The O···H−O Hydrogen Bond in the Gas Phase. Microwave Structure of Ethylene Oxide−Water

Walther Caminati,* Paolo Moreschini, Ivan Rossi, and Paolo G. Favero

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

Received May 22, 1998

Abstract: The free jet millimeter wave spectra of five isotopomers of the 1:1 complex between ethylene oxide and water have been assigned. The water molecule lies in the plane of symmetry of ethylene oxide perpendicular to the ring; the water hydrogen involved in the hydrogen bond points toward the ring oxygen, while the "free" hydrogen is *entgegen* to the ring. The H bond parameters are $r(O_{ring}\cdots H) = 1.92$ Å, $\angle(O_{ring}\cdots H-O) \cong 163°$, and $\angle(ring-O_{ring}\cdots H) \cong 103°$, respectively. The large differences of the two angles with respect to those of 1,4-dioxane−water and tetrahydropyran−water are mainly due to dipole−dipole interaction energy effects. The MP2 method using a 6-311++G(d,p) is shown to be a reliable approach for this kind of study. An experimental measure of the difference in zero-point energy between the O···D−O−H and the O···H−O−D species is given by the intensity ratio 3/1 of corresponding lines when a sample of water 50% enriched in D is used.

Introduction

Hydrogen bonding governs processes in aqueous surrounding, which are very common in nature.[1] The first step to a molecular-scale understanding of the energetics and dynamics involved in these processes is the investigation of the interaction of a water molecule with a substrate molecule. Rotationally resolved spectroscopy of jet-cooled samples is the technique that provided the most detailed and precise experimental data on these solvation phenomena, as shown and summarized by Zwier.[2]

In this paper we focus our interest on the O−H···O hydrogen bond. High-resolution investigations are already available for complexes of water with itself[3,4] and with carbon dioxide,[5,6] carbon oxide,[7] ozone,[8] and phenols.[9] Two adducts of water with ethers, 1,4-dioxane−water[10] and tetrahydropyran−water,[11] have been studied very recently. Free jet millimeter wave absorption and also molecular beam Fourier Transform microwave spectroscopies, for the second case, have been applied to these problems. In both cases the water molecule was found to lie in the plane of symmetry of the partner molecule, with one hydrogen (H′, involved in the hydrogen bond) pointing toward the axial lone pair of the ring oxygen and the second hydrogen (H, "free") *entgegen* with respect to the ring (*axial-entgegen*, *ae*, conformer). We investigated first the system 1,4-dioxane−water, and found that the highest stability of the observed conformer could simply have been explained in terms of dipole−dipole interaction energy.[10] Later on, to understand the influence of the dipole moment of the partner molecule in the adduct, we studied the complex of water with tetrahydropyran. It is a polar molecule, which differs from nonpolar 1,4-dioxane by a CH_2 group replacing an oxygen atom. Large deviations on the H bond structure and on the centrifugal distortion constants, clearly due only to dipole moment effects, have been found.

Another interesting aspect of hydrogen bond complexes, related to the values of the zero-point energies, is that when the water isotopomer HDO acts as a proton donor to a generic base B, the species H−O−D···B always overwhelms the species D−O−H···B (see, for example, refs 10 and 11, for which the second species was not observed). The understanding of this feature can be very important for the observation of hydrogen-bonded complexes in low temperature−low pressure conditions, as, for example, in interstellar space, where the D/H ratio is much larger than on earth.

To better understand the effects of the dipole moment of the "solvated" molecule in determining the shape and energetics of the hydrogen bond, and the other above-mentioned evidences, in particular between water and ethers, we decided to investigate the system ethylene oxide−water (EO−W, see Figure 1), a

---

* 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. Jeffrey, J. A.; Saenger, W. *Hydrogen bonding in biological structures*; Springer-Verlag: Berlin, 1991. Jeffrey, J. A. *Introduction to hydrogen bonding*; University Press: Oxford, 1997.

(2) Zwier, T. S. *Annu. Rev. Phys. Chem.* **1996**, *47*, 205−241.

(3) Dyke, T. R.; Mack, K. M.; Muenter, J. S. *J. Chem. Phys.* **1977**, *66*, 498−510. Fraser, G. T.; Suenram, R. D.; Coudert, L. H. *J. Chem. Phys.* **1989**, *90*, 6077−6085.

(4) 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.

(5) Peterson, K. I.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1991**, *94*, 106−117.

(6) Columberg, G.; Bauder, A.; Heineking, N.; Stahl, W.; Makarewicz, J. *Mol. Phys.* **1998**, *93*, 215−228.

(7) Yaron, D.; Peterson, K. I.; Zolanz, D.; Klemperer, W.; Lovas, F. J.; Suenram, R. D. *J. Chem. Phys.* **1990**, *92*, 7095−7109.

(8) Gillies, J. Z.; Gillies, C. W.; Suenram, R. D.; Lovas, F. J.; Schmidt, T.; Cremer, D. *J. Mol. Spectrosc.* **1991**, *146*, 493−512.

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

(10) Caminati, W.; Dell' Erba, A.; Melandri, S.; Favero, P. G. *J. Am. Chem. Soc.* **1998**, *120*, 5555−5558.

(11) Spoerel, U.; Stahl, W.; Caminati, W.; Favero, P. G. *Chemistry, Eur. J.* **1998**, *4*, 1974−1981.

10.1021/ja9817895 CCC: $15.00

Table 1. Rotational and Centrifugal Distortion Constants for Normal and Four Isotopic Species of EO−W Complex

	EO−H_2O	EO−$H_2{}^{18}O$	EO−DOH	EO−HOD	EO−D_2O
A/MHz	14827.5(25)[a]	14806.3(32)	14745.5(32)	14719.3(49)	14665.1(26)
B/MHz	3603.067(16)	3384.842(15)	3556.990(13)	3406.650(16)	3367.974(11)
C/MHz	3486.472(15)	3282.723(16)	3447.110(13)	3305.022(17)	3271.758(13)
D_J/kHz	14.754(21)	13.323(18)	14.156(20)	12.378(25)	11.987(14)
D_{JK}/kHz	105.45(16)	93.75(22)	94.58(29)	93.37(55)	83.34(12)
d_1/kHz	0.199(38)	0.191(35)	0.222(30)	0.226(43)	0.18(3)
d_2/kHz	−0.0328(63)	−0.0276(56)	−0.0406(63)	−0.0293(65)	−0.010(4)
H_{JK}/Hz	−6.67(85)	−6.4(10)	−3.4(12)	−3.7(24)	4.5(6)
H_{KJ}/Hz	46.2(11)	40.0(24)	47.9(30)	41.2(54)	32.8(10)
N[b]	34	31	28	21	34
J_{max}	11	11	11	11	11
σ/MHz	0.054	0.047	0.050	0.034	0.037
M_{bb}/uÅ^2 [c]	19.387	19.437	19.389	19.401	19.448

[a] Errors in parentheses are expressed in units of the last digit. [b] Number of transitions in the fit. [c] Planar moment of inertia perpendicular to the plane of symmetry of the complex (see text). The corresponding value for isolated EO is M_{bb} = 19.432 uÅ^2.

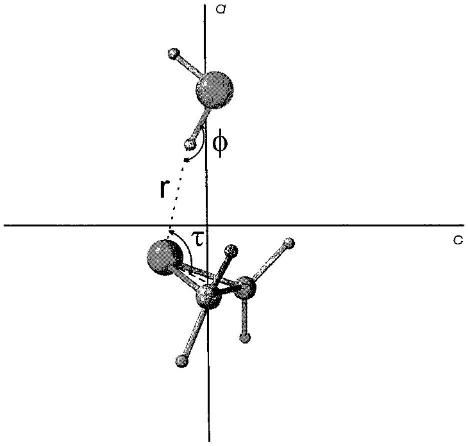

Figure 1. Plausible conformations and principal axes system of the observed conformer (*entgegen*) of EO−W.

molecular system small enough to allow high-level ab initio calculations, and with promisingly strong microwave spectra.

Since ab initio calculations of geometries and energetics of hydrogen-bonded systems often rise difficulties, we tried several approaches to find which one is the most suitable for this kind of problem.

Experimental Section

The 60−78 GHz Stark and pulse modulated free jet absorption millimeter wave spectrometer used in this study has been described elsewhere.[12,13] The adducts were formed expanding argon, containing about 2% of water and 2% of EO in moles, at room temperature and at a pressure of ca. 0.5 bar, 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

Trial rotational constants were calculated on the basis of the geometries of isolated EO[14] and water assuming hydrogen bond parameters intermediate between those of 1,4-dioxane−water[10] and tetrahydropyran−water,[11] that is an O···H distance of 1.90 Å within an O···H−O linear arrangement, and the "free" H *entgegen* to the ring. Differently from 1,4-dioxane−water and tetrahydropyran−water, the notation *axial* or *equatorial* is no longer required to specify the position of water, because the two lone pairs of the ring oxygen are equivalent in EO.

The rotational lines (μ_a-R type lines) of the normal isotopic species, which was investigated first, were found far away—at higher frequency—with respect to the calculated values because, despite a right conformational guess, the angle τ (see Figure 1) was much smaller than in the two previous cases. No μ_c type transitions have been observed, probably due to the accidentally low value of this dipole moment component. To locate exactly the position of the water atoms in the complex, the microwave spectra of four isotopomers (EO with $H_2{}^{18}O$, D′OH, H′OD, and D_2O) were assigned. The measured transition frequencies of all isotopic species are available as Supporting Information.

Two points concerning the main features of the spectrum are worth mentioning: (i) differently from the cases, for example, of the phenol−water[9] and pyrazine−water[15] 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 EO···H_2O complex, and (ii) when measuring the spectra of the species EO···D′OH and EO···H′OD, obtained in the same experiment by using water 50% enriched in D, the spectrum of the EO···D′OH species was about 3 times stronger than that of the twin isotopomer. This latter effect is in agreement with a lower zero-point energy of EO···D′OH, as described later on. Because of this effect we could not observe the O···H′OD isotopomers for the 1,4-dioxane−water and tetrahydropyran−water complexes, whose spectra were quite weaker than that of EO−W.

The rotational frequencies have been fitted with Watson Hamiltonian[16] (I^r-representation, *S*-reduction). Besides the rotational constants, four quartic and two sextic centrifugal distortion parameters have been determined. The results of the fittings are shown in Table 1. The centrifugal distortion parameters may be regarded as effective fitting parameters. Their interpretation is discussed in a later section.

Conformation and Structure

The planar moment of inertia M_{bb} (=$\Sigma_i m_i b_i^2$) is obtained from the rotational constants through $M_{bb} = h/(16\pi^2)(-1/B + 1/A + 1/C)$. It represents the mass extension along the principal axis *b*, which is perpendicular to the plane of symmetry (see Figure 1). The M_{bb} values are reported at the bottom of Table 1 for the five isotopic species, and for isolated EO. Since all

---

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

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

(14) Hirose, C. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1311−1318.

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

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

Table 2. Experimental Substitution Coordinates of the Water Atoms of EO−Water Compared to the Model Calculated Values after the Structural Refinement, that is with the Hydrogen Bond Parameters Reported at the Bottom of the Table (Å and deg)[a]

(1) r_s Coordinates

		$\lvert a \rvert$		$\lvert b \rvert$		$\lvert c \rvert$	
parent molecule	atom	exptl	calcd[b]	exptl	calcd[b]	exptl	calcd[b]
EO−H_2O	O	2.152(1)[c]	2.171	0.0	0.0	0.162(8)	0.160
	H′	1.282(5)	1.321	0.15(4)	0.0	0.442(15)	0.280
	H	2.821(1)	2.810	0.25(2)	0.0	0.456(8)	0.553

(2) r_0 Hydrogen Bond Parameters (see Figure 2)

$r = 1.92(1)$	$\tau = 103(1)$	$\phi = 163(2)$	$R^d = 2.84$

[a] The quoted errors of these parameters are just fitting errors: supplementary uncertainties come, for example, from the assumption that the geometries of water and EO have been fixed to those of the isolated molecules (see text). The primed hydrogen participates in the hydrogen bond. [b] Calculated with the r_0 structure (see bottom of the table and text). [c] Error (in parentheses) is expressed in units of the last digit. [d] Distance between the centers of mass of the monomers.

five M_{bb} values are about the same, we can argue that all atoms of the water moiety lie in the *ac* plane of symmetry of EO, and therefore the *ac* plane is also a symmetry element of the complex. From the experimental rotational constants we obtained a local r_0 structure at the H bond, fixing the geometries of EO and H_2O as in the isolated molecules, and the r_s substitution coordinates[17] of the water atoms. These data are reported in Table 2. Although the large-amplitude motions of the water moiety and the Ubbelohde effect,[18] that is the shrinking of the O−H bond upon deuteration, make the r_s substitution coordinates not exactly reliable, they are precise enough for conformational discrimination. It is easy to see that the experimental data nicely match the calculated values for the *entgegen* configuration of the "free" water hydrogen. The small nonzero $|b|$ values are likely due to the large-amplitude motions which are usually present in this kind of molecular complexes (see, for example, ref 19), and therefore are compatible with zero equilibrium values.

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 as 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[9] and pyrazine−water[15] these internal rotations connect equivalent minima and generate Coriolis doubling of rotational lines. This is not the case of EO−H_2O and of other ether−water adducts,[10,11] for which only one set of rotational lines has been observed. As to the stretching and bending motions of water with respect to the EO ring, their effects are reflected in the anomalously high values of the D_J and D_{JK} centrifugal distortion parameters, as was suggested also for several of the complexes of aromatic molecules with rare gases. Millen developed some equations to obtain the stretching force constant for high-symmetry complexes,[20] considering them as "pseudodiatomic" complexes. It has been shown by Read et al.[21] that similar equations can be used also for asymmetric top complexes, provided that the stretching coordinate is near-parallel to the inertial *a* axis. This condition is satisfied by EO−W, so that the equation

$$k_s = 16\pi^4 \mu_D R_{CM}^2 [4\mathrm{B}_D^4 + 4\mathrm{B}_D^4 - (B_D - C_D)^2 (B_D + C_D)^2]/hD_J \quad (1)$$

can be used to derive the stretching force constant k_s. μ_D, R_{CM}, and D_J are the reduced mass, the distance between the centers of mass, and the first-order centrifugal distortion constant, respectively. The value $k_s = 7.3$ N/m, corresponding to a harmonic stretching frequency of 98 cm^{-1}, has been calculated. Our O−H···O internal hydrogen bond appears to be weaker, for instance, than the O−H···O internal hydrogen bond of the water dimer[22] ($k_s = 10.8$ N/m).

Computational Results for the Geometries and the H-Bond Energies. It is well-known that systems involving intra- and/or intermolecular hydrogen bond imply difficulties in obtaining good results with theoretical calculations. Both to better understand the experimental evidences previously reported and to check the reliability of some theoretical methods to calculate geometries and energetics related to this problem, we performed several calculations with various theoretical approaches. First the potential energy surface associated with the EO−W cluster has been calculated at the MP2 level[23] with use of the 6-311++G(d,p) basis set.[24] Optimization has been tried for two configurations of the water subunit with respect to the EO ring, that is with the nonbonded water hydrogen *entgegen* or *zusammen* with respect to the ring. Only one minimum geometry has been found and fully optimized, corresponding to the *entgegen* orientation of the free water hydrogen, in agreement with the experimental findings. The *zusammen* form resulted from a saddle point, an energy maximum for the coordinate corresponding to the internal rotation of water roughly about the O−H···O internal hydrogen bond. This maximum is 6.7 kJ/mol above the *entgegen* minimum.

The geometry of the *entgegen* EO−H_2O cluster has also been optimized by using the pure and hybrid Density Functionals BLYP[25,26] and B3LYP[27] with the same basis set. While all three methods report a similar overall geometry for the *entgegen* minimum, the MP2 geometrical parameters are in better agreement with the experimentally determined ones, as can be seen from the values reported in Table 3.

---

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

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

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

(20) Millen, D. J. *Can. J. Chem.* **1985**, *63*, 1477−1479.

(21) Read, W. G.; Campbell, E. J.; Henderson, G. *J. Chem. Phys.* **1983**, *78*, 3501−3508.

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

(23) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229−236.

(24) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654.

(25) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(27) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

Table 3. Comparison between Experimental and Calculated Hydrogen Bond Parameters

		calcd			
	exptl	MP2[a]	B3LYP[a]	BLYP[a]	QCISD(T)[b]
r/Å	1.92(1)	1.913	1.903	1.915	
τ/deg	103(1)	107.37	115.262	116.85	
ϕ/deg	163(2)	151.58	159.954	162.68	
E_d/kJ mol^{-1}		22.74	23.04	21.18	22.72

[a] Basis set used is 6-311++G(d,p). [b] QCISD(T)/6-311++G(2d,p)//MP2/6-311++G(d,p).

Table 4. Zero-Point Vibrational Energy (ZPVE) Corrections (kJ mol^{-1}) for the Various H/D Isotopomers of Entgegen EO−W

	EO−H_2O	EO−D_2O	EO−HOD	EO−DOH
ZPVE	212.92	196.38	205.04	204.26
ΔE	−16.54[a]		−0.78[b]	

[a] Difference between the ZPVE of EO−D_2O and EO−H_2O. [b] Difference between the ZPVE of EO−DOH and EO−HOD.

The binding energy for the *entgegen* EO−W cluster has been evaluated by performing single-point QCISD(T)[28]/6-311++G(2d,p) calculations at the cluster and fragment MP2/6-311++G(d,p) optimized geometries, according to:

$$E_{\mathrm{stab}} = E_{\mathrm{EO-W}} - E_{\mathrm{EO}} - E_{\mathrm{W}} + E_{\mathrm{BSSE}} \tag{2}$$

The basis set superposition error (BSSE) has been evaluated by means of the counterpoise[29,30] procedure, which includes fragment relaxation energy terms.[31−32] The fragment relaxation terms to the binding energy are on the order of 0.2 kJ/mol, thus supporting the correctness of considering the fragment geometries conserved in the adduct. The binding energy is calculated to be 22.7 kJ/mol.

All the calculations have been performed with the Gaussian-94[34] software package.

Chemical "Equilibrium" between the EO−H′OD and EO−D′OH Species. As outlined in a previous section, we observed that when EO is expanded with water that is 50% D enriched, the intensities of corresponding lines of the EO−H_2O, EO−H′OD, EO−D′OH, and EO−D_2O have ratios 2/1/3/2, that is the EO−D′OH species is much more abundant than the EO−H′OD one. Entropic factors would require the four intensities to be equivalent, so that the different population among the EO−H′OD and EO−D′OH species must be imputed to an energy difference. For this reason ZPVEs have been calculated for the four different water H/D cluster isotopomers. In this calculation the 0.9748 scale factor suggested by Scott and Radom[33] has been used. The results are shown in Table 5. Since at least the mentioned six large amplitude motions are not strictly harmonic, which is the approximation inherent in Gaussian-94, these values are not necessarily precise, but useful for qualitative considerations. The large ZPVE difference between EO−H_2O and EO−D_2O is not reflected in a different relative population, because they are formed from different reactants; vice versa the relatively small ZPVE difference between EO−H′OD and EO−D′OH results in a large difference in the "equilibrium" concentrations because the two latter species are formed from the same reactants, with the D atom reaching a different position in the complex. The smallest ZPVE results are associated with the EO−DOH structure, in qualitative agreement with the experimental observation. It is not exactly appropriate to use the word "equilibrium" for the reaction

$$\mathrm{EO{-}H'OD} \rightleftharpoons \mathrm{EO} + \mathrm{HDO} \rightleftharpoons \mathrm{EO{-}D'OH} \tag{3}$$

when we consider it in jet conditions. Nevertheless, the 3:1 ratio in favor of EO−D′OH indicates that the formation of the most stable species is favored in our experimental context, at least indicating that the system is moving toward equilibrium. Anyway this kind of equilibrium must be intermediate between the initial (preexpansion) and the final (plume) states. If the energy difference of Table 4 (−0.78 kJ/mol, practically coinciding with ΔG) were correct, and assuming a Boltzmann distribution law to be valid, from the thermodynamic relation

$$\Delta G = -RT \ln K \tag{4}$$

the effective temperature (86 K) to which the "equilibrium" is referred could be estimated. This suggests that the energy necessary to detach HDO from EO represents a high activation energy at T = 86 K and below that temperature the reaction does not practically take place in jet conditions.

Dependence of the O−H···O Geometries and Energies on the Properties of the "Solvated" Molecule. The present investigation is the third, but the most detailed, high resolution spectral investigation of a 1:1 adduct of water with ethers, after the results recently reported for 1,4-dioxane−water[10] and tetrahydropyran−water.[11] The H-bond geometries are considerably different in the three complexes, as shown in Table 5. Although strong hydrogen bonds are generally believed to be linear, the contrasting behavior given by Table 6 is not so surprising, because even relatively small forces, such as those due to dipole−dipole interaction energy, can alter the slightly stronger forces involved in the H bond. The observed structural differences can be interpreted in terms of ab initio calculations, for example, at the HF/6-31**G level (this kind of calculation has been chosen because it is already available for tetrahydropyran−water[11]). The small forces underlying the bending motions of water with respect to EO are comparable to the forces arising from the dipole−dipole interactions. As a consequence the "imperturbed" shape of the hydrogen bond ($\tau \cong 120°$, $\phi \cong 180°$, see Figure 1) changes to the values 103/163 and 128/163 for EO−W and 1,4-dioxane−W, while it remains almost unaltered for tetrahydropyran, as shown for the three adducts in Table 5. These differences appear to be related to dipole−dipole interaction energy differences beetwen the *entgegen* and *zusammen* forms, which are 7.5, 4.2, and 2.5 kJ/mol for the three adducts, respectively. These values are roughly proportional to the distortion of τ and ϕ.

Conclusions

This is one of the first reports of the rotational spectrum of an adduct formed by one molecule of water and an ether. Since EO is the smallest ether, the EO−W system represents the simplest model for ab initio investigations. We performed

---

[28] Pople, J. A.; Head-Gordon, M. *J. Chem. Phys.* **1985**, *82*, 284−298.

[29] Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553−566.

[30] For a recent review on the subject see: van Duijneveldt, F. B.; van Duijneveldt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873−1885.

[31] Emsley, J.; Hoyte, O. P. A.; Overill, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 3303−3306.

[32] Xantheas, S. S. *J. Chem. Phys.* **1996**, *104*, 8821−8824.

[33] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

[34] 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. Gaussian 94-Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

Table 5. Comparison of the Experimental and Calculated Hydrogen Bond Parameters of EO−W to Those of the Previously Investigated Ether−Water Adducts (see Figure 1)

	EO−W			1,4-dioxane−W			tetrahydropyran−W	
	exptl	calcd[a]	calcd[b]	exptl[c]	calcd[a]	calcd[b]	exptl[d]	calcd[a,d]
r/Å	1.92(1)	2.04	2.01	1.90(3)	2.02	1.99	1.91(2)	2.01
τ/deg	103(1)	104.7	116.9	128(3)	127.4	144.9	122(2)	142.1
ϕ/deg	163(2)	149.2	160.2	163(6)	161.3	171.6	176(4)	180

[a] Geometry optimized at the HF/6-31G(d,p) level. [b] Geometry optimized at the HF/6-31++G(d,p) level. [c] From ref 10. [d] From ref 11.

indeed several ab initio calculations wth different approaches, and found that the MP2/6-311++G(d,p) level gives results in better agreement with experiment.

We could also measure the intensity ratio for the corresponding transitions of the EO−D′OH and EO−H′OD complexes, and interpret it as due to different zero-point energies.

While the −O−H···O intermolecular hydrogen bond is generally believed to be linear, we show that it can fall far away from linearity depending mainly on the dipole−dipole interaction energy.

Only one set of rotational transitions of the EO−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 conformer with the "free" water hydrogen *entgegen* with respect to the ring (see Figure 1). The second plausible conformer, with the "free" water hydrogen *zusammen*, has been found to be a saddle point by MP2/6-311++G(d,p) calculations. It is difficult to give experimental confirmation of this theoretical result. In fact the *zusammen* species, if formed at room temperature or in an intermediate step, would relax during the adiabatic expansion to the most stable one.[35]

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

Supporting Information Available: Table of experimental transition frequencies of ethylene oxide−water (1 page, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9817895

---

(35) Godfrey, P. D.; Rodgers, F. M.; Brown, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 2232−2239.