Interactions Between Organic Molecules and Water: Rotational Spectrum of the 1:1 Oxetane–Water complex

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Abstract: The 1:1 molecular complex between oxetane and water has been investigated by using free-jet millimeter-wave spectroscopy. The rotational spectra of five isotopomers (with H_2O, D_2O, DOH, HOD and $H_2{}^{18}O$) have been assigned. Partial r_0 and r_s structures of the complex have been derived. The water moiety lies in the plane of symmetry of oxetane, with the "free" hydrogen *E* with respect to the ring. The oxetane ring appears to be slightly nonplanar, with the C_β carbon tilted on the opposite side of the water unity. The three atoms involved in the hydrogen bond adopt a linear arrangement with an $O_{ring}{\cdots}H$ distance of about 1.86 Å, and the angle between the COC bisector and the $O_{ring}{\cdots}H$ bond being ≅106°. Additionally, quantum-chemical calculations for the complex were performed and were found to be in agreement with the experimental results.

Keywords: ab initio calculations · free-jet spectroscopy · hydrogen bonds · molecular adducts · rotational spectroscopy

Introduction

The study of isolated 1:1 complexes of organic molecules with water helps in the understanding of their solvation mechanism. Several spectroscopic techniques, generally associated with supersonic expansions, have been used for this purpose. We believe that rotationally resolved spectroscopies provide the most detailed and precise experimental data. When the "solvated" molecules contain a chromophoric group, either laser-induced fluorescence (LIF) and related techniques, or pure rotational spectroscopy can be used. This is the case, for example, of the indole–water complex.[1,2]

Aliphatic ethers are not chromophores, therefore the use of LIF is not suitable to study their complexes with water. This is probably the reason why only pure rotational spectra has been reported for just a few of these systems. We studied the rotational spectra of the first adducts of water with ethers. We found that in 1,4-dioxane–water[3] and tetrahydropyran–water,[4] the water molecule is linked in an axial arrangement, with the "free" hydrogen *E* with respect to the ring. In the cases of oxirane–water and dimethylether–water the notation "axial" or "equatorial" is meaningless, since for both oxirane and dimethylether the two lone pairs of the oxygen ring are equivalent. The water molecule can tunnel between these two equivalent lone-pairs, and the effects of this motion on the rotational spectrum can be useful to determine the potential-energy surface for the transfer of the protic group. This is the case, indeed, for dimethylether–water,[5] while in the case of oxirane–water,[6] no tunneling effects have been observed.

Oxetane (OXE) is somehow intermediate between oxirane and dimethyl ether, for example the COC angle is 91.5°, intermediate with respect to the values 61.7 and 111.7° for oxirane and dimethyl ether, respectively. In addition, since OXE executes a ring-puckering motion with a barrier below the vibrational ground-state, its conformation is "effectively" planar, but not exactly planar.[7,8] These two factors could alter the features of the rotational spectrum of the complex with water (OXE–W, see Figure 1), with respect to the ether–water adducts previously reported. For this reason, we decided to investigate its free-jet millimeter-wave absorption spectrum. Complexes of OXE with Ar,[9] HF,[10] and HCl[11] have already been investigated, and no doubling of lines from internal motions have been observed.

Results and Discussion

Rotational spectrum: We started the search with an estimate geometry based upon the structure of the oxetane monomer,[12] and upon the parameters of the hydrogen bond in

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DOI: 10.1002/chem.200305516

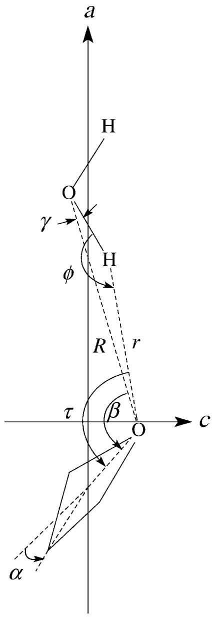

Figure 1. Observed configuration and definition of the main structural parameters of OXE–W.

the complex 1,4-dioxane-water.[3] We found four μ_a-type R bands, typical of a near-prolate top, evenly spaced by the $B+C$ value, and with J in the range from 11 to 16. We could measure single transitions with K_a, in the range from 0–10. The rotational frequencies have been fitted with Watsons hamiltonian (I^r representation, S reduction),[13] which determine all the quartic-centrifugal-distortion constants, except for D_K, and the sextic H_{KJ} parameter. No detectable inversion splitting was observed.

We then recorded the rotational spectrum of the other four isotopomers (oxetane with D_2O, DOH, HOD, and $H_2{}^{18}O$), and the fitting procedure described above was repeated for each isotopomer.

All measured transitions are listed in Table 1, while the fitted spectroscopic parameters are shown in Table 2.

Abstract in Italian: *Il complesso molecolare 1:1 fra ossetano ed acqua è stato studiato con spettroscopia millimetrica di assorbimento in espansione supersonica. Sono stati assegnati gli spettri rotazionali di cinque isotopomeri dell'acqua (H_2O, D_2O, DOH, HOD and $H_2{}^{18}O$) nel complesso. Sono state ottenute strutture parziali r_0 ed r_s del complesso. L'acqua si trova nel piano di simmetria dell'ossetano che passa per gli atomi O e C_β, con L'atomo di idrogeno "libero" e rispetto all'anello. L'ossetano è lievemente non-planare, con L'atomo di carbonio C_β piegato dalla parte opposta rispetto a quella in cui si trova l'acqua. I tre atomi coinvolti nel legame a ponte idrogeno hanno una configurazione lineare, con una distanza $O_{ring}\cdots H$ di circa 1.86 Å, e con l'angolo fra la bisettrice di COC ed il legame $O_{ring}\cdots H$ di circa 106°. Sono inoltre stati fatti dei calcoli ab initio per il complesso, che sono risultati in accordo con i dati sperimentali.*

We may note from their spectra that the transitions of the two monodeuterated species have different intensities, that is, the spectrum of the OXE–DOH species is about three times stronger than that of the OXE–HOD species. Such an effect, observed also for oxirane–water,[5] is due to the lower zero-point energy of the monodeuterated species.

The centrifugal distortion parameters, which are much larger than those of "normal" molecules, may be regarded as effective-fit parameters. In a more detailed analysis, the large values of the D_J and D_{JK} parameters could give information on the low-energy motions of the water molecule with respect to the ring. The value of D_{JK} (−68.7 kHz) is, for example, almost the opposite of the corresponding value for the similar oxirane–water complex ($D_{JK} = 104.4$ kHz). However, the interpretation of this discrepancy appears to be prohibitive, in that the water moiety is characterized by six large-amplitude vibrations with respect to the OXE moiety. Even though it is not directly related to these constants, the observation of vibrational doubling of lines would give some more easily-handling information on such a multidimensional potential-energy surface.

Conformation and structure: In all the studied ether–water complexes, the water molecule lies on the *ac* plane of symmetry of the ether molecule, which is also the plane of symmetry of the complex. This feature is clearly shown when taking into account the planar moment of inertia for the complex (M_{bb}) along the *b* axis.

M_{bb} ($=\Sigma_i m_i b_i^2$) represents the mass extension along the principal axis *b*, which is perpendicular to the *ac* plane, and is obtained from the rotational constants, through Equation (1).

$$M_{bb} = h/(16\pi^2)(-1/B + 1/A + 1/C) \qquad (1)$$

The M_{bb} values of OXE and the five isotopomers of OXE–W are reported in Table 3. One can see that they have almost the same values, which indicates that all the water atoms lie in the *ac* plane.

The values of r_s coordinates[14] for the water atoms (see Table 4) rule out the *Z* configuration of the the "free" water hydrogens. The small non-zero $|b|$ values are consistent with the contributions due to the large amplitude motions of the water moiety in the complex. Caution is needed to consider the r_s position of a hydrogen atom involved in a hydrogen bond, since the H→D isotopic substitution produces a shrinking of the distance between the heavy atoms involved in the hydrogen bond (Ubbelhode effect[15]). The water H–H distance, obtained from the r_s coordinates of the two water hydrogens for the OXE–H_2O and OXE–D_2O are quite similar (1.449 and 1.436 Å, respectively); this suggests the Ubbelhode effect, as well as other vibrational effects, to be almost negligible.

A partial r_0 structure was calculated from the experimental rotational constants of the five isotopomers. The geometries of oxetane and water were kept constant, while fitting the *R* (the O–O distance), α and β parameters of Figure 1, except for the non-zero value of α, which measures the degree of non-planarity of OXE upon the formation of the

Table 1. Frequencies for measured transitions of OXE···W [MHz].

$J'(K_a',K_c')\leftarrow J''(K_a'',K_c'')$	OXE···H_2O	OXE···$H_2{}^{18}O$	OXE···DOH	OXE···HOD	OXE···D_2O
12(0,12)-11(0,11)	60613.60		59781.36		
12(1,12)-11(1,11)	60267.08				
12(1,11)-11(1,10)	61998.47		61126.00		
12(2,11)-11(2,10)	61216.53		60358.29		
12(2,10)-11(2,9)	61944.33		61053.14		
12(3,10)-11(3,9)	61439.49		60570.32		
12(3,9)-11(3,8)	61513.24		60638.43		
12(4,9)-11(4,8)	61434.34		60565.64		
12(4,8)-11(4,7)	61436.86				
12(5)-11(5)[a]	61428.41		60560.97		
12(6)-11(6)[a]	61434.92		60567.90		
12(7)-11(7)[a]	61449.44		60583.36		
12(8)-11(8)[a]	61469.62		60603.86		
12(9)-11(9)[a]	61494.19		60629.00		
12(10)-11(10)[a]	61522.84		60658.07		
12(11)-11(11)[a]	61554.97				
13(0,13)-12(0,12)	65542.42	61915.56	64644.83	62563.47	61768.10
13(1,13)-12(1,12)		61588.52	64329.46	62239.10	61440.83
13(1,12)-12(1,11)	67083.48	63225.66	66143.07	63919.12	63089.73
13(2,12)-12(2,11)	66264.14	62486.44	65337.21	63163.20	62345.55
13(2,11)-12(2,10)	67146.52	63176.39	66181.36	63890.07	63043.93
13(3,11)-12(3,10)	66539.98	62698.25	65600.07	63386.76	62560.03
13(3,10)-12(3,9)	66649.85	62768.66	65701.17	63464.03	62631.80
13(4,10)-12(4,9)	66537.93	62694.24	65597.63	63382.60	62555.87
13(4,9)-12(4,8)	66542.41	62696.67	65601.40	63385.41	62558.33
13(5,9)-12(5,8)	66528.01	62689.44	65589.13	63376.38	62550.77
13(6)-12(6)[a]	66532.91	62696.67	65594.93	63382.64	62557.73
13(7)-12(7)[a]	66547.23	62711.55	65610.20	63396.79	62572.47
13(8)-12(8)[a]	66568.39	62731.87	65631.53	63416.52	62592.47
13(9)-12(9)[a]	66594.28	62756.67	65658.27		62617.43
13(10)-12(10)[a]	66624.90	62785.20			62646.00
14(0,14)-13(0,13)	70456.73	66566.57	69494.07	67262.52	66409.64
14(1,14)-13(1,13)	70184.67	66270.80	69215.93	66971.37	66113.96
14(1,13)-13(1,12)	72145.90	68013.83	71138.83	68758.10	67868.74
14(2,13)-13(2,12)	71299.07	67241.47	70303.87	67969.90	67091.79
14(2,12)-13(2,11)	72342.86	68066.67		68837.24	67926.50
14(3,12)-13(3,11)	71633.79	67499.54	70623.17	68242.15	67353.00
14(3,11)-13(3,10)	71791.90	67601.20	70768.80	68353.69	67456.77
14(4,11)-13(4,10)	71637.54	67498.19		68241.06	67351.56
14(4,10)-13(4,9)	71645.19	67502.34	70632.63	68245.72	67355.83
14(5)-13(5)[a]	71623.05	67489.98	70613.07	68231.20	67342.97
14(6)-13(6)[a]	71625.72	67495.80	70616.93	68235.89	67348.56
14(7)-13(7)[a]	71639.64			68250.00	67363.27
14(8)-13(8)[a]	71661.17		70653.87	68270.34	67384.33
14(9)-13(9)[a]	71688.69		70681.90		67410.40
14(10)-13(10)[a]	71721.10		70714.87		67440.80
15(0,15)-14(0,14)	75359.14		74331.28		71038.83
15(1,15)-14(1,14)	75125.53		74090.88		70776.83
15(1,14)-14(1,13)	77183.31		76111.08		72628.89
15(2,14)-14(2,13)	76320.27		75257.71		71826.94
15(2,13)-14(2,12)			76419.14		72804.15
15(3,13)-14(3,12)	76719.72		75638.94		72139.87
15(3,12)-14(3,11)			75842.43		72285.53
15(4,12)-14(4,11)	76732.79		75650.00		72143.57
15(4,11)-14(4,10)	76745.34		75661.13		72150.53
15(5)-14(5)[a]			75632.53		72131.17
15(6)-14(6)[a]			75633.67		72134.73
15(7)-14(7)[a]	76726.26		75647.73		72149.13
15(8)-14(8)[a]	76748.21		75670.43		72170.80
15(9)-14(9)[a]	76776.86				72198.17
15(10)-14(10)[a]					72230.33
16(0,16)-15(0,15)					75657.42
16(1,16)-15(1,15)					75429.42
16(1,15)-15(1,14)					77368.38
16(2,15)-15(2,14)					76550.89
16(2,14)-15(2,13)					77672.99
16(3,14)-15(3,13)					76919.93
16(3,13)-15(3,12)					77119.15

Table 1. (Continued)

$J'(K_a',K_c')$←$J''(K_a'',K_c'')$	OXE···H_2O	OXE···$H_2^{18}O$	OXE···DOH	OXE···HOD	OXE···D_2O
16(4,13)-15(4,12)					76931.47
16(4,12)-15(4,11)					76942.53
16(5)-15(5)[a]					76914.83
16(6)-15(6)[a]					76916.07
16(7)-15(7)[a]					76929.80
16(8)-15(8)[a]					76951.90
16(9)-15(9)[a]					76980.47
16(10)-15(10)[a]					77014.50

[a] Doubly overlapped transitions due to the asymmetry degeneration of the K_a levels. Only K_a is indicated.

Table 2. Spectroscopic constants for the OXE···W complex.

	OXE···H_2O	OXE···$H_2^{18}O$	OXE···DOH	OXE···HOD	OXE···D_2O
A/[MHz]	8099.3(5)[a]	8070.5(6)	8103.9(8)	8069.(2)	8075.4(7)
B/[MHz]	2635.78(1)	2478.61(1)	2597.70(1)	2506.61(5)	2473.30(1)
C/[MHz]	2487.99(1)	2349.92(1)	2453.35(1)	2374.15(5)	2343.47(1)
D_J/[kHz]	20.337(7)	18.44(1)	19.30(1)	17.75(4)	16.868(6)
D_{JK}/[kHz]	−68.70(4)	−63.76(3)	−69.1(7)	−61.81(5)	−63.21(5)
d_1/[kHz]	2.29(1)	1.96(2)	2.17(2)	2.00(7)	1.87(1)
d_2/[kHz]	−0.064(3)	−0.047(2)	−0.053(4)	−0.056(8)	−0.041(5)
H_{KJ}/[Hz]	−7.4(3)	−9.7(4)	−4.9(8)	−6.3[b]	−6.3(5)
N[c]	56	26	53	27	59
σ/[MHz]	0.08	0.03	0.1	0.1	0.09

[a] Error (in parenthesis) are expressed in units of the last digit. [b] Fixed at the values of the OXE···DOD species. [c] Number of transitions in the fit.

Table 3. M_{bb} planar moments of inertia for OXE and OXE···W.

	OXE	OXE···H_2O	OXE···DOH
M_{bb}/uÅ^2	36.99	36.89	36.90
	OXE···HOD	OXE···D_2O	OXE···$H_2^{18}O$
M_{bb}/uÅ^2	36.93	36.95	36.89

complex. The deviation from linearity of the O–H···O linkage (γ of Figure 1) has been estimated from the r_s position of the water H_{free} hydrogen to be 0 ± 5°. The derived, but more significant parameters r (the O···H distance), ϕ and τ of Figure 1, are given in Table 5, in which they are compared to the corresponding values of the previously studied ether–water complexes.

Quantum chemical calculations: The experimental evidence seems to indicate that the oxetane ring in OXE–W is slightly nonplanar, with the C_β apex away from the water molecule. We performed some ab initio and density functional calculations for this complex in order to get a better insight about this aspect of the structure, and its energetics. Oxetane is a molecule which is "effectively" planar, with a small barrier to ring-puckering below the ground state.[7,8] Upon formation of the complex, with water at one side of the ring, the two small minima could no longer be equivalent. We ran MP2 and B3LYP calculations with the 6-311++G** basis set. We found that the global minimum with both MP2 and B3LYP had a distorted oxetane ring, being the α angle of Figure 1 of 16 and 6°, respectively. While the former method gives a barrier of 83 cm^{-1} to the planarity, for the latter one the minimum stands at 6 cm^{-1} below the energy of the planar configuration, and consequently it describes a very shallow potential-energy function. In addition, MP2 calculations give a secondary minimum (38 cm^{-1} above the absolute minimum) with the C_β apex pointing towards the water molecule with an opposite non-planar angle ($\alpha \cong -16°$). The two potential-energy functions, $E(\alpha)$, are qualitatively shown in Figure 2, and are compared to the ones relative to OXE. B3LYP calculations for this monomer give a single

Table 4. The experimental substitution coordinates for the water atoms of OXE···W are compared with the model calculated values after the structural refinement, that is, with the r_0 hydrogen bond parameters reported at the bottom of the table. The primed hydrogen participates in the hydrogen bond.

r_s coordinates		|a|		|b|		|c|	
Parent molecule	Atom	Exptl	Calcd[a]	Exptl	Calcd	Exptl	Calcd
OXE–W	O	2.473(1)[b]	2.480	0.10(1)	0.0	0.34(1)	0.35
	H′	1.696(1)	1.615	0.11(2)	0.0	0.22(1)	0.06
	H	3.122(2)	3.093	0.22(2)	0.0	0.45(1)	0.38
2) r_0 hydrogen-bond parameters (see Figure 1)							
R(O–O) = 2.82(1) Å			β = 106(1)°		α = 3(1)°		γ = 0(5)°

[a] Calculated with the r_0 structure. [b] Error (in parentheses) are expressed in units of the last digit.

Table 5. Hydrogen-bond parameters for some of the ether–water adducts (see Figure 1)

	1,4-Dioxane–W[a]	Tetrahydropirane–W[b]	Oxirane–W[c]	Dimethylether–W[d]	OXE–W[e]
r/[Å]	1.90(3)	1.91(2)	1.92(1)	1.88(1)	1.86(2)
ϕ/[°]	163(6)	184(4)	163(2)	172(1)	180(5)
τ/[°]	128(3)	122(2)	103(1)	141(2)	106(3)

[a] From ref. [3]. [b] From ref. [4]. [c] From ref. [6]. [d] From ref. [5]. [e] From this work.

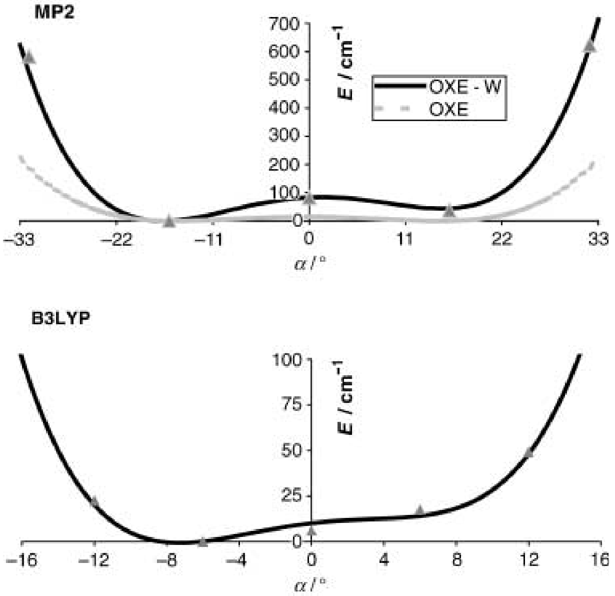

Figure 2. Calculated (6-311++G**) potential-energy functions as a function of α (deviation from the planarity of the oxetane ring) with MP2 (above) and B3LYP (below) methods for OXE–W. The MP2 function is relative to that calculated for isolated OXE by using the same method.

Table 6. Experimental and theoretical 6-311++G** structural parameters for OXE W (see Figure 1).

	Exptl	MP2	B3LYP
r_{OH}/[Å]	1.86(2)	1.851	1.857
ϕ/[°]	180(5)	159	167
τ/[°]	106(3)	120	130
α/[°]	3(1)	16	6

minimum, therefore the comparison is not significant. The ground-state average distortion of the ring in OXE–W is qualitatively in agreement with the experimental indication, $\alpha = 3°$.

The hydrogen-bond structural parameters calculated with MP2 and B3LYP methods are shown in Table 6 and are relative to the experimental values.

All calculations have been done with the Gaussian 98 program.[16]

Conclusion

The configuration of the global minimum of the OXE–W complex has been determined by studying the millimeter-wave free-jet absorption spectra of several isotopomers. The water moiety lies in the plane of symmetry of oxetane, with the "free" hydrogen *E* the ring. Both experimental data and MP2 and B3LYP theoretical calculations at the 6-311++G** level, indicate that the linkage with a water molecule distorts the oxetane ring from planarity, with the CH_2 apex in the β position on the opposite side with respect to the water subunit. MP2 calculations suggest a secondary minimum with C_β on the same side, however the minimum is too shallow to allocate any vibrational state.

In contrast, to the previously investigated ether–water complexes, the O–H···O linkage appears to be linear. It seems that the shape of the O–H···O linkage depends on secondary interactions (such as the weak C–H···O hydrogen bonds), so that the partner molecule can engage with water. MP2 and B3LYP calculations failed to reproduce this structural aspect (see Table 6).

We cannot exclude the stability of a second conformer, with the "free" water hydrogen *Z* with respect to the ring. This species, however, if formed at room temperature or in an intermediate step, would relax during the adiabatic expansion to the most stable one.[17]

Experimental Section

The description of the Stark- and pulse-modulated free-jet absorption millimeter-wave spectrometer used in this study has been reported previously.[18,19] The adducts were formed by flowing argon at room temperature at a pressure of about 0.7 bar over a solution of OXE and water, in a molecular ratio of 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; the mixture reached an estimated "rotational" temperature of about 10 K.

Acknowledgement

We thank Mr. A. Millemaggi for technical help, the University of Bologna (funds for special topics), the Ministero dell' Universita' e della Ricerca Scientifica e Tecnologica, and the C.N.R. for financial support.

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Received: September 5, 2003 [F5516]