

The Fourier transform rotational spectrum of difluoromethane–water: internal motion of water

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Abstract

The Fourier transform rotational spectra of the normal and the ¹³C species of the 1:1 complex between difluoromethane and water have been measured. The rotational transitions are split into two component lines, due to the internal rotation of the water moiety. The barrier to this motion has been estimated to be 340(20) cm⁻¹. An improved structure of the complex has been obtained.

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1. Introduction

The free jet millimeter wave spectrum of difluoromethane–water (since now on DFM–H₂O) has been reported recently [1]. Information on the configuration and on the structural and energetic details of the O–H⋯F–C hydrogen bond have been obtained, leading to the shape of the complex shown in Fig. 1. No splittings due to the internal rotation of the water moiety were observed. However, the rotational spectra of several complexes of water with organic molecules displayed splittings of the rotational transitions, which enabled the determination of the potential energy surface of the motions of water in the complex. This analysis was successfully performed, e.g. for pyrazine–water [2], phenol–water [3], indole–water [4], benzonitrile–water [5], anisole–water [6]. Since Fourier transform microwave spectroscopy (FT-MW) does have a higher resolution power than free jet absorption millimetre wave spectroscopy, we pursued a high-resolution measurement of the spectrum of DFM–H₂O utilizing the FT-MW technique. We observed indeed narrow splittings of the rotational

transitions, which allowed for an estimate of the barrier to the internal rotation of the water subunit. In addition, with the superior sensitivity provided by FT-MW spectroscopy we could detect the rotational spectrum of the ¹³C-isotopomer in natural abundance, thereby obtaining an improvement of the molecular structure.

2. Experimental

The MB-FTMW spectrum in the 6–18.5 GHz frequency region was measured using a COBRA-type [7] pulsed supersonic-jet Fourier-transform microwave (FT-MW) spectrometer [Balle-Flygare] described elsewhere [8], recently updated with the FTMW++ set of programs [9]. A mixture of 2% DFM in Ne was flown over water at room temperature, and expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry–Pérot cavity. The frequencies were determined after Fourier transformation of the 8k data points time domain signal, recorded with 100 ns sample intervals. Each rotational transition is split by Doppler effect due to the molecular beam expansion in the coaxial arrangement of the supersonic jet and resonator axes. The rest frequency is

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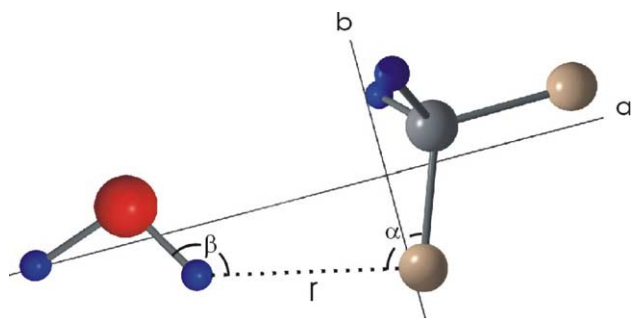


Fig. 1. Principal axes and hydrogen bond parameters of DFM-H₂O.

calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

3. Rotational spectra

From the rotational constants of Ref. [1] it has been easy to locate new rotational lines for the normal species of the DFM-H₂O in the 8–18 GHz region: six new μ_a - and six μ_b -type transitions have been measured. All of them were split into two component lines, with a relative intensity of about 1:3, as expected from the statistical weight 1:3 calculated for a large amplitude motion introduced by the internal rotation of water. μ_b -type transitions are much weaker than μ_a ones—in general approximately 1/100—and required a higher polarisation power. The splittings of μ_b -type transitions were much larger than those of the μ_a -type transitions. Fig. 2 shows the two tunnelling component lines of the $3_{13}-2_{12}$ μ_a transition. The frequencies of the newly measured lines are reported in Table 1. These, together with the frequencies previously measured in the millimeter wave range [1], have been used to determine the spectroscopic

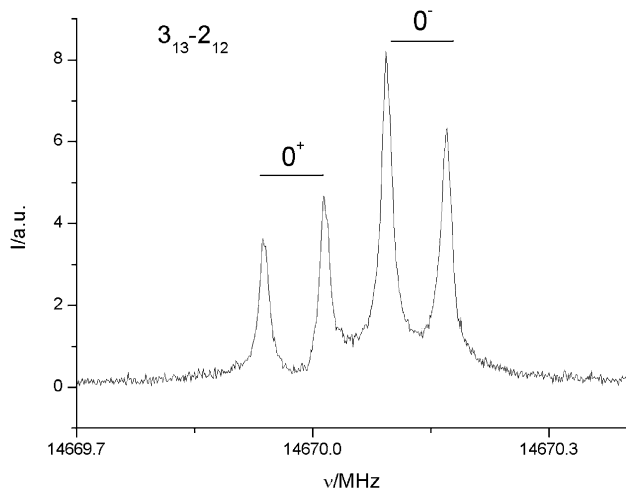


Fig. 2. The 0^+ and 0^- component lines of the $3_{13}-2_{12}$ μ_a transition of normal DFM-H₂O.

Table 1
Fourier transform experimental transition frequencies (MHz) of the ^{12}C and ^{13}C species of DFM-H₂O

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	^{12}C		^{13}C	
	0^+	0^-	0^+	0^-
<i>μ_a transitions</i>				
2(0,2)–1(0,1)	10,073.6934	10,073.7245	10,057.5792	10,057.6083
2(1,2)–1(1,1)	9781.8641	9781.9664	9765.2831	9765.3939
2(1,1)–1(1,0)	10,373.6103	10,373.5766	10,358.0310	10,357.9991
3(0,3)–2(0,2)	15,100.0160	15,100.0739	15,075.7621	15,075.8199
3(1,3)–2(1,2)	14,669.9716	14,670.1282	14,645.0906	14,645.2405
3(1,2)–2(1,1)	15,557.4634	15,557.4040	15,534.0686	15,534.0122
<i>μ_b transitions</i>				
1(1,0)–1(0,1)	16,281.0514	16,279.5145		
2(1,1)–2(0,2)	16,580.9823	16,579.3824		
3(1,2)–3(0,3)	17,038.4253	17,036.7102		
4(1,3)–4(0,4)	17,662.3651	17,660.4966		
5(0,5)–4(1,4)	10,406.5967	10,407.8617		
6(0,6)–5(1,5)	16,058.8139	16,059.9696		

constants reported in Table 2. The fit has been performed with a Pickett-type coupled Hamiltonian [10,11], here given in a very simple form:

$$H = H_R(0^+) + H_R(0^-) + H_{CD} \quad (1)$$

$H_R(0^+)$ and $H_R(0^-)$ represent the rigid rotational parts of the Hamiltonian for the 0^+ and 0^- states, respectively. The centrifugal distortion contributions (analyzed using the S-reduction and Γ -representation [12]) are represented by H_{CD} , and were assumed to be the same in both states. The transition frequencies of the two tunnelling components did not show any appreciable interaction between the two symmetry species, so that it was not possible to determine parameters such as ΔE (the energy difference between the two states), or Coriolis' coupling terms.

From the structure of the complex given in Ref. [1] the spectrum of the ^{13}C species was readily assigned. Twelve μ_a -type transitions, reported in Table 1, have been measured in natural abundance. Spectroscopic constants for the ^{13}C species have been fitted to the transition frequencies with the same procedure mentioned above, but fixing the values of the centrifugal distortion parameters to those of the normal species. The obtained rotational constants are given in Table 2.

4. Structure

The geometry of the complex as reported in Ref. [1] was quite good already, since it allowed to easily locate the spectrum of the ^{13}C species. From the rotational constants of this isotopomer we can obtain, however, additional precise structural information, such as the r_s substitution coordinates [13] of the carbon atom, reported in Table 3. These data, combined with the corresponding coordinates of the oxygen atom [1], supply a reliable O–C r_s distance.

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