

For the water dimer, the work of Feller\(^{31}\) indicates that at the complete basis set limit, the HF+MP2 interaction energy is \(\Delta E = 4.95 \pm 0.05\) kcal/mol. At the basis set level employed here, this extrapolated interaction energy is bracketed from above by the uncorrected HF interaction energy of the HF optimized structure (4.41 kcal/mol) and from below by the uncorrected MP2 binding energy of the MP2 optimized structure (5.90 kcal/mol); the HF energy is closer to the extrapolated limit. Similarly, the experimental O···O distance of \(R = 2.977\) Å (Ref. 34) is bracketed by the calculated HF distance \(R_{HF} = 3.00\) Å and the MP2 distance \(R_{MP2} = 2.91\) Å. Again the calculated HF distance is closer to experiment. Based on these results for the dimer, we expect that for the trimer, the experimental binding energy of (H\(_2\)O)\(_2\) will also lie between the CP-uncorrected values calculated at the HF and MP2 levels with the 6-311+G(d,p) basis. The analogous estimate for the experimental O···O distance yields \(R_{exp} = 2.87 \pm 0.03\) Å, somewhat shorter than derived by Pugliano and Saykally.\(^{21}\)

A comparison with the water trimer structures predicted by the empirical EPEN model of Scheraga and co-workers\(^{19}\) shows astonishingly close agreement with the HF geometries. Thus, the \{uud\} structure is the minimum, the O···O distances are \(R = 2.89–2.91\) Å, and the deviation of the hydrogen bonds from linearity are 27°-30°, quite close to the calculated values at the HF level. The EPEN model predicts \(\alpha_i\) to be \(\alpha_i = 57°–60°\), somewhat larger than calculated here. The EPEN model also predicts a \{udp\} transition structure in semiquantitative agreement with the HF geometry in Table II (cf. Table IX in Ref. 19), the exception again being the inclinations of the "up" and "down" O–H bonds, which are \(\pm 60°\). The EPEN potential energy of the transition structure is 0.62 kcal/mol above the minimum, substantially above both the calculated HF and MP2 barriers.

Summarizing the above results, we note that the intermolecular PES is extremely flat as a function of the flipping coordinates. There exist a number of distinct pathways with low barriers, which give rise to large-amplitude tunneling motions in the water trimer (cf. Fig. 2) (i) the cyclic pseudorotational path along the equatorial rhombohedron edges connecting six isometric chair structures via the \{udp\} transition structures; (ii) three equivalent inversion pathways, along the dashed edges, each interconnecting a pair of three homochiral chair structures via a common "crown" stationary point; (iii) three equivalent inversion paths connecting chair enantiomers via the \{ppp\} stationary point, giving rise to symmetric double-minimum potentials. The one-dimensional cuts of the intermolecular potential surface along these interconversion pathways give rise to potentials with \(C_2\) symmetry for (i) and with \(C_1\) symmetry for (ii) and (iii), respectively. Taking into account quantum tunneling through the very small barriers, especially along path (i), we expect the water trimer to be delocalized over all six equivalent chair minima even in its vibrational ground state.

IV. VIBRATIONAL FREQUENCIES AND MODES

Twelve intermolecular modes arise from the relative translations/rotations of the three separated water molecules upon cluster formation. Since the chair minimum has no symmetry, the translational and librational motions of the constituent monomers may be strongly coupled in the normal modes. This was found for (H\(_2\)O)\(_3\) for which simple descriptions of the low-frequency intermolecular modes cannot be given. However, for (D\(_2\)O)\(_3\), the translation/libration coupling is fortuitously low.

Table III presents the harmonic intermolecular frequencies and corresponding IR intensities for the chair isomers of (H\(_2\)O)\(_3\) and (D\(_2\)O)\(_3\), respectively, calculated at the HF 6-311+G(d,p) level. Intra- and intermolecular modes are separated by an extended frequency gap of 800 and 600 cm\(^{-1}\) for (H\(_2\)O)\(_3\) and (D\(_2\)O)\(_3\), respectively. The intramolecular vibrations will be discussed elsewhere.

Figures 3 and 4 show the six lowest-frequency normal modes of (D\(_2\)O)\(_3\). Two types of motions can be identified:
TABLE III. Calculated harmonic frequencies (cm⁻¹) and IR intensities (km/mol) of (H₂O)₃ and (D₂O)₃ [HF/6-311+ +G(d,p) level].

<table>
<thead>
<tr>
<th>Mode*</th>
<th>Frequency</th>
<th>Intensity</th>
<th>Mode*</th>
<th>Frequency</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H₂O)₃</td>
<td></td>
<td></td>
<td>(D₂O)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>τ₁</td>
<td>111.4</td>
<td>85.8</td>
<td>τ₁</td>
<td>82.7</td>
<td>44.1</td>
</tr>
<tr>
<td>Stretch/torsion</td>
<td>147.3</td>
<td>121.7</td>
<td>τ₂</td>
<td>113.9</td>
<td>136.9</td>
</tr>
<tr>
<td>σ₂</td>
<td>158.6</td>
<td>7.1</td>
<td>σ₁</td>
<td>144.4</td>
<td>6.9</td>
</tr>
<tr>
<td>τ₂</td>
<td>165.6</td>
<td>151.6</td>
<td>σ₂</td>
<td>148.8</td>
<td>13.8</td>
</tr>
<tr>
<td>Torsion/stretch</td>
<td>191.9</td>
<td>12.6</td>
<td>τ₃</td>
<td>152.8</td>
<td>42.8</td>
</tr>
<tr>
<td>τ₃</td>
<td>207.5</td>
<td>40.1</td>
<td>σ₃</td>
<td>184.3</td>
<td>1.2</td>
</tr>
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<td>Libration</td>
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<td>96.8</td>
<td>Libration</td>
<td>227.3</td>
<td>35.2</td>
</tr>
<tr>
<td>Libration</td>
<td>322.0</td>
<td>72.1</td>
<td>Libration</td>
<td>235.1</td>
<td>31.3</td>
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<tr>
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<tr>
<td>Libration</td>
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<td>353.7</td>
<td>85.5</td>
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<tr>
<td>OOP b</td>
<td>630.3</td>
<td>503.7</td>
<td>OOP b</td>
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<td>288.7</td>
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<tr>
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<td>21.0</td>
<td>Libration</td>
<td>540.1</td>
<td>11.9</td>
</tr>
</tbody>
</table>

*Mode numbering based on (D₂O)₃ modes (cf. Figs. 3 and 4). (H₂O)₃ modes are partially mixed. Where possible, (D₂O)₃ and (H₂O)₃ modes were correlated by shape.

Collective out-of-plane libration (cf. large IR intensity).

(i) torsional modes (τ₁,τ₂,τ₃) shown in Fig. 3, which involve predominantly the Δαₗ flipping coordinates; (ii) the H-bond-stretching modes (σ₁,σ₂,σ₃) shown in Fig. 4. The pair of modes σ₁, σ₂ are calculated to be close in frequency; they correlate in frequency and shape with the degenerate e′(e) pair which arises for both the planar {ppp} and crown {uuu} stationary points. The third H-bond-stretching mode σ₃ is a “breathing” motion which correlates with the totally symmetric a′(a) breathing mode of the planar and crown stationary points.

For the H-bond stretching modes σ₁, σ₂, and σ₃, the...
energy barriers correspond to H-bond dissociation and are thus substantially higher than those for the \( \tau \) modes. Here, the harmonic vibrational frequencies may serve as first approximations to the true frequencies, although large corrections may occur due to anharmonicity along and between the \( \sigma \)-type normal coordinates. The remaining six higher-frequency intermolecular modes are of mixed librational/stretching character. Since the change in dipole moment of the cluster is larger for flipping coordinates than for H-bond stretching, the torsional modes generally have stronger IR band strengths than the H-bond stretching modes (cf. Table III).

The modes \( \tau_1, \tau_2, \) and \( \tau_3 \) of \( (\text{D}_2\text{O})_3 \) are of main interest in the present context. In the SALC coordinate system pictured in Fig. 5, consider the \( \tau_1 \) eigenvectors of \( \{d\text{uu}\} \) as an example. The \( \tau_1 \) eigenvector lies within the plane containing the \{uud\} structures of same chirality and tangential to the sphere encompassing the six corners. The \( \tau_2 \) eigenvector is oriented vertically in Fig. 5, i.e., parallel to SALC \( \phi_1 \) connecting the crown structures. Finally, the \( \tau_3 \) eigenvector is oriented approximately along the SALC \( \phi_3 \).

Figure 6 shows the torsional normal modes at the \{upd\} transition structures. The vibrational eigenvector of the \( \tau_1 \) mode with imaginary frequency shows a significant component only on the H atom lying close to the O-O-O plane. This motion corresponds to one of the internal \( \Delta \alpha \) coordinates, i.e., the normal mode is almost exactly parallel to of the equatorial rhombohedron edges in Figs. 2 and 5. The \{upd\} \( \tau_3 \) mode points almost exactly towards the (ppp) structure. The directions of these normal mode eigenvectors is also indicated in Fig. 5. The \{upd\} \( \tau_2 \) mode is orthogonal to both \( \tau_1 \) and \( \tau_3 \).

The information on the location of the minima and first-order transition structures, together with the eigenvectors of the three lowest-frequency vibrations, is projected along SALC \( \phi_1 \) in Fig. 5. Although the exact symmetry is only \( S_6 \), the stationary points and eigenvectors conform very closely to \( D_{3d} \) symmetry. The two independent distances between the minima and the transition structures are \( 34.4^\circ \) and \( 33.3^\circ \). At both sets of stationary points, the \( \tau_1 \) eigenvectors point along the low energy interconversion path. The absolute values of the corresponding harmonic frequencies differ by only 2 cm\(^{-1}\). The harmonic frequencies of the \( \tau_1 \) modes perpendicular to the interconversion path are also within 5 cm\(^{-1}\).

**Pseudorotation model**

For the flipping modes \( \tau_1 \) the harmonic approximation is clearly inappropriate, since the harmonic fundamental frequencies are much larger than the relevant barrier height along the equatorial interconversion path.
\( \nu_1 \approx 83 \text{ cm}^{-1}, B^2 - E_{\text{min}} \approx 20 \text{ cm}^{-1} \). This and the cyclic topology of the interconversion path suggest a pseudorotational model for the anharmonic vibrational level structure of mode \( \nu_1 \) based on the following assumptions: (a) The pathway describing the pseudorotational flipping motion is approximately separable from the other two tunnelling pathways through the crown or planar saddle points discussed in Sec. III. Kinetic and potential energy coupling terms in the Hamiltonian between the pseudorotation coordinate and the other two coordinates which are closely orthogonal to it are neglected. (b) A one-dimensional effective cut through the intermolecular PES along the pseudorotational coordinate is approximated by a cyclic potential function \( V(\phi) = V_0(1 - \cos \theta)/2 \), where \( V_0 \) denotes the barrier height calculated for the \{upd\} structure. In view of the approximate \( D_{3d} \) symmetry of the potential, higher terms such as \( V_{12}[1 - \cos(12\theta + \phi_0)])/2 \), etc., are neglected in our model. (c) The reduced masses calculated for \( \tau_1 \) at the \{uud\} and the \{upd\} configurations are 2.34 and 2.44 amu, respectively. Since these are so similar, the reduced rotational constant for pseudorotation is calculated at the transition structure, where only the planar H atom is moving. From the calculated geometry, one obtains an effective internal rotation constant \( a \) of \( \text{cm}^{-1} \) or \( F(D_2O) = 11.75 \text{ cm}^{-1} \).

The level structure and wave functions for this coordinate were calculated using an internal rotation Schrödinger equation with the above periodic potential function \( V(\phi) \), and solved in a basis of 21 free rotor functions of the form \( \psi_n = (2\pi)^{-1/2} e^{i m \phi} \). In Fig. 7, the energies of the six lowest vibrational levels are plotted as a function of the barrier height \( V_6 \). There and in the following, we employ symmetry labels of the \( C_6 \) group. The correlations with symmetry labels of the related groups are \((C_6 \rightarrow S_6 \rightarrow C_{3h}) a \leftrightarrow a^* \leftrightarrow a^* \leftrightarrow a^* \leftrightarrow a^* \leftrightarrow a^* \). The lowest level \( m=0 \) in the free-rotor limit) is of \( a \) symmetry with no nodal plane. The \( m= \pm 1 \) and \( m= \pm 2 \) levels are of \( e_1 \) and \( e_2 \) symmetries with one and two nodal planes, respectively; they remain degenerate for any barrier height. The \( m= \pm 3 \) levels split into two \( b \) levels, each with three nodal planes. For the lower \( b \) level, these are aligned with the barriers (\{upd\} structures), for the upper \( b \) function they are aligned with the minima (\{uud\} structures). With a barrier in the range given in Table II and a low reduced mass, pseudorotation along the equatorial path comes very close to free rotation, as indicated by the nearly constant level spacing among the \( a, e_1, \) and \( e_2 \) levels (Fig. 7).

Analogous considerations can be made for the \( \tau_2 \) and \( \tau_3 \) normal modes. For \( \tau_2 \), the harmonic fundamental of \( 147 \text{ cm}^{-1} \) for \((\text{H}_2\text{O})_3 \) [114 \text{ cm}^{-1} for \((\text{D}_2\text{O})_3 \)] is of the same magnitude as the barrier height along path (ii), viz., \{uud\} \( \rightarrow \{uuuu\} \rightarrow \{udd\} \), which is in the range between 121 \text{ cm}^{-1} \) (HF, CP corrected) to 213 \text{ cm}^{-1} \) (HF+MP2, CP corrected). For \( \tau_3 \), the harmonic fundamental of 159 \text{ cm}^{-1} \) for \((\text{H}_2\text{O})_3 \) [144 \text{ cm}^{-1} for \((\text{D}_2\text{O})_3 \)] is also similar to the barrier along path (iii) \{uud\} \( \rightarrow \{ppp\} \rightarrow \{ddu\} \), which are 90 \text{ cm}^{-1} \) (HF, CP corrected) and 101 \text{ cm}^{-1} \) (HF+MP2, CP corrected), respectively. Both the anharmonicity of the corresponding potential energy cuts and the existence of tunneling lead to modification of the level structure relative to the harmonic frequencies. Anharmonic coupling between these two modes and the pseudorotational mode may be expected at vibrational frequencies \( > 100 \text{ cm}^{-1} \).

V. DISCUSSION

The far-infrared vibrational transitions of \((\text{D}_2\text{O})_3 \) found by Pugliano and Saykally\(^2\) form a \( c \)-type band centered at 89.6 cm\(^{-1} \). They have assigned it as a flipping-type transition with a large dipole derivative along the (near) oblate-top axis. Based on the harmonic and anharmonic calculations presented above, there are two possible assignments.

1) An excitation of the \( \tau_1 \) mode from the lowest \( |m| = 0 \) pseudorotational level of \( a \) symmetry to the lower \( |m| = 3 \) level of \( b \) symmetry. Such a transition is allowed and polarized mainly along the \( c \) axis (under \( C_{3h} \) symmetry, it would be a pure \( c \)-type transition). According to Fig. 7, a potential barrier of \( \approx 70 \text{ cm}^{-1} \) would yield the observed transition frequency. A barrier of this magnitude is compatible with the range of values given in Table II.
(2) Alternatively, the transition may be due to the fundamental excitation of the $(\Delta DO)_{3}$ $\tau_3$ mode which is also of c type. The calculated harmonic frequency $\nu(\tau_3) = 114$ cm$^{-1}$ will be lowered due to anharmonicity and tunneling effects (see above). Note that both the $\tau_1$ and $\tau_2$ modes have large calculated band strengths (Table III).

The simple pseudorotational model allows predictions of two further low-frequency transitions from the lowest vibrational level. There is a second $a_1 \rightarrow b_1(\{m\} = 3)$ transition which is allowed as a c-type band and is predicted to lie at $\approx 125$ cm$^{-1}$, using the above value of 70 cm$^{-1}$ for the barrier height. Figure 7 shows that the splitting between the two $a \rightarrow b(\{m\} = 3)$ transitions is a sensitive measure of the barrier height. The fundamental vibrational excitation $a \rightarrow c_1$ is allowed in $(x,y)$ polarization, i.e., as a perpendicular band with a center frequency of $\approx 12$ cm$^{-1}$. This transition frequency hardly varies with barrier height, as seen in Fig. 7. For more accurate predictions, two- or three-dimensional anharmonic calculations based on the intermolecular potential energy surface as a function of all three $\tau_i$ or $\Delta \alpha_i$ coordinates are indispensable since the $\tau_1/\tau_2$ interactions may be quite strong.

Table IV compares the rotational constants calculated for the chair and crown structures obtained at the HF and MP2 levels with the 6-311+ +G(d,p) basis with the experimental values recently measured by Pugliano and Saykally for states in our first assignment which correspond to the $a_2(m=0)$ and $b_2(m=\pm 3)$ levels. For the $\{uud\}$ structure, the agreement for the $C$ constant is quite good at the HF level, while the calculated $A$ and $B$ values are too small by about 5%. At the MP2 level, the $A$ and $B$ constants are reproduced with deviations of 1%–2%, whereas now the calculated $C$ constant is almost 8% too large. All three constants are sensitive to the O···O distances, whereas the $A$ and $B$ constants are also sensitive to the flipping angles $\alpha_i$.

Note that in this system, the equilibrium structure differs substantially from the vibrationaly averaged structure for any given $m$ state: (i) each of the pseudorotational states is a vibrational average over $\{uud\}$ and $\{udp\}$ sets; (ii) the probability of each isometric structure within either set is equal for a given $m$; (iii) the relative probability of the two sets differs from level to level; (iv) vibrational averaging is rapid compared to rotation. Due to the vibrational averaging, the system will behave like an effective oblate symmetric top, at least for low $J$ and $K$. Note that due to the different number of nodes in the pseudorotational wave functions, the average flipping angles and thus the $B(\approx A + B/2)$ rotational constant should show a slight dependence on the pseudorotational constant $m$, as is experimentally observed [cf. assignment (1) and Ref. 21].

The intermolecular restoring forces along the $\alpha_i$ coordinates are relatively small, implying that centrifugal distortion effects will be large. Thus, increased rotation around the $c$ axis (increase of $K$ for fixed $J$) leads to a flattening of the trimer, i.e., a decrease of $\alpha_i$ and distortion towards the $(ppp)$ geometry. Increased rotation around the $a$ or $b$ axes increases one of the $\alpha_i$ angles and lowers the other two, distorting the geometry towards the $(upp)$ structure. Also, angular momentum coupling between rotation and vibration should occur for the $m > 0$ states.

Pugliano and Saykally report a 7% increase of the $C$ constant for the excited vibrational state relative to the lower state, indicating that the O···O distances must decrease substantially on excitation. We find this difficult to reconcile with either of the tentative vibrational assignments given above, since for both assignments, the main structural changes are expected for the flipping angles and not for the O···O distances.

Summarizing the results obtained, we note the following.

(1) $Ab$ initio calculations of $(\text{H}_2\text{O})_3$ were performed at the Hartree–Fock and MP2 levels with the 6-311+ +G(d,p) basis set. The intermolecular potential energy surface was explored as a function of the three flipping angles $\alpha_i$. The equilibrium structure is found to be a cyclic trimer with two O–H bonds on one side and the third on the other side of the O$_3$ plane. For a given handedness of the hydrogen-bond cycle, six permutations of “up” and “down” free O–H bonds occur in the subspace of the three flipping angles $\alpha_i$; the set of six structures is denoted $\{uud\}$.

Three energetically low-lying transition structures (stationary points of the intermolecular PES) were found. The lowest is a first-order saddle point with one of the O–H bonds almost coplanar with the O$_3$ plane, denoted $\{udp\}$. Relative to the $\{uud\}$ structures, the interaction energy is only marginally different ($\approx 20$ to $\approx 5$ cm$^{-1}$). The second set of transition structures are the crown $(uuu)$ and $(ddd)$
configurations with all three O–H bonds on the same side of the O₂ plane. The relative interaction energies are in the range 170±50 cm⁻¹, depending on the level of the calculation. The third transition structure is a planar configuration of C₃ᵥ symmetry denoted (ppp), with a relative interaction energy 90–200 cm⁻¹ above the {uud} set. The relative energetic ordering of these two saddle points is not definitely established on the basis of the present calculations, but the (ppp) configuration is lower at all levels except at the CP uncorrected HF level. The lower of these two transition structures is a second-order, the higher a third-order saddle point.

(2) These minima and stationary points can be represented efficiently in a three-dimensional coordinate system of flipping displacement angles Δα₁. In these coordinates, the (ppp) configuration is the origin, all other stationary points falling on a rhombohedron. The {uud} minima are the six equivalent “equatorial” vertices, the {upd} saddle points lie very close to the six equivalent “equatorial” edge midpoints, and the (uuu)/(ddd) saddle points are represented as the axial vertices. The flipping-type normal coordinates and isomerization paths can be mapped onto this rhombohedron. We note that the nuclear framework structure is chiral at every point in this configuration subspace, except at the (ppp) origin. Thus, the spectroscopic finding that {D₂O₃} is nonplanar²¹ is equivalent to saying that it is classically chiral; see, however point (6) below.

(3) The six lowest intermolecular vibrations can be classified as flipping (τ₂,3) and stretching (σ₁,2,3) fundamentals with harmonic frequencies in the range 80–210 cm⁻¹. The six higher-frequency fundamentals are in the range 220–750 cm⁻¹, and are mixed librational/torsional/stretching modes.

(4) The three barriers {upd}, {uuu}, and (ppp) to interconversion among the six equivalent {uud} structures are very low, and comparable to the torsional vibrational fundamentals τ₂,3 which may be considered as the incipient interconversion motions. The relative ordering of the {uuu} and (ppp) barriers should be investigated at higher levels of calculation.

(5) The interconversion between the {uud} and {upd} sets lies on a slightly warped circular path in Δα₁ configurational space (see Fig. 5), equivalent to a pseudorotation. The pseudorotation is locally close to the normal coordinates τ₁ at both the {uud} and {upd} points. The potential energy profile is probably close to a sinusoidal \( V(\phi) = V₀(1 - \cos 6\phi)/2 \) potential. Using an internal rotational Hamiltonian and a pseudorotation barrier of \( V₀ = 70 \) cm⁻¹ leads to level structure in qualitative agreement with an experimentally observed vibration band,²¹ but further data and calculations are needed to validate this model.

(6) Viewed classically, the pseudorotational motion interconverts enantiomers. Curiously enough, the transition structure is also chiral [see note (2) above], and the system never passes through a nonchiral configuration along the pseudorotation path. Quantum mechanically, however, the pseudorotational wave functions are completely delocalized over the two enantiomeric sets of three {uud} minima, with equal amplitudes on either set. Also, the \( \nu=0/1 \) tunneling splitting is \( \approx 100 \) times larger than the rotational constants \([\approx 12 \text{ cm}^{-1}/24 \text{ cm}^{-1}] \) compared to \( 0.1-0.2 \text{ cm}^{-1} \) for \((\text{D}_2\text{O})_3/\text{(H}_2\text{O})_3\), respectively), implying that delocalization is complete on the rotational time scale. Thus, quantum mechanically, none of the water trimer vibrational states discussed here is chiral (barring high J,K rotational effects).

(7) The \( \tau_3 \) mode corresponds to an incipient inversion tunneling path which leads towards a homochiral enantiomer via the (uuu) or (ddd) saddle point. Since there are three equivalent homochiral starting points, the saddle points represent branch points along this path with two equal negative curvatures.

(8) The third flipping mode \( \tau_3 \) leads towards the (ppp) saddle point. It is also an incipient inversion tunneling path; however, this path interconverts enantiomers, e.g., \( \text{(uud)} \rightarrow \text{(ddu)} \).

The H-bond-breaking internal motions not considered here \((C_2 \text{ tunneling, clockwise/counterclockwise tunneling})²¹ \) lead to energetically higher saddle points, and to further small level splittings, as observed experimentally.²¹ Further studies involving higher levels of calculation should also be directed to these coordinates.

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