Rotational Spectra of Fluorodiacetylene and Fluorotriacetylene Produced by Electrical Discharge

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The rotational spectra of discharge produced ^{13}C isotopomers of fluorodiacetylene were recorded with high sensitivity to improve the centrifugal distortion analysis. Stimulated by the sensitivity attained by the spectrometer the investigation was extended to detect the *hitherto unknown fluorotriacetylene*. The spectrum of a linear molecule was found, which with high probability belongs to fluorotriacetylene.

Key words: Rotational Spectra; Fluoropolyacetylenes; Discharges; Molecular Beam; Fourier Transform Spectroscopy.

Introduction

In the recent years the rotational spectra of many molecules, which were produced by an electrical discharge in a pulsed beam nozzle, were investigated by molecular beam Fourier transform microwave (MB FTMW) spectroscopy [1]. After the initial experiments of Grabow, Heineking, and Stahl [2] this field was subsequently investigated by several groups with great success: Gerry et al. [3, 4], Endo et al. [5], Thaddeus et al. [6]. In Kiel, Sutter and Dreizler contributed to the field by two publications [7, 8]. In this paper we report an extension of this work.

It was possible to study many new molecular species, which were otherwise difficult to synthesize. Many of them were observed in the interstellar space [6]. Further deuteration was possible, and reaction paths in the discharge were proposed [7, 8].

Experimental

Following these lines the MB FTMW spectrometer [9] in Valladolid was equipped with a discharge nozzle similar to that given in Fig. 1 of [8] or that described in the appendix B of [6]. The discharge tube is of 3 mm diameter and 16 mm length, the ring electrodes have a distance of 4 mm. The downstream following reaction tube is of 4.5 mm diameter and 16 mm length. A positive upstream electrode proved to result in higher sensitivity. The downstream electrode was on ground. Further, the parts 28 to 33 of Fig. 1 of [7] (HV power supply, HV switch, pulse generator, limiting resistor, HV probe, oscilloscope) were incorporated into the spectrometer.

To test the set up with discharge produced fluorodiacetylene, $F(C{\equiv}C)_2H$, [8], a sample prepared with neon as carrier gas and approximately 1% of 1,1 difluoroethene, CF_2CH_2, as precursor gas (Aldrich Chemical Co) was used. Backing pressures up to 5 bar and discharge voltages between 800 to 1400 V were applied. With a valve opening time of 0.8 to 1 ms the high voltage was on for 0.75 ms with a delay of 0.25 ms relative to the starting of the gas pulse. We were able to measure the $J = 2 - 1$ and $3 - 2$ transitions of all four ^{13}C isotopomers in natural abundance of 1%. About 8192 experiment cycles were necessary. The results are given in Table 1. The measurements were used to improve the centrifugal distortion analysis with the Hamiltonian

$$H = BJ(J + 1) + D_J J^2(J + 1)^2. \qquad (1)$$

Using the program of Pickett [10] and including the high J transitions given in [11, 12] results in the

Table 1. Low J rotational transitions of ^{13}C-isotopomers of fluorodiacetylene, FCCCCH [MHz]. Estimated experimental uncertainty 2 kHz.

Isotopomer	J = 2-1	J = 3-2	Ref.
$F^{13}CCCCH$	8116.7033	12175.0500	
$FC^{13}CCCH$	8151.4269	12227.1354	
$FCC^{13}CCH$	8077.5380	12116.2989	
$FCCC^{13}CH$	7916.7035	11875.0506	
FCCCCH	8152.3905	12228.5810	[8]

Table 2. Rotational [MHz] and centrifugal distortion [kHz] constants of fluorodiacetylene and fluorotriacetylene. Higher order centrifugal distortion terms are not determinable.

	B	D_J	Ref.
FCCCCH	2038.09840(14)	0.08459(18)	[8]
$F^{13}CCCCH$	2029.17650(28)	0.083252(606)	
$FC^{13}CCCH$	2037.85741(28)	0.084207(535)	
$FCC^{13}CCH$	2019.38480(28)	0.083069(606)	
$FCCC^{13}CH$	1979.17652(28)	0.079141(513)	
$F(C\equiv C)_3H$	755.74895(33)	0.00807(195)	

rotational and centrifugal distortion constants given in Table 2.

The results for the main isotopomer $F(C\equiv C)_2H$, [8] have been included in Table 2. By adding the low J lines, the results gain in precision compared to [12].

Stimulated by the results and experience given in [6] that by adding another $(C\equiv C)$-group the intensity of the lines of the extended species reduces to 10 to 20%, and by the sensitivity demonstrated above by the ^{13}C isotopomers we searched for the hitherto unknown fluorotriacetylene, $F(C\equiv C)_3H$.

For prediction we transferred the structural data from $F(C\equiv C)_2H$ [12] and $HC\equiv CH$ [13] in the following way:

$$\begin{array}{ccccccc} & 1.203 & & 1.203 & & 1.208 & \\ F - C & \equiv & C - C & \equiv & C - C & \equiv & C - H \\ 1.273 & & 1.371 & & 1.371 & & 1.056 \end{array}$$

Bond lengths in Å.

A moment of inertia of I = 668.6 amu Å^2 resulted. The predicted rotational constant was B = 755.8 MHz.

Ab initio calculations were additionally performed using GAUSSIAN 98 [14] programs in order to predict the rotational constants of $F(C\equiv C)_3H$. First we tested the reliability of these calculations on the $F(C\equiv C)_2H$ molecule. We initially compared the rotational constants calculated using 6-31G(d,p) and 6-311+G(d,p) basis sets in combination with MP2 and B3LYP methods with the corresponding experimental value given in [12]. The MP2 calculation gave bond distances larger than those reported, and this resulted in values of B smaller than the experimental value. The density functional B3LYP hybrid method predicts a rotational constant in better agreement with the experimental observation and finally we decided to use a B3LYP/6-311+G(d,p) level of theory to obtain the quantum chemical value B_{QC} for $F(C\equiv C)_3H$. The predicted value B_{QC} MHz was scaled with the ratio $B_{\mathrm{OBS}}(F(C\equiv C)_2H) / B_{\mathrm{QC}}(F(C\equiv C)_2H)$ to give the final prediction B_{SC} = 756.3 MHz.

Table 3. Rotational transitions of fluorotriacetylene, $F(C\equiv C)_3H$. Estimated experimental uncertainty 2 kHz.

J'	-	J	ν_{exp} [MHz]	$\nu_{\mathrm{exp}} - \nu_{\mathrm{calc}}$ [kHz]
5	-	4	7557.48650	1.08
6	-	5	9068.97990	–0.48
7	-	6	10580.47390	–0.27
8	-	7	12091.96660	–0.01
9	-	8	13603.45780	0.3
10	-	9	15114.94470	–1.95
11	-	10	16626.43440	0.54
12	-	11	18137.91970	0.7

An extended search by scans [15] in the region of the J = 8 - 7 resulted in a weak signal. Improving with higher backing pressures up to 7 bar and higher voltages to 1400 V resulted in the frequencies given in Table 3. Figure 1 gives an example. The results of a centrifugal distortion analysis have been included in Table 2. It may be noted that the rotational constant B = 755.74895(33) MHz is very close to the predicted one and that the centrifugal distortion constant D_{J} is about one order of magnitude smaller for $F(C\equiv C)_3H$ than for $F(C\equiv C)_2H$, indicating a slower rotation.

Discussion

The agreement between experiment and prediction is a strong indication that the spectrum of the linear molecule is really that of fluorotriacetylene, $F(C\equiv C)_3H$. Also the reduction of the centrifugal distortion constant supports this conclusion. It must be a dipolar molecule composed only of hydrogen, carbon and fluorine, as the precursor only provides these atoms.

Comparing the normalized $(\frac{S}{N})_{\mathrm{norm}} = \frac{S}{N} n_{\mathrm{c}}^{-1/2}$ [8] signal to noise ratio with n_{c}, the number of cycles as a rough measure of the intensity of the signals we estimated a decrease of the signals, from $F(C\equiv C)_2H$ to $F(C\equiv C)_3H$ by a factor of 26(6). This rough method

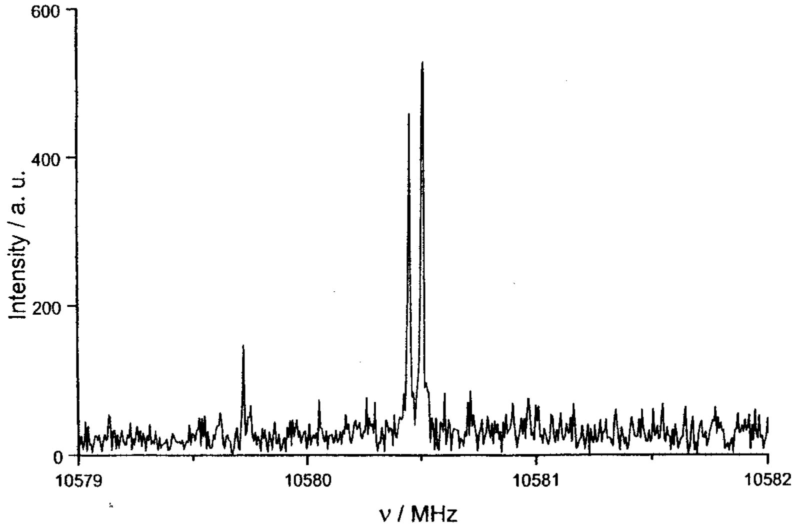

Fig. 1. A section of 3 MHz of the amplitude spectrum of fluorotriacetylene, $F(C{\equiv}C)_3H$, showing the Doppler doublet of the $J = 7 - 6$ transition. 4 k data points in the time domain with 40 ns interval, polarizing frequency 10580.47 MHz, 1024 averaging cycles, +1400 V discharge voltage. This recording results from an optimal adjustment of all parameters. The line width (HWHH) is about 6 kHz. A coherent perturbation is visible at lower frequencies.

was checked for $F(C{\equiv}C)_2H$ and its ^{13}C-species. It resulted a factor of 143(35). This value is not far from 99, which results from the natural abundance of ^{13}C.

Presently it seems not possible for reasons of sensitivity to find the ^{13}C isotopomers in natural abundance, which would prove definitely that $F(C{\equiv}C)_3H$ is the observed molecule.

It is interesting to mention that the hexatriynyl radical, C_6H, has been observed in the interstellar space [16] and in the laboratory [17].

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