

# Jet-Cooled Rotational Spectra and Ab Initio Investigations of the Tetrahydropyran – Water System

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**Abstract:** The tetrahydropyran–water system was investigated by molecular-beam Fourier-transform microwave and free-jet millimeter-wave spectroscopies and by ab initio calculations. The spectra of the  $^{13}\text{C}$  isotopomers in natural abundance of tetrahydropyran and of the 1:1 complex between tetrahydropyran and three isotopomers of water ( $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , and  $\text{H}_2^{18}\text{O}$ ) have been assigned. A partial  $r_s$  structure of the tetrahydropyran

monomer has been derived. In the complex, the water molecule lies in the plane of symmetry of tetrahydropyran; 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 slightly bent arrangement with an  $\text{O}_{\text{ring}} \cdots \text{H}$  distance of about 1.91 Å and  $\angle(\text{O}_{\text{ring}} \cdots \text{H}-\text{O}) \approx 176^\circ$ . Additionally, ab initio calculations for the complex were performed and found to be in agreement with the experimental results.

**Keywords:** ab initio calculations • free jet spectroscopy • hydrogen bonds • molecular complexes • rotational spectroscopy

## Introduction

Most chemical, biochemical, and atmospheric processes take place in aqueous surroundings. The first step in understanding the energetics and dynamics involved in such processes is the investigation of the interaction of a water molecule with a substrate molecule. Rotationally resolved spectroscopy of jet-cooled samples has provided the most detailed and precise experimental data; most of the important results have been summarized by Zwiernicki.<sup>[1]</sup>

Complexes of water with itself,<sup>[2,3]</sup> nitrogen,<sup>[4]</sup> carbon dioxide,<sup>[5,6]</sup> carbon monoxide,<sup>[7]</sup> ozone,<sup>[8]</sup> benzene,<sup>[9]</sup> amines,<sup>[10–13]</sup> nitrogen-containing aromatics,<sup>[14,15]</sup> and phenols<sup>[16]</sup> have been investigated. Only one adduct with an ether, 1,4-dioxane–water, has been studied so far.<sup>[17]</sup> In order to understand the influence of the dipole moment of the partner molecule of water in the adduct, we decided to study the complex of water (W) with tetrahydropyran (THP). THP is a polar molecule which differs with respect to the nonpolar 1,4-dioxane by a  $\text{CH}_2$  group replacing an oxygen atom. As in the case of 1,4-dioxane–water, assuming that the hydrogen bond is formed along one of the oxygen lone electron pairs

(LEP), four conformational possibilities exist for the overall configuration of the complex THP–W: ax-E, ax-Z, eq-E, and eq-Z (see Figure 1). The first two letters indicate the axial or

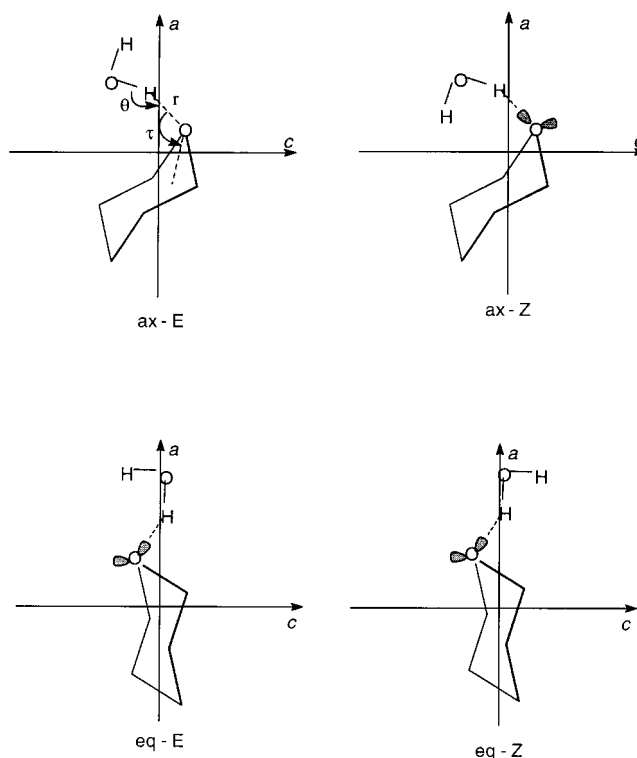


Figure 1. Plausible conformers of THP–W. Ax-E is the species observed.

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equatorial position of the hydrogen (H') involved in the hydrogen bond, while the third one refers to the *entgegen* (E) or *zusammen* (Z) position of the water hydrogen (H) not involved in the hydrogen bond. Two different techniques, molecular-beam Fourier-transform microwave spectroscopy (MB-FTMW) and free-jet millimeter-wave absorption spectroscopy, have been applied to this problem. Their complementarity in studying this kind of problem is discussed below.

In the case of the MB-FTMW measurements not only was the THP–W complex analyzed, but the  $^{13}\text{C}$  isotopomers of the THP monomer were also assigned. This enabled us to calculate an improved structure of THP and compare it with *ab initio* results.

## Results and Discussion

### The tetrahydropyran monomer:

**Rotational spectra:** The main isotopomer of THP has already been investigated by Lowe and Kewley<sup>[23]</sup> and by Lopez et al.,<sup>[24]</sup> who also measured vibrationally excited states. In order to derive a partial  $r_s$  structure, we decided to analyze the spectra of the monosubstituted  $^{13}\text{C}$  isotopomers in natural abundance. Assuming the structure of THP to be analogous to that of cyclohexane<sup>[25]</sup> we predicted a- and c-type spectra of the  $^{13}\text{C}$  isotopomers. The dipole moment of THP has already been determined by Rao and Kewley.<sup>[26]</sup>

We were able to measure lines for all monosubstituted  $^{13}\text{C}$  isotopomers. Most lines exhibit small additional  $^{13}\text{C}$  spin-rotation splittings that were too small to be analyzed. Because the isotopomers were measured in natural abundance, the lines were too weak to observe transitions with high  $J$  values. Centrifugal distortion constants could therefore not be determined. Instead, we used the fourth-order centrifugal distortion constants (Watson's A reduction) of the main isotopomer after reanalyzing the transitions measured by Lowe and Kewley<sup>[23]</sup> with the program ZFAP4.<sup>[27]</sup> The measured transitions are given in Table 1. The derived

**Abstract in Italian:** *Il sistema tetraidropirano–acqua è stato studiato in fasci supersonici con spettroscopia a microonde a trasformate di Fourier e con spettroscopia millimetrica di assorbimento, e con calcoli ab initio. Sono stati assegnati gli spettri degli isotopomeri  $^{13}\text{C}$  in abbondanza naturale del tetraidropirano e del complesso 1:1 fra tetraidropirano e tre isotopomeri dell'acqua ( $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , e  $\text{H}_2^{18}\text{O}$ ). È stata derivata una parziale struttura  $r_s$  del monomero del tetraidropirano. Per quanto riguarda il complesso, la molecola d'acqua è nel piano di simmetria del tetraidropirano; l'idrogeno dell'acqua coinvolto nel legame a ponte idrogeno è assiale, mentre l'idrogeno libero è *entgegen* rispetto all'anello. I tre atomi coinvolti nel legame a ponte idrogeno assumono una conformazione lievemente piegata, con la distanza  $O_{\text{anello}} \cdots H$  di circa 1.91 Å e l'angolo  $O_{\text{anello}} \cdots H-O$  di circa 176°. Sono inoltre stati fatti dei calcoli ab initio per il complesso, che sono risultati in accordo con i dati sperimentali.*

Table 1. Observed transitions of  $^{13}\text{C}$  isotopomers of THP. Numbering of atoms according to Figure 2, observed transitions in MHz, observed-minus-calculated values  $\Delta$  in kHz.

$J(K_a, K_c) - J''(K_a', K_c')$	$^{13}\text{C}(1)$		$^{13}\text{C}(2)$		$^{13}\text{C}(3)$	
	obs.	$\Delta$	obs.	$\Delta$	obs.	$\Delta$
1 1 0–0 0 0	9086.0557	–0.1	9078.1333	0.9	9078.7905	–0.3
1 0 1–0 0 0	7041.0345	0.0	7036.7258	–0.1	6979.4859	0.0
2 2 1–1 1 1	18328.6550	–0.2	18308.4545	0.2	18421.9808	–0.4
2 2 1–1 0 1	18015.5240	0.8	18004.0747	0.4		
2 2 1–1 1 0			16419.2298	–0.2		
2 2 0–1 1 0	18181.4213	0.1	18165.0888	0.1	18184.1192	0.0
2 1 1–1 1 0	15970.5112	0.0	15962.6594	0.1	15793.8349	0.1
2 1 1–1 0 1					17893.1376	0.0
2 1 2–1 1 1	12193.6025	0.0	12184.2153	–0.2	12124.0789	0.2
2 0 2–1 0 1	12340.8286	–0.3	12327.5740	–0.2	12361.9295	0.1
2 1 2–1 0 1	12350.1647	–0.2	12336.4038	–0.2		
2 0 2–1 1 1	12184.2154	5.0	12175.3837	0.0		
2 2 1–1 1 0	16440.1952	–0.1				
3 1 2–2 1 1	21546.2724	0.2	21522.7406	0.1	21600.5531	0.5
3 2 1–2 2 0					24466.8889	0.0
3 2 2–2 2 1	21123.0553	0.3	21110.1233	0.5	20983.4094	0.1
3 0 3–2 0 2	17427.7600	–0.4	17410.9313	–0.6	17409.9156	–1.5
3 1 3–2 1 2	17418.7694	–0.1	17402.4226	–0.4	17385.0156	1.2
3 1 2–3 1 3			9788.0062	–0.6		
4 0 4–3 0 3	22542.1657	0.0				
4 1 4–3 1 3	22540.5753	–0.1				
4 1 3–4 1 4	13748.6029	0.2				
4 2 2–4 2 3	9726.3335	–0.4	9724.9955	0.0	9538.4063	0.4
4 2 2–4 1 3			9727.2365	0.1		
5 3 2–5 3 3	9598.1899	–0.4	9603.4616	–0.5	9207.1422	–0.4
5 2 3–5 2 4					13663.6397	0.1

rotational constants of the isotopomers and the rotational and centrifugal distortion constants of the main isotopomer are compiled in Table 2. The correlation matrices for the rotational constants resulting from the fits for the  $^{13}\text{C}$  isotopomers are given in Table 3.

Table 2. Rotational and fourth-order centrifugal distortion constants (Watson's A reduction) of THP and  $^{13}\text{C}$  isotopomers, planar moment  $M_{\text{bb}}$  of THP. Standard deviation  $\sigma$ , numbering of atoms according to Figure 2.

	THP <sup>[a]</sup>	$^{13}\text{C}(1)$	$^{13}\text{C}(2)$	$^{13}\text{C}(3)$
$A$ [MHz]	4673.499(46)	4621.31005(50)	4615.16775(69)	4671.6054(10)
$B$ [MHz]	4495.065(47)	4464.74950(37)	4462.97917(46)	4407.18644(47)
$C$ [MHz]	2601.291(47)	2576.28900(23)	2573.74946(30)	2572.30284(35)
$\Delta_J$ [kHz]	0.63(21)			
$\Delta_{JK}$ [kHz]	–0.596(62)		centrifugal distortion constants of	
$\Delta_K$ [kHz]	0.960(42)		main isotopomer used	
$\delta_J$ [kHz]	0.211(11)			
$\delta_K$ [kHz]	0.366(23)			
$M_{\text{bb}}$ [ $\text{u}\text{\AA}^2$ ]	94.9938			
number of lines	68	18	19	18
$\sigma$ [kHz]	127	3	4	6

[a] These constants were derived by reanalyzing the measured lines of Lowe and Kewley<sup>[23]</sup> with the program ZFAP4<sup>[27]</sup>.

Table 3. Correlation matrices for rotational constants of  $^{13}\text{C}$  isotopomers of THP. Numbering of atoms according to Figure 2.

	$^{13}\text{C}(1)$			$^{13}\text{C}(2)$			$^{13}\text{C}(3)$		
$A$	1.00			1.00			1.00		
$B$	–0.48	1.00		–0.47	1.00		–0.21	1.00	
$C$	–0.04	0.43	1.00	0.61	0.41	1.00	–0.13	0.27	1.00

**Molecular structure:** After analysis of the spectra of the monosubstituted  $^{13}\text{C}$  isotopomers, a partial  $r_s$  structure was calculated. The  $r_s$  coordinates were determined according to Kraitchman's equation (Table 4).<sup>[28]</sup>

Table 4. The  $r_s$  coordinates for monosubstituted  $^{13}\text{C}$  isotopomers determined according to Kraitchman's equation.

	C(1)	C(2)	C(3)
$ a $	0.7232	0.7286	1.4868
$ b $	1.1734	1.2507	0.0000
$ c $	0.2262	0.2227	0.2232

The numbering of atoms is shown in Figure 2. The  $b$  value of C(3) was set to zero because of symmetry restrictions. Otherwise a small imaginary value results, which is physically

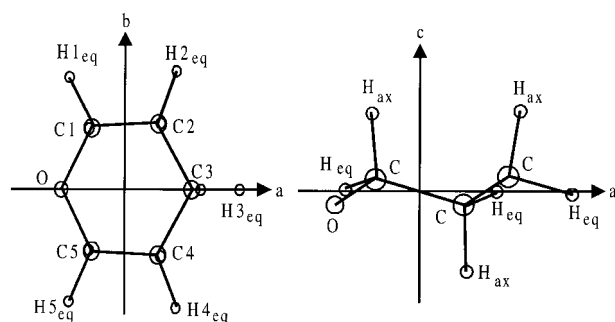


Figure 2. Structure of THP.

not acceptable and is due to the proximity of C(3) to the  $b$  axis. The bond lengths and bond angles that could not be determined were adopted from cyclohexane<sup>[25]</sup> or from standard bond parameters.<sup>[29]</sup> The bond lengths and bond angles are given in Table 5. The experimentally undetermined values are given in parentheses.

We also performed structure optimizations with *ab initio* calculations at the HF/6-31G\*\* and MP2/6-31G\*\* levels using the program packages Gaussian92<sup>[30]</sup> and Gaussian94,<sup>[31]</sup> respectively. The results are in good agreement with experimental findings. Only for bond lengths and angles that could not be determined by experiment did the deviations from the calculated values exceed 1%. The largest deviations were found for the C–O bonds adopted from standard values. The MP2/6-31G\*\*-optimized bond lengths and angles are also given in Table 5.

### The tetrahydropyran–water complex

**Rotational spectrum:** Trial rotational constants were calculated for the four conformers by using the geometries of isolated THP and water and assuming an  $\text{O}_{\text{ring}}\text{--H}$  distance of 1.90 Å<sup>[17]</sup> within a linear  $\text{O--H}\cdots\text{O}$  arrangement.

With the millimeter-wave apparatus we could observe and measure the rotational transitions for the normal species, as well as for the isotopomers with  $\text{D}_2\text{O}$  and  $\text{H}_2^{18}\text{O}$ . As was the case for 1,4-dioxane–water,<sup>[17]</sup> none of the observed transitions were split or shifted by large-amplitude motion effects of the water moiety. In order to check if these internal motions, often associated with a double-minimum potential, were causing some hyperfine structure in the rotational

Table 5. Experimental and MP2/6-31G\*\* optimized structure of THP. Bond lengths<sup>[a]</sup> in Å, bond angles<sup>[a]</sup> in degrees, rotational constants in MHz, experimental-minus-optimized values in %, numbering of atoms according to Figure 2.

	Experimental	MP2/6-31G**	Deviation [%]
OC(1)	(1.413)	1.426	1.0
C(1)C(2)	1.516	1.522	0.4
C(2)C(3)	1.530	1.528	0.2
C(1)H(1) <sub>ax</sub>	(1.101)	1.100	0.1
C(1)H(1) <sub>eq</sub>	(1.093)	1.089	0.4
C(2)H(2) <sub>ax</sub>	(1.101)	1.092	0.9
C(2)H(2) <sub>eq</sub>	(1.093)	1.093	0.0
C(3)H(3) <sub>ax</sub>	(1.101)	1.095	0.6
C(3)H(3) <sub>eq</sub>	(1.093)	1.091	0.2
(C(5)OC(1))	(114.8)	110.78	3.5
(OC(1)C(2))	(114.66)	111.38	2.8
(C(1)C(2)C(3))	110.17	109.94	0.3
(C(2)C(3)C(4))	109.73	109.88	0.2
(C(2)C(1)H(1) <sub>ax</sub> )	(108.83)	109.84	1.0
(C(2)C(1)H(1) <sub>eq</sub> )	(110.55)	111.64	1.0
(C(1)C(2)H(2) <sub>ax</sub> )	(108.83)	108.46	0.4
(C(1)C(2)H(2) <sub>eq</sub> )	(110.55)	109.80	0.7
(C(1)H(1) <sub>ax</sub> H(1) <sub>eq</sub> )	(106.65)	108.22	1.5
(C(2)H(2) <sub>ax</sub> H(2) <sub>eq</sub> )	(106.65)	107.63	1.0
(C(3)H(3) <sub>ax</sub> H(3) <sub>eq</sub> )	(106.65)	106.94	0.3
(OC(5)C(1))(C(5)C(1)C(2))	(132.31)	124.67	5.8
(C(4)C(3)C(2))(C(5)C(4)C(2))	132.31	131.84	0.5
rotational constants in MHz	from bond parameters	MP2/6-31G**	from spectrum <sup>[23]</sup>
A	4672.499	4696.141	4673.498(4)
B	4497.147	4521.442	4495.069(8)
C	2577.355	2617.180	2601.272(5)

[a] Bond parameters that could not be determined from experimental data are approximated by standard values and are therefore given in parentheses.

transitions, we investigated the spectrum of the normal species with a FTMW spectrometer in detail. Since we observed no splittings, we can deduce that water is quite rigid in this complex. The measured frequencies are reported in Table 6 for the normal species and in Table 7 for the isotopic species. They have been fitted with Watson's Hamiltonian<sup>[32]</sup> (*I* representation, *S* reduction). The full set of quartic and four sextic centrifugal distortion parameters were determined for the normal species. Some of these parameters were kept constant at the values of the normal species for the  $\text{D}_2\text{O}$  and  $\text{H}_2^{18}\text{O}$  species. The results of the fits are shown in Table 8. The combined measurements of the millimeter-wave and Fourier-transform spectrometers allow a very precise determination of the spectroscopic parameters.

The centrifugal distortion parameters may be regarded as effective fit parameters. For example, in a more detailed analysis the large values of the  $D_J$ ,  $D_{JK}$ , and  $D_K$  parameters could be interpreted in terms of the low-energy motions of the water molecule with respect to the ring.

**Conformation and structure:** The planar moments of inertia,  $M_{\text{gg}}$ , defined in Equation (1), are easily obtained from the rotational constants through Equation (2).

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

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

Table 6. Frequencies of measured transitions of normal THP–W (MHz). Observed-minus-calculated values in parentheses in units of the last digit.

Individual transitions		Doubly overlapped transitions <sup>[a]</sup>	
$J'(K_a, K_c) - J''(K_a, K_c)$	$\nu$ [MHz]	$J'(K_a) - J''(K_a)$	$\nu$ [MHz]
1(0,1)–0(0,0)	3531.015(1)	6(1,6)–5(1,5)	20844.058(0)
1(1,0)–0(0,0)	4709.822(0)	6(1,5)–5(1,4)	21419.276(–1)
2(0,2)–1(0,1)	7055.559(1)	6(4,3)–6(3,3)	7863.048(0)
2(1,2)–1(1,1)	6963.768(5)	6(3,3)–5(2,3)	26720.875(3)
2(1,1)–1(1,0)	7160.097(3)	6(2,5)–5(1,5)	25301.738(–3)
2(1,1)–1(0,1)	8338.904(1)	6(3,4)–5(2,4)	26913.801(1)
2(2,0)–1(1,0)	10408.415(3)	7(3,4)–6(2,4)	30149.571(–1)
2(2,1)–1(1,1)	10500.177(–2)	7(1,6)–6(0,6)	27423.106(0)
3(3,0)–2(2,0)	16238.960(–7)	7(2,5)–6(1,5)	27785.936(1)
3(0,3)–2(0,2)	10567.334(0)	8(0,8)–7(0,7)	27842.786(4)
3(1,2)–2(1,1)	10735.828(–1)	8(1,7)–7(1,6)	28473.825(–1)
3(1,3)–2(1,2)	10441.548(1)	8(1,8)–7(1,7)	27748.849(4)
3(3,1)–2(2,1)	16245.098(3)	8(2,7)–7(2,6)	28163.726(4)
3(1,2)–2(0,2)	12019.175(1)	8(2,6)–7(1,6)	31389.582(–1)
3(2,1)–2(1,1)	13866.312(–2)	9(0,9)–8(0,8)	31262.431(3)
3(2,2)–2(1,2)	14129.016(–12)	9(1,9)–8(1,8)	31192.786(–1)
4(0,4)–3(0,3)	14060.888(–2)	9(1,8)–8(1,7)	31969.699(–2)
4(1,4)–3(1,3)	13914.764(–2)	9(2,8)–8(2,7)	31656.215(–1)
4(1,3)–3(1,2)	14306.012(–2)	9(2,7)–8(2,6)	32156.470(1)
4(2,2)–3(2,1)	14180.475(–3)	9(2,7)–8(1,7)	35072.226(0)
4(2,3)–3(2,2)	14118.122(–1)	10(0,10)–9(0,9)	34681.155(–2)
4(0,4)–3(1,2)	12609.046(–4)	10(1,9)–9(1,8)	35441.111(–4)
4(2,2)–3(1,2)	17310.966(3)	10(1,10)–9(1,9)	34631.932(–1)
4(3,1)–3(3,0)	14136.541(6)	10(2,9)–9(2,8)	35139.796(2)
4(3,2)–3(3,1)	14134.981(8)	10(5,5)–10(4,7)	10087.968(–4)
4(2,3)–3(1,3)	17805.603(0)	11(0,11)–10(0,10)	38100.537(–2)
4(3,2)–3(2,2)	19787.460(2)	13(7,6)–12(6,6)	60551.47(3)
4(4,1)–3(3,1)	22032.101(0)	13(7,7)–12(6,7)	60551.90(33)
4(4,0)–3(3,0)	22031.857(8)	14(6,9)–13(5,9)	61791.30(–1)
5(0,5)–4(0,4)	17532.990(0)	14(6,8)–13(5,8)	61780.93(11)
5(1,5)–4(1,4)	17382.454(–1)	17(6,12)–16(6,11)	60126.17(–3)
5(1,4)–4(1,3)	17868.163(–1)	18(6,12)–17(6,11)	63683.54(6)
5(2,3)–4(2,2)	17759.458(–2)	18(7,12)–17(7,11)	63624.09(5)
5(1,4)–4(0,4)	19565.127(0)	18(7,11)–17(7,10)	63624.52(–4)
5(2,3)–4(1,3)	20764.411(1)	19(6,14)–18(6,13)	67222.42(5)
5(0,5)–4(1,3)	15836.021(–6)	19(6,13)–18(6,12)	67239.95(–5)
5(1,4)–4(2,2)	14863.212(–2)	19(7,13)–18(7,12)	67165.75(1)
5(3,2)–5(2,4)	5709.961(–3)	19(7,12)–18(7,11)	67166.79(–4)
6(0,6)–5(0,5)	20984.109(1)		

[a] Only  $K_a$  is indicated in the notation because these transitions are doubly overlapped due to the near-prolate degeneracy of the involved levels.

These moments are very useful in visualizing the mass extension along a given axis, and are reported in Table 8 for the three isotopic species. Because the three  $M_{\text{bb}}$  values have approximately the same values, very similar to that of isolated THP, we can argue that all atoms of water lie in the  $ac$  symmetry plane of THP, and therefore that the  $ac$  plane is also a symmetry element of the complex. In Table 9 we compare the experimental rotational constants, their shifts in going from the normal to the  $\text{D}_2\text{O}$  and  $\text{H}_2^{18}\text{O}$  species, and the  $r_s$  substitution coordinates<sup>[28]</sup> of the water oxygen to the model-calculated values for the four conformers of Figure 1. The values of the rotational constants and the  $r_s$  coordinates rule out the equatorial configurations of water, while the  $\Delta A$ ,  $\Delta B$ , and  $\Delta C$  values show that the ax-E conformer is the only one which is consistent with all the experimental evidence. The small non-zero  $|b|$  value for the water oxygen is consistent with the contributions due to the large-amplitude motions of the water moiety in a van der Waals complex (see for example ref. [33]).

A plausible  $r_0$  structure of the atoms involved in the hydrogen bond has been calculated from the rotational

constants. The  $r_0$  geometries of the two subunits were taken as in the isolated water and THP. The hydrogen-bond parameters ( $\text{\AA}$  and degrees) obtained are given at the top of Table 10, which also lists the experimental and calculated values of the rotational constants and of the  $r_s$  coordinates for comparison.

*Internal motions:* The three translational and three rotational degrees of freedom of the isolated water molecule are replaced by six low-energy vibrational modes upon formation of the complex. One of these motions can be considered the stretching between the two centers of mass of the constituent molecules, while the remaining ones can be thought of as two bends and three internal rotations of the water moiety. In the cases of phenol–water<sup>[16]</sup> and pyrazine–water<sup>[14]</sup> at least one of these internal rotations connects equivalent minima and generates Coriolis doubling of rotational lines. As in the case of 1,4-dioxane–water, only one set of rotational lines has been observed for THP–W. As to the stretching and bending motions of water with respect to the THP ring, their effects

Table 7. Frequencies of measured transitions of isotopic species of THP–W (MHz). Observed-minus-calculated values in parentheses in units of the last digit.

$J'(K'_a) - J''(K''_a)^{[a]}$	H <sub>2</sub> <sup>18</sup> O	D <sub>2</sub> O
11(10)–10(9)	59695.25(–2)	59914.90(3)
11(11)–10(10)	62086.10(–4)	62336.89(–4)
12(9)–11(8)	60661.86(–5)	60843.22(5)
12(10)–11(9)	63052.27(0)	63265.13(2)
12(11)–11(10)	65442.90(5)	65686.97(–2)
12(12)–11(11)	67833.92(–1)	68109.07(3)
13(8)–12(7)	61626.46(–3)	61768.95(–6)
13(9)–12(8)	64017.60(–1)	64192.10(0)
13(10)–12(9)	66408.00(1)	66614.19(1)
13(11)–12(10)	68798.43(6)	69035.98(0)
13(12)–12(11)	71189.17(7)	71457.77(–4)
13(13)–12(12)	73580.33(–8)	73879.85(1)
14(7)–13(6)		62687.10(–7)
14(8)–13(7)		65115.42(1)
14(9)–13(8)		67539.53(2)
14(10)–13(9)	69762.31(3)	
15(7)–14(6)		66027.89(9)
15(8)–14(7)		68459.57(–3)
18(7)–17(7)	60563.94(9)	
18(8)–17(8)	60539.87(11)	60413.25(1)
18(9)–17(9)	60522.34(–5)	60395.06(–4)
18(10)–17(10)	60508.97(–2)	60381.38(0)
18(11)–17(11)		60370.46(4)
18(12)–17(12)		60361.22(–4)
18(13)–17(13)		60353.36(3)
19(8)–18(8)	63902.38(3)	63770.33(–2)
19(9)–18(9)	63882.16(–1)	63749.20(1)
19(10)–18(10)	63866.65(–7)	
19(11)–18(11)	63854.24(6)	63720.68(–1)
19(12)–18(12)	63843.47(–4)	
20(10)–19(10)		67084.83(6)
20(11)–19(11)		67070.33(–2)
20(12)–19(12)		67058.48(–2)
18(6,13)–17(6,12)	60599.20(–2)	60476.48(–2)
18(6,12)–17(6,11)	60602.05(–3)	60480.04(6)
19(6,14)–18(6,13)	63971.52(–6)	63844.02(–3)
19(6,13)–18(6,12)	63976.82(3)	63850.38(0)

[a] Only  $K_a$  is indicated in the notation because all but the last four transitions are doubly overlapped due to the near-prolate degeneracy of the involved levels. For the last four transitions the full notation,  $J'(K'_a, K'_c) - J''(K''_a, K''_c)$  is used.

are reflected in the anomalously high values of the  $D_J$ ,  $D_{JK}$ , and  $D_K$  centrifugal distortion parameters, as observed in several of the complexes of aromatic molecules with rare gases. Rather surprisingly, as shown in Table 11, the quartic centrifugal distortion parameters of THP–W are much smaller than those of 1,4-dioxane–water, indicating that the water is more tightly bound in THP–W.

The pseudodiatomic force constant for the van der Waals stretch can be obtained rather straightforwardly from the rotational spectrum when such a stretching takes place along a symmetry axis of the complex.<sup>[34]</sup> The value of this force constant has been determined also for complexes without this symmetry element, but with the stretching accidentally almost along the  $a$  axis.<sup>[35]</sup> It is not possible to apply this approximation to THP–H<sub>2</sub>O because the angle between the  $a$  axis and the H–O bond is about 40°.

*Ab initio calculations:* We performed ab initio calculations in order to obtain more information on the stabilization energies

Table 8. Rotational and centrifugal distortion constants (S reduction and I representation) and planar moments of inertia of THP–water.

	H <sub>2</sub> O	H <sub>2</sub> <sup>18</sup> O	D <sub>2</sub> O
$A$ [MHz]	2895.2487(3) <sup>[a]</sup>	2877.534(4)	2889.64(2)
$B$ [MHz]	1814.5903(2)	1723.39(2)	1721.35(5)
$C$ [MHz]	1716.4666(2)	1640.24(2)	1634.31(7)
$D_J$ [kHz]	3.387(1)	3.31(2)	2.86(4)
$D_{JK}$ [kHz]	4.22(1)	4.39(3)	3.9(1)
$D_K$ [kHz]	–2.87(2)	–3.20(2)	–2.29(9)
$d_1$ [kHz]	0.3771(5)	[0.3771] <sup>[b]</sup>	0.43(6)
$d_2$ [kHz]	0.0276(3)	[0.0276]	[0.0276]
$H_J$ [Hz]	–0.043(4)	[–0.043]	–0.16(4)
$H_{JK}$ [Hz]	–0.34(3)	[–0.34]	[–0.37]
$H_{KJ}$ [Hz]	1.8(1)	[1.8]	1.6(4)
$H_K$ [Hz]	–1.18(9)	[–1.18]	–1.6(3)
$N^c$	111	26	33
$\sigma$ [MHz] <sup>[d]</sup>	0.05	0.09	0.04
$M_{aa}$ [ $\mu\text{Å}^2$ ]	199.1945	212.8660	213.9663
$M_{bb}$ [ $\mu\text{Å}^2$ ] <sup>[e]</sup>	95.2405	95.2476	95.2647
$M_{cc}$ [ $\mu\text{Å}^2$ ]	79.3141	80.3816	79.6290

[a] Error in parentheses expressed in units of the last digit. [b] Values in bracket fixed to those of the normal species. [c] Number of transitions in the fit. [d] Standard deviation of the fit. [e] To be compared to the value of 94.9938  $\mu\text{Å}^2$  for isolated THP.

Table 9. Comparison of the experimental rotational constants, of their shifts upon isotopic substitution, and of the substitution coordinates of the water oxygen to the trial calculated values of the four conformers. The ax-E conformer best matches the observed data. The geometries of water and THP have been fixed, and an O–H–O linear arrangement with an O–H distance of 1.90 Å was assumed.

	Exptl	Calcd			
		ax-E	ax-Z	eq-E	eq-Z
Rotational constants of the normal species [MHz]					
$A$	2895.2	2933.2	2889.6	4511.9	4469.7
$B$	1814.6	1861.4	1891.5	1431.8	1442.2
$C$	1716.5	1752.1	1795.2	1174.8	1184.7
Shifts of rotational constants upon substitution of H <sub>2</sub> O with D <sub>2</sub> O [MHz]					
$\Delta A$	–17.7	–19.7	–15.5	–5.5	–2.6
$\Delta B$	–91.2	–93.6	–97.0	–83.9	–85.2
$\Delta C$	–76.2	–76.7	–82.2	–56.7	–57.9
Shifts of rotational constants upon substitution of H <sub>2</sub> O with H <sub>2</sub> <sup>18</sup> O [MHz]					
$\Delta A$	–5.6	–1.7	–39.3	–11.7	–49.7
$\Delta B$	–93.2	–96.8	–73.1	–78.5	–70.6
$\Delta C$	–82.2	–85.5	–51.6	–52.7	–44.8
$r_s$ coordinates of water oxygen [Å]					
a	2.62	2.58	2.61	3.33	3.34
b	0.07	0.0	0.0	0.0	0.0
c	0.78	0.81	0.74	0.27	0.19

of the various possible structures of THP–W and to confirm some assumptions made for the structure determination. The 6-31G\*\* basis set was selected based on the good results Schütz et al. obtained for phenol–water<sup>[37]</sup> and, for reasons pointed out previously, for aniline–water.<sup>[38]</sup> We started with structure optimization at HF/6-31G\*\* level using the Gaussian packages.<sup>[30, 31]</sup> When optimizing structures of complexes one must be aware that the basis set superposition error (BSSE) will not be corrected by the implemented optimization procedure. As a result the stabilizing energy will be overestimated; this will cause, for example, the calculated hydrogen bond length to be too short. Recently Simon et al.<sup>[39]</sup> proposed a method for structure optimization correcting the BSSE by the counterpoise procedure (CP).<sup>[40]</sup> Another

Table 10.  $r_0$  hydrogen bond parameters obtained by fixing the geometries of water and THP to the values of the isolated molecules. The experimental  $r_s$  coordinates of the water oxygen and rotational constants are compared to the values calculated with this geometry.

$r_0$ hydrogen bond parameters [ $\text{\AA}$ and degrees, see Figure 1] <sup>[a]</sup>						
$r = 1.91(2)$		$\tau = 122(2)$		$\theta = 184(4)$		
$R^{[b]} = 3.324(4)$						
$r_s$ coordinates of the water oxygen [ $\text{\AA}$ ]						
exptl	a		b		c	
	calcd <sup>[c]</sup>		calcd <sup>[c]</sup>		calcd <sup>[c]</sup>	
2.669(5) <sup>[d]</sup>	2.652		0.00		0.783	
rotational constants [MHz]						
	$\text{H}_2\text{O}$		$\text{H}_2^{18}\text{O}$		$\text{D}_2\text{O}$	
	exptl	calcd <sup>[c]</sup>	exptl	calcd <sup>[c]</sup>	exptl	calcd <sup>[c]</sup>
A	2895.2	2890.3	2877.5	2872.6	2889.6	2889.2
B	1814.6	1813.7	1723.4	1720.9	1721.4	1720.3
C	1716.5	1717.3	1640.2	1639.6	1634.3	1633.7

[a] Obtained from  $r_{\text{O-O}} = 2.866$  (4),  $\alpha = 123.3(1)$ , and  $\angle(\text{H-O-O}) = 2.5(25)$ , the parameters which were actually fitted. [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.

Table 11. Comparison of quartic centrifugal distortion constants [kHz] of THP–W and 1,4-dioxane–water.

	THP–W	1,4-dioxane–water
$D_J$	3.385(3)	4.07(2)
$D_{JK}$	4.21(2)	16.2(2)
$D_K$	–2.85(3)	–13.7(3)
$d_1$	0.376(2)	0.45(2)
$d_2$	0.026(2)	0.105(4)

difficulty is caused by the flatness of the energy potential of the complex. Thus the quality of the resulting optimized structure will be strongly related to the quality of the structure at the starting point. The flat energy potential might also give rise to more than one minimum for the structure of the complex. So, not surprisingly, three structures of type eq-E could be found.

The structure optimizations were performed at the HF/6-31G\*\* level. The optimization took place under  $C_s$  symmetry constraint for the complex; the hydrogen bond was not constrained to linearity. At the HF level four structures were found. Three correspond to the eq-E structure and one to ax-E. The three eq-E structures resemble each other closely; minor differences occur in the hydrogen bond. The structures are given in Table 12. We calculated the stabilization energies,  $E_{\text{stab}}$ , of these structures using the CP method to correct for the BSSE with all energies being calculated in the basis set used for the complex [Eq. (3)]. The BSSE-corrected stabilization energies are  $-4.437$  ( $-4.430$ )  $\text{kcal mol}^{-1}$  for structure eq-E and  $-4.229$   $\text{kcal mol}^{-1}$  for structure ax-E.

$$E_{\text{stab}} = E_{\text{complex}} - E_{\text{thp}} - E_{\text{water}} \quad (3)$$

When deriving the experimental structure of a complex it is usually assumed that the structures of the monomers do not change upon complexation. In order to prove this assumption for THP–W we compared the optimized structures of THP–

Table 12. HF/6-31G\*\* optimized structures of THP–W. Bond lengths in  $\text{\AA}$ , bond angles in degrees, numbering of atoms of THP according to Figure 2, deviation  $\Delta_{\text{str}}$  of structure ax-E to HF/6-31G\*\* optimized structures of monomers in %.

	eq-E, 1	eq-E, 2	eq-E, 3	ax-E	$\Delta_{\text{str}}$
OC(1)	1.408	1.408	1.408	1.409	0.5
C(1)C(2)	1.523	1.523	1.523	1.524	0.0
C(2)C(3)	1.531	1.531	1.531	1.531	0.0
C(1)H(1) <sub>ax</sub>	1.090	1.090	1.090	1.091	0.2
C(1)H(1) <sub>eq</sub>	1.082	1.082	1.082	1.083	0.0
C(2)H(2) <sub>ax</sub>	1.086	1.087	1.087	1.086	0.1
C(2)H(2) <sub>eq</sub>	1.087	1.087	1.087	1.087	0.0
C(3)H(3) <sub>ax</sub>	1.089	1.089	1.089	1.090	0.0
C(3)H(3) <sub>eq</sub>	1.086	1.086	1.086	1.086	0.1
OO	2.959	2.961	2.961	2.938	
OH <sub>a</sub> <sup>[a]</sup>	0.947	0.948	0.948	0.948	0.5
OH <sub>b</sub> <sup>[b]</sup>	0.943	0.943	0.942	0.943	0.0
OC(1)C(2)	111.01	111.00	110.98	111.27	0.1
C(1)C(2)C(3)	110.28	110.31	110.33	110.27	0.1
C(2)C(3)C(4)	110.08	110.06	110.03	109.99	0.0
C(5)OC(1)	113.72	113.76	113.71	113.60	0.0
C(2)C(1)H(1) <sub>ax</sub>	110.41	110.35	110.37	110.46	0.4
C(1)C(2)H(2) <sub>ax</sub>	108.81	108.76	108.77	108.72	0.1
C(2)C(1)H(1) <sub>eq</sub>	111.52	111.51	111.50	111.37	0.1
C(1)C(2)H(2) <sub>eq</sub>	109.55	109.61	109.61	109.48	0.3
C(1)H(1) <sub>ax</sub> H(1) <sub>eq</sub>	107.90	107.92	107.92	107.93	0.2
C(2)H(2) <sub>ax</sub> H(2) <sub>eq</sub>	107.49	107.40	107.40	107.59	0.2
C(3)H(3) <sub>ax</sub> H(3) <sub>eq</sub>	106.73	106.78	106.78	106.82	0.1
(OC(1)C(5))(C(5)C(1)C(2))	125.46	125.49	125.41	126.02	0.2
(C(2)C(3)C(4))(C(5)C(1)C(2))	132.58	132.65	132.67	132.49	0.3
(C(1)OC(5))(OO)	142.08	144.74	141.88	158.96	
H <sub>a</sub> OH <sub>b</sub>	105.70	105.68	105.76	106.40	0.4
$\Delta$ (linear hydrogen bond)	0.25	0.63	0.06	4.60	
$E_{\text{stab}}$ [kcal mol <sup>-1</sup> ]	–4.430	–4.437	–4.437	–4.229	

[a] H<sub>a</sub> is the water proton involved in the hydrogen bond. [b] H<sub>b</sub> is the ‘free’ water proton.

W and the HF/6-31G\*\*-optimized structures of the monomers THP and water. As an example, the deviation of the HF-optimized structures of the monomers to the optimized structure of ax-E is also given in Table 12. One can see that the optimized structures of the monomers do not differ much from the partial structure they have in the optimized structure of the complex. The deviations are in the range of 0.5% or less. The biggest differences occur with those atoms that are involved in the hydrogen bond. For example the O–H bond length of water with H forming the hydrogen bond increases by 0.5%, as does the bond length between C(1) and O in THP. These very small effects result directly because of the newly formed hydrogen bond.

A linear hydrogen bond was not imposed during optimization. The deviations from linearity of the hydrogen bond are given in Table 12. For structure eq-E it is less than 0.7°, and for structure ax-E it is 4.6°. The hydrogen bond is not a stiff bond; therefore, these deviations are not significant enough to indicate nonlinear hydrogen bonding. Furthermore, calculations at the MP2 level suggest that the ax-E structure is the global but not the only minimum. We will refer to this again later.

After optimizing the complex structures at the HF level we also performed calculations at the MP2 level. Because of the amount of computer time needed for the optimization procedure we did not perform complete structure optimizations but optimized the hydrogen bond length and angle by

calculating single-point energies with the MP2/6-31G\*\*-optimized monomers. The fit parameters  $r_G$  and  $\alpha$  are depicted in Figure 3. The bond lengths and angles were fitted

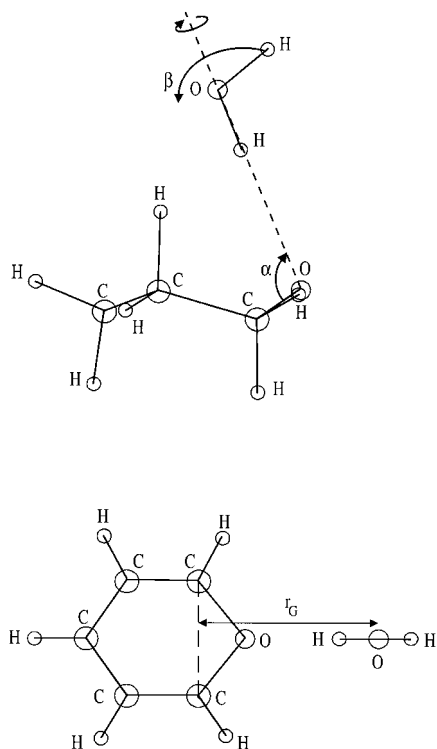


Figure 3. Fit parameters for THP–W.

by parabolic fits of the BSSE-corrected stabilization energies. For all calculations we assumed a linear hydrogen bond according to the results at the HF level, with the hydrogen bond located in the symmetry plane of THP according to the experimental results. With the optimized hydrogen bond length and angle, the ability of the free water proton to move out of the symmetry plane was tested. These structures are described by the angle  $\beta$ , which is also depicted in Figure 3. The calculations confirmed the assumed  $C_s$  symmetry. The results after optimizing the structures eq-E and ax-E are given in Table 13; the MP2/6-31G\*\*-optimized structure of THP is given in Table 5. Structure ax-E is more stable than structure eq-E by 0.24 kcal mol<sup>-1</sup>. Also with these calculations it was not possible to optimize structures analogous to structure eq-Z or

Table 13. MP2/6-31G\*\* optimized parameters of the hydrogen bond of THP–W. Definition of parameters  $r_G$ ,<sup>[a]</sup>  $\alpha$ ,<sup>[b]</sup>  $\beta$  according to Figure 3,  $r_{O-O}$  in Å,  $\alpha$ ,  $\beta$  in degrees, stabilisation energy  $E_{stab}$  in kcal mol<sup>-1</sup>.

	eq-E	ax-E
$r_{O-O}$	3.008(23)	3.006(20)
$\alpha$	138.11(97)	132.61(17)
$\beta$	0.0(210)	0.0(130) <sup>[c]</sup>
$E_{stab}$	-4.920	-5.164

[a] Instead of the fit parameter  $r_G$  the more informative distance between the two oxygens of the hydrogen bond is given. [b]  $\alpha$  refers to the angle between the THP ring and a linear O...H–O hydrogen bond. Such a linear hydrogen bond is not a requirement for the angle  $\tau$  in Figure 1. [c] Only the five parameters lowest in energy were used for the fit.

ax-Z. When varying the angle  $\alpha$  the structures eq-Z and ax-Z resulted in the corresponding structures eq-E and ax-E. This seems sensible, inasmuch as in the structures eq-Z and ax-Z the LEPs of the two oxygens are directed towards each other, whereas in the structures eq-E and ax-E they are directed away from each other. In structure ax-E additional weak interactions between the lone-pair electrons of the water oxygen, which are directed almost towards the axial hydrogens of C(3) and C(5), can result. These hydrogens are only 3.42 Å away. In structure eq-E the lone-pair electrons are directed almost towards the axial hydrogens of C(2) and C(4), but these hydrogens are 4.03 Å away. Structure ax-E is thus the most stable one, in contradiction to the results at the HF level. Because of the difficulties in optimizing structures of complexes and because of the flatness of the potential energy surface, however, we assume that the ax-E structure optimized at the HF level is the result of a local but not a global minimum.

## Conclusions

This is, to our knowledge, one of the first reports of the rotational spectrum of an adduct formed by one molecule of water and one molecule of an ether. In agreement with the facts that O–H...O is a very strong intermolecular hydrogen bond, and that THP does not have a high molecular symmetry, only one set of rotational transitions of the THP–water complex was observed and assigned in the jet-cooled mixture. Based on investigations of several isotopic species, the observed spectrum was assigned to the ax-E conformer (see Figure 1). The fact that this conformer appears to be the most stable one is in agreement with ab initio calculations at the MP2/6-31G\*\* level. The remaining three plausible conformers (Figure 1), if formed at room temperature or in an intermediate step, relax during the adiabatic expansion to the most stable one. This suggests relatively low barriers to the conformational interconversion.<sup>[36]</sup>

## Experimental section

**Free-jet absorption millimeter-wave spectroscopy:** The Stark- and pulse-modulated free-jet absorption millimeter-wave spectrometer used in this study has been described elsewhere.<sup>[18, 19]</sup> The adducts were formed by allowing argon to flow, at room temperature and a pressure of ca. 0.7 bar, over a solution of THP and water in a 2:1 molar ratio. The mixture was then expanded to approx.  $5 \times 10^{-3}$  mbar through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm, reaching an estimated rotational temperature of ca. 10 K.

**MB-FTMW spectroscopy:** The rotational spectra, in the range 3–26.5 GHz, were recorded with MB-FTMW spectrometers.<sup>[20–22]</sup> Helium containing 1% THP was used as a carrier gas at a backing pressure of 1 bar. For the measurements of the water complex a small container filled with water was additionally mounted upstream from the nozzle.

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