Conformation and Stability of Adducts of Sulfurated Cyclic Compounds with Water: Rotational Spectrum of Tetrahydrothiophene−Water

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The ground-state rotational spectrum of the tetrahydrothiophene···water complex ($C_4H_8S \cdots H_2O$) has been studied by free jet millimeter wave absorption and molecular beam Fourier transform microwave spectroscopy. The spectra of H_2O and D_2O combined with $C_4H_8{}^{32}S$ and $C_4H_8{}^{34}S$ were assigned. The rotational parameters have been interpreted in terms of a geometry in which the water molecule acts as proton donor lying close to the plane bisector to the CSC angle of tetrahydrothiophene. The "free" hydrogen is *entgegen* to the ring. The parameters characterizing the hydrogen bond are the distance between the sulfur and hydrogen atoms, $r(S \cdots H) = 2.37(4)$ Å, and the angle between the line bisecting the CSC angle of tetrahydrothiophene and the S···H bond, $\phi = 85.(3)°$. The deviation from collinearity of the atoms S···H−O is suggested from $\theta = 162.(12)°$.

Introduction

Hydrogen bonding governs solvation processes in water. Its importance in chemistry and biology has already been summarized in several books.[1] The combination of various spectroscopic techniques with the supersonic expansion,[2] which enables the controlled formation of a-few-molecules clusters, allowed for a molecular-scale understanding of molecular forces and solvation effects already in several cases.[3] Reviews are available describing the studies of molecular complexes by microwave,[4−6] Raman,[7] infrared,[8−10] electronic,[11,12] rotational coherence,[13] and zero electron kinetic energy[14] spectroscopies. The role of the van der Waals systems in physical chemistry and in the biodisciplines has been summarized by Hobza and Zahradnik.[15]

Several adducts of water with saturated ring molecules have been studied in detail by rotationally resolved spectroscopy. Precise information has been obtained on the conformation, H-bond structure, and dissociation energies of complexes 1/1 of water/cyclic alkanes[16] (hydrophobic effect), water/cyclic ethers[17−19] (O−H···O H-bond), and water/cyclic amines[20] (O−H···N H-bond).

Little attention has been paid to the hydrogen bond of the O−H···S kind. Two hydrogen bond complexes involving the fully aliphatic tetrahydrothiophene (THT, C_4H_8S) with HCl[21] and HF[22] have been recently reported. In both complexes the proton donor (HCl or HF) lies on the plane bisector to the CSC angle of THT with the HCl or HF being hydrogen-bonded to the sulfur atom. The angle formed between the line bisecting the CSC angle and the S···H internuclear line is around 90°. The deviation from collinearity of the atoms S···H−Cl and S···H−F of 14° and 10° has been rationalized in terms of secondary attractive interactions between X (F, Cl) and the CH_2 groups of the THT ring.

In this work, we attempt a detailed analysis of the hydrogen-bonded THT···H_2O complex. The equilibrium structure of the complex is of primary interest. Two different hydrogen-bonded conformations are possible, as shown in Figure 1, due to the *entgegen* or *zusammen* positions of the "free" water hydrogen.

Experimental Approaches

A commercial sample of THT (Aldrich) has been used without further purification. Supersonic expansions[2] have been used to generate molecular clusters, at conditions optimized for 1:1 cluster formation. Two different experimental setups have been used: a millimeter wave free jet absorption spectrometer (Bologna), and a molecular beam Fourier transform microwave spectrometer (Valladolid), which provided complementary results.

(a) Free Jet Absorption Millimeter Wave Spectroscopy. This relatively simple technique has been only recently systematically applied to the study of molecular adducts. The Stark and pulse modulated free jet absorption millimeter wave spectrometer used in this study has already been described elsewhere.[23,24] The adducts were formed by flowing argon, at room temperature and at a pressure of ca. 0.7 bar, over a solution of THT and water at 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, reaching an estimated "rotational" temperature of about 8 K. The high speed of the scans (10 GHz/day) and the preserved natural intensity of lines allow rapid acquisition of spectra and simplifies their assignment.

(b) MB−FTMW Spectroscopy. The details of the spectrometer, which covers the range 6−18.5 GHz, has been described previously.[25] For production of THT···H_2O complexes Ar gas at a backing pressure of ~2 bar was mixed with THT vapor at 20 mbar. This gas mixture was flowed through a reservoir with water situated just before the solenoid valve

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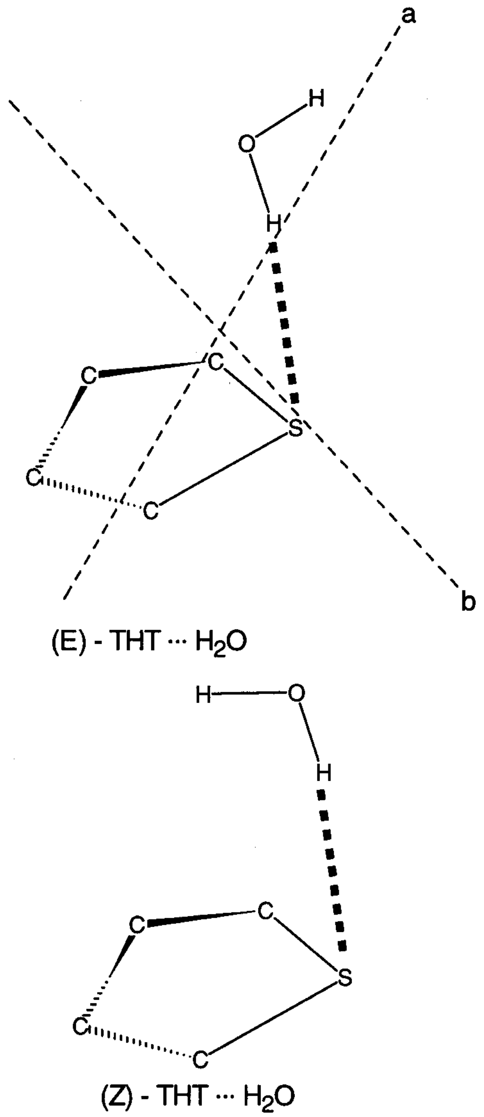

Figure 1. Plausible conformers of the THT−water adduct.

(General Valve, Series 9) and expanded into the cavity (nozzle diameter 0.8 mm). The frequencies were determined after Fourier transformation of the 8k data points time domain signal, recorded with a 40 ns sample interval. The pulsed nozzle valve is mounted near the center of one of the mirrors in such a way that the supersonic beam propagates parallel to the resonator axis. Due to this setup, all lines appear as Doppler doublets. The line position is the arithmetic mean of both Doppler components.

Rotational Spectra

THT is a five-membered ring with a twisted (C_2) equilibrium conformation.[21,26−30] Trial rotational constants based on the structures of THT[21] and water[31] have been predicted for the two conformations of Figure 1, attaching a water hydrogen to the sulfur atom. The H_2O subunit was considered to lie on the plane bisector to the CSC angle, as shown in Figure 2, with the H−O axis nearly perpendicular to the CSC plane and assuming an H···S distance of 2.3 Å.

A series of μ_a-type R-branch transitions for the normal and D_2O species were first observed and assigned in the region 60−72 GHz with the millimeter wave spectrometer of Bologna. The rotational spectrum for the THT···DOD isotopomer allowed us to distinguish between the two conformers for the complex shown in Figure 1 since it was found to be consistent with only an *entgegen* position of the "free" hydrogen of water. The transitions in the region 7−18.5 GHz were then measured in Valladolid with the MB-FTMW, which provides a higher sensitivity and resolution. In addition, we could measure the spectrum of the ^{34}S isotopomer in natural abundance. A few μ_b-type transitions were also observed for the parent species. Exhaustive search for the μ_c-type transitions was made, but with unfruitful results.

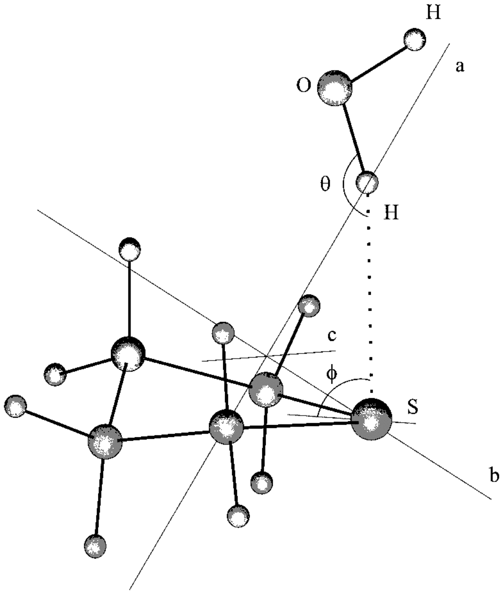

Figure 2. Structure of the observed (*engegen*) conformer of the THT−water adduct.

All the measured frequencies, displayed in Table 1, were fitted using the A-reduced semirigid Hamiltonian of Watson[32] in the I^r representation. The derived spectroscopic constants for all the isotopic species are given in Table 2. Line uncertainties of 50 kHz for the rotational transitions measured in Bologna and of 5 kHz for the lines measured in Valladolid were considered. In all cases, the calculated frequencies were commensurate with the experimental uncertainties, as can be readily seen from the residuals of Table 1.

It was found that some rotational transitions of the $C_4H_8{}^{32}S$···HOH and $C_4H_8{}^{32}S$···DOD isotopomers measured with the MB-FTMW spectrometer show hyperfine structure. The observed hyperfine splittings are very small (ca. 10−30 kHz), and its analysis is discussed in the next section. For these transitions the hypothetical unsplit frequencies used in the rotational analysis were calculated by averaging the frequencies of the hyperfine components.

Hyperfine Structure

Some rotational transitions of the isotopic species $C_4H_8{}^{32}S$···HOH and $C_4H_8{}^{32}S$···DOD appear split into two or three components. The hyperfine structure of the H_2O species has been attributed to the H,H spin−spin interaction of the two water protons. For the D_2O species the splittings have been interpreted in terms of the D-nuclear quadrupole coupling.

The fact that some lines appear as triplets precludes a tunneling motion that exchanges the protons or deuterons of the water molecule from being the origin of such splittings, since this motion would give rise to two different states. Moreover, these two states would have spin statistical weights of 1:3 in the case of $C_4H_8{}^{32}S$···HOH and of 2:1 for $C_4H_8{}^{32}S$···DOD, according to Fermi−Dirac and Bose−Einstein statistics, re-

TABLE 1: Line Center Frequencies (MHz) of THT⋯Water and Their Differences with the Calculated Frequencies

						$C_4H_8{}^{32}S\cdots HOH$		$C_4H_8{}^{32}S\cdots DOD$		$C_4H_8{}^{34}S\cdots HOH$	
J''	K''_{-1}	K''_{+1}	J'	K'_{-1}	K'_{+1}	obs	obs − cal	obs	obs − cal	obs	obs − cal
2	0	2	1	0	1	7468.2045	0.0010			7424.8438	−0.0012
2	1	2	1	1	1	7309.8974	−0.0029				
2	1	1	1	1	0	7670.7475	0.0016				
2	1	2	1	0	1	8317.4226	−0.0021				
2	2	1	1	1	0	10693.3154	0.0028				
2	2	0	1	1	1	10895.8810	−0.0004				
3	0	3	2	0	2	11148.9130	−0.0016	10547.2155	−0.0056	11070.9430	0.0002
3	1	3	2	1	2	10951.6003	−0.0014			10864.6771	0.0004
3	1	2	2	1	1	11491.1048	0.0007	10841.9122	0.0025	11457.8176	0.0005
3	2	2	2	2	1	11235.2222	−0.0029				
3	2	1	2	2	0	11321.6343	0.0033				
3	0	3	2	1	2	10299.6956	0.0022				
3	1	3	2	0	2	11800.8224	−0.0005				
3	2	2	2	1	1	14257.7912	−0.0006				
4	0	4	3	0	3	14776.2937	−0.0008	13994.5674	−0.0040	14654.1586	0.0010
4	1	4	3	1	3	14579.6704	−0.0014	13796.0646	−0.0032	14458.6759	−0.0009
4	1	3	3	1	2	15291.0197	0.0004	14434.0786	−0.0026	15238.0920	−0.0003
4	2	3	3	2	2	14962.6343	−0.0048	14134.9624	−0.0099		
4	2	2	3	2	1	15166.3141	0.0031				
4	3	2	3	3	1	15019.4001	−0.0018				
4	3	1	3	3	0	15029.5695	−0.0074				
4	0	4	3	1	3	14124.3865	0.0003				
4	1	4	3	0	3	15231.5808	0.0006				
5	0	5	4	0	4	18356.4676	0.0031	17399.9668	0.0062	18187.4532	−0.0007
5	1	5	4	1	4	18192.9163	0.0023	17220.5857	0.0025	18035.2494	0.0006
5	1	4	4	1	3			18004.4843	−0.0001		
5	2	4	4	2	3			17647.9871	−0.0030		
5	2	3	4	2	2			17931.8444	0.0027		
5	0	5	4	1	4	17901.1820	0.0031				
16	5	12	15	5	11	60335.5400	−0.0406				
16	6	11	15	6	10	60336.7700	0.0333				
16	6	10	15	6	9	60429.9700	0.0673				
16	7	10	15	7	9	60242.6000	0.0217				
16	7	9	15	7	8	60250.4100	0.0799				
16	8	9	15	8	8	60164.8600	0.0748				
16	8	8	15	8	7	60165.2100	0.0154				
16	9		15	9[a]		60110.8000	−0.0321				
16	10		15	10[a]		60072.3200	0.0039				
16	11		15	11[a]		60043.6100	0.0200				
16	12		15	12[a]		60021.2900	−0.0356				
17		17	16		16[b]	61016.4300	0.0170				
17	1	16	16	1	15	61943.8900	0.0755				
17	2	15	16	2	14	62935.5900	0.0964				
17	3	15	16	3	14	62854.4300	−0.0369				
17	4	14	16	4	13	63643.7100	−0.0582	60236.6200	0.0792		
17	4	13	16	4	12	65066.1800	0.0428				
17	5	13	16	5	12	64080.0700	0.0155				
17	5	12	16	5	11	64884.9600	−0.0034	60953.9700	0.0001		
17	6	12	16	6	11	64138.1600	0.0533				
17	6	11	16	6	10	64308.7900	0.0234	60548.3000	0.0875		
17	7	11	16	7	10	64043.2300	−0.0603	60395.5500	0.0109		
17	7	10	16	7	9	64060.3200	−0.0288	60400.5000	0.0401		
17	8	10	16	8	9	63951.5400	0.0185	60326.6100	0.0577		
17	8	9	16	8	8	63952.5100	−0.0740	60326.6100	0.0577		
17	9		16	9[a]		63886.5500	0.0114	60278.5100	−0.0360		
17	10		16	10[a]		63840.2900	−0.0256	60244.0800	−0.0075		
17	11		16	11[a]		63806.0000	0.0164	60218.1500	0.0595		
17	12		16	12[a]		63779.5200	0.0316				
18		18	17		17[b]	64572.1800	−0.0789	61173.1800	−0.0027		
18	1	17	17	1	16	65496.4600	−0.0209				
18	2	17	17	2	16	65493.8900	0.0371				
18	5	14	17	5	13	67800.1200	−0.0567	64051.8000	0.0457		
18	5	13	17	5	12	68846.6400	0.0218				
18	6	13	17	6	12	67933.3200	−0.0613	64070.2100	0.0243		
18	6	12	17	6	11			64184.9600	0.0003		
18	7	12	17	7	11	67848.6400	−0.0431	63976.8800	−0.0077		
18	7	11	17	7	10	67883.8800	−0.0574	63987.2100	−0.0433		
18	9	10	17	9	9	67665.9100	0.0206	63838.7200	−0.0136		
18	10		17	10[a]				63797.9200	0.0004		
18	11		17	11[a]		67570.1500	−0.0235	63767.3200	0.0379		
18	12		17	12[a]		67538.9100	0.0054				
18	13		17	13[a]		67514.0900	0.0098				

TABLE 1 (Continued)

						$C_4H_8{}^{32}S\cdots HOH$		$C_4H_8{}^{32}S\cdots DOD$		$C_4H_8{}^{34}S\cdots HOH$	
J''	K''_{-1}	K''_{+1}	J'	K'_{-1}	K'_{+1}	obs	obs − cal	obs	obs − cal	obs	obs − cal
19		19	18		18[b]			64540.6400	0.0451		
19	5	14	18	5	13			68432.5600	0.0568		
19	6	14	18	6	13			67653.5700	−0.0828		
19	6	13	18	6	12			67848.1900	−0.0161		
19	7	13	18	7	12			67562.2200	−0.0731		
19	7	12	18	7	11			67582.9300	−0.0630		
19	9		18	9[a]				67401.5000	−0.0248		
19	10		18	10[a]				67353.4900	−0.0478		
20		20	19		19[b]			67907.1200	−0.0086		
21		21	20		20[b]			71272.7000	−0.0237		

[a] Doubly overlapped transitions due to the near prolate degeneracy of the involved levels: only K_a is given. [b] Doubly overlapped transitions due to the near prolate degeneracy of the involved levels: only K_c is given.

TABLE 2: Spectroscopic Constants for the THT$\cdots$H$_2$O Complex

	$C_4H_8{}^{32}S\cdots HOH$	$C_4H_8{}^{32}S\cdots DOD$	$C_4H_8{}^{34}S\cdots HOH$
A/MHz	2970.3564(29)[a]	2963.814(26)	2918.600(45)
B	1962.81712(53)	1849.09054(56)	1962.4712(29)
C	1782.40249(37)	1688.02747(57)	1763.9206(17)
Δ_J/kHz	3.1331(19)	2.6822(20)	3.072(61)
Δ_{JK}	3.972(11)	4.279(13)	3.6 (14)
Δ_K	−2.53(60)	[−2.53][b]	[−2.53]
δ_J	0.43953(64)	0.36902(72)	0.502(36)
δ_K	−5.563(57)	−4.954(71)	[−5.563]
N[c]	67	40	9
J max.	18	21	5
σ[d]/kHz	35	38	0.7
P_c[e]/u Å^2	72.03958(57)	72.2192(13)	72.0854(21)

[a] Standard error in parentheses in units of the last digit. [b] Parameters in square brakets were fixed to the corresponding $C_4H_8{}^{32}S\cdots HOH$. [c] Number of fitted transitions. [d] rms deviation of the fit. [e] $P_c = (I_a + I_b - I_c)/2 = \sum_i m_i c_i^2$.

spectively. Such an intensity ratio of the hyperfine components is not observed. Apart from this, if the splittings observed for the H$_2$O species were due to a tunneling motion, the corresponding splittings in the D$_2$O species should reflect a mass-dependence reduction. Thus, given the magnitude of the splittings observed for the parent species, they would be too small in THT$\cdots$DOD to be detected.

The closely spaced hyperfine structure of the $C_4H_8{}^{32}S\cdots HOH$ isotopomer was analyzed in the first place. It was found that the splittings observed were described satisfactorily by a Hamiltonian containing the semirigid rotor terms and the standard operator H_{ss} which takes into account the spin−spin interaction of the two water protons.[33] The fit of the hyperfine frequencies of Table 3 gave a value of the coupling constant $D_{aa} = -57.2(59)$ kHz.

In the case of $C_4H_8{}^{32}S\cdots DOD$ the hyperfine structure was similar to that arising for a single quadrupole D nucleus. The Hamiltonian for the molecular rotation extended with the quadrupole interaction[34] was used to analyze the splittings. Different quadrupole coupling Hamiltonians were considered, including coupling from one single D nucleus or from two D nuclei. In both cases the corresponding χ_{aa} constants were determined. The fittings revealed the effective equivalence of the two deuterium nuclei. The available set of observed hyperfine components does not allow us to adjust independently the constants of both nuclei. When this is done, similar values for the χ_{aa} are obtained but with errors of the same order as the determined constants. However, when these constants are constrained to have the same value for each deuterium, the fit yields $\chi_{aa} = 166(43)$ kHz. The same result was obtained when it was considered one single nucleus. The hyperfine components with the assignments for one single quadrupole nucleus as well as the residuals from the fit are shown in Table 4.

TABLE 3: Observed and Calculated Spin−Spin Hyperfine Frequencies (MHz) for $C_4H_8{}^{32}S\cdots HOH$

J''	K''_{-1}	K''_{+1}	J'	K'_{-1}	K'_{+1}	I''	F''	I'	F'	obs	obs − cal
2	0	2	1	0	1	1	3	1	2	7468.2045	0.0000
2	1	2	1	1	1	1	2	1	1	7309.8844	−0.0014
						0	2	0	1	7309.9002	0.0001
						1	3	1	2	7309.9076	0.0040
2	1	1	1	1	0	1	2	1	1	7670.7306	−0.0004
						0	2	0	1	7670.7493	0.0023
						1	3	1	2	7670.7493	0.0023
						1	1	1	0	7670.7625	−0.0042
2	1	2	1	0	1	1	3	1	2	8317.4226	−0.0010
2	2	1	1	1	0	1	3	1	2	10693.3062	−0.0021
						0	2	0	1	10693.3062	−0.0021
						1	2	1	1	10693.3132	−0.0036
						1	2	1	2	10693.3268	0.0015
2	2	0	1	1	1	1	3	1	2	10895.8761	−0.0007
						0	2	0	1	10895.8761	−0.0007
						1	2	1	1	10895.8858	0.0007
3	0	3	2	0	2	1	4	1	3	11148.9130	−0.0019
3	1	3	2	1	2	1	4	1	3	10951.6003	−0.0028
3	1	2	2	1	1	1	4	1	3	11491.1048	0.0001
3	2	2	2	2	1	1	3	1	2	11235.2112	0.0009
						0	3	0	2	11235.2182	−0.0064
						1	2	1	1	11235.2371	−0.0018
3	2	1	2	2	0	1	3	1	2	11321.6174	0.0017
						1	4	1	3	11321.6394	0.0051
							2	1	1	11321.6462	0.0016
3	0	3	2	1	2	1	4	1	3	10299.6956	−0.0001
3	1	3	2	0	2	1	4	1	3	11800.8224	0.0001
3	2	2	2	1	1	1	4	1	3	14257.7912	0.0043
4	0	4	3	0	3	1	5	1	4	14776.2937	−0.0010
4	1	4	3	1	3	1	5	1	4	14579.6704	−0.0022
4	1	3	3	1	2	1	5	1	4	15291.0197	0.0006
4	2	3	3	2	2	1	4	1	3	14962.6264	−0.0064
						1	5	1	4	14962.6422	0.0006
						1	3	1	2	14962.6422	0.0006
4	2	2	3	2	1	1	5	1	4	15166.3141	0.0022
4	3	2	3	3	1	1	4	1	3	15019.3907	0.0027
						0	4	0	3	15019.4000	−0.0009
						1	5	1	4	15019.4095	0.0044
4	3	1	3	3	0	1	4	1	3	15029.5595	−0.0034
						0	4	0	3	15029.5685	−0.0074
						1	5	1	4	15029.5805	0.0004
4	0	4	3	1	3	1	5	1	4	14124.3865	−0.0008
4	1	4	3	0	3	1	5	1	4	15231.5808	0.0008
5	0	5	4	0	4	1	6	1	5	18356.4676	0.0028
5	1	5	4	1	4	1	6	1	5	18192.9163	0.0017
5	0	5	4	1	4	1	6	1	5	17901.1820	0.0025

Conformation and Structure

First indications on the relative disposition of the monomers can be provided by examination of the planar moments of inertia. They are defined as $P_g = \sum m_i g_i^2$ ($g = a, b, c$) and are

TABLE 4: Observed and Calculated Quadrupole Hyperfine Frequencies (MHz) for $C_4H_8{}^{32}S\cdots DOD$

J''	K''_{-1}	K''_{+1}	J'	K'_{-1}	K'_{+1}	F''	F'	obs	obs − cal
3	0	3	2	0	2	4	3	10547.2155	−0.0033
3	1	2	2	1	1	4	3	10841.9033	−0.0013
						3	2	10841.9211	0.0019
4	0	4	3	0	3	5	4	13994.5674	−0.0027
4	1	4	3	1	3	5	4	13796.0603	−0.0039
						4	3	13796.0688	−0.0019
4	1	3	3	1	2	5	4	14434.0786	0.0005
4	2	3	3	2	2	5	4	14134.9624	−0.0028
5	0	5	4	0	4	6	5	17399.9668	0.0067
5	1	5	4	1	4	6	5	17220.5857	0.0052
5	1	4	4	1	3	6	5	18004.4811	−0.0014
						5	4	18004.4874	0.0017
5	2	4	4	2	3	6	5	17647.9835	−0.0013
						4	3	17647.9835	−0.0013
						5	4	17647.9907	−0.0063
5	2	3	4	2	2	6	5	17931.8449	0.0037
						4	3	17931.8449	0.0037
						5	4	17931.8562	0.0022

easily obtained from combinations of the inertial moments. They are reported at the bottom of Table 2 for all the isotopic species observed for the complex. The P_c parameters have practically the same value for the three isotopomers, indicating that the isotopically substituted atoms lie in the *ab* plane of the complex. These values are slightly smaller than the P_b value of the isolated THT ($P_b = 74.4128$ u Å^2), so suggesting that the *ab* plane of the heterodimer is almost coincident with the *ac* plane of THT (an axes switching takes place upon hydration). The latter one is, in turn, very close to the plane bisector to the CSC angle of THT, which we will take as a reference in our structural calculations.

The r_0 hydrogen bond structural parameters were obtained from least-squares fits of the nine experimental rotational constants. The geometries of the monomers were assumed to remain unchanged by complexation. Initially, the water molecule was constrained to lie in the plane bisector to the CSC angle of THT and, according to the rotational spectra observed, with its "free" hydrogen located away from the THT ring. In this way the following parameters characterizing the hydrogen bond were obtained: $r(S\cdots H) = 2.37(4)$ Å, $\phi = 85.(3)°$, and $\theta = 162.(12)°$, where ϕ is the angle between the S···H bond and the line bisecting the CSC angle of THT and θ is the ∠SHO angle (see Figure 2). To confirm the assumption about the location of H_2O, the angle δ of deviation of the water subunit from the CSC bisector plane was also adjusted. A value of $\delta = 1.9(15)°$ was obtained, which indicates that the water molecule lies "effectively" in the CSC bisector plane in the equilibrium conformation. The agreement between experimental and calculated values of the rotational constants, as well as of the sulfur r_s coordinates, is shown in Table 5.

The determined structure is also consistent with the additional information supplied by the hyperfine coupling constants. Considering the spin−spin interaction in $C_4H_8{}^{32}S\cdots HOH$, there is a relation[35] between the determined D_{aa} constant and the spin−spin constant D_0 along a line connecting the two protons of the water molecule:

$$D_{aa} \approx \frac{1}{2} D_0 [3\langle \cos^2 \beta \rangle - 1] \tag{1}$$

where β is the angle between the *a* principal inertial axis of the complex and a line connecting the two hydrogens of H_2O. D_0, calculated from ref 31, is −69.1 kHz, while β is calculated to be 12.1° from the geometry of the complex. Substitution of these values in eq 1 yields a constant $D_{aa} = -64.6$ kHz, in good agreement with the value obtained from the fit of the hyperfine frequencies ($D_{aa} = -57.2(59)$ kHz). On the other hand, the χ_{aa} nuclear quadrupole coupling constant determined for $C_4H_8{}^{32}S\cdots DOD$ relates in a similar way to the quadrupole coupling constant χ_{zz} along the O−D bond:[35]

$$\chi_{aa} \approx \frac{1}{2} \chi_{zz} [3\langle \cos^2 \beta \rangle - 1] \tag{2}$$

where β is now the angle between the *a* principal inertial axis of the complex and the O−D bond. Two different quadrupole coupling constants χ_{aa} arise from eq 2 depending on the deuterium nucleus considered, 230 kHz for the "free" and 49 kHz for the "bound" one. Nevertheless, the fit of the hyperfine splittings indicates an effective equivalence of both nuclei, thus only allowing an average value to be determined. This average value of χ_{aa} was calculated to be 139.5 kHz, which is comparable to that obtained from the fit of the hyperfine structure ($\chi_{aa} = 166(43)$ kHz). The equivalence of the two deuterium nuclei can be explained in terms of a tunneling motion that interchanges them, and so it would average the coupling constants,[35] leading to the observation of identical quadrupole coupling constants. The nonobservation of tunneling splittings in the rotational spectra does not exclude the existence of this motion. Given that THT is a rather heavy molecule, a reduced mass for this vibration high enough to overlap the tunneling states can be expected.

TABLE 5: r_0 Hydrogen Bond Parameters Obtained by Fixing the Geometries of Water and THT to the Values of the Isolated Molecules

(1) r_0 Hydrogen Bond Parameters (Å and deg, See Figure 2)

$r_{S-H} = 2.37(4)^b$ $\phi = 85(3)$ $\theta = 162(12)$

(2) r_s Coordinates of the S Atom (Å)

|*a*|		|*b*|		|*c*|	
exptl	calc[c]	exptl	calc[c]	exptl	calc[c]
0.0	0.006	1.2305(2)	1.233	0.162(2)	0.155

(3) Rotational Constant

	normal		^{34}S		D_2O	
MHz	exptl	calc[c]	exptl	calc[c]	exptl	calc[c]
A	2970.4	2966.9	2918.6	2915.2	2963.8	2964.9
B	1962.8	1958.5	1962.5	1958.1	1849.1	1842.3
C	1782.4	1789.8	1763.9	1771.1	1688.0	1692.2

[a] The experimental substitution coordinates of the S atom and rotational constants are compared to the values calculated with this refined geometry. [b] Error (in parentheses) is expressed in units of the last digit. [c] Calculated with the r_0 structure (see top of the table and text).

Internal Motions of the Water Subunit

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 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 cases, for example, of cyclopropane−water,[16] phenol−water,[36] and pyrazine−water[37] these internal rotations connect equivalent minima and generate Coriolis doubling of rotational lines. This is not the case for THT−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 partner molecule, their effects are generally reflected in the anomalous high values of the Δ_J, Δ_{JK}, and Δ_K centrifugal distortion parameters, as it 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.[38] 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.[39] It is not possible to apply this approximation to THT−H_2O because the angle between the *a*-axis and the H···S bond is about 45°.

Conclusions

The rotational spectra of several isotopomers of the 1/1 complex of water/THT in the jet-cooled mixtures have been assigned and measured with millimeter wave free jet absorption and molecular beam Fourier transform microwave spectroscopies. A geometry of the complex was determined where the water subunit lies in the CSC bisector plane, being hydrogen-bonded to the sulfur atom of THT. This is consistent with the results previously obtained for related complexes,[21,22] and it has been interpreted as an interaction between the electrophilic region of the proton donor, H_2O in one case, and the nucleophilic regions in the acceptor molecule, the nonbonding electron pairs of the S atom for THT. The O−H···S H-bond is nearly linear with a H···S “bond length” of about 2.37 Å. The nonbonded water hydrogen is *entgegen* with respect to the ring, as generally observed (see for example refs 17−20, 36). So, almost certainly, the *entgegen* conformer corresponds to the global minimum. However, a local stability of the *zusammen* conformer is not excluded, even if this species has not been observed, because during the expansion it would easily relax to the most stable one. This topic is clearly described by Godfrey et al.[40]

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