Deuterium Quadrupole Coupling Constants of Deuterohalogenoacetylenes

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Employing the high resolution of microwave Fourier transform spectroscopy, we investigated the lowest rotational transitions of fluoro-, bromo-, and iodoacetylene-d. Along with the rotational, centrifugal distortion, halogen nuclear quadrupole, and halogen spin-rotation coupling constants, we determined the deuterium quadrupole coupling constants of bromo- and iodoacetylene-d. For fluoroacetylene-d, we redetermined the deuterium nuclear quadrupole coupling constants with higher accuracy.

Introduction

Because of the small quadrupole moment and nuclear charge of the deuterium nucleus, coupling effects in the rotational spectra of linear molecules containing deuterium are only measurable in low-J transitions. Even then, the small splittings often lead to partial overlaps of different hyperfine structure components. Therefore, the analysis of such measurements has to be carried out very carefully. In this work, we employed our recently developed fit procedures [1]. The measurements were performed with our microwave Fourier transform (MWFT) spectrometers in J-band (5.3–8.0 GHz) [2] and Ku-band (12.4–18.0 GHz) [3].

For chloro(35)acetylene-d, a very accurate value for the deuterium quadrupole coupling constant has been given by Tack and Kukolich [4]. For fluoroacetylene-d (DCCF), only less reliable data are available [5]. We therefore reinvestigated the $J = 1-0$ rotational transition of deuterofluoroacetylene. In the case of deuterobromoacetylene (DCCBr), we recorded the $J = 1-0$ and part of the $J = 2-1$ rotational transitions of both bromine isotopomers. In addition, we detected the $J = 1-0$ and $J = 3-2$ rotational transitions of deuteroiodoacetylene (DCCI).

Experimental

a) Normal fluoroacetylene was prepared by dehalogenation of 1,2-dibromo-fluoroethylene with magnesium in tetrahydrofurane [6]. Deuteration was performed by treating the product with an excess of deuterium oxide. The product of unknown isotopic contents was distilled off at low pressure and temperature.

We performed several recordings of the $J = 1-0$ transition in Ku-band under different experimental conditions. No additional splittings due to magnetic coupling of the fluorine nucleus ($I = 1/2$) could be observed. All measurements were performed at temperatures of 225–235 K and pressures of 0.1–0.2 Pa (0.7–1.5 mTorr).

b) Normal bromoacetylene was prepared by dehydrobromination of 1,2-dibromoethylene (purchased from Aldrich Chemie, Steinheim) with molten potassium hydroxide [7]. Deuteration was performed as described above.

Because of the large quadrupole moment of the bromine nuclei, the molecular rotation angular momentum couples strongly with the bromine nuclear spin ($I = 3/2$ for both isotopes) to give an "intermediate" angular momentum F_1. The resulting F_1-components are further split by coupling of the deuterium spin, so that each rotational transition consists of several narrow multiplets with different F_1 quantum numbers. The multiplet patterns vary strongly with F_1. We analysed the $J = 1-0$ transitions (in J-band) and some of the F_1-multiplets of the $J = 2-1$ transitions (in Ku-band) of both bromine isotopomers.

c) Deuteroiodoacetylene was prepared by first producing dideuteroacetylene from calcium carbide and deuterium oxide. This gas was then led through an alcaline solution of iodine in deuterium oxide and the substitution product trapped by cooling the exhaust gases to $-80°$ C [8].

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Because the rotational spectrum of deuteroiodoacetylene had not yet been assigned, we first searched for the carbon-13 isotopic satellites in the spectrum of normal iodoacetylene in order to refine the assumed structure of DCCI. After these lines had been found, the respective transitions of the deuterated species could easily be assigned (the structure determination thus possible will be published elsewhere). We recorded the $J = 1-0$ transition in J-band and one F_1-group of the $J = 3-2$ transition in Ku-band.

Deuterium Quadrupole Coupling in the Spectrum of DCCF

When only the deuterium nuclear spin ($I = 1$) couples to the molecular rotation, the $J = 1$ rotational energy level splits into three sublevels with F quantum numbers 0, 1, 2 (F for overall angular momentum). Their first order energies are (B = rotational constant, D_J = centrifugal distortion constant, eQq = quadrupole coupling constant, $c_I(\mathrm{D})$ = spin-rotation coupling constant of deuterium)

$$E/h(F=2) = 2B - 4D_J - 0.05\,eQq + c_I(\mathrm{D}), \quad (1\,\mathrm{a})$$

$$E/h(F=1) = 2B - 4D_J + 0.25\,eQq - c_I(\mathrm{D}), \quad (1\,\mathrm{b})$$

$$E/h(F=0) = 2B - 4D_J - 0.50\,eQq - 2c_I(\mathrm{D}). \quad (1\,\mathrm{c})$$

The $J = 0$ rotational level does not split, so that the transition frequencies v_i are expressed by

$$h\,v_i = E(F = i, J = 1) - E(F = 1, J = 0). \quad (2)$$

To eliminate the rotational, centrifugal distortion, and spin-rotation coupling constant, we calculated the linear combination

$$3\,v_1 - 2\,v_0 - v_2 = 1.8\,eQq. \quad (3)$$

We evaluated the v_i as arithmetic mean values out of four recordings. This calculation also yielded standard errors of the v_i and, via error propagation, the uncertainty of eQq. It was not possible to determine the spin-rotation coupling constants of deuterium and fluorine. The experimental frequencies and derived mean values as well as the derived deuterium quadrupole coupling constant are given in Table 1.

Table 1. Experimental frequencies of the hyperfine components of the $J = 1-0$ rotational transition of deuterofluoroacetylene.

	$F = 2-1$ MHz	$F = 1-1$ MHz	$F = 0-1$ MHz
First recording (weighted twice)	17472.0349	174.72.0969	17471.9431
2nd recording	17472.0353	17472.0974	17471.9417
3rd recording	17472.0352	17472.0971	17471.9441
4th recording	17472.0353	17472.0971	17471.9440
Mean values	17472.0351 (2)	17472.0971 (2)	17471.9432 (10)

Quadrupole coupling constant $eQq = 205.4(12)$ kHz.

Table 2. Experimental frequencies and derived molecular constants of deuterobromo(79)acetylene and deuterobromo(81)-acetylene. – * Δv = observed minus calculated frequency.

Quantum numbers	Bromine-79		Bromine-81	
$J', 2F_1', 2F' - J'', 2F_1'', 2F''$	v (MHz)	Δv (kHz)	v (MHz)	Δv (kHz)
1 1 3 0 3 5	7149.3877	−0.4	7135.4476	−0.8
1 5 3 0 3 1	7278.3241	−0.4	7243.2525	−0.2
1 5 7 0 3 5	7278.3427	+0.1	7243.2709	+0.1
1 5 5 0 3 3	7278-3861	+0.5	7243.3141	+0.6
1 3 3 0 3 3	7440.7652	−0.4	7378.8932	+0.3
1 3 5 0 3 5	7440.8074	−0.4	7378.9346	0.0
1 3 1 0 3 3	7440.8413	+1.2	7378.9674	+0.7
1 3 1 0 3 1	7440.8413	−0.2	7378.9674	−0.5
2 3 1 1 3 1	14492.2455	+0.4	14432.6383	+1.6
2 3 5 1 3 5	14492.2775	−0.1	14432.6681	−0.8
2 3 3 1 3 3	14492.3188	+0.6	14432.7101	+0.8
2 5 3 1 3 1	14606.5343	−0.6	14528.3064	−1.2
2 5 7 1 3 5	14606.5779	+0.4	14528.3490	−0.9
2 5 5 1 3 3	14606.6394	−1.8	14528.4117	−1.3
2 7 5 1 5 3	14606.8052	+0.3	14328.5147	−0.2
2 7 9 1 5 7	14606.8052	+2.1	14528.5147	+1.6
2 7 7 1 5 5	14606.8155	−1.4	14528.5269	+0.4
Standard deviation:	1.04 kHz		1.01 kHz	
Molecular parameters:				
B (MHz)	3655.12193(27)		3634.99449(26)	
D_J (MHz)	0.00059(4)		0.00066(4)	
eQq (Br) (MHz)	+648.1381(21)		+541.4454(20)	
c_I (Br) (kHz)	+6.40(18)		+6.70(17)	
eQq (D) (kHz)	+207.7(18)		+205.8(18)	

Coupling Effects in the Spectrum of DCCBr

The strong coupling of the bromine nuclei perturbs the rotational energy levels, so that a first order treatment is no longer sufficient. Instead, the complete Hamiltonian [9] has to be set up and the energy matrix must be diagonalized. The $J = 0$ level remains unsplit ($F_1 = 3/2$), while the $J = 1$ level is split into three F_1-sublevels ($F_1 = 1/2, 3/2, 5/3$), and the $J = 2$ level into four ($F_1 = 1/2,\ 3/2,\ 5/2,\ 7/2$). Magnetic dipole interaction with the bromine nuclear magnetic moment has to be considered at this step of the analysis. The

Table 3. Experimental frequencies and derived molecular constants of deuteroiodoacetylene. Sign of c_I (I) as defined in [9].

J,	$2F_1'$,	$2F'$ –	J'',	$2F_1''$,	$2F''$	ν (MHz)	$\Delta\nu$ (kHz)
1	5	5	0	5	5	5466.3938	+0.6
1	5	7	0	5	7	5466.4407	−0.8
1	5	3	0	5	3	5466.4625	+0.2
1	7	5	0	5	3	5938.2963	−1.2
1	7	9	0	5	7	5938.3124	+1.9
1	7	7	0	5	5	5938.3522	−0.7
1	3	5	0	5	7	6145.3081	−0.1
1	3	3	0	5	5	6145.3210	+0.1
3	5	3	2	3	1	17288.6158	−0.1
3	5	7	2	3	5	17288.6446	−0.9
3	5	5	2	3	3	17288.6828	+1.0
Standard deviation:						1.19 kHz	
Molecular parameters:							
B (MHz)						2910.21394(24)	
D_J (MHz)						0.00040(2)	
eQq (I) (MHz)						−2254.1785(34)	
c_I (I) (kHz)						+8.55(18)	
eQq (D) (kHz)						+209.5(32)	

Table 4. Comparison of deuterium quadrupole coupling constants of the deuterohalogenoacetylenes (in kHz).

	This work	Older data
DCCF	205.4(12)	212(10) [3]
DCC^{35}Cl	–	208.5(15) [2]
DCC^{79}Br	207.7(18)	–
DCC^{81}Br	206.6(18)	–
DCCI	209.5 (32)	–

F_1-sublevels are further split by the deuterium quadrupole coupling. Employing our programme SYM 2 QS [10] we analysed the three F_1-groups of the $J = 1-0$ transitions and the three most suitable F_1-multiplets ($F_1 = 7/2-5/2$, $5/2-3/2$, $3/2-3/2$) of the $J = 2-1$ transitions. From the frequencies of $2 \cdot 17$ recorded hyperfine components, five parameters (B, D_J, eQq(Br), eQq(D), and c_I(Br)) for each isotopomer were determined by simultaneous least squares fit (the centrifugal distortion constant was only included for completeness and is not well determined because of the low-J transitions involved in the analysis). The standard deviation was one kilocycle/sec in both cases. Experimental frequencies and derived data are given in Table 2.

Coupling Effects in the Spectrum of DCCI

Because of the iodine spin of 5/2, the hyperfine patterns of the rotational transitions are more complicated than those of DCCBr, and the F_1-multiplets are narrower. Furthermore, the achievable signal intensities are lower due to the very small dipole moment of DCCI. Nevertheless, all three F_1-groups of the $J = 1-0$ rotational transition (in J-band) and one ($F_1 = 5/2-3/2$) of the $J = 3-2$ transition (in Ku-band) could be recorded and at least partially resolved. From the frequencies of 11 hyperfine components, five molecular parameters (same as above) were determined. The accuracy of these is worse than those of the other investigated molecules but still satisfactory. The experimental frequencies and the derived parameters are presented in Table 3. A compilation of all determined deuterium quadrupole coupling constants, along with those taken from other authors, is given in Table 4. The differences are small, i.e., hardly beyond the error limits, and no systematic variation is obvious.

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