Microwave and Millimeterwave Spectrum of Bromofluoroacetylene (Br—C≡C—F)

M. Andolfatto, B. Kleibömer, and A. Guarnieri

Institut für Physikalische Chemie, Abteilung Chemische Physik der Universität Kiel

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The microwave and millimeterwave spectra of Bromofluoroacetylene ^{79}Br—C≡C—F and ^{81}Br—C≡C—F in natural abundance have been investigated. The molecule has been found to be linear. The rotational constant, the centrifugal distortion constants D_0, the Bromine quadrupole coupling constant and the electrical dipole moment have been determined.

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

Introduction

In a preceding paper the microwave and millimeterwave spectrum of Chlorofluoroacetylene has been investigated [1]. As a second molecule of this series we report now the results of our investigations on Bromofluoroacetylene, a substance which, we believe, has not previously been prepared.

Experimental

Bromofluoroacetylene (BFA) has been prepared following a method developed in this laboratory and described in what follows:

To 22 ml of 1,2-dibromo-1fluoroethane (II), purchased from C.O.C., Columbia, 130 ml of a solution of potassium hydroxide in water (50 g to 100 ml H_2O) were slowly added.

The reaction mixture was heated at 100 °C with reflux for about 30 minutes. After cooling the mixture to room temperature, about 20 g of bromofluoroethylene mixture (II) were obtained. (Mostly cis-trans-1-bromo-2-fluoroethylene and little 1-bromo-1-fluoroethylene; azeotrope b. p. 31 °C.)

To the mixture (II), a small excess of bromine was added very slowly at 0 °C. At the end of the reaction a mixture of 60% 1,1,2-tribromo-2-fluoroethane, 30% 1,1,2-tribromo-1-fluoroethane, and 10% bromine was obtained (III).

Ten ml of the mixture (III) were treated in the same way as (I) to perform the dehydrohalogenation. After distillation, 5 ml of a mixture of 95% cis-trans-1,2-dibromo-1-fluoroethylene and 5% of 1,1-dibromo-2-fluoroethylene (azeotrope b.p. 85 – 90 °C) were obtained (IV).

About 100 g of pure potassium hydroxide were melted in vacuum at about 150 °C to free it from oxygen, which may react with bromofluoroacetylene. After this treatment, KOH was allowed to reach room temperature, and then reduced to very small pieces. It was then placed in a horizontal glass tube of about 10 mm diameter and heated to 110 °C under vacuum of 10^{-3} Torr for about 1 hour. One ml of the mixture (IV) after vaporization was allowed to pass very slowly through the KOH at 110 °C.

The reaction products were collected in a trap cooled at liquid air temperature. After a fractional distillation between −20 °C and −190 °C we obtained a small amount of bromofluoroacetylene (V), which had to be stored at liquid air temperature.

Bromofluoroacetylene is likely to be very reactive, and therefore it must be handled very carefully. A small explosion has been observed during one preparation. The mixed products mentioned above were analysed by gas-chromatography over an SE 30 silicone column.

As vapor, at low pressure, BFA 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 in a brass cell of about 20 min.

The millimeterwave spectrum was observed with a conventional spectrometer using klystrons in the range 30 – 40 GHz as primary sources and frequency multiplication up to the millimeter frequencies.

X- and Ku-Band microwave Fourier transform spectrometers [2] have been used for the recording of

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Reprint requests to Prof. Dr. A. Guarnieri, Institut für Phys. Chemie der Universität Kiel, Olshausenstraße 40–60, Haus S 12c, D-2300 Kiel.

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low frequency lines. Due to the second order effect of the bromine quadrupole coupling spectra, some lines had to be recorded with high resolution. A Stark modulation spectrometer in the low frequency range was used for the measurement of the dipole moment.

Frequency measurements are believed to be accurate to 10 kHz or 20 kHz, for the millimeterwave measurements, depending on the frequency, and to 20 kHz in the case of the low frequency measurements.

Table 1a. Microwave Spectrum of ^{79}Br—C≡C—F. Frequencies of lines are given in MHz.

J	*J′*	Frequencies		$\Delta\nu$
		calculated	measured	(kHz)
2	3	9068.266	9068.266*	0
3	4	12091.013	12091.013*	0
4	5	15113.754	15113.753*	− 1
31	32	96718.608	96718.66	52
32	33	99740.432	99740.48	47
33	34	102762.199	102762.12	− 79
34	35	105783.906	105783.91	4
35	36	108805.550	108805.53	− 20
36	37	111827.131	111827.10	− 31
44	45	135997.278	135997.26	− 18
45	46	139018.208	139018.29	82
46	47	142039.055	142039.05	− 5
47	48	145059.820	145059.84	20
48	49	148080.500	148080.45	− 50

* Zero line obtained after correction for quadrupole coupling splitting.

Table 1b. Microwave Spectrum of ^{81}Br—C≡C—F. Frequencies of lines are given in MHz.

J	*J′*	Frequencies		$\Delta\nu$
		calculated	measured	(kHz)
2	3	9000.093	9000.093*	0
3	4	12000.116	12000.116*	0
4	5	15000.131	15000.132*	1
31	32	95991.572	95991.55	− 22
32	33	98990.687	98990.66	− 27
33	34	101989.744	101989.77	26
34	35	104988.742	104988.75	8
35	36	107987.680	107987.65	− 30
36	37	110986.554	107986.59	36
44	45	134975.089	134975.13	41
45	46	137973.322	137973.33	8
46	47	140971.474	140971.46	− 14
47	48	143969.545	143969.52	− 25
48	49	146967.533	146967.53	− 3

* Zero line obtained after correction for quadrupole coupling splitting.

Spectrum

The investigation of the prepared substance began with the observation in the millimeterwave range of a double sequence of single lines almost equally spaced, confirming the presence of two linear molecules.

The obtained rotational constants were in agreement with those calculated "a priori" for BFA 79 and BFA 81 within a few MHz. The intensity of the observed lines was comparable with the intensity of OCS lines in the first excited vibrational state

Table 2. Lines split by quadrupole coupling effect of the bromine nucleus. Frequencies (MHz). — Calculated frequencies result from the molecular parameters listed in Table 3 via a complete diagonalisation of the ± subblocks of the Hamiltonian matrix including quadrupole hfs and centrifugal distortion.

J	*J′*	*F*	*F′*	Frequencies (MHz)		$\Delta\nu$
				measured	calculated	(kHz)
^{79}Br—C≡C—F						
1	2	1/2	3/2	6216.810	6216.811	1
		3/2	5/2	6031.122	6031.122	0
		5/2	5/2	6200.401	6200.404	3
		5/2	7/2	6031.665	6031.669	− 4
2	3	1/2	3/2	9102.583	9102.588	5
		3/2	5/2	9100.572	9100.572	0
		5/2	7/2	9060.337	9060.337	0
		7/2	9/2	9060.559	9060.559	0
3	4	3/2	5/2	12105.399	12105.405	6
		5/2	7/2	12104.856	12104.862	6
		7/2	9/2	12085.983	12085.990	7
		9/2	11/2	12086.102	12086.102	0
4	5	5/2	7/2	15121.675	15121.682	7
		7/2	9/2	15121.455	15121.460	5
		9/2	11/2	15110.350	15110.349	− 1
		11/2	13/2	16110.278	15110.285	7
^{81}Br—C≡C—F						
1	2	1/2	3/2	6142.755	6142.753	− 2
		3/2	5/2	5988.040	5988.039	− 1
		5/2	5/2	6129.312	6129.312	0
		5/2	7/2	5988.428	5988.421	− 7
2	3	1/2	3/2	9028.667	9028.673	6
		3/2	5/2	9027.260	9026.256	− 4
		5/2	7/2	8993.458	8993.459	1
		7/2	9/2	8993.618	8993.615	− 3
3	4	3/2	5/2	12012.135	12012.142	7
		5/2	7/2	12011.756	12011.760	4
		7/2	9/2	11995.991	11995.989	− 2
		9/2	11/2	11995.907	11995.910	3
4	5	5/2	7/2	15006.775	15006.766	− 9
		7/2	9/2	15006.607	15006.610	3
		9/2	11/2	14997.276	14997.272	− 4
		11/2	13/2	14997.224	14997.226	2

Table 3. Rotational constant, centrifugal distortion constant, quadrupole coupling constant and electric dipole moment for $^{79}Br-C \equiv C-F$ and $^{81}Br-C \equiv C-F$ in the ground vibrational state. Errors are three times the standard errors of the fitting procedure.

	$^{79}Br-C \equiv C-F$	$^{81}Br-C \equiv C-F$
B_0 (MHz)	1511.3790 ± 0.0015	1500.0168 ± 0.0009
D_0 (MHz)	$0.7361 \cdot 10^{-4}$ $\pm 0.3 \cdot 10^{-6}$	$0.7248 \cdot 10^{-4}$ $\pm 0.2 \cdot 10^{-6}$
χ_z (MHz)	672.6 ± 0.3	561.9 ± 0.3
μ (D)	0.449 ± 0.006	0.446 ± 0.006

(l-doublets). Splittings due to the quadrupole coupling effect were not resolved in the millimeter frequency region. The measurement of the quadrupole coupling constant, χ_z, was possible by recording the low frequency lines in X- and Ku-Band.

Table 4a. Stark Effect of the $J = 1 - 2$ Transition of 79 BFA.

Fieldstrength = Voltage/0.4738 cm

Voltage (Volt)	F	F'	MF	ν_{calc} (MHz)	ν_{obs} (MHz)	$\Delta\nu$ (kHz)
201	3/2	5/2	3/2	6030.941	6030.943	— 2
201	5/2	7/2	5/2	6031.945	6031.951	— 6
300	3/2	5/2	3/2	6030.717	6030.726	— 9
300	5/2	7/2	1/2	6031.325	6031.336	— 11
300	3/2	5/2	1/2	6031.781	6031.790	— 9
300	5/2	7/2	5/2	6032.289	6032.288	1
304	1/2	1/2	1/2	6045.433	6045.415	18
399	1/2	3/2	1/2	6216.629	6216.635	— 6
400	3/2	5/2	3/2	6030.397	6030.396	1
400	5/2	7/2	1/2	6031.054	6031.054	0
400	5/2	7/2	3/2	6031.657	6031.670	— 13
400	3/2	5/2	1/2	6032.292	6032.288	4
400	5/2	7/2	5/2	6032.774	6032.778	— 4
400	1/2	1/2	1/2	6045.384	6045.380	4
501	1/2	1/2	1/2	6045.332	6045.330	2
505	5/2	7/2	3/2	6031.669	6031.680	— 11
506	3/2	5/2	3/2	6029.949	6029.956	— 7
506	5/2	7/2	1/2	6030.670	6030.668	2
600	1/2	1/2	1/2	6045.288	6045.295	— 7
603	3/2	5/2	3/2	6029.437	6029.430	7
603	5/2	7/2	1/2	6030.227	6030.233	— 6
603	5/2	7/2	3/2	6031.699	6031.709	— 10
603	3/2	5/2	1/2	6033.771	6033.781	— 10
699	1/2	1/2	1/2	6045.264	6045.258	6
713	5/2	7/2	1/2	6029.608	6029.592	16
716	1/2	3/2	1/2	6216.403	6216.411	— 8
801	1/2	1/2	1/2	6045.271	6045.267	4
878	5/2	7/2	3/2	6031.950	6031.961	— 11
1247	5/2	7/2	3/2	6033.027	6032.997	30

Tables 1 a, 1 b and 2 report the measured and calculated frequencies of the lines for the two isotopic species.

The constants listed in Table 3 have been obtained by fitting the measured frequencies and by taking for the error three times the standard error of the fitting procedure.

Table 4 b. Stark Effect of the $J = 1 - 2$ Transition of 81 BFA.

Fieldstrength = Voltage/0.4738 cm

Voltage (Volt)	F	F'	MF	ν_{calc} (MHz)	ν_{obs} (MHz)	$\Delta\nu$ (kHz)
300	5/2	7/2	1/2	5988.087	5988.088	— 1
300	5/2	7/2	3/2	5988.416	5988.422	— 6
300	3/2	5/2	1/2	5988.688	5988.697	— 9
373	3/2	5/2	3/2	5987.384	5987.392	— 8
373	5/2	7/2	1/2	5987.899	5987.904	— 5
400	5/2	7/2	1/2	5987.818	5987.810	8
427	3/2	5/2	3/2	5987.176	5987.180	— 4
427	5/2	7/2	1/2	5987.731	5987.738	— 7
427	5/2	7/2	3/2	5988.425	5988.433	— 8
452	3/2	5/2	3/2	5987.069	5987.078	— 9
452	5/2	7/2	1/2	5987.644	5987.656	— 12
500	5/2	7/2	1/2	5987.461	5987.458	3
500	5/2	7/2	3/2	5988.440	5988.451	— 11
500	3/2	5/2	3/2	5986.846	5986.846	0
501	1/2	3/2	1/2	6142.553	6142.559	— 6
546	3/2	5/2	3/2	5986.608	5986.616	— 8
546	5/2	7/2	1/2	5987.266	5987.274	— 8
599	1/2	1/2	1/2	5999.913	5999.911	2
601	3/2	5/2	3/2	5986.291	5986.296	— 5
601	5/2	7/2	1/2	5987.004	5986.996	8
601	5/2	7/2	3/2	5988.481	5988.484	— 3
615	1/2	3/2	1/2	6142.505	6142.512	— 7
653	1/2	3/2	1/2	6142.497	6142.503	— 6
700	1/2	3/2	1/2	6142.493	6142.496	— 3
703	3/2	5/2	3/2	5985.609	5985.615	— 6
703	5/2	7/2	1/2	5986.434	5986.452	— 18
703	1/2	1/2	1/2	5999.923	5999.922	1
798	1/2	3/2	1/2	6142.516	6142.522	— 6
800	3/2	5/2	3/2	5984.838	5984.842	— 4
800	5/2	7/2	1/2	5985.782	5985.806	— 24
800	5/2	7/2	3/2	5988.669	5988.680	— 11
902	1/2	3/2	1/2	6142.602	6142.617	— 5
1005	3/2	7/2	3/2	5989.100	5989.121	— 21
1030	1/2	3/2	1/2	6142.826	6142.831	— 5
1100	1/2	1/2	1/2	6000.526	6000.541	— 15
1198	1/2	3/2	1/2	6143.378	6143.349	29

Dipole Moment

The Stark effect of hfs-quadrupole components of the $J = 1 \rightarrow 2$ transition have been measured with a *J*-Band Stark modulated spectrograph with fields up to 2650 V/cm. As in this case the shift given by the Stark field is smaller than the separation between the hfs-levels, the case of weak field is applicable. This means that the Stark-quadrupole effect can be represented in the basis of the eigenfunctions $|I\,J\,F\,M_F\rangle$ and with the microwave electric field component $\bar{E}$ parallel to the Stark field the selection rule $\Delta M_F = 0$ is to be used. For the evaluation of the electric dipole moment a computer program has been written which sets up and diagonalizes the complete Hamiltonian Matrix, including all matrix elements which would contribute to a second order perturbation treatment.

The values of the dipole moment obtained for the two isotopic species are given in Table 4. The calibration of the cell has been made using the value of 0.71521 D [10] for the dipole moment of OCS.

Quadrupole Coupling Constant

The quadrupole coupling constant of Bromine in BFA is reported in Table 5 together with those of other similar molecules for comparison. According to the quadrupole coupling discussion given in [4] σ-bond ionic character, double bond character, resultant ionic character and bond distances are also listed.

Taking for the ionic character of the σ-bond Hal – C ⁝ the formula [4]

$$i_\sigma = \left| \frac{X_A - X_B}{2} \right|, \qquad (1)$$

where X_A and X_B are the electronegativities of the halogen and of the $-\mathrm{C} \equiv \mathrm{X}$ group respectively, the expression

$$\pi_c = 2\left(1 - i_\sigma + \frac{\chi_{zz}}{e\,Q\,q_{n10}}\right) \qquad (2)$$

is obtained for the amount of double bond character.

The resultant ionic character of the bond including both i_σ and π_c components was given as

$$i_c = i_\sigma - \pi_c\,. \qquad (3)$$

A high value of π_c would mean a strong tendency to conjugation of the C-Halogen bond with the adjacent triple bond. Structures of the type $\mathrm{Hal}^{(+)} = \mathrm{C} = \mathrm{N}^{(-)}$ and $\mathrm{Hal}^{(+)} = \mathrm{C} = \mathrm{C}^{(-)} - \mathrm{X}$ seem to contribute from 22% to 15% to the ground structure configuration of the molecules listed in Table 5.

Structure

A precise calculation of the structure is not possible because only two isotopic species have been investigated. Nevertheless, as it was reported in [1], the distance of the C ≡ C bond changes in other similar molecules between 1.200 and 1.209 Å and so

Table 6. r_0-Structure data in Å for Br—C≡C—F calculated using the rotational constants and by assuming the C≡C Distance fixed to the values given in parenthesis. For comparison the calculated values for Cl—C≡C—F (1) are given below. Conversion factor 505.376 GHz · AMU · Å².

C≡C	C—F	C—Br		
(1.200)	1.2789	1.7883	Values obtained are solutions of a system set up with both rotational constants:	
(1.203)	1.2763	1.7873		
(1.206)	1.2737	1.7862	^{79}Br—C≡C—F	1511.379 MHz
(1.209)	1.2711	1.7852	^{81}Br—C≡C—F	1500.017 MHz
C≡C	**C—F**	**C—Cl**		
(1.200)	1.2773	1.6353	^{35}Cl—C≡C—F	2224.844 MHz
(1.203)	1.2748	1.6342	^{37}Cl—C≡C—F	2171.664 MHz
(1.206)	1.2722	1.6332		
(1.209)	1.2696	1.6322		

	χ_z	i_σ*	π_c	i_c	Hal—C≡	Ref.
Br—C≡N	685.6 ± 0.4	0	0.22	0.22	1.790	[5]
Br—C≡C—H	648.1 ± 0.1	0.05	0.22	0.17	1.791_3	[6]
Br—C≡C—CN	660 ± 6	0.05	0.19	0.14	1.785_8	[7]
Br—C≡C—F	672.6 ± 0.3	0.05	0.15	0.10	—	this work
For comparison same chlorine substituted molecules.						
Cl—C≡N	– 83.4 ± 0.2	0.10	0.28	0.18	1.629_3	[8]
Cl—C≡C—H	– 79.7 ± 0.2	0.15	0.24	0.09	1.636_8	[9, 11]
Cl—C≡C—CN	– 74 ± 4	0.15	0.36	0.21	1.624_5	[7]
Cl—C≡C—F	– 83.0 ± 0.1	0.15	0.18	0.03	—	[1]

Table 5. Quadrupole coupling constants: χ_z, σ-bond ionic character: i_σ, double bond character: π_c, resultant ionic character: i_c, and bond distance for the Br—C≡ bond in related molecules.

* For the electronegativities following values (4) have been used: $X_{\mathrm{Br}} = 2.6$; $X_{\mathrm{Cl}} = 3.0$; $X_{\mathrm{C \equiv C - X}} = 2.7$.

it is possible, taking fixed values for the C ≡ C distance, to calculate the other two parameters using the measured rotational constants.

Four sets of parameters have been in this way obtained. They are listed in Table 6 together with the corresponding values obtained for Cl – C ≡ C – F for comparison.

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[1] A. Guarnieri and M. Andolfatto, Z. Naturforsch. **36a**, 899 (1981).
[2] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35a**, 392 (1980).
[3] W. Gordy, Disc. Faraday Soc. **19**, 9 (1955).
[4] W. Gordy and R. L. Cook, Microwave Molecular Spectra-Interscience Publ. New York 1970, p. 587.
[5] T. Oka and H. Hirakawa, J. Phys. Soc. Japan **12**, 820 (1957).
[6] A. P. Porter and P. D. Godfrey, J. Mol. Spectr. **68**, 492 (1977); H. Jones, J. Sheridan, and O. C. Stiefvater, Z. Naturforsch. **32a**, 866 (1977).
[7] T. Bjorvatten, J. Mol. Structure **20**, 75 (1974).
[8] W. S. Lafferty, D. R. Lide, and R. A. Toth, J. Chem. Phys. **43**, 2063 (1965).
[9] J. Jones, M. Takami, and J. Sheridan, Z. Naturforsch. **33a**, 156 (1978).
[10] J. S. Muenter, J. Chem. Phys. **48**, 5455 (1968).
[11] A. A. Westenberg, J. M. Goldstein, and E. B. Wilson Jr., J. Chem. Phys. **17**, 1319 (1949).