The Microwave Spectrum and Dipole Moment of Hexafluoropropanone

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We recorded the microwave spectrum of hexafluoropropanone between 7 and 15 GHz using a pulsed molecular beam microwave Fourier transform spectrometer. The rotational constants were determined to be $A = 2181.71980(14)$ MHz, $B = 1037.22930(7)$ MHz, $C = 934.89233(8)$ MHz, the quartic centrifugal distortion constants are $D'_J = 0.07378(39)$ kHz, $D'_{JK} = 0.10002(75)$ kHz, $D'_K = -0.07269(266)$ kHz, $\delta'_J = 0.00623(29)$ kHz and $R'_6 = 0.00755(12)$ kHz. Stark effect measurements yielded a dipole moment $\mu = \mu_b = 0.3949(18)$ D.

Introduction

In the course of our studies of multiply fluorinated compounds we found that hexafluoropropanone CF_3COCF_3 had not been investigated by microwave spectroscopy before. This is probably due to a very dense spectrum at room temperature crowded by many high-J transitions and lines of vibrationally excited states. Therefore we decided to analyze the spectrum by means of our pulsed molecular beam microwave Fourier transform (MB-MWFT) spectrometer. This method is very advantageous in such cases because due to the low rotational temperature in the molecular beam no highly excited states occur.

From electron diffraction studies [1] structural data were available which enabled us to predict approximate rotational constants.

Experimental

We recorded the spectrum of hexafluoropropanone using an MB-MWFT spectrometer [2] with parallel molecular beam and resonator axes [3]. A gas mixture containing 2% hexafluoropropanone in argon and a stagnation pressure of approximately 50 kPa was used throughout. We used commercially available hexafluoropropanone.

Spectral Analysis

A rough prediction of the rotational constants of hexafluoropropanone was made utilizing the structural information obtained by Hilderbrandt et al. [1] from electron diffraction measurements. From the corresponding Fortrat diagram (Fig. 1) it is obvious that the most characteristic structure in the b-type spectrum is a series of strong and equally spaced Q-branches. We used our MB-MWFT spectrometer in its automatic scan mode in order to search for these groups of lines first. A J assignment of the individual Q-branch lines became possible from their predicted asymmetry splittings (see Fig. 2, e.g.). Subsequently the Q-branch data were used to determine two rotational constants. The third constant $(B+C)$ remained indeterminate. We found that within the range of our scan several lines remained unassigned. In order to obtain an unambiguous R-branch assignment, we searched for and found the $J, K_- = 3, 3-2, 2$ K-doublet transitions. It was now easy to assign quantum numbers to the isolated R-branch lines already recorded. This information fixed the $(B+C)$ constant, and with a new prediction a number of further R-branch lines were found which confirmed our assignment.

Finally the lines were remeasured with the spectrometer in its high resolution mode, where a typical line width of 2 kHz (FWHH) can be achieved. Some lines were considerably broader than this, which could be caused by fluorine spin-rotation coupling. Internal rotation of the trifluoromethyl groups seems to be less probable because no increase from low to high-J transitions was observed.

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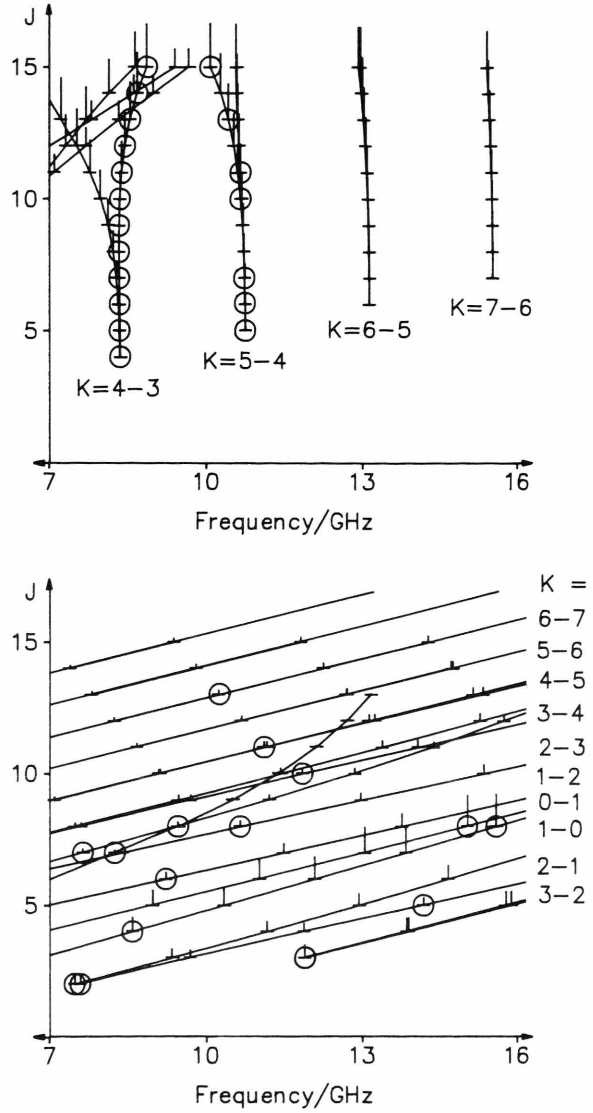

Fig. 1. Fortrat diagram of hexafluoropropanone. For simplification, R-branches (lower diagram) and Q-branches (upper diagram) are shown separately. Observed transitions are circled, theoretical line strengths are indicated by vertical bars.

Table 1. Observed transitions of hexafluoropropanone.

J	K_-	K_+	J'	K'_-	K'_+	ν [GHz]	Dev.[a] [kHz]
R-branch transitions							
4	1	4	3	0	3	8.588725	1
8	1	8	7	0	7	15.597756	1
2	2	0	1	1	1	7.588949	3
2	2	1	1	1	0	7.480050	2
5	2	3	4	1	4	14.176245	−1
3	3	0	2	2	1	11.898889	0
3	3	1	2	2	0	11.892064	−1
8	0	8	7	1	7	15.033926	0
6	1	5	5	2	4	9.230116	−1
7	1	7	6	2	4	8.250452	−1
8	1	8	7	2	5	9.460427	−1
7	2	5	6	3	4	8.387840	−1
8	2	6	7	3	5	10.649577	−0
8	2	7	7	3	4	9.461126	−0
10	3	7	9	4	6	11.847880	1
11	4	8	10	5	5	11.108230	1
13	6	7	12	7	6	10.239447	−1
13	6	8	12	7	5	10.239077	−0
Q-branch transitions							
4	4	0	4	3	1	8.356547	1
5	4	1	5	3	2	8.345786	−1
4	4	1	4	3	2	8.358381	3
5	4	2	5	3	3	8.353037	−0
6	4	3	6	3	4	8.346098	−2
7	4	4	7	3	5	8.339071	−2
8	4	5	8	3	6	8.334808	−1
9	4	6	9	3	7	8.337606	−2
10	4	7	10	3	8	8.353119	−2
11	4	8	11	3	9	8.388069	−0
12	4	9	12	3	10	8.449812	−0
13	4	10	13	3	11	8.545831	1
14	4	11	14	3	12	8.683193	0
15	4	12	15	3	13	8.868066	1
5	5	0	5	4	1	10.747337	3
6	5	1	6	4	2	10.741234	−2
7	5	2	7	4	3	10.731257	−1
10	5	5	10	4	6	10.656723	−1
13	5	8	13	4	9	10.423466	−0
15	5	10	15	4	11	10.075245	1
5	5	1	5	4	2	10.747415	3
6	5	2	6	4	3	10.741625	−1
7	5	3	7	4	4	10.732676	−1
11	5	7	11	4	8	10.656431	−0

[a] Observed minus calculated frequencies.

Table 2. Spectroscopic constants for hexafluoropropanone (representation I^r and centrifugal distortion constants of van Eijck and Typke), and correlation matrix.

			A	B	C	D'_J	D'_{JK}	D'_K	δ'_J	R'_6
A/MHz	= 2181.71980(14)[a]	A	1.000							
B/MHz	= 1037.22930(7)	B	0.722	1.000						
C/MHz	= 934.89233(8)	C	0.699	0.602	1.000					
D'_J/kHz	= 0.07378(39)	D'_J	0.791	0.781	0.851	1.000				
D'_{JK}/kHz	= 0.10002(75)	D'_{JK}	−0.031	−0.070	−0.506	−0.367	1.000			
D'_K/kHz	= −0.07269(266)	D'_K	0.824	0.533	0.584	0.788	−0.304	1.000		
δ'_J/kHz	= 0.00623(29)	δ'_J	−0.204	0.074	−0.666	−0.344	0.674	−0.212	1.000	
R'_6/kHz	= 0.00755(12)	R'_6	−0.251	−0.041	−0.643	−0.377	0.698	−0.254	0.945	1.000

[a] Numbers in parentheses are single standard errors in units of least significant figures.

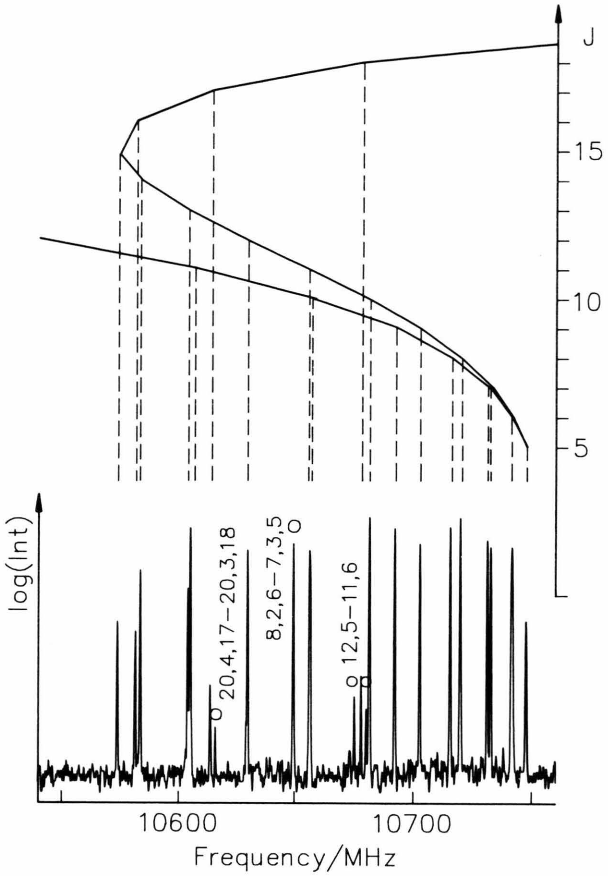

Fig. 2. Automatic scan plot of the $K_- - K'_- = 5-4$ Q-branch of hexafluoropropanone with corresponding Fortrat diagram. Isolated R-branch lines are indicated by circles.

A fit of 24 Q-branch lines (Table 1) ranging from $J=4$ to 15 and 18 R-branch lines ranging up to $J=13$ yielded three rotational constants and a complete set of well determined quartic centrifugal distortion constants. The results are presented in Table 2.

Dipole Moment Determination

For Stark effect measurements two parallel aluminum Stark plates (250 × 250 mm) were mounted symmetrically around the mirror axis in a distance of 275 mm. In contrast to our standard setup for this purpose the nozzle was positioned above the Stark plates perpendicular to the mirror axis. For calibration of the plate distance, we used the 1←0 transition of carbonylsulfide and a dipole moment of 0.715196 D [4]. The field vectors of the static electric field and the electric component of the microwave field were parallel to each other so that a $\Delta M = 0$ selection rule was used throughout.

For dipole moment determination three different transitions were recorded (Table 3) at different Stark fields. Using our program ADS [5], a dipole moment of 0.3949(18) D parallel to the *b*-axis was found.

Table 3. Observed Stark shifts $\Delta\nu$ of selected rotational transitions of hexafluoropropanone.

J	K_-	K_+	J'	K'_-	K'_+	M	$E/\mathrm{V \cdot cm^{-1}}$	$\Delta\nu$/MHz	Dev. [a] [kHz]
1	1	0	2	2	1	1	145.45	−0.153	−7
1	1	0	2	2	1	0	218.2	0.048	−7
1	1	0	2	2	1	1	218.2	−0.338	−10
1	1	1	2	2	0	0	218.2	−0.112	−11
1	1	1	2	2	0	1	218.2	0.084	−2
1	1	1	2	2	0	0	290.8	−0.183	−3
1	1	1	2	2	0	1	290.8	0.151	−2
2	2	0	3	3	1	1	436.3	−0.044	−2
2	2	0	3	3	1	2	436.3	−0.144	6
2	2	0	3	3	1	1	509.1	−0.058	−1
2	2	0	3	3	1	2	509.1	−0.196	7
2	2	0	3	3	1	1	581.85	−0.074	1
2	2	0	3	3	1	2	581.85	−0.256	10

[a] Observed minus calculated frequencies.

Table 4. Observed intensity ratios of selected K doublets of hexafluoropropanone.

J	K_-	K_+	J'	K'_-	K'_+	/	J	K_-	K_+	J'	K'_-	K'_+	I_1/I_2
7	5	3	7	4	4	/	7	5	2	7	4	3	0.83
6	5	1	6	4	2	/	6	5	2	6	4	3	0.825
9	6	4	9	5	5	/	9	6	3	9	5	4	0.85
13	6	8	12	7	5	/	13	6	7	12	7	6	0.82

Discussion

From the spectroscopic point of view hexafluoropropanone may be considered as a rigid C=O frame with two internal CF_3 rotors. This is very similar to the acetone molecule where both CF_3 groups are substituted by CH_3 groups. Due to the higher internal moment of inertia of the CF_3 groups, internal rotation splittings are considerably smaller than in acetone and, if a barrier to internal rotation of 1470 cal/mol [6] or 2800 cal/mol [7] as yielded by thermodynamic and infrared measurements respectively is assumed, beyond the resolution of our spectrometer.

It is difficult to get structural information of the molecule from microwave measurements because no isotopic substitution of the fluorine nuclei is possible. We therefore tried to get information on the point group of the molecule from nuclear spin statistics. If hexafluoropropanone contains a C_2 axis, this would cause a spin weight of 28 for ee – oo transitions and 36 for eo – oe transitions. We carefully measured the intensities of the K doublets (6_{51}–6_{42}; 6_{52}–6_{43}), (7_{52}–7_{43}; 7_{53}–7_{44}), (9_{64}–9_{55}; 9_{63}–9_{54}) and (13_{68}–12_{75}; 13_{67}–12_{76}) and indeed found an intensity ratio of approximately 7:9 (see Table 4). Whenever intensity measurements are not very accurate we believe that hexafluoropropanone belongs to the C_{2V} point group like acetone or C_2 if the trifluoromethyl groups are twisted against each other. A C_S symmetry with fully staggered internal rotors and a plane of symmetry spanned by the carbon atoms would cause equal statistical weights for both components of a K doublet, which does not agree with our measurements.

The dipole moment of hexafluoropropanone ($\mu = 0.3949(18)$ D) is surprisingly small if compared with that of acetone ($\mu = 2.90$ D); the dipole moment of carbonylfluoride, COF_2, is 0.951 (10) D [8].

Acknowledgement

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