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A Microwave Spectroscopic Investigation of the Networked Structure of 3-Hydroxytetrahydrofuran-H_2O

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The rotational spectra of nine isotopomers of the 3-hydroxytetrahydrofuran−water complex were recorded using a Fourier transform microwave spectrometer. The spectra are assigned to the networked structure of the complex, with intermolecular hydrogen bonds from the hydroxyl to the water oxygen and from water to the furanose-ring oxygen. Ab initio calculations, at the MP2/6-31G** level, indicate that this is the lowest energy structure of the complex, and it is based on the lowest-energy ring-puckering conformation of the 3-hydroxytetrahydrofuran monomer, $C_{4'}$-endo. Stark effect measurements were used to determine the projections of the dipole moment on the principal inertial axes: $\mu_a = 1.2$ (3) D, $\mu_b = 1.8$ (2) D, $\mu_c = 0.7$ (4) D, and $\mu_{tot} = 2.2$ (2) D.

Introduction

Molecular complexes have been the focus of continuing study because the weakly attractive forces between complex partners also stabilize the conformations of large molecules. Complexes with water are particularly interesting because water complexes can model the hydrogen bonding interactions that are prevalent in biochemical systems; the structures and dynamics of many water van der Waals complexes have been studied by Fourier transform microwave spectroscopy. The water dimer is prototypical of many of these systems:[1] the oxygen−oxygen distance[2] was found to be 2.976 Å and the dimer can tunnel between eight equivalent configurations, giving rise to a rich and complex spectrum. Many other water complexes have similar heavy-atom separations and display some evidence of exchange tunneling dynamics. In only a few systems, however, does water simultaneously act as a hydrogen bond donor and as an acceptor.[3−5] In both formamide−water[3] and alaninamide−water,[5] the water was found to donate a hydrogen bond to the carbonyl oxygen while accepting one from the amide nitrogen. The hydrogen bond angles in these systems are considerably less than 180° (<NHO = 143° and 139°; <OHO = 143° and 155°), but the hydrogen bond lengths are typical for hydrogen-bonded water clusters (1.9−2.0 Å).

Like many other five-membered rings, the furanose ring puckers to relieve strain caused by eclipsing methylene groups around the ring. The minimum energy structure of tetrahydrofuran remains controversial. X-ray[6] and neutron diffraction[7] experiments have shown that the preferred crystal-phase structure is a twist conformation with the two beta carbons on opposite sides of the plane established by the oxygen and the two alpha carbon atoms. Recent ab initio calculations (MP2/6-31G**) also support this twist structure.[8] The microwave spectrum of tetrahydrofuran is heavily perturbed by pseudorotation,[9,10] and spectra arising from four different pseudorotational states of jet-cooled tetrahydrofuran have been recorded.[10] The spacing of the lowest vibrational levels and the effective moments of inertia from these states were used to determine the potential energy function along the pseudorotational pathway.[9,10] These minimum-energy structures, however, were identified as envelope structures with one of the alpha carbon atoms out of plane; small barriers were located at the envelope structure with oxygen out of plane (45 cm^{-1}) and at the twist structure with the two beta carbon atoms on opposite sides of the plane established by the oxygen and alpha carbon atoms (16 cm^{-1}).

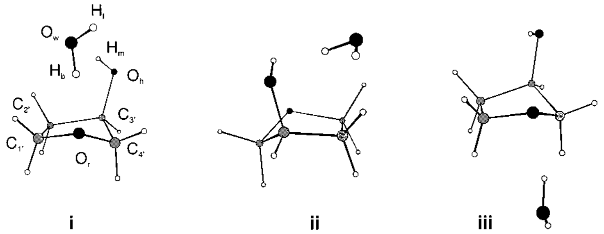

Figure 1. Ab initio structures of 3-hydroxytetrahydrofuran−water. Structure **i** has a network of hydrogen bonds from the hydroxyl to the water oxygen and from water to the furanose oxygen; structure **i** also indicates the labeling scheme used throughout the paper. Structure **ii** has a single hydrogen bond from water to the hydroxyl oxygen, and structure **iii** has a single hydrogen bond from water to the furanose oxygen.

We have recently recorded the microwave spectrum of 3-hydroxytetrahydrofuran,[11] a simple model system of the furanose rings found in nucleosides. Spectroscopic constants obtained from five isotopic species were used to determine the ring-puckering conformation. The best-fit structure was found to be a $C_{4'}$-endo envelope; MP2/6-31G** calculations predicted this to be the lowest energy conformation.[11,12] The experimental and ab initio studies were consistent with a weak intramolecular hydrogen bond in 3-hydroxytetrahydrofuran from the hydroxyl to the furanose oxygen. As in ref 11, we use the ring numbering system and endo/exo convention appropriate for nucleosides instead of that for furans; see Figure 1.

Because 3-hydroxytetrahydrofuran has two different hydrogen bonding sites, there are a number of different possible structures of its water complex. This complex may have a hydrogen-bonding network in which the water inserts itself into the 3-hydroxytetrahydrofuran monomer intramolecular hydrogen bond (water accepting a hydrogen bond from the hydroxyl and donating one to the furanose oxygen); it is unknown if the ring-puckering conformation of 3-hydroxytetrahydrofuran would

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need to adjust to better accommodate insertion of the water. Various single hydrogen-bonded structures of the 3-hydroxytetrahydrofuran−water complex are also possible, but these structures are likely higher in energy than the doubly bonded complex. We have undertaken this spectroscopic study of 3-hydroxytetrahydrofuran−water in order to determine its preferred structure.

Experimental Section

Rotational spectra were recorded using a Fourier transform microwave spectrometer.[13,14] The resonant cavity consists of two 36 cm diameter mirrors, one of which can be moved to tune the frequency (5−18 GHz). Microwave radiation is generated by a Hewlett-Packard 83711B synthesized frequency generator and coupled into the cavity by an L-shaped antenna. The cavity is used in reflection mode: molecular emission is detected using the same antenna. The molecular signal is routed into a heterodyne circuit, frequency reduced, and digitized by a Keithley-MetraByte DAS-4101 data acquisition board in a personal computer.

The resonant cavity is straddled by two solid aluminum plates, 30 × 30 × 0.5 cm. These plates can be charged up to 10 000 V with opposite polarity to perform Stark effect experiments. The effect of field inhomogeneities can be minimized by using shorter gas pulses and adjusting the timing of the microwave pulse; line widths remained 35 kHz (see below) up to ±8000 V. The electric field was calibrated after each measurement by measuring the Stark shift of the $1 \leftarrow 0$ transition of OCS ($\mu = 0.715\,196$ D).[15]

3-Hydroxytetrahydrofuran (Aldrich) was incorporated into a supersonic expansion by warming to 50 °C. The sample contained enough water so that it was unnecessary to further seed the expansion to form the water complex. Deuteration of the 3-hydroxytetrahydrofuran monomer was achieved by dissolving the sample in D_2O for 1 h followed by concentration under vacuum. Mixed isotopomers of the complex were formed by seeding the expansion to 2% with various H_2O/D_2O mixtures.

The current spectrometer design requires the heated nozzle to be oriented perpendicular to the cavity axis; the resulting rotational line widths are 35 kHz (full width at half-maximum), with line centers accurate to 4 kHz. The backing pressure of the argon carrier gas was typically 2 atm.

Results

***d*-3-hydroxytetrahydrofuran.** Sixteen transitions were measured for the monodeuterated 3-hydroxytetrahydrofuran monomer. The deuterium nuclear quadrupole hyperfine splittings could not be fully resolved for these transitions, but the transitions were partially split and broadened up to 200 kHz. Transition frequencies were estimated from the centers of the broadened transitions; these frequencies are given in the Supporting Information. The transitions were fit to the Watson A-reduction Hamiltonian,[16] yielding the following rotational and centrifugal distortion constants: $A = 5469.091$ (3) MHz, $B = 3558.671$ (3) MHz, $C = 2900.492$ (3) MHz, $\Delta_J = 1.8$ (4) kHz, $\Delta_{JK} = -8.8$ (2) kHz, and $\Delta_K = 13.1$ (3) kHz.

3-hydroxytetrahydrofuran-H_2O. A total of 25 *a*-, *b*-, and *c*-type transitions, given in Table 1, have been measured for the most abundant isotopomer of the 3-hydroxytetrahydrofuran−water complex. The transitions were fit to a Watson A-reduction Hamiltonian,[16] and the spectroscopic constants are given in Table 2. Twenty-one transitions were recorded for 3-hydroxytetrahydrofuran-$H_2{}^{18}O$ isotopomer. Transition frequencies for the $H_2{}^{18}O$ complex and the deuterated complexes are available in the Supporting Information. Spectra of the ^{13}C isotopomers of the complex could not be found in natural abundance. The alcohol proton and two water protons readily exchange with deuterium, so seven unique deuterated isotopic species are possible. A minimum of 13 transitions have been measured for each of the seven isotopomers; spectroscopic constants for the deuterium isotopomers are also given in Table 2. In the table, *d*-furan indicates substitution of the alcohol proton, H_m, DOH indicates substitution of the hydrogen-bonded water proton, H_b, and HOD indicates substitution of the non-hydrogen-bonded water proton, H_f. The deuterium nuclear quadrupole hyperfine splitting was not resolved for these transitions, but resulted in transitions broadened up to 100 kHz for the *d*-3-hydroxytetrahydrofuran-D_2O complex. Many of the smaller centrifugal-distortion constants were poorly determined for the deuterated species because partially resolved quadrupole hyperfine splittings resulted in greater uncertainty of the transition frequencies (~25 kHz). Assignment of the deuterium isotopomer spectra was made difficult because several isotopomers would be present in the beam at any given time and because the hydrogen/deuterium ratio would shift throughout the day.

TABLE 1: Frequencies of the Assigned Transitions of 3-Hydroxytetrahydrofuran-H_2O

J'_{KpKo}	J''_{KpKo}	ν/MHz	$\Delta\nu$/kHz
2_{02}	1_{11}	7675.075	2.2
2_{12}	1_{11}	7836.445	1.6
2_{02}	1_{01}	8080.809	0.2
2_{12}	1_{01}	8242.177	−2.5
2_{11}	1_{10}	8880.216	0.7
2_{11}	1_{01}	9807.846	−2.0
2_{21}	1_{10}	10 097.426	−1.0
2_{20}	1_{10}	10 374.955	2.0
2_{21}	1_{11}	10 619.328	4.3
2_{20}	1_{11}	10 896.849	−0.7
2_{20}	1_{01}	11 302.595	9.3
3_{03}	2_{12}	11 565.500	3.6
3_{13}	2_{12}	11 609.590	−0.5
3_{03}	2_{02}	11 726.866	−1.0
3_{13}	2_{02}	11 770.957	−4.2
3_{12}	2_{02}	14 793.270	−2.3
3_{21}	2_{11}	14 842.620	−6.3
4_{04}	3_{13}	15 300.134	1.7
4_{14}	3_{13}	15 310.012	−3.3
3_{22}	2_{12}	15 320.238	−4.0
4_{04}	3_{03}	15 344.226	−0.4
4_{14}	3_{03}	15 354.108	−1.5
3_{30}	2_{20}	15 847.189	−1.3
4_{23}	3_{22}	16 484.700	12.2
4_{13}	3_{12}	16 897.155	−3.7

The fully deuterated complex was formed by co-expanding *d*-3-hydroxytetrahydrofuran and D_2O. The assignment of this spectrum could be made because the transitions of this species had the largest frequency shift relative to the normal isotopomer; the broad, unresolved band shape arising from the three quadrupoler deuterium nuclei served as a further guide for assignment. Various singly deuterated forms predominated when *d*-3-hydroxytetrahydrofuran was expanded with H_2O, whereas the other partially deuterated forms could be formed by expanding 3-hydroxytetrahydrofuran with a 50:50 H_2O:D_2O mix. The relative intensities of the normal and fully deuterated species served as a guide to the extent of deuteration, and thus served as a guide to assignment. Correct assignment of the many deuterated species also relied on predictions based on the ab initio structures; further verification of the assignment was provided by Kraitchman calculations of the atomic coordinates. Atomic coordinates for each of the three substitution positions could be calculated using seven different sets of moments of

TABLE 2: Spectroscopic Constants for the Isotopic Species of 3-Hydroxytetrahydrofuran-H_2O

species[a]	A/MHz	B/MHz	C/MHz	Δ_J/kHz	Δ_{JK}/kHz	Δ_K/kHz	δ_j/kHz	N[b]
furan-H_2O	2756.284 (1)	2350.548 (1)	1828.6480 (8)	1.80 (5)	1.3 (3)	−0.8 (3)	−0.45 (3)	25
d-furan-H_2O	2735.399 (12)	2338.551 (3)	1813.108 (2)	1.4 (2)	4. (2)	−3.5 (9)	−0.39 (6)	15
furan-DOH	2741.762 (4)	2323.996 (2)	1807.006 (1)	1.99 (8)	−0.9 (6)	1.1 (5)	−0.54 (3)	16
d-furan-DOH	2718.476 (10)	2314.314 (3)	1791.942 (2)	1.3 (2)	4. (1)	−1.9 (8)	−0.34 (6)	15
furan-HOD	2750.190 (6)	2248.586 (2)	1765.692 (1)	1.69 (10)	2.3 (7)	−4. (1)	−0.52 (6)	16
d-furan-HOD	2726.768 (6)	2240.165 (2)	1751.6612 (9)	1.41 (7)	2.5 (7)	−1.1 (4)	−0.37 (2)	13
furan-D_2O	2737.879 (12)	2223.883 (2)	1746.146 (2)	1.06 (10)	1. (1)	0.0[c]	0.0[c]	14
d-furan-D_2O	2712.782 (11)	2217.050 (3)	1732.524 (3)	1.1 (1)	3.4 (8)	0.0[c]	0.0[c]	20
furan-$H_2{}^{18}O$	2750.509 (1)	2236.397 (2)	1757.6257 (8)	1.92 (5)	0.0[c]	0.0[c]	−0.55 (3)	21

[a] See text for explanation of the labeling system. [b] Number of transitions included in the fit. [c] Held constant in the fit.

TABLE 3: Comparison of the Observed and Calculated Stark Effects for 3-Hydroxytetrahydrofuran-H_2O

transition	$\|M\|$	$\Delta\nu/\mathscr{E}^2$/(MHz cm^2/kV^2) observed	$\Delta\nu/\mathscr{E}^2$/(MHz cm^2/kV^2) calculated[a]
$3_{13} - 2_{12}$	0	−2.22 (3)	−2.27
$2_{21} - 1_{10}$	0	19.96 (7)	19.93
$2_{02} - 1_{01}$	0	9.98 (4)	9.94
$3_{03} - 2_{12}$	0	−2.40 (3)	−2.49
$2_{12} - 1_{01}$	0	11.88 (4)	11.94

[a] Calculated using $\mu_a = 1.2$ D, $\mu_b = 1.8$ D, $\mu_c = 0.7$ D, and the rotational constants in Table 2.

TABLE 4: Ab Initio Structures of 3-Hydroxytetrahydrofuran-H_2O

structure	ΔE^a/kJ mol^{-1}	ΔI_{rms}/amu Å^2
i	0	9.3
ii	12.6	165.7
iii	15.3	191.9

[a] Relative to structure **i**.

inertia; see below. The good agreement for the coordinates indicates a correct assignment of the spectra.

Many weakly bonded water complexes are subject to tunneling processes which exchange equivalent protons. Despite an extensive spectral search, no transitions were found that could be assigned to another tunneling state.

Dipole Moment. Second-order Stark coefficients for the 3-hydroxytetrahydrofuran−water complex were calculated from the rotational constants in Table 2, and the M^2-coefficients were found to be large for all observed transitions. Since the lobes arising from $M = 1$ or higher shifted very quickly with low fields, they could not be calibrated with OCS. Instead, Stark shifts for the $M = 0$ lobes of five different transitions were tracked up to 1.2 MHz. The A-Stark coefficients for these lobes were highly correlated, however, so fits of the dipole components to the experimental Stark shifts have large uncertainties. The best-fit values were $\mu_a = 1.2$ (3), $\mu_b = 1.8$ (2), $\mu_c = 0.7$ (4), and $\mu_{tot} = 2.2$ (2) D; the observed and calculated Stark shifts, as listed in Table 3, are in very good agreement. The largest deviations occur for the $M = 0$ lobes of the $3_{13}-2_{12}$ and $3_{03}-2_{12}$ transitions, which were only tracked up to 800 kHz.

Structure and Discussion

The structure of the monomer was reinvestigated including the moments of inertia of *d*-3-hydroxytetrahydrofuran. In ref 11, an ab initio calculation was used to fix the hydroxyl hydrogen parameters: the O_h−H bond length was 0.965 Å, the $C_{3'}$−O_h−H angle was 104.5°, and the H−$C_{3'}$−O_h−H torsional angle was 169.2°. These parameters were virtually unchanged when fit to the moments of inertia of *d*-3-hydroxytetrahydrofuran: 0.993 (39) Å, 104.8° (27), and 169.5° (20), respectively. This new structure fit indicates a weak hydrogen bond from the hydroxyl hydrogen to the furanose oxygen, since the hydrogen-to-oxygen distance is 2.461 Å. Kraitchman coordinates of the hydroxyl hydrogen were found to be $a = \pm1.154$ Å, $b = \pm0.299$ Å, and $c = \pm1.351$ Å, which are in agreement with the least-squares fit structure.

Complete optimizations of the structure of the 3-hydroxytetrahydrofuran-H_2O complex were performed using Gaussian94[17] at the MP2/6-31G** level.[18−20] Starting structures for the optimizations were based on the experimental and ab initio (MP2/6-31G**) structures[11] of the 3-hydroxytetrahydrofuran monomer. Three structural minima were found; these structures are shown in Figure 1 and listed in Table 4 along with their relative energies. In the minimum energy structure, the water donates a hydrogen bond to the furanose oxygen and accepts one from the hydroxyl group of the 3-hydroxytetrahydrofuran. Thus, the water is positioned directly above the furanose ring in the networked structure. The two singly hydrogen-bonded structures are much higher in energy: 12.6 kJ mol^{-1} for the water-to-hydroxyl-oxygen complex and 15.3 kJ mol^{-1} for the water-to-furanose-oxygen complex. Another optimization, beginning from a singly bonded hydroxyl-to-water complex, converged instead on the water-to-hydroxyl-oxygen structure. Interestingly, the three optimized structures of the complex retained the $C_{4'}$-endo ring puckering conformation of the 3-hydroxytetrahydrofuran monomer.

Root-mean square averages of the differences between the experimental moments of inertia and those calculated from the ab initio structures, ΔI_{rms} where $\Delta I = I_x(\text{exp}) - I_x(\text{calcd})$ and $x = a$, b, and c for each isotopomer, are also given in Table 4. The experimental moments of inertia of the isotopic species of the complex are in good agreement with the networked structure, but the large values of ΔI_{rms} for the two singly hydrogen-bonded complexes make them unlikely structures.

Attempts to least-squares fit the structure of the complex to the experimental moments of inertia were unsuccessful. The lowest-energy ab initio structure was used as a starting structure for least-squares fits of the complex structure to the experimental moments of inertia. Comprehensive fits, using all of the isotopic data and fitting the six intermolecular coordinates shown in Figure 2, failed to converge; it was evident that some coordinates (especially the angular and dihedral angle coordinates) were not well determined even with this large isotopic data set. Restrictive fits attempted to fit to a more limited set of isotopic data (moments of inertia of the normal, *d*-3-hydroxytetrahydrofuran-D_2O, and 3-hydroxytetrahydrofuran-$H_2{}^{18}O$ complexes), fit a smaller set of structural parameters (the center-of-mass distance and the tilt angles θ_1 and θ_2), or only fit structural parameters to the *b*- and *c*- moments of inertia. These fits either did not converge or predicted atomic coordinates significantly different from the ab initio model and Kraitchman coordinates.

More extensive fits of the structure of 3-hydroxytetrahydrofuran−water included structural parameters of the 3-hydroxy-

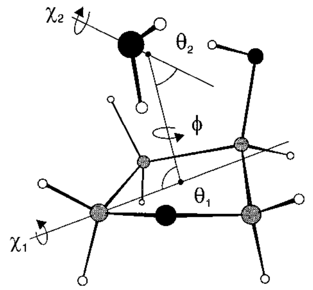

Figure 2. Intermolecular coordinates used in fitting the structure of 3-hydroxytetrahydrofuran−water. Not shown is R_{cm}, the distance between the centers of mass.

TABLE 5: Principal-Axis-System Coordinates (Å) of Isotopically Labeled Atoms from Kraitchman and ab Initio Calculations

	Kraitchman	ab initio
H_m		
a	±0.997 (2)	1.096
b	±1.175 (1)	−1.114
c	±0.264 (6)	−0.214
H_b		
a	±1.529 (1)	1.671
b	±0.990 (2)	0.792
c	±0.248 (6)	0.269
H_f		
a	±3.0911 (5)	3.038
b	±0.562 (3)	0.137
c	±0.408 (4)	0.401
O_w		
a	±2.342 (1)	2.347
b	±0.430 (3)	0.315
c	±0.233 (6)	−0.239

tetrahydrofuran monomer. While structure fits that adjusted the positions of the hydroxyl oxygen and hydrogen converged, these fits result in implausible bond lengths (1.516 Å for the $C_{3'}-O_h$ bond and 0.714 Å for the O_h-H_m bond) and poorly match the Kraitchman coordinates for all the substituted atom positions. Likewise, structure fits of the complex that also adjust the dihedral angles that define the ring pucker converged after adjusting the structure to a $C_{3'}$-exo ring pucker. This structure, too, is unlikely because of implausible bond lengths (0.826 Å for the O_h-H_m bond), bond angles (122° for the $C_{4'}-C_{3'}-O_h$ bond angle).

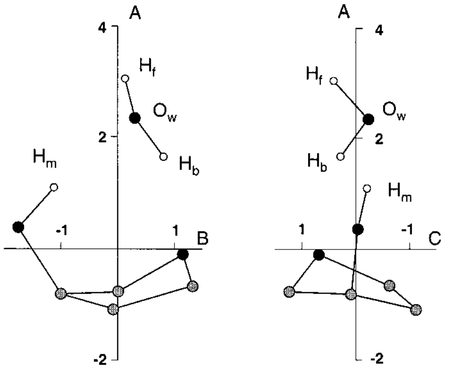

Figure 3. Projections of the lowest energy ab initio structure onto the *ab* and *ac* planes in the principal-inertial-axis coordinate system (Å) of the most abundant isotopic species.

TABLE 6: Kraitchman Coordinates (Å) of the Hydroxyl and Water Hydrogens in Principal-axis Coordinate Systems of Additional Isotopic Species

parent	H_m	H_b	H_f
furan-HOD	*d*-furan-HOD $a = \pm0.867$ $b = \pm1.243$ $c = \pm0.260$	furan-D_2O $a = \pm1.549$ $b = \pm0.901$ $c = \pm0.248$	furan-H_2O $a = \pm3.086$ $b = \pm0.439$ $c = \pm0.366$
furan-DOH	*d*-furan-DOH $a = \pm0.897$ $b = \pm1.246$ $c = \pm0.267$	furan-H_2O $a = \pm1.558$ $b = \pm0.913$ $c = \pm0.236$	furan-D_2O $a = \pm3.103$ $b = \pm0.367$ $c = \pm0.408$
d-furan-H_2O	furan-H_2O $a = \pm1.031$ $b = \pm1.127$ $c = \pm0.253$	*d*-furan-DOH $a = \pm1.461$ $b = \pm1.080$ $c = \pm0.251$	*d*-furan-HOD $a = \pm3.037$ $b = \pm0.752$ $c = \pm0.407$
furan-D_2O	*d*-furan-D_2O $a = \pm0.781$ $b = \pm1.292$ $c = \pm0.262$	furan-HOD $a = \pm1.563$ $b = \pm0.844$ $c = \pm0.238$	furan-DOH $a = \pm3.087$ $b = \pm0.290$ $c = \pm0.368$
d-furan-HOD	furan-HOD $a = \pm0.893$ $b = \pm1.209$ $c = \pm0.250$	*d*-furan-D_2O $a = \pm1.499$ $b = \pm0.973$ $c = \pm0.250$	*d*-furan-H_2O $a = \pm3.051$ $b = \pm0.575$ $c = \pm0.364$
d-furan-DOH	furan-DOH $a = \pm0.931$ $b = \pm1.204$ $c = \pm0.256$	*d*-furan-H_2O $a = \pm1.498$ $b = \pm1.000$ $c = \pm0.239$	*d*-furan-D_2O $a = \pm3.065$ $b = \pm0.544$ $c = \pm0.404$

The isotopic data were used to calculate the Kraitchman coordinates,[21,22] in the principal-axis coordinate system of the most abundant isotopomer, of the oxygen and hydrogen atoms of water, as well as of the hydroxyl hydrogen. Kraitchman and ab initio coordinates are compared in Table 5, and the ab initio structure is shown projected onto the principal axes in Figure 3. (The complete set of coordinates for the lowest energy ab initio structure is given in the Supporting Information.) The extensive data set for deuterated isotopomers allowed the calculation of Kraitchman coordinates for the water and hydroxyl hydrogens in the principal axis coordinates of six more parent isotopic species for each hydrogen; Kraitchman coordinates in these axis systems are given in Table 6. The coordinates are very similar, with small differences arising from rotation of the principal axes upon isotopic substitution. The similarity of the coordinates provides substantial evidence for the correct assignment of the spectra to the deuterated isotopomers. The *b*-coordinate of H_f, however, is inconsistent among the Kraitchman data set. The assignments of the spectra to these species are correct, however, because the same isotopic species (furan-H_2O, furan-D_2O, *d*-furan-HOD, furan-DOH, *d*-furan-H_2O, and *d*-furan-D_2O) were used in Kraitchman calculations of the hydroxyl and hydrogen-bonded water proton and give consistent coordinate values for those atomic coordinates.

The Kraitchman coordinates in Table 5 were used to calculate the water O_w-H bond lengths and the hydrogen bond length from the hydroxyl proton to the water oxygen. Sign information is lost for Kraitchman coordinates because only the squared coordinate values can be obtained from differences in the moments of inertia upon isotopic substitution. We used the signs of the ab initio atomic coordinates to calculate the interatomic distances of the substituted atoms and found 1.098 Å for the O_w-H_b bond length, 0.995 Å for the O_w-H_f bond length, and 2.094 Å for the H_m-O_w hydrogen bond length. While the Kraitchman value for the hydrogen bond length is reasonable, the water O_w-H_b bond length is 13% longer than in the water monomer.[23] The inconsistent structural data indicate that the experimental structures, from the Kraitchman method and least-squares fitting, represent average structures at the zero-point level of a large-amplitude vibrational coordinate.

Structure determinations of many water complexes have been complicated by large-amplitude vibrational motions. In many instances an angular momentum contribution to the rotational

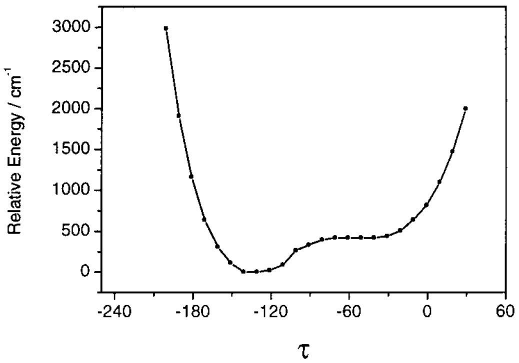

Figure 4. Relative energy (MP2/6-31G**) as a function of the wagging motion of water, $\tau = H_f-O_w-H_b-O_r$. The minimum energy configuration is at $\tau = -141°$.

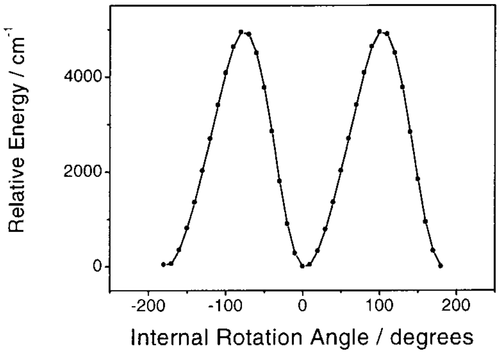

Figure 5. Relative energy (MP2/6-31G**) as a function of internal rotation about the water C_2 axis. The barrier to internal rotation is 4900 cm^{-1}.

constants arises from internal rotations if the spectra are analyzed using a semirigid-rotor model. If the internal motion exchanges equivalent protons (or any equivalent nuclei with nonzero spin), separate spectra arising from the even and odd spin states will arise; in such a case, the angular momentum from the internal rotation can be separated from the angular momentum of rotation by using an internal rotation Hamiltonian. Even if the internal motion does not exchange equivalent nuclei, differences in the extent of zero-point vibrational averaging among the isotopic species may make the isotopic moments of inertia inconsistent with any single structure. Structural analysis of the alaninamide−water[5] and dimethylamine−water[24] complexes, for example, was limited by vibrational-averaging effects despite the use of many isotopically labeled species.

3-Hydroxytetrahydrofuran−water has a hydrogen-bonded network similar to that found in alaninamide−water,[5] so a wagging motion of the free water hydrogen, H_f, is likely to have large amplitude. We mapped out the potential energy for the wagging motion by performing single-point calculations (MP2/6-31G**) of the energy along the τ coordinate, defined by the $H_f-O_w-H_b-O_r$ dihedral angle. The potential energy along this coordinate is plotted in Figure 4, and has a shallow minimum at $\tau = -141°$. This configuration directs one the lone pairs of the water oxygen toward the hydroxyl hydrogen, and the nonhydrogen-bonded water proton is oriented toward the pucker. We did not find a second minimum along the wagging coordinate at this level of theory, but the potential energy surface is shallow over a large range of the wagging coordinate. It should also be noted, that further geometry optimization along coordinates orthogonal to the wagging coordinate will reduce the single-point energies with respect to the minimum energy − further flattening the well. The shallow potential energy surface suggests that the 3-hydroxytetrahydrofuran−water complex undergoes a large amplitude vibrational motion along this coordinate.

We also calculated the barrier to internal rotation of water about its C_2 axis with a series single-point energy calculations (MP2/6-31G**). The potential energy surface for C_2 internal rotation of water is shown in Figure 5; the minimum energy orientation corresponds to an internal rotation angle of 0°. The 4900 cm^{-1} barrier between the wells is high enough to quench the appearance of tunneling doublets in the rotational spectrum.

Because of vibrational averaging, the ab initio calculations provide the most reliable details of the networked structure of 3-hydroxytetrahydrofuran−water. The weak intramolecular hydrogen bond reported for the 3-hydroxytetrahydrofuran monomer (2.351 Å in the ab initio structures;[11,12] 2.461 Å in the least-squares-fit structure − see above) is replaced by two stronger intermolecular hydrogen bonds between the monomer and water. The hydroxyl-to−water hydrogen bond length is 1.899 Å, the water-to-furanose hydrogen bond is 1.850 Å, and the hydrogen bond angles are 168° and 151°, respectively, in the lowest energy ab initio structure. Improved calculations, using a higher level of theory and including diffuse functions, are needed, however, to fully characterize the potential energy surface and floppy structure of this complex.

Conclusions

Rotational spectra have been recorded for nine isotopic species of the 3-hydroxytetrahydrofuran−water complex. The spectra are assigned to a doubly hydrogen-bonded structure of the complex, which is also the lowest energy ab initio structure (MP2/6-31G**). The structure of this complex is based on the lowest-energy ring-puckering conformation of the 3-hydroxytetrahydrofuran monomer ($C_{4'}$-endo). The ab initio structure was found to provide the best detailed description of the hydrogen bonds because least-squares fitting and Kraitchman analysis were affected by vibrational averaging along a wagging coordinate of the complex.

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Supporting Information Available: Nine tables of transitions frequencies for *d*-3-hydroxytetrahydrofuran and the isotopic species of 3-hydroxytetrahydrofuran−water and one table of principal-axis coordinates of the lowest energy ab initio structure. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Fraser, G. T. *Int. Rev. Phys. Chem.* **1991**, *10*, 189−206.

(2) Odutola, J. A.; Dyke, T. R. *J. Chem. Phys.* **1980**, *72*, 5062−5070.

(3) Lovas, F. J.; Suenram, R. D.; Fraser, G. T.; Gillies, C. W.; Zozom, J. *J. Chem Phys.* **1988**, *88*, 722−729.

(4) Held, A.; Pratt, D. W. *J. Am. Chem. Soc.* **1993**, *115*, 9708−9717.

(5) Lavrich, R. J.; Tubergen, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 2938−2943.

(6) Luger, P.; Buschmann, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 410.

(7) David, W. I. F.; Ibberson, R. M. *Acta Crystallogr., Sect. C.: Cryst. Struct. Commun.* **1992**, *48*, 301−303.

(8) Han, S. J.; Kang, Y. K. *J. Mol. Struct.* **1996**, *369*, 157−165.

(9) Engerholm, G. G.; Luntz, A. C.; Gwinn, W. D.; Harris, D. O. *J. Chem. Phys.* **1969**, *50*, 2446−2457.

(10) Meyer, R.; López, J. C.; Alonso, J. L.; Melandri, S.; Favero, P. G.; Caminati, W. *J. Chem. Phys.* **1999**, *111*, 7871−7880.

(11) Lavrich, R. J.; Rhea, R. L.; McCargar, J. W.; Tubergen, M. J. *J. Mol. Spectrosc.* **2000**, *199*, 138−143.

(12) Berthier, G.; Cadioli, B.; Gallinella, E.; Aamouche, A.; Ghomi, M. *J. Mol. Struct.* **1997**, *390*, 11−21.

(13) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33−45.

(14) Tubergen, M. J.; Flad, J. E.; Del Bene, J. E. *J. Chem. Phys.* **1997**, *107*, 2227−2231.

(15) Tanaka, K.; Ito, H.; Harada, K.; Tanaka, T. *J. Chem. Phys.* **1984**, *80*, 5893−5905.

(16) Watson, J. K. G. *J. Chem. Phys.* **1967**, *46*, 1935−1949.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94*, Revision E.3. Gaussian, Inc.: Pittsburgh, PA, 1995.

(18) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622.

(19) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1−19.

(20) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193−2218.

(21) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17−24.

(22) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Wiley: New York, 1984.

(23) Cook, R. L.; De Lucia, F. C.; Helminger, P. *J. Mol. Spectrosc.* **1974**, *53*, 62−76.

(24) Tubergen, M. J.; Kuczkowski, R. L. *J. Mol. Struct.* **1995**, *352*, 335−344.