Dipole–Dipole Interactions

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Dynamical Behavior and Dipole–Dipole Interactions of Tetrafluoromethane–Water**

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Water and tetrafluoromethane form a stable complex with dipole–dipole interaction as a leading factor in determining its configuration, according to the rotational spectra of several isotopologues of the complex observed in supersonic expansions. All of these spectra display the features of a symmetric top.

Nonbonding interactions play important roles in biology, supramolecular chemistry, and in solvation processes and have been the subject of numerous investigations.[1] Hydrogen bonding is the most important of such interactions; it involves many scientific areas and is invoked to explain the energetic and structural features of inorganic, organic, and biological systems.[2] Classical hydrogen bonds are O–H···O,[3] O–H···N,[4] O–H···S,[5] and N–H···O.[6] All of these are relatively

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strong hydrogen bonds with energies in the range 15–25 kJ mol^{-1}.

The hydrogen bonding of water with halogens (O–H···X) is somewhat elusive. The O–H···F and O–H···Cl bonds have been characterized through analysis of the rotational spectra of the complexes of water with Freon-32 (difluoromethane)[7] and Freon-31 (chlorofluoromethane),[8] respectively. It has been shown that the O–H···Cl hydrogen bond is slightly preferred to the O–H···F one,[8] but their energies have been estimated to be rather small (4–5 kJ mol^{-1}).[8] These energy values are similar to those estimated for weak C–H···O,[9] C–H···F[10] or C–H···π[11] interactions, which are classified as weak[12] or blue-shifted hydrogen bonds.[1] The simplest molecules containing halogen atoms (F_2 and ClF) react with water. However, by using a fast-mixing nozzle, Legon and coworkers observed non-hydrogen-bonding adducts $H_2O\cdots F_2$ and $H_2O\cdots ClF$, which display an O···F or an O···Cl interaction.[13]

CF_4 is intermediate between CH_2F_2 and F_2 in that it has no permanent dipole moment, like F_2, but each of its C–F bonds is polar, like those in CH_2F_2. So, is the leading interaction in the complex $CF_4\cdots H_2O$ a hydrogen-bonding contact as in $CH_2F_2\cdots H_2O$, or an O···F contact as in $H_2O\cdots F_2$? Investigation of its rotational spectrum provides the answer.

$CF_4\cdots H_2O$ is an interesting quantum-mechanical system. It is a combination of a spherical top (CF_4) and of a planar top (H_2O). Classically it would be an asymmetric top, but its quantum mechanical behavior depends on the barriers hindering the internal motions of the water molecule, thus approaching the classical representation in the very high barrier limit. A detailed understanding of the system would require the use of permutation-inversion theory, which takes into account all feasible motions,[14] as is necessary in the case of methane–water.[15] However, we show that the higher mass of the CF_4 group allows the problem to be treated in a relatively simple way.

We assigned the spectra of the $CF_4\cdots H_2O$, $CF_4\cdots D_2O$, $CF_4\cdots HDO$, and $CF_4\cdots H_2{}^{18}O$ isotopologues by free-jet millimeter-wave absorption spectroscopy. All spectra consisted of evenly spaced bands. For each band, the band head at higher frequency showed the features of a symmetric-top spectrum. An example of such a symmetric-top spectrum is shown for $CF_4\cdots D_2O$ in Figure 1. The lower-frequency region of the bands is quite rich in lines, some of which are up to twice the intensity of those of the symmetric-top band head. Fitting these transitions was quite troublesome. To understand these features better, we performed some measurements at lower frequency with a supersonic expansion on a Fourier transform microwave spectrometer. The overall pattern was similar to that observed in the high-frequency region, but was simpler because of the smaller number of lines. All measured line frequencies are available in the Supporting Information. The spectroscopic constants obtained by fitting to the lines for a symmetric top are reported in Table 1 for all isotopologues.

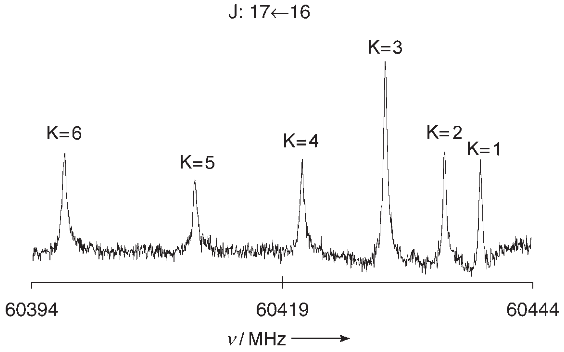

Figure 1. The rotational spectra of tetrafluoromethane–water isotopologues display symmetric-top behavior. The $J=17\leftarrow16$ transition of $CF_4–D_2O$ is shown. The intensity differences are caused by the statistical weight resulting from the three equivalent F atoms of the CF_3 symmetric top with nuclear spin 1/2. The $K=0$ component is missing because it is not Stark-modulated.

Table 1: Effective spectroscopic constants (A-state transitions) of the symmetric top $CF_4\cdots$water.

	$CF_4\cdots H_2O$	$CF_4\cdots H_2{}^{18}O$	$CF_4\cdots HDO$	$CF_4\cdots D_2O$
B/MHz	1918.0364(2)[a]	1814.684(5)	1845.5936(2)	1780.3609(2)
D_J/kHz^{-1}	5.391(4)	5.165(7)	5.078(5)	4.659(3)
D_{JK}/kHz	30.23(4)	28.0(3)	33.30(3)	34.47 (2)
H_{JJJ}/Hz	−0.081(7)		−0.10(1)	−0.079(5)
H_{JJK}/Hz	−1.36(8)	−1.0(3)	−0.59(7)	−0.67(5)
H_{JKK}/kHz	4.0(5)	3.5(15)	0.9(5)	−2.0(5)
N[b]	29	19	35	52
σ/σ_{exp}[c]	1.06	0.80	0.96	1.28

[a] Standard errors are given in parentheses in units of last digit. [b] Number of transitions in the fit. [c] Reduced deviation of the fit, relative to measurement errors of 3 and 50 kHz for the FTMW and conventional spectrometer, respectively.

The symmetric-top behavior can be explained by assuming water undergoes an almost free internal rotation. Ab initio computations at the MP2/6-311++G(d,p) level[16] converge to a global minimum that is in agreement with the experimental configuration (theoretical rotational constants are $A=5603.4$, $B=2052.2$, and $C=2043.4$ MHz). The calculations also indicate that the barriers to the motions of the water molecule between CF_3 hollows are relatively high (Figure 2), whereas the barrier to the internal rotation of water is low ($V_3\approx 24$ cm^{-1}; Figure 2). A calculation[17] with a simple flexible model indicates that in this case the ground-state torsional wavefunction describes a water molecule with

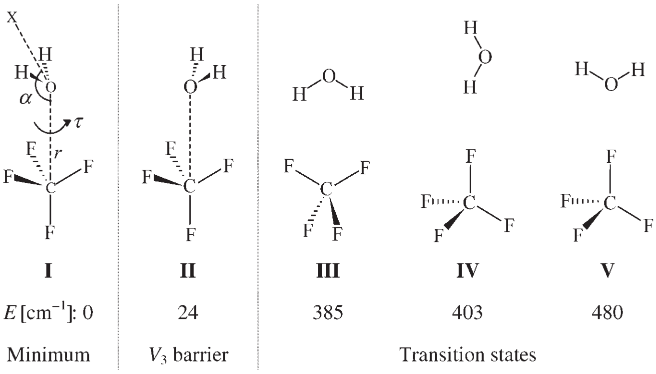

Figure 2. MP2/6-311++G** energy minimum of $CF_4–H_2O$ and transition states for the motions of water between CF_3 hollows.

the two hydrogen atoms completely delocalized with respect to the C_3 symmetry axis. As a consequence, the quantum-mechanical object is a symmetric top, and rotational constants B and C have the same value. The overall picture of the complex is shown in Figure 3.

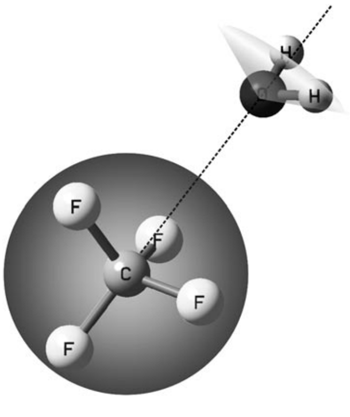

Figure 3. Cone of uncertainty of the orientation of the water moiety within a CF_3 hollow.

The parameters r (the distance between the C and O atoms; 3.371(3) Å) and α (125(2)°; see Figure 2) were estimated by assuming that the structures of water[18] and CF_4[19] are not altered upon formation of the complex. The shortest F···H, F···O, and C···O distances are 3.13, 2.75, and 3.30 Å, respectively, and the C–F bonds are nearly parallel with the axis of the cone of uncertainty defined by the delocalized H–O bonds.

The behavior of the "nonsymmetric-top" transitions (E-type) of $CF_4\cdots H_2O$ is very similar to that of benzene–water;[20] it cannot be interpreted with simple Hamiltonians,[21] but is described in Appendix 1 of the Supporting Information.

In view of the geometry and symmetry of the complex, it is likely that the stretching motion that leads to the dissociation of the complex is almost parallel to the a axis. This allows us to estimate the stretching force constant (k_s) by using the approximate Equation (1),[22] in which μ_{PD} is the pseudo-

$$k_s = 16\pi^4(\mu_{PD}R_{CM})^2[(B^2+C^2)^2+2(B^4+C^4)]/(h\,D_J) \qquad (1)$$

diatomic reduced mass, R_{CM} is distance between the centers of mass, and D_J is the first-order centrifugal-distortion constant. A k_s value of 4.2 N m^{-1}, corresponding to a harmonic stretching frequency of 69 cm^{-1}, was obtained. The dissociation energy (E_D) was evaluated to be 5.0 kJ mol^{-1} by assuming a Lennard–Jones potential function and using the approximated Equation (2).[23] This energy is similar to that estimated

$$E_D = 1/72\,k_s R_{CM}{}^2 \qquad (2)$$

for molecular complexes with three weak C–H···F–C or C–H···O hydrogen bonds. This seriously limits the consideration of weak hydrogen bonds as major factors in estimating the conformations of molecular complexes, as their energy is very similar to those of dispersion forces.

We believe that the configuration shown in Figure 3 results from favorable dipole–dipole interactions between the C–F and H–O bonds, whose electric dipole moments are almost antiparallel. Dipole–dipole interaction energy has been shown to be the leading factor also in determining the conformation of $CH_3F\cdots CF_3H$.[10b]

Experimental Section

Two experimental setups were used:

a) The 60–78-GHz Stark and pulse-modulated free-jet absorption millimeter-wave spectrometer used in this study is described elsewhere.[24] The best conditions to generate the adduct were obtained when flowing a mixture of approximately 30 mol % CF_4 (Linde) in helium at a pressure of 1.8 bar over water at room temperature and expanding it to about 5×10^{-3} mbar through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm. An estimated "rotational" temperature of about 10–20 K was reached. All samples were obtained from commercial sources and used without further purification. The accuracy of the frequency measurements was estimated to be 0.05 MHz.

b) The COBRA-type[25] pulsed supersonic-jet Fourier transform microwave (FTMW) spectrometer[26] is described elsewhere.[27] It was recently updated with the FTMW++ set of programs.[28] A mixture of 2 % in pressure CF_4 in He was flown over water at room temperature, and expanded to about 10^{-5} mbar. Each rotational transition is split by the Doppler effect and enhanced by the molecular-beam expansion in the direction of the coaxial supersonic-jet and resonator axes. The rest frequency was calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz and lines separated by more than 7 kHz are resolvable.

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[1] A full issue of Chemical Review has been dedicated to this topic: see for example the introduction: B. Brutschy, P. Hobza, *Chem. Rev.* **2000**, *100*, 3861, and the article: P. Hobza, Z. Havlas, *Chem. Rev.* **2000**, *100*, 4253–4264.

[2] See, for example, the two more recent books on the topic: a) A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, **1997**; b) S. Scheiner, *Hydrogen Bonding*, Oxford University Press, New York, **1997**.

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