Conformational equilibrium and internal dynamics in the iso-propanol–water dimer†

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The molecular complex between iso-propanol and water has been investigated by Fourier transform microwave spectroscopy. Two distinct rotational spectra have been assigned, corresponding to two different isomers of the adduct. In both cases the water molecule acts as a proton donor to the alcoholic oxygen atom of iso-propanol in its gauche arrangement. The isomer in which the water molecule is oriented along the symmetry plane of the iso-propanol molecule (inner) is more stable than the second isomer, where the water is positioned outside the iso-propanol symmetry plane (outer). The rotational transitions of the inner isomer display a doubling, due to the two equivalent minima related to the internal rotation of the hydroxyl group (concerted with a rearrangement of the water unit). The tunneling splitting has been determined to be 25.16(8) GHz, corresponding to a $B_2$ barrier of $\sim 440$ cm$^{-1}$.

In the pioneering rotational study of methanol–water it was shown that the observed species consisted of a water–donor, methanol–acceptor complex. The spectrum was complicated by the internal rotation of the methyl group, such that the spectroscopic parameters were reported only for the internal rotation A-state.

Similarly, water acts as proton donor in the adduct tert-butanol–water. The tert-butanol hydroxyl group tunnels between two equivalent minima – involving also a considerable rearrangement of water – that generates splittings of the rotational transitions. From these splittings, the corresponding potential energy function has been estimated. The same hydrogen bonding motif (where water serves as the proton donor) has been recently found in the adduct of water with ethanol, and in glycidol–water, the water moiety acts both as a proton donor and a proton acceptor forming two strong O–H···O hydrogen bonds within a cyclic structure.

A different behavior has been encountered in phenol–water, where water has the role of proton acceptor. Here, water undergoes a two dimensional (2D) motion (a combination of internal rotation and inversion) between four (2 × 2 equivalent) minima on the 2D intermolecular potential energy surface.

Additional studies of the rotational spectra of adducts of water with larger aliphatic alcohols, such as water–propanol, would help to understand the interplay between the hydrophobic and -philic interactions in such clusters. Here we are interested in the adduct of water with iso-propanol (IP–W), a dimer with a conformational equilibrium taking place between the gauche and trans forms of the iso-propanol. In a related complex, hexafluoroisopropanol–water, only one conformer was observed, wherein trans-hexafluoroisopropanol acts as a proton donor to the water, a motif similar to phenol–water. Most likely, it is the high degree of fluorination that inverts...
the usual conformational behavior observed for the aliphatic alcohol–water complexes.

2. Experimental section

The rotational spectra of IP–W isotopologues have been measured in two different laboratories:

(a) UNIBO. Measurements were performed between 6–18.5 GHz using a pulsed jet Fourier Transform MicroWave (PJFTMW) spectrometer described elsewhere,\(^\text{10}\) based on the pioneering designs of Flygare\(^\text{11}\) and Grabow.\(^\text{12}\) Adducts were formed by flowing helium through a stainless steel reservoir containing a 50% by mole mixture of iso-propanol and water, and running the resulting gaseous mixture through a pulsed supersonic expansion. Rotational frequencies were determined after the Fourier transform of 8k-data point time domain free induction decays, recorded with 40 ns sampling intervals. The pulsed molecular beam was introduced parallel to the axis of the Fabry–Pérot resonator. Consequently, each observed transition appeared as a Doppler doublet, and the line frequency was determined as the arithmetic mean of the frequencies of the two Doppler components. The accuracy of frequency measurements is estimated to be better than 3 kHz.

(b) Caltech. Data were collected from 6–18 GHz using a previously described Chirped Pulse-Fourier Transform MicroWave (CP-FTMW) spectrometer.\(^\text{6}\) A reservoir nozzle was filled with a 1 : 1 molar mixture of iso-propanol and water, and heated to ~40 Celsius. Argon at 46 psi pressurized the nozzle. The nozzle was pulsed at 10 Hz, creating a supersonic expansion perpendicular to two waveguide horns. Forty 1 microsecond duration chirps were broadcast with each gas pulse. Data were collected for 300 seconds at each local oscillator setting. Line centers were measured to an accuracy of 20 kHz.

3. Preliminary calculations of the conformational energies

Before searching for the rotational spectrum, we ran several theoretical calculations, in order to constrain reliable starting conformations for spectral assignment. The MP2/6-311++G(d,p) level of theory was used, in Gaussian09.\(^\text{13}\)

Five energy minima were found, shown in Fig. 1, corresponding to the trans or gauche conformation of iso-propanol, to the proton donor or proton acceptor role of water, and to the orientation of water with respect to the symmetry plane of gauche iso-propanol (inner indicates water is oriented along the IP symmetry plane; outer indicates water is oriented perpendicular to the IP symmetry plane). The corresponding spectroscopic parameters are listed in Table 1.

As has been seen for the simpler aliphatic alcohol adducts, the complexes where the water acts as a proton donor are more stable, and, as for ethanol–water dimer, the gauche conformation of the alcohol is preferred. Cooperative water donor/iso-propanol acceptor structures (GAI, GAO, and TA) comprise the three lowest energy dimers, while anti-cooperative hydrogen bonding increases the GD and TD dimer energies by over 100 cm\(^{-1}\). The relative energy difference between GAI, GAO, and TA indicates the trans/gauche position of the alcohol hydroxyl may account for ~20 cm\(^{-1}\) in energy. However, a significant stabilization of 100 cm\(^{-1}\) occurs when the water is oriented symmetrically between the alcohol’s two methyl groups, as in GAI. This stabilization is likely attributable to increased opportunities and/or improved alignment for secondary stabilizing C–H···OH\(_2\) bonding interactions.

4. GAI (inner) isomer

**Rotational spectrum**

The rotational spectrum of this isomer was assigned at Caltech, using the SPFTT/SPCAT suite of programs\(^\text{4,14}\) and a graphical Python fitting program. Double resonance of assigned transitions was performed to validate the fit. Later on, complementary measurements were performed at UNIBO. Rotational transitions are split into two component lines, with an intensity ratio of about 5 : 1, corresponding to a vibrational splitting of about 1 cm\(^{-1}\). The doublet of the 2\(^{1}\)\( \leftrightarrow \) 1\(^{1}\) transition is shown in Fig. 2.

Isotopologues were not assigned for the GAI isomer due to their complex spectra. Instead, the justification for our structural assignment comes from the good agreement between predicted and experimental rotational constants. The intensities of the

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Table 1 MP2/6-311++G(d,p) calculated spectroscopic parameters of the five most stable IP–W dimers

|                  | GAI  | GAO  | TA   | GD   | TD   |
|------------------|------|------|------|------|------|
| **A/MHz**        | 5121.4 | 8058.8 | 7528.5 | 8039.6 | 5188.1 |
| **B/MHz**        | 2527.4 | 2073.1 | 2155.3 | 1996.1 | 2364.8 |
| **C/MHz**        | 2388.2 | 1758.2 | 1837.5 | 1701.5 | 2225.1 |
| \(\mu_\text{a}/D\) | 1.95  | –2.62 | 2.42  | 3.07  | –2.69 |
| \(\mu_\text{b}/D\) | 0.20  | –1.17 | 0.87  | –0.83 | 0.00  |
| \(\mu_\text{c}/D\) | 1.51  | –0.64 | 0.37  | –0.48 | 1.62  |

\(^a/G\) = Gauche, \(T\) = Trans, \(A\) = Acceptor (Alcohol), \(D\) = Donor (Alcohol), \(I\) = Inner (position of water), \(O\) = Outer (position of water). Absolute energy = \(-270.134153\) \(E_h\).
GAI and GAO transitions also agree with relative populations consistent with the \textit{ab initio} energies. Finally, the flexible model analysis based upon the GAI structure (mentioned next) faithfully reproduces splitting of transitions ascribed to that isomer.

The fitting of the transition frequencies was complicated by the Coriolis’ interactions between the $v = 0$ and $v = 1$ vibrational levels. The following coupled Hamiltonian was therefore used:

\[ H = H_0^R + H_1^R + H^{CII} + H^{int} \]  

where $H_0^R$ and $H_1^R$ account for the rotational energies for the 0 and 1 substates, respectively, $H^{CII}$ represents the centrifugal distortion corrections (forced to the same value for $v = 0$ and $v = 1$), and $H^{int}$ the interaction between the $v = 0$ and $v = 1$ states, expressed as:

\[ H^{int} = \Delta E_{01} + F_{bc} \times (P_c P_b + P_b P_c + P_a P_b) + F_{ab} \times (P_a P_b + P_b P_a) \]  

\[ \Delta E_{01} = E_1 - E_0 \]

$\Delta E_{01}$ is the energy difference between the 0 and 1 substates, while $F_{bc}$ and $F_{ab}$ are Coriolis’ coupling parameters. The $\{P_c P_a + P_a P_c\}$ Coriolis term was not used in the fit, consistent with an inversion motion through the $b$-axis. This inversion motion is further verified in the \textit{ab initio} structure, which confirms that the proton movements occur along the $b$-axis.

Measurement transition frequencies have been fitted using Pickett’s SPFIT program.\textsuperscript{14} Since the GAI isomer is a near symmetric top, the $S$-reduction and $f$-representation have been chosen.\textsuperscript{15} The fitted spectroscopic parameters are reported in Table 2. The measured transition frequencies are given in the ESL.\textsuperscript{†}

**Flexible model analysis of the tunneling motion**

The determined $\Delta E_{01}$ splitting is related to the barrier connecting the two equivalent minima depicted in Fig. 3 as a function of the dihedral angle ($\tau$) describing the internal rotation of the OH group, to the amplitude of the motion (in our case a ca. 120° rotation of the OH group), and to the reduced mass of the motion, which is a function of $\tau$ and also of the structural relaxation which takes place in the complex.

Meyer’s flexible model\textsuperscript{16} is especially suitable to determining the basic properties of potential energy surfaces from rotational and vibrational experimental data. In our case we consider $\tau$ as the key parameter to describe the motion, with any structural relaxations of the dimer taken into account as a function of $\tau$.

\[ V(\tau) = B_2[1 - (\tau/\tau_0)^2]^2, \]  

where $B_2$ is the barrier at $\tau = 0$ and $\tau_0$ is the equilibrium value of the inversion angle (see Fig. 3). Since we have only one data point, we fixed $\tau_0$ at its \textit{ab initio} value (62.7°). Guided by the \textit{ab initio} structural differences between the energy minimum ($\tau = \tau_0$) and the transition state ($\tau = 0$), we took into account the structural relaxations of four structural parameters as a function of the leading parameter $\tau$, according to the following expressions (see Fig. 4 for labelling):

\[ \text{H}_2\text{O}_2-\text{OIC1}^\circ = 180 - 30.7(\tau/\tau_0) \]  
\[ \text{HFO2-}^{18}\text{H}_2\text{O1}^\circ = 180 - 10.3(\tau/\tau_0) \]  
\[ \text{H}_2\text{O}_2\text{O1}^\circ = 15.3 - 3(1 - \cos 3\tau) \]  
\[ \text{R(O2-}^{18}\text{O1})\text{Å} = 2.843 + 0.006(1 - \cos 3\tau). \]

Applying Meyer’s one-dimensional flexible model, a barrier of $B_2 \sim 440$ cm$^{-1}$ best reproduced the experimental value of

| $\nu$ | 0 | 1 |
|------|---|---|
| $A$/MHz | 5098.624(3)\textsuperscript{a} | 5099.953(3) |
| $B$/MHz | 2485.250(1) | 2484.560(1) |
| $C$/MHz | 2353.833(1) | 2352.743(1) |
| $D_1$/kHz | 7.98(4) | |
| $D_1$/kHz | 21.6(2) | |
| $D_2$/kHz | $-17.3(6)$ | |
| $d_4$/kHz | 0.27(2) | |
| $\Delta E_0$/GHz | 25.16(8) | |
| $F_{ab}$/MHz | 47.87(2) | |
| $F_{bc}$/MHz | 4.2(1) | |
| $\sigma'$/kHz | 3.7 | |
| $N'$ | 33 | |

\textsuperscript{a} Errors in parenthesis are expressed in units of the last digit. \textsuperscript{b} Standard deviation of the fit. \textsuperscript{c} Number of fitted transitions.
ΔE_01. In the flexible model calculations the τ coordinate has been considered in the ±120° range and solved into 81 mesh points.\textsuperscript{16}

5. GAO (outer) isomer

Rotational spectra

The spectrum of this species was observed only at UNIBO, using He as carrier gas. It is possible that a supersonic expansion with Ar encourages GAO to conformationally relax into GAI.\textsuperscript{17} Here, the μ_α-dipole moment component has the highest value; for this reason we first scanned the frequency region expected to include the J = 2 ← 1 μ_α-bands of all species. We could identify only one triplet composed of the 2_{12} ← 1_{11}, 2_{02} ← 1_{01}, 2_{1,1} ← 1_{10} individual transitions. We could easily extend the assignment up to the J = 3 μ_α-band and to 4 additional μ_β- and μ_γ-transitions, for a total of 16 rotational lines. The measured transition frequencies have been fitted with a semi-rigid Hamiltonian,\textsuperscript{15} obtaining the spectroscopic parameters (rotational constants and 4 quartic centrifugal distortion constants) reported in the first column of Table 3.

The experimental values of the rotational constants match best with those calculated for the GAO species, that is iso-propanol in the gauche isomer acting as a proton acceptor, and with H_2O in the outer position. This interpretation was confirmed by the assignment of the rotational spectra of four additional isotopologues, obtained by deuteration of the water hydrogens, or by replacing H_2O with H_2^{18}O in the pre-expansion mixture. The rotational frequencies (generally a smaller number with respect to the parent species) of the isotopologues were fitted with the same procedure used for the parent species. Occasionally, some centrifugal distortion constants are not determinable and therefore have been fixed to the values of the parent species. All the obtained spectroscopic parameters are listed in Table 3, while the measured transition frequencies are given in the ESI.\textsuperscript{\textdagger}

### Structural information

Some structural information has been obtained from the six available rotational constants. First the Kraitchman coordinates\textsuperscript{18} of the water oxygen and of the water hydroxyl hydrogen atoms were calculated in the principal axis system of the parent species.

The obtained values are reported in Table 4 (see Fig. 5 for atom numbering), where the \textit{ab initio} and the partial r_0 (see below) values are also given for comparison.

The \textit{ab initio} values correspond to the bottom of the vibrational potential energy surface and are indicated by the notation r_0 (or equilibrium structure).

A partial r_0 structure, suitable to reproduce the rotational constants in the vibrational ground state, has been determined by adjusting, with respect to the \textit{ab initio} geometry (given in the ESI\textdagger), the O5–O3 distance and the \( \angle \) O5O3–C2C1 and \( \angle \) H15O5–O3C2 dihedral angles (see Table 5). The discrepancies between the experimental and calculated values of the rotational constants with such an effective structure have been reduced by

| Table 4 | Experimental (r_0 and r_0), and \textit{ab initio} (r_0, MP2/6-311+G(d,p)) coordinates of the substituted atoms of the GAO (outer) isomer of IP–W |
|----------|-----------------|
|          | O5               | H14 | H15 |
| \(|\alpha|/Å\) | \( r_0 \) | 2.8098(5) | 1.8454(8) | 3.2916(5) |
| \(|\beta|/Å\) | \( r_0 \) | 0.03(3) | 0.370(4) | 0.237(6) |
| \(|\gamma|/Å\) | \( r_0 \) | 0.0189 | 0.3411 | 0.0535 |
| \(|\delta|/Å\) | \( r_0 \) | 0.0073 | 0.3550 | 0.1835 |
| \(|\epsilon|/Å\) | \( r_0 \) | 0.193(7) | 0.071 | 0.693(2) |
| \(|\zeta|/Å\) | \( r_0 \) | 0.1983 | 0.0703 | 0.6119 |
|         | \( r_0 \) | 0.1642 | 0.0667 | 0.6162 |

\* A Error in parenthesis are in units of the last digits. \*b Calculated from the partial r_0 structure of Table 5, combined with the \textit{ab initio} structure given in the ESI.

| Table 3 | Experimental spectroscopic parameters of the isotopologues of the GAO (outer) isomer of IP–W |
|----------|-------------------------------|
|          | IP–H_2O                       | IP–H_2^{18}O | IP–DOH       | IP–HOD       | IP–D_2O     |
| A/MHz     | 7918.293(1)\textsuperscript{a} | 7909.561(1) | 7902.499(2) | 7855.730(2) | 7845.81(1) |
| B/MHz     | 2049.4385(7)                  | 1928.2259(3) | 2021.8036(3) | 1960.3019(3) | 1934.9157(3) |
| C/MHz     | 1745.1053(7)                  | 1656.8025(3) | 1724.2112(4) | 1682.2996(4) | 1662.4514(4) |
| D_{J}/kHz | 7.15(1)                       | 6.878(5)     | 6.642(7)     | 7.485(7)     | 6.374(9)    |
| D_{R}/kHz | −36.43(6)                     | −39.2(2)     | −34.5(2)     | −50.7(2)     | [36.43]     |
| D_{Q}/kHz | −0.29(2)                      | [−0.29]      | [−0.29]      | [−0.29]      | [−0.29]     |
| N^c       | 16                            | 15           | 12           | 12           | 9           |
| \( \sigma^d \)/kHz | 2.3                         | 2.7          | 3.2         | 4.2         | 4.0         |

\*a Error in parentheses in units of the last digit. \*b Values in brackets were fixed at the corresponding value of the parent species. \*c Number of lines in the fit. \*d Root-mean-square-deivation of the fit.
Derived H-bond distance $r_{e}$ and $r_{0}$ geometry, and derived hydrogen bond length of the GAO (outer) isomer of IP–W

| Fitted parameters | $r_{e}$ Å | $r_{0}$ Å |
|-------------------|-----------|-----------|
| $r_{OSO3}$ Å      | 2.8602    | 2.869(3)  |
| $r_{OSO3-C2C1}$ Å | 178.3     | 184.0(2)  |
| $r_{H1SO5-O3C2}$ Å | −144.6    | −138(8)   |

Derived H-bond distance $r_{OH-O}$ Å

| $r_{OH-O}$ Å | 1.898 | 1.908 |

$^{a}$ MP2/6-311+G(d,p) values. $^{b}$ Error in parentheses in units of the last digit.

7. Conclusions

The present study confirms the inclination of aliphatic alcohols to play a proton acceptor role in their complexes with water, as observed in the previous investigations of this kind.\(^1,5-7\) Such a trend appears to be inverted upon fluorination of the aliphatic chain, as shown by Shahi and Arunan in the case of hexafluoro-isopropanol–water.\(^9\) In addition, aromatic alcohols (phenols) adopt a proton donor role upon complexation with one water molecule.\(^5\)

Secondary weak hydrogen bonding interactions between alkyl protons also appear to play a stabilizing role. Orientation of the water to maximize the number of secondary CH–O interactions may stabilize the GAI isomer by a significant amount (prediction $\sim 100$ cm\(^{-1}\), experiment $\sim 370$ cm\(^{-1}\)) compared to GAO. This is despite the known energetic cost of water accepting more than one hydrogen bond.\(^4\) The acceptance of more than one weak CH–O interaction by the water oxygen may be achieved by changes to hydrogen bond lengths in GAI cf. GAO. Ab initio structures indicate weak hydrogen bond lengths of 2.83 Å and 2.94 Å for GAI, and 2.79 Å for GAO. Therefore, we may conclude that multiple, comparatively weaker hydrogen bonding interactions may be favoured over a single stronger hydrogen bond in certain alcohol–water complexes. That ab initio calculations successfully predict the structures of iso-propanol–water dimers indicates appropriate consideration of weaker hydrogen bonds into structural calculations.

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