J. Am. Chem. Soc. **1998,** *120,* 5555−5558

Conformation and Stability of Ether−Water Adducts: Free Jet Absorption Millimeter Wave Spectrum of 1,4-Dioxane−Water

Walther Caminati,* Adele Dell'Erba, Sonia Melandri, and Paolo G. Favero

Contribution from the Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna,
Via Selmi 2, I-40126 Bologna, Italy

Received November 18, 1997

Abstract: The free jet millimeter wave spectra of the 1:1 complex between 1,4-dioxane and four isotopomers of water (H_2O, D_2O, HDO, and $H_2{}^{18}O$) have been assigned. The water molecule lies in the plane of symmetry of 1,4-dioxane; the water hydrogen involved in the hydrogen bond is *axial* with respect to the ring, while the "free" hydrogen is *entgegen* to the ring. The three atoms involved in the hydrogen bond adopt a bent arrangement with a distance $O_{ring}\cdots H$ of about 1.90 Å and $\angle(O_{ring}\cdots H-O) \cong 163°$.

Introduction

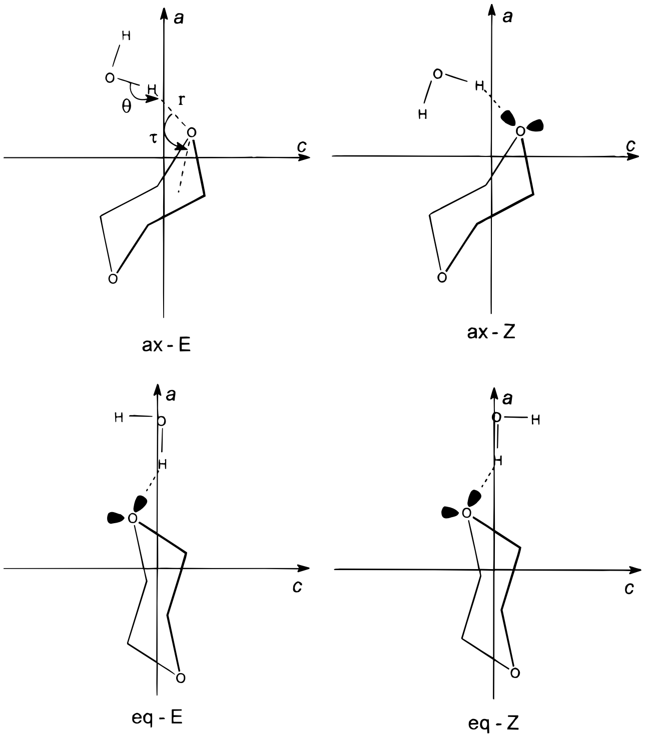

Figure 1. Plausible conformations and principal axes system in 14DX-water. *Ax-E* is the observed species.

The importance and role of intermolecular hydrogen bonding in chemistry, biology, and physics are well-known and have been discussed in several reviews.[1] Precise conformational, structural, and dynamical information has been obtained in the past decade on several hydrogen bonded adducts by free jet microwave or rotationally resolved spectroscopy. As to the microwave techniques, Molecular Beam Fourier Transform Microwave Spectroscopy (MBFTMW) has been mostly used.[2−10] Hydrogen bonds of the O−H···O kind, formed by a hydroxyl group as proton donor and an oxygen atom as proton acceptor, have the highest binding energy, about 20 kJ/mol; this energy rises to more than 50 kJ/mol when the hydrogen bond is resonance assisted.[11] This is for example the case for adducts of the kind R−COOH···R′−COOH, whose stability allowed the detection of the low-resolution rotational spectrum, consisting of μ_a-type bands, even at room temperature.[12] Later on the high-resolution spectrum has been obtained by MBFTMW[13] and this has given information on the dynamics of the proton transfer. The interest in the O−H···O bond lies in the fact that it is the leading interaction in the aqueous environment; nevertheless, not many adducts of this kind have been investigated by high-resolution spectroscopic techniques. Several investigations have been dedicated to the water dimer[14,15] or to water polymers.[16] Recently the rotational spectrum of the phenol−water[17] complex has been reported: the water molecule behaves as a proton acceptor and as a result of its internal

---

* To whom correspondence should be addressed.

(1) Pimentel, G. C.; McClellan, A. C. *The hydrogen bond*; Pauling, L., Ed.; Freeman: San Francisco, 1960. Vinogradov, S. N.; Linnell, R. H. *Hydrogen bonding*; van Nostrand Reinhold Co.: New York, 1971.

(2) Legon, A. C.; Suckley, A. P. *Chem. Phys. Lett.* **1988**, *150*, 153−158 and references therein.

(3) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, 257, 942.

(4) Lovas, F. J.; Zobov, N.; Fraser, G. T.; Suenram, R. D. *J. Mol. Spectrosc.* **1995**, *171*, 189−199.

(5) Lovas, F. J.; Lugez, C. L *J. Mol. Spectrosc.* **1996**, *179*, 320−323.

(6) Consalvo, D.; Stahl, W.; *J. Mol. Spectrosc.* **1995**, *174*, 520−535.

(7) Tubergen, M. J.; Andrews, A. M.; Kuczkowski, R. L. *J. Phys. Chem.* **1993**, *97*, 7451−7457.

(8) Andrews, A. M.; Kuczkowski, R. L. *J. Chem. Phys.* **1993**, *98*, 791−795.

(9) Makarewicz, J.; Ha, T. K.; Bauder, A. *J. Chem. Phys.* **1993**, *99*, 3694−3699.

(10) Leung, H. O.; Marshall, M. D.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1989**, *90*, 700−712.

(11) Borisenko, K. B.; Hargittai, I. *J. Phys. Chem.* **1993**, *97*, 4080−4084.

(12) Constain, C. C.; Srivastava, G. P. *J. Chem. Phys.* **1961**, *35*, 1903; **1964**, *41*, 1620.

(13) Martinache, L.; Kresa, W.; Wegener, M.; Vonmont, U.; Bauder, A. *Chem. Phys.* **1990**, *148*, 129−140.

(14) Dyke, T. R.; Mack, K. M.; Muenter, J. S. *J. Chem. Phys.* **1977**, *66*, 498.

(15) Fraser, G. T.; Suenram, R. D.; Coudert, L. H. *J. Chem. Phys.* **1989**, *90*, 6077−6085.

(16) Olthof, E. H. T.; van der Avoird, A.; Wormer, P. E. S.; Liu, K.; Saykally, R. J. *J. Chem. Phys.* **1996**, *105*, 8051−8063. Cruzan, J. D.; Brown, M. G.; Liu, K.; Braly, L. B.; Saykally, R. J. *J. Chem. Phys.* **1996**, *105*, 6634−6644.

(17) Gerhards, M.; Schmitt, M.; Kleinermanns, K.; Stahl, W. *J. Chem. Phys.* **1996**, *104*, 967−971.

S0002-7863(97)03958-9 CCC: $15.00

Table 1: Frequencies of Measured Transitions of 14DX-water (MHz)

$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	H_2O	$H_2{}^{18}O$	DOH	D_2O
10(10)−9(9)[a]	60672.14	60214.78	60669.82	60451.11
11(9)−10(8)[a]	61561.21	60794.23	61463.91	60989.5
11(10)−10(9)[a]	64212.22	63580.76	64163.94	63809.62
11(11)−10(10)[a]	66865.28		66865.65	66631.28
12(7)−11(6)[a]	59803.53			
12(8)−11(7)[a]	62452.21	61375.61	62258.97	61529.07
12(9)−11(8)[a]	65100.85	64159.59	64957.2	64347.47
12(10)−11(9)[a]	67750.78	66945.03	67656.38	67166.70
12(11)−11(10)[a]	70402.72		70357.12	69987.44
12(12)−11(11)[a]	73056.85		73059.82	72809.83
13(6,8)−12(5,8)	60688.01		60349.01	
13(6,7)−12(5,7)	60686.84		60348.19	
13(7)−12(6)[a]	63341.29	61956.70	63052.09	62067.43
13(8)−12(7)[a]	65990.22	64739.88	65750.82	64885.85
13(9)−12(8)[a]	68638.43	67523.09	68448.65	67703.72
13(10)−12(9)[a]	71287.49	70307.59	71147.03	70522.2
13(11)−12(10)[a]	73938.21		73846.82	73342.00
13(12)−12(11)[a]	76591.19		76548.41	76163.39
14(5,10)−13(4,10)	61562.44	59738.62	61126.42	59768.41
14(5,9)−13(4,9)	61505.16	59713.76	61076.18	59738.78
14(6,9)−13(5,9)	64219.46	62531.32	63834.53	62597.59
14(6,8)−13(5,8)	64217.05	62530.31	63832.47	62596.50
14(7)−13(6)[a]	66875.90	65318.59	66540.68	65421.53
14(8)−13(7)[a]	69525.87	68102.06	69240.35	68240.59
14(9)−13(8)[a]	72174.00	70884.56	71937.94	71058.17
14(10)−13(9)[a]	74822.21	73668.13	74635.79	73876.02
14(11)−13(10)[a]	77471.83		77334.65	76694.88
15(4,12)−14(3,12)	62699.50	60450.49	62144.56	60456.12
15(4,11)−14(3,11)	61786.44	59902.37	61293.76	59837.68
15(5,11)−14(4,11)	65093.33	63094.29	64610.15	63115.98
15(5,10)−14(4,10)	64992.79	63050.44	64521.53	63063.71
15(6,10)−14(5,10)	67746.72	65887.85	67316.00	65945.94
15(6,9)−14(5,9)	67741.74	65886.18	67311.87	65943.76
15(7)−14(6)[a]	70407.33	68678.18	70025.97	68773.12
15(8)−14(7)[a]		71461.76	72727.32	
15(9)−14(8)[a]	75706.57	74243.91	75425.29	
15(10)−14(9)[a]		77026.62		77227.88
16(4,13)−15(3,13)	66338.40	63869.72	65728.33	63875.47
16(4,12)−15(3,12)	65101.70	63099.57	64567.94	63012.03
16(5,12)−15(4,12)	68625.00	66448.12	68093.98	66462.29
16(5,11)−15(4,11)	68457.33	66373.85	67946.01	66373.93
16(6,11)−15(5,11)	71269.34	69240.57		69290.34
16(6,10)−15(5,10)	71259.33	69237.21		69286.20
16(7)−15(6)[a]	73934.35	72034.03		72121.73
16(8)−15(7)[a]	76588.57	74819.23		
16(9)−15(8)[a]		77601.00		
17(4,14)−16(3,14)	70005.94	67307.04	69339.35	67315.62
17(4,13)−16(3,13)	68402.15	66266.11	67822.76	66156.44
17(5,13)−16(4,13)	72160.00	69801.12		69808.28
17(5,12)−16(4,12)	71892.20	69680.35		69665.16
17(6,12)−16(5,12)	74787.00	72589.15		72630.82
17(6,11)−16(5,11)	74768.17	72582.68		72622.66
17(7)−16(6)[a]	77457.61	75386.59		75466.76
17(8)−16(7)[a]		78173.35		
18(4,15)−17(3,15)	73706.06	70765.38		
18(4,14)−17(3,14)	71707.24	69409.12		
18(5,14)−17(4,14)	75701.94	73154.61		
18(5,13)−17(4,13)	75291.00	72965.7		
18(6,13)−17(5,13)		75933.15		
18(6,12)−17(5,12)		75921.7		
19(4,16)−18(3,16)		74248.38		
19(4,15)−18(3,15)		72539.88		
19(5,15)−18(4,15)		76510.88		
19(5,14)−18(4,14)		76224.38		

[a] Transitions doubly overlapped due to the near prolate degeneracy of the involved levels. Only K_a is given.

motions a doubling of each rotational transition was observed. Rotationally resolved laser induced fluorescence also has been applied to these kinds of problems, for example, in the case of pyridinone−water,[18] which is stabilized by a double hydrogen bond.

Table 2. Rotational and Centrifugal Distortion Constants ("S" Reduction and I^r Representation) and Planar Moments of Inertia of 1,4-Dioxane−Water

water:	normal	$H_2{}^{18}O$	D′OH[a]	D_2O
A (MHz)	3101.25(4)[b]	3081.75(6)	3102.29(4)	3094.34(4)
B (MHz)	1817.60(2)	1723.64(2)	1793.03(2)	1720.76(2)
C (MHz)	1735.79(2)	1655.55(2)	1712.83(2))	1648.72(2)
D_J (kHz)	4.07(2)	3.82(2)	3.92(3)	3.47(2)
D_{JK} (kHz)	16.2(2)	16.5(2)	14.0(2)	13.1(1)
D_K (kHz)	-13.7(3)	-13.8(5)	-11.7(2)	-10.3(2)
d_1 (kHz)	0.45(2)	0.40(1)	0.42(2)	0.38(2)
d_2 (kHz)	0.105(4)	0.078(4)	0.088(7)	0.083(6)
H_{KJ} (Hz)	4.9(8)	5.4(10)	3.5(8)	4.9(8)
H_K (Hz)	-4.6(6)	−5.1(15)	-3.9(5)	-4.6(6)
N[c]	54	55	41	46
σ (MHz)	0.10	0.09	0.07	0.06
M_{aa} (u Å^2)	203.120	217.239	207.003	218.450
M_{bb} (u Å^2)	88.032	88.025	88.051	88.078
M_{cc} (u Å^2)	74.928	75.965	74.855	75.246

[a] The primed hydrogen participates in the hydrogen bond. [b] Error in parentheses is expressed in units of the last digit. [c] Number of transitions in the fit.

Table 3: Comparison of the Experimental Rotational Constants (MHz) and of the Substitution Coordinates (Å) of the Normal Species to the Trial Calculated Values of the Four Conformers

		calcd[a]			
	exptl	*ax-E*	*ax-Z*	*eq-E*	*eq-Z*
A	3101.2	3071.9	3024.4	4887.7	4839.7
B	1817.6	1874.6	1905.8	1429.7	1440.2
C	1735.8	1797.2	1843.1	1185.7	1195.8
$\lvert a\rvert$ (O)	2.67	2.60	2.63	3.36	3.37
$\lvert b\rvert$ (O)	0.0	0.0	0.0	0.0	0.0
$\lvert c\rvert$ (O)	0.76	0.81	0.74	0.26	0.18
$\lvert a\rvert$ (H′)	1.98	1.89	1.91	2.44	2.45
$\lvert b\rvert$ (H′)	0.14	0.0	0.0	0.0	0.0
$\lvert c\rvert$ (H’)	0.28	0.16	0.10	0.00	0.07
$\lvert a\rvert$ (H)[b]	3.40	3.40	2.19	3.85	3.36
$\lvert b\rvert$ (H)	0.17	0.0	0.0	0.0	0.0
$\lvert c\rvert$ (H)	0.65	0.30	1.59	0.56	1.14

[a] The geometries of water and 14DX have been fixed and (see text) an O···H−O linear arrangement with a O···H distance of 1.90 Å was assumed. The primed hydrogen participates in the hydrogen bond. [b] Obtained from the *a*-coordinate of H in the 14DX-D′OH principal system by adding the difference between the *a*-coordinates of H in the 14DX-H_2O and 14DX-D′OH principal systems.

Rather surprisingly, while infrared spectroscopy studies of hydrogen bonded complexes of water with ethers have been reported,[19] no data are available, to our knowledge, concerning their rotationally resolved spectra. For this kind of adduct the water moiety must act as a proton donor. Since with supersonic jet millimeter-wave absorption spectroscopy (a simpler technique with respect to MBFTMW) we have recently been successful in investigating molecular complexes of ring molecules with argon[20−22] and water,[23] we also applied this technique to the study of complexes of water with cyclic ethers. We chose 1,4-dioxane (14DX, see Figure 1) as a prototype because in this case only the spectrum of the adduct is observable in the ether/water mixture since 14DX does not possess a rotational spectrum (the electric dipole moment, μ, is zero by symmetry). Moreover,

---

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

(19) Paul, S. O.; Ford, T. A. *Spectrochim. Acta* **1981**, *37A*, 415−420.

(20) Melandri, S.; Maccaferri, G.; Maris, A.; Millemaggi, A.; Caminati, W.; Favero, P. G. *Chem. Phys. Lett.* **1996**, *261*, 267−271.

(21) Caminati, W.; Melandri, S.; Favero, P. G.; Meyer, R. *Chem. Phys. Lett.* **1997**, *268*, 393−400.

(22) Caminati, W.; Melandri, S.; Favero, P. G.; Makarewicz, J. *Mol. Phys.* **1997**, *91*, 663−667.

(23) Caminati, W.; Favero, L. B.; Favero, P. G.; Maris, A.; Melandri, S. *Angew.Chem., Int. Ed. Engl.* **1998**, *37*, 792−795.

Table 4. r_0 Hydrogen Bond Parameters Obtained by Fixing the Geometries of Water and 14DX to the Values of the Isolated Molecules

(1) r_0 Hydrogen Bond Parameters (Å and deg, see Figure 1)

$r = 1.90(3)$	$\tau = 128(3)$	$\theta = 163(6)$	$R^b = 3.34(4)$

(2) r_s Coordinates (Å)

	$\|a\|$		$\|b\|$		$\|c\|$	
atom	exptl	calcd[c]	exptl	calcd[c]	exptl	calcd[c]
O	2.669(5)[d]	2.659	0.00	0.0	0.76(2)	0.791
H′	1.97(1)	2.080	0.14(18)	0.0	0.28(9)	0.029
H	3.40(1)[e]	3.542	0.17(17)	0.0	0.65(5)	0.422

(3) Rotational Constant

rot. const. (MHz)	normal		$H_2{}^{18}O$		D′OH[a]		D_2O	
	exptl	calcd[c]	exptl	calcd[c]	exptl	calcd[c]	exptl	calcd[c]
A	3101.3	3105.5	3081.8	3084.4	3102.3	3105.4	3094.3	3102.4
B	1817.6	1820.5	1723.6	1726.3	1793.0	1792.6	1720.8	1716.3
C	1735.8	1736.7	1655.6	1656.8	1712.8	1711.4	1648.7	1642.5

[a] The experimental substitution coordinates of the water atoms and rotational constants are compared to the values calculated with this geometry. The primed hydrogen participates in the hydrogen bond. [b] Distance between the centers of mass of the monomers. [c] Calculated with the r_0 structure (see top of the table and text). [d] Error (in parentheses) is expressed in units of the last digit. [e] Obtained from the *a*-coordinate of H in the 14DX-D′OH principal system by adding the difference between the *a*-coordinates of H in the 14DX-H_2O and 14DX-D′OH principal systems.

interaction of water with 14DX is of interest in the atmospheric degradation of 14DX.[24]

Experimental Section

The 60−78 GHz Stark and pulse modulated free jet absorption millimeter-wave spectrometer used in this study has been described elsewhere.[20,25] The adducts were formed with flowing Argon, at room temperature and at a pressure of ca. 0.7 bar, over a solution of 14DX and water in a molecular ratio 2/1. The mixture was then expanded to about 5×10^{-3} mbar through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm, reaching an estimated "rotational" temperature of about 10 K. All samples were commercial and have been used without further purification. The accuracy of the frequency measurements was estimated to be 0.05 MHz.

Rotational Spectrum

If one assumes that the hydrogen bond takes place along one of the oxygen lone electronic pairs (LEP) and that the complex possesses a plane of symmetry, four conformational possibilities are left for the overall configuration of the adduct: *ax-E*, *ax-Z*, *eq-E*, and *eq-Z* (see Figure 1). The first letter indicates the *axial* or *equatorial* position of the hydrogen involved in the hydrogen bond (H′), while the second one is relative to the *entgegen* (*E*) or *zuzammen* (*Z*) position of the water hydrogen not involved in the hydrogen bond (H). Trial rotational constants were calculated for these four cases based on the geometries of isolated 14DX,[26] and water, and assuming an O···H distance of 1.90 Å[17] within an O···H−O linear arrangement.

The microwave spectrum of each isotopic species (14DX with H_2O, D_2O, HDO, and $H_2{}^{18}O$) consisted of one set of rotational transitions whose frequencies are reported in Table 1. Two points concerning the main features of the spectrum are worth mentioning: first of all differently from the case of the phenol−water[16] and pyrazine−water[23] complexes, none of the observed transitions was split or shifted for large amplitude motion effects of the water moiety, suggesting that water should be quite "rigid" within the 14DX−H_2O complex. It is also interesting to note that in the case of the 14DX−HDO complex, in principle two isotopomers could have been formed, with H or D involved in the intermolecular bond, but only the spectrum of the 14DX−D′OH species was observed (the primed atom is the one involved in the hydrogen bond). This effect is probably due to the lower zero point energy of the 14DX···D′OH complex with respect to the 14DX···H′OD one.

The rotational frequencies have been fitted with the Watson Hamiltonian[27] (I^r, representation; S, reduction); the full set of quartic and two sextic centrifugal distortion parameters have been determined. The results of the fittings are shown in Table 2. The centrifugal distortion parameters may be regarded as effective fitting parameters. Their interpretation is discussed in a following section.

Conformation and Structure

The planar moments of inertia, M_{aa}, M_{bb}, M_{cc}, defined as:

$$M_{aa} = \sum m_i a_i^2, \text{ etc.} \tag{1}$$

are easily obtained from the rotational constants through the following relation:

$$M_{aa} = h/(16\pi^2)(-1/A + 1/B + 1/C), \text{ etc.} \tag{2}$$

They are very useful in visualizing the mass extension along a given axis, and are reported in Table 2 for the four isotopic species. Since the M_{bb} values are about the same for the four species, we can argue that all atoms of the water moiety lie in the *ac* plane of symmetry of 14DX, and therefore the *ac* plane is also a symmetry element of the complex. In Table 3 the experimental rotational constants and the r_s substitution coordinates[28] of O, H′, and H of the normal species are compared to the values calculated from the above-mentioned geometry of the four conformers of Figure 1, i.e. assuming a O···H distance of 1.90 Å[17] within an O···H−O linear arrangement. Although the large-amplitude motions of the water moiety and the Ubbelhode effect,[29] that is the shrinking of the hydrogen bond upon deuteration, make the r_s substitution coordinates[28] not highly reliable, they have often been used for qualitative

---

(24) Platz, J.; Sehested, J.; Møgelberg, T.; Nielsen, O. J.; Wallington, T. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2855−2863.

(25) Melandri, S.; Caminati, W.; Favero, L. B.; Millemaggi, A.; Favero, P. G. *J. Mol. Struct.* **1995**, *352/353*, 253−258.

(26) Davis, M.; Hassel, O. *Acta Chem. Scand.* **1963**, *17*, 1181.

(27) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York/Amsterdam, 1977; Vol. 6, p 1.

(28) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17−25.

(29) Ubbelhode, A. R.; Gallagher, K. J. *Acta Crystallogr.* **1955**, *8*, 71−83.

considerations. In this way it is easy to see that the best match between calculated and experimental data is for the *ax-E* configuration. The small nonzero $|b|$ values of the oxygen atom and of the hydrogen involved in the hydrogen bond are likely due to the large-amplitude motions which are usually present in this kind of molecular complex (see for example ref 21), and therefore are compatible with zero equilibrium values. The larger $|c|$ value for the hydrogen not involved in the hydrogen bond is indicative that this atom does not lie along the *a*-axis, but in any case, it lies in the *ac*-plane.

Rough dipole−dipole interaction energy calculations based on bond dipoles indicate the *ax-E* conformer to be the most stable one, in agreement with our observations. With respect to *ax-E*, the energies of the remaining species were calculated to be 1.02, 0.99, and 0.37 kcal/mol for *ax-Z*, *eq-E*, and *eq-Z*, respectively. In the calculations standard bond moments[30] were used for 14DX, while the dipole moment of the monomer was used for water. This is somehow arbitrary because a considerable enhancement of the dipole moment of water has been observed[31] in water clusters (about 15% for water dimer), but it is difficult to estimate this effect for the present adduct.

After having assigned the observed spectrum to conformer *ax-E* we performed a partial refinement of the structure in order to have a better agreement, with respect to that of Table 3, between observed and calculated rotational constants and substitution coordinates. The hydrogen bond parameters were adjusted while the geometries of the two subunits were taken as in the isolated water and 14DX.[26] The so obtained r_0 hydrogen bond parameters (in units of angstroms and degrees) are given in Table 4, together with experimental and calculated rotational constants and substitution coordinates. The main result of this structural refinement is that the O···H−O arrangement is not linear.

Internal Motions

Upon formation of the molecular complex, the three translational and the three rotational degrees of freedom of the isolated water molecule are replaced by six low-energy vibrational modes. One of these motions can be considered the stretching between the two centers of mass of the two constituent molecules, while the remaining ones can be thought of as two bendings and three internal rotations of the water moiety. In the case of phenol−water and pyrazine−water these internal rotations connect equivalent minima, and generate Coriolis doubling of rotational lines. This is not the case for 14DX−H_2O, for which only one set of rotational lines has been observed. As to the stretching and bending motions of water with respect to the 14DX ring, their effects are reflected in the anomalous high values of the D_J, D_{JK} and D_K centrifugal distortion parameters, as was suggested also for several of the complexes of aromatic molecules with rare gases. The pseudodiatomic force constant of the van der Waals stretching vibration can be rather straightforwardly obtained from the rotational spectrum when such a motion takes place along a symmetry axis of the complex.[32] The value of this force constant was obtained also for complexes without this symmetry element, but with the stretching coordinate accidentally almost along the *a*-axis.[4] It is not possible to apply this approximation to 14DX−H_2O because the angle between the *a*-axis and the H···O bond is about 45°.

Conclusions

This is, to our knowledge, the first report of the rotational spectrum of an adduct formed by one molecule of water and an ether. In agreement with the fact that −O−H···O is a very strong intermolecular hydrogen bond, and that 14DX does not have high molecular symmetry, only one set of rotational transitions of the 14DX−water complex has been observed and assigned in the jet-cooled mixture. By investigating several isotopic species the observed spectrum has been assigned to the *ax-e* conformer (see Figure 1). The results of simple dipole−dipole interaction energy calculations confirm that the observed conformer is the most stable one. The three remaining plausible conformers (see Figure 1), if formed at room temperature or in an intermediate step, relax during the adiabatic expansion to the most stable one, and this suggests relatively low barriers to the conformational interconversion.[33]

The structure compatible with the experimental observations is characterized by a nonlinear O···H−O hydrogen bond. This has been observed also in complexes of ethers with halogenhydric acids in the cases of 2,5-dihydrofuran···H−Cl[34] and 2,5-dihydrofuran···H−Br.[35]

Acknowledgment. We thank Mr. A. Millemaggi for technical help, and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica and the C.N.R. for financial support.

JA973958B

---

[30] Minkin, V. I.; Ossipov, O. A.; Zhdanov, Yu. A. *Dipole Moments in Organic Chemistry*; Plenum: New York, 1970.

[31] Gregory, J. K.; Clary, D. C.; Liu, K.; Brown, M. G.; Saykally, R. J. *Science* **1997**, *275*, 814−820.

[32] Millen, D. J. *Can. J. Chem.* **1985**, *63*, 1477−1479.

[33] Godfrey, P. D.; Rodgers, F. M.; Brown, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 2232−2239.

[34] Legon, A. C.; Thorn, J. C. *Chem. Phys. Lett.* **1994**, *227*, 472−479.

[35] Cooke, S. A.; Corlett, G. K.; Evans, C. M.; Legon, A. C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2973−2976.