Microwave and Millimeterwave Spectrum of Chlorofluoroacetylene (Cl—C≡C—F)

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The microwave and millimeterwave spectra of chlorofluoroacetylene $^{35}Cl-C\equiv C-F$ and $^{37}Cl-C\equiv C-F$ in natural abundance, have been investigated. The molecule has been found to be linear. The rotational constant, the centrifugal distortion constant D_0 and the chlorine quadrupole coupling constant have been determined.

Some r_0-structures have been calculated assuming different values for the C≡C distance.

Introduction

During a previous study of the millimeterwave spectrum of Fluoroacetylene [1] it has been found that no investigations have been reported for dihaloacetylenes containing fluorine, although dihaloacetylenes with Cl, Br and Cl, I have been studied [2]. We report here the results of our investigations on Chlorofluoroacetylene as the first molecule of this serie.

Experimental

Chlorofluoroacetylene (CFA) was prepared for the first time by Delavarienne and Viehe [3] from 2-Fluoro-1, 1-Dichloroethylene [4]. We have used a similar method of synthesis starting from 1,2-Dichloro-1-Fluoroethylene [5] which can be purchased from PCR (Florida, USA). About 1 mole of pure potassium hydroxide (KOH) has been melted in vacuum at about 150 °C to get it free from oxygen which may react very strongly with CFA and also cause explosion [3].

After this treatment KOH was allowed to reach room temperature, and then, reduced to very small pieces, has been put into a horizontal glasstube of about 10 mm diameter and heated up to 110 °C under a vacuum of 10^{-3} Torr for about 24 hours. 1 g of 1,2-Dichloro-1-Fluoroethylene after vaporization was allowed to pass through the KOH at 110 °C very slowly. The reaction products were collected in a trap cooled at liquid air temperature. After a fractionated distillation between −190 °C and −70 °C we obtained a small amount of CFA which had to be stored at liquid air temperature.

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Chlorofluoroacetylene is very reactive and must be handled very carefully. It reacts with air giving explosion. As vapor, at low pressures, it was sufficiently stable to be studied by millimeterwave, Stark or microwave Fourier transform spectroscopy. The pressure in the cell was about 30 mTorr with a substance lifetime of about 15 min.

The millimeterwave spectrum was observed with a conventional spectrometer using Gordy-Type frequency multiplication and OKI-Klystrons as source [6]. Because of the weekness of the absorption lines, source modulation with second derivative presentation was used.

Due to the relative insensitivity to the Stark modulation the low frequency lines have been recorded at first using a Ku-Band-microwave Fourier transform spectrometer described elsewhere [7]. Later, with the purpose of guessing a value for the dipole moment, we performed measurements in the Ku-Band with the Stark modulation spectrometer with fields of 4000 V/cm to obtain a sufficiently modulated line. Frequency measurements are believed to be accurate to 10 kHz or 30 kHz, for the millimeterwave measurements, depending on the frequency, and to 20 kHz in the case of the Ku-Band measurements.

Spectrum

The investigation of the prepared compound began with the observation in the millimeterwave range of a sequence of single lines almost equally spaced, confirming the presence of a linear molecule. The obtained rotational constant was in agreement with the one calculated "a priori" within a few MHz. The intensity of the observed lines was comparable with the intensity of the ^{13}C OCS lines.

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A second weeker spectrum with the same characteristics was assigned to the isotopic species with chlorine 37.

No splittings due to the quadrupole coupling effect was visible in this frequency region.

The measurement of the chlorine quadrupole coupling constant χ_z was possible by observing the low frequency lines which appeared as doublets. Tables 1a, 1b and 2 report the measured and calculated frequencies of the lines for the two isotopic species.

With the measured data the rotational constant B_0 and the centrifugal distortion constant D_0 could be well determined for the two isotopic species.

Table 1a. Microwave Spectrum of ^{35}Cl—C≡C—F. Frequencies of lines are given in MHz.

J	J'	Frequencies		$\Delta\nu$
		calculated	measured	(kHz)
2	3	13349.050	13349.055*	5
3	4	17798.716	17798.715*	— 1
14	14	62294.052	62294.013	— 39
14	15	66743.376	66743.382	6
18	19	84540.116	84540.17	53
10	20	88989.145	88989.14	— 5
20	21	93438.105	93438.04	— 65
21	22	97886.992	97886.98	— 12
22	23	102335.803	102335.78	— 22
23	24	106784.533	106784.57	36
24	25	111233.181	111233.14	— 41
30	31	137923.125	137923.26	134
31	32	142371.093	142371.06	— 33
32	33	146818.950	146818.95	— 0
38	39	173503.569	173503.57	1
39	40	177950.552	177950.52	— 32

* Corrected for the quadrupole coupling splitting.

Table 1b. Microwave Spectrum of ^{37}Cl—C≡C—F. Frequencies of lines are given in MHz.

J	J'	Frequencies		$\Delta\nu$
		calculated	measured	(kHz)
2	3	13029.971	13029.973*	2
3	4	17373.279	17373.282*	3
13	14	60805.087	60805.070	— 17
14	15	65148.068	65148.095	27
20	21	91204.796	91204.76	— 36
22	23	99889.853	99889.85	— 3
23	24	104232.269	104232.32	51
24	25	108574.605	108574.60	— 5
32	33	143310.045	143310.04	— 5
33	34	147651.519	147651.49	— 29
39	40	173697.887	173697.93	43
40	41	178038.505	178038.48	— 25

* Corrected for the quadrupole coupling splitting.

Table 2. Lines split by quadrupole coupling effect of chlorine nucleus. — Frequencies of Lines are in MHz.

J	J'	F	F'	Frequencies		$\Delta\nu$
				Measured	Calculated	(kHz)
^{35}Cl—C≡C—F						
2	3	3/2	5/2	13344.910	13344.905	5
		1/2	3/2			
		9/2	7/2	13350.038	13350.043	5
		7/2	5/2			
3	4	5/2	7/2	17796.931	17796.932	— 1
		3/2	5/2			
		9/2	11/2	17799.347	17799.348	— 1
		7/2	9/2			
^{37}Cl—C≡C—F						
2	3	3/2	5/2	13026.694	13026.692	2
		1/2	3/2			
		7/2	9/2	13030.752	13030.753	— 1
		5/2	7/2			
3	4	5/2	7/2	17371.875	17371.872	+ 3
		3/2	5/2			
		9/2	11/2	17373.780	17373.777	3
		7/2	9/2			

Table 3. Rotational constant, centrifugal distortion constant and quadrupole coupling constant for ^{35}Cl—C≡C—F and ^{37}Cl—C≡C—F in the ground state. Errors are three times the standard errors of the fitting procedure. — All Data are in MHz.

^{35}Cl—C≡C—F		
B_0	2224.8442	± 0.0012
D_0	$1.445 \cdot 10^{-4}$	$\pm 0.6 \cdot 10^{-6}$
χ_{zz}	83.0	± 0.1
^{37}Cl—C≡C—F		
B_0	2171.6642	± 0.0012
D_0	$1.377 \cdot 10^{-4}$	$\pm 0.6 \cdot 10^{-6}$
χ_{zz}	65.6	± 0.1

All the determined molecular parameters are given in Table 3.

Structure

As only two isotopic species have been studied, an approach to the r_0-structure of F—C≡C—Cl involves necessarily a comparison with the structures of other mono- or bihalogenated acetylenes which have been already studied by microwave spectroscopy. We listed the interesting data for these molecules in Table 4. As it can be seen the C≡C triple bond distance has been found to lie between 1.200 and 1.209 Å. Assuming four values for the C≡C distances in this range it is possible to fit the C—F

Table 4. Structure data for monohalo- and bihaloacetylenes as studied by Microwave Spectroscopy. Bond lengths are given in Å.

H 1.053 C 1.198 C 1.279 F	a)
H 1.055 C 1.203 C 1.637 Cl	b)
H 1.055 C 1.203 C 1.791 Br	c)
NC 1.369 C 1.209 C 1.625 Cl	d)
NC 1.369 C 1.204 C 1.786 Br	d)
Br 1.790 C 1.209 C 1.628 Cl	e)
I 1.989 C 1.209 C 1.627 Cl	e)

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Table 5. r_0-Structure data in Å for Cl−C≡C−F. C≡C Distances are assumed fixed to the values in parenthesis.

C≡C	C−F	C−Cl	B_0(calc) MHz	
			^{35}Cl−C≡C−F	^{37}Cl−C≡C−F
(1.200)	1.278	1.636	2224.073	2170.910
(1.203)	1.276	1.634	2224.769	2171.512
(1.206)	1.274	1.633	2224.126	2170.976
(1.209)	1.270	1.632	2225.374	2172.185

Conversion factor 505.531 GHz/AMU · A^2.

and C−Cl distances on the basis of the rotational constants obtained from the spectra.

The four sets of obtained parameters are listed in Table 5.

Quadrupole Coupling Constant

The quadrupole coupling constant of −83.0 MHz for ^{35}Cl−C≡C−F (−65.6 MHz for ^{37}Cl−C≡C−F) agrees with the value of −83.4 MHz found for ^{35}Cl−CN [8] (−65.8 MHz for ^{37}Cl−CN) and with the values of −79.7 MHz and −74 ± 4 MHz found, respectively, for ^{35}Cl−C≡C−H [9] (−62.7 MHz for ^{37}Cl−C≡C−H) and ^{35}Cl−C≡C−CN [10] (−62 ± 3 MHz for ^{37}Cl−C≡C−CN). A comparison of these values indicates a large similarity in the electric field gradient of the electrons on the chlorine nucleus.

A strong tendency for conjugation of the C-Halogen bond with the adjacent triple bond [11, 12] is found for all these substances with calculated π-character percentage of 22−28%. Following the well known formulas given in [12] a percentage of π-character in the C−Cl bond of 20% is found in F−C≡C−Cl using for the ionic character of the σ-bond a value of 0.15.

Dipole Moment

Due to the complicated hyperfine quadrupole coupling structure and to the impossibility to reach fields higher than 4000 V/cm with the conventional Stark spectrometer, a rough value for the electric dipole moment was guessed observing the sensitivity to the modulation of the strongest of the two quadrupole satellites of the $J = 2-2$ line at 13350 MHz. A dipole moment of about 0.25 ± 0.1 D was found.

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