Study of the C-D Stretching Vibration Bands ν_1 of DCCF and DCCBr

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The rotational structures of the ν_1 bands of the deuterated monohaloacetylenes DCCF and DCCBr were investigated. The rotational constants B in the ground state and in the vibrational states involved were obtained. The centrifugal distortion constants D were calculated from the force constants and the geometrical data, too. The results $D = 8.7 \times 10^{-8}\ \mathrm{cm}^{-1}$ for DCCF and $D = 1.9 \times 10^{-8}\ \mathrm{cm}^{-1}$ for DCCBr are compatible with the experimental values $(12 \pm 4) \times 10^{-8}\ \mathrm{cm}^{-1}$ and $(2 \pm 2) \times 10^{-8}\ \mathrm{cm}^{-1}$, respectively.

Introduction

The low resolution infrared spectra of monohaloacetylenes have previously been studied by Hunt and Wilson [1], who also assigned the fundamentals of DCCF and DCCBr.

The rotational constant of fluoroacetylene has been measured by Tyler and Sheridan [2] from the microwave spectrum. In their investigation a value $B_0 = 8736.04$ MHz, corresponding to $B_0 = 0.291403\ \mathrm{cm}^{-1}$, was obtained. The microwave spectra of bromoacetylenes HCCBr and DCCBr have been studied by Jones et al. [3]. These measurements give the values $B_0 = 3655.11$ MHz and $B_0 = 3634.99$ MHz for the rotational constants of the isotopic molecules DCCBr^{79} and DCCBr^{81}, corresponding to the values $0.121921\ \mathrm{cm}^{-1}$ and $0.121250\ \mathrm{cm}^{-1}$, respectively.

The aim of the present work is to continue the previous measurements of the C – H stretching bands of monohaloacetylenes [4, 5] with deuterated derivatives, to get more accurate vibrational data, and also to obtain the rotational constants in the corresponding vibrational states.

Experimental

Monofluoroacetylene was synthesized by the method of Viehe and Franchimont [6]. The bromine compound, using the method of Bashford et al. [7], changed so that the synthesis was performed at helium atmosphere. The deuterated compound was then produced in both cases by passing the gas through weakly alkaline D_2O. More than a 80% deuteration was obtained.

The measurements were performed with the grating spectrometer in the Department of Physics at the University of Oulu [8]. The detector used was an indium antimonide cell, cooled with liquid nitrogen. The wavenumbers were derived by interpolating between absorption lines of CO [9], HCl [9], N_2O [10], and HBr [11].

The path length used in both cases was 10 cm. The spectra were recorded at room temperature, at gas pressures varying from 30 to 100 mm Hg, according to the absorption. The spectral slit width used was about $0.07\ \mathrm{cm}^{-1}$.

Results

The ν_1 band of DCCF

The recorded spectrum showed a central minimum and therefore corresponded to a $\Sigma - \Sigma$ type band of a linear molecule. However, the position of the gap was not self-evident because of the strong lines caused by the overlaping hot bands. When recording the spectrum at low pressure the origin was, however, easy to locate.

The observed wavenumbers assigned to the fundamental ν_1 are given in Table 1. The lines were treated graphically and also fitted by least squares to the third order polynomial

$$\nu = \nu_0 + (B' + B'')\, m + (B' - B'')\, m^2 - 4\, D\, m^3\,, \quad (1)$$

where the letters have their usual meaning. The fit of 100 lines led to

$$\nu = 2645.090 + 0.58168\, m - 1.240 \times 10^{-3}\, m^2 - 4.9 \times 10^{-7}\, m^3\,. \quad (2)$$

The average deviation between an observed and calculated value was $0.011\ \mathrm{cm}^{-1}$.

The coefficients of the polynomial (2) give

$$\begin{aligned} \nu_0 &= 2645.090\ \mathrm{cm}^{-1}\,, \\ B'' = B_0 &= 0.29146\ \mathrm{cm}^{-1}\,, \\ B'' - B' = \alpha_1 &= 1.240 \times 10^{-3}\ \mathrm{cm}^{-1}\,, \\ D &= 12 \times 10^{-8}\ \mathrm{cm}^{-1}\,. \end{aligned}$$

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Table 1. The observed vacuum wavenumbers (cm^{-1}) of the lines in the ν_1 band of deuterated monofluoroacetylene. 2600 cm^{-1} should be added to the numbers given. The values placed in parentheses are clearly perturbed by hot bands or otherwise and they have been omitted in the calculations.

J	*P(J)*	*R(J)*	*J*	*P(J)*	*R(J)*
2		—	33	24.559	63.423
3		—	34	—	63.922
4		—	35	23.247	64.383
5		(48.561)	36	22.553	64.873
6		49.121	37	21.893	65.355
7	40.946	49.674	38	21.214	65.853
8	40.331	50.223	39	(20.500)	66.348
9	39.731	50.760	40	(19.835)	66.823
10	39.166	(51.304)	41	19.188	67.285
11	38.551	51.891	42	18.528	67.748
12	37.932	52.445	43	—	68.234
13	37.334	53.000	44	—	68.728
14	36.718	53.540	45	16.421	69.165
15	36.080	54.073	46	15.763	69.625
16	35.455	54.624	47	15.068	70.090
17	34.841	55.188	48	14.380	70.553
18	34.239	55.709	49	—	71.020
19	33.610	56.235	50	—	71.472
20	32.972	56.736	51	—	71.926
21	32.337	57.270	52	11.560	72.365
22	31.710	57.795	53	10.850	72.804
23	31.071	58.323	54	10.132	73.242
24	30.417	58.869	55	9.442	73.683
25	29.769	59.363	56	—	74.132
26	29.132	59.872	57	7.995	74.566
27	28.471	60.416	58		74.994
28	27.813	60.918	59		75.423
29	27.165	*61.418*	60		75.832
30	26.538	61.930	61		76.267
31	25.881	62.412	62		76.716
32	25.236	62.924	63		77.128
			64		77.532

The main band was accompanied by hot bands. The strongest of these is $\nu_1 + \nu_5 - \nu_5$. The intensity of this band can be calculated to be 35% of that of the main band and this is also in accordance with the observed intensity. Because this band is a $\pi - \pi$ transition, it has, in addition to the P and R branches, also a weak Q branch. From the band shape contour the origin of this band could be approximately located at 2634 cm^{-1}. The weak Q branch could be detected there, even though it was partly hidden behind the lines of the main band.

In the analysis of the band 34 lines were used. The wavenumbers are given in Table 2. By fitting them to the polynomial (1) the result was

$$\nu = 2634.33 + 0.5823\, m - 1.22 \times 10^{-3}\, m^2 - 4.6 \times 10^{-7}\, m^3 , \qquad (3)$$

and the average deviation between an observed value and one from (3) was 0.011 cm^{-1}.

Table 2. The observed vacuum wavenumbers (cm^{-1}) of the lines assigned to the hot band $\nu_1+\nu_5-\nu_5$ of deuterated monofluoroacetylene. 2600 cm^{-1} should be added to the numbers given.

J	*P(J)*	*R(J)*	*J*	*P(J)*	*R(J)*
8	29.60		26	18.37	—
9	28.98		27	17.73	—
10	28.36		28	17.09	—
11	—		29	—	—
12	—		30	—	—
13	—	(42.21)	31	—	—
14	—	42.78	32	—	—
15	25.35	43.33	33	—	—
16	24.70	43.88	34	—	53.18
17	24.10	44.44	35	—	53.68
18	23.44	44.96	36	11.81	54.20
19	(22.79)	45.49	37	11.17	
20	22.22	46.03	38	10.46	
21	—	46.55	39	9.79	
22	(20.97)	47.05	40	9.12	
23	20.29	47.60	41	8.43	
24	19.65	—	42	7.73	
25	19.01	—			

The coefficients of the above polynomial give

$$\nu_0 = 2634.33\ cm^{-1} ,$$
$$B'' = B_5 = 0.2918\ cm^{-1} ,$$
$$B'' - B' = \alpha_1 = 1.22 \times 10^{-3}\ cm^{-1} ,$$
$$D = 12 \times 10^{-8}\ cm^{-1} .$$

Another hot band which overlaps the fundamental and can be detected, has a lower relative intensity than the band stated above. This is obviously the hot band $\nu_1 + \nu_4 - \nu_4$. Because only a few lines were measured no analysis of them is given here.

The ν_1 band of DCCBr

The appearance of the ν_1 band deviated from that of the $\Sigma - \Sigma$ type band, expecially at the central region of the spectrum. The lines were broadened and in some places the rotational structure was difficult to resolve. The origin of the ν_1 band was thus not obvious, but it could be located approximately around 2611 cm^{-1}.

In the region of the band about 160 lines were measured. Because the lines in the central region and in the P branch between 2600 – 2604 cm^{-1} did not fit in with the other lines assigned to this band, only 100 wavenumbers were suitable for calculation. The exact position of the origin was selected so that the value for B'', derived from the analysis, was in the best attainable agreement with the value $B'' = 0.121589\ cm^{-1}$ calculated from the data of Jones et al.[3] for natural bromine,

Table 3. The observed vacuum wavenumbers (cm^{-1}) of the lines in the ν_1 band of DCCBr. 2500 cm^{-1} should be added to the numbers given.

J	$P(J)$	$R(J)$	J	$P(J)$	$R(J)$
11	—	113.73	49	98.12	122.08
12	—	113.96	50	97.83	122.27
13	—	114.18	51	97.54	122.48
14	—	114.41	52	97.26	122.68
15	—	114.64	53	96.98	122.87
—	—	—	54	96.70	123.07
20	—	(115.77)	55	96.44	123.29
21	—	116.01	56	96.16	123.49
22	—	116.25	57	95.85	123.69
23	(104.14)	116.45	58	95.56	123.90
24	(104.89)	116.70	59	—	124.09
25	104.59	—	60	94.98	124.30
26	104.31	—	61	94.70	124.51
27	104.05	117.36	62	94.44	124.70
28	—	117.58	63	94.13	124.89
29	—	117.82	64	93.84	125.09
30	—	(118.02)	65	93.55	125.29
31	—	—	66	93.27	125.47
32	—	—	67	92.96	125.66
33	—	118.67	68	92.68	125.86
34	—	118.91	69	92.39	126.06
35	—	119.15	70	92.10	126.24
36	—	119.37	71	91.82	126.43
37	—	119.57	72	91.50	126.62
38	—	119.78	73	91.23	126.81
39	100.87	119.98	74	90.94	127.00
40	—	120.20	75	90.64	127.16
41	(100.34)	120.42	76	90.35	127.36
42	100.03	120.64	77	90.05	127.55
43	99.75	120.85	78	89.77	127.72
44	99.48	121.04	79	89.47	127.93
45	(99.24)	121.25	80	89.17	
46	(98.98)	121.46	81	88.88	
47	(98.70)	121.67	82	88.57	
48	98.41	121.88			

The lines assigned to the ν_1 band are given in Table 3. They are rounded off to two decimal places, although, in the original calculations three decimal places were used. When fitting the lines to the polynomial (1) the result was

$$\nu = 2610.858 + 0.24275\,m - 3.63 \times 10^{-4}\,m^2 - 7.5 \times 10^{-8}\,m^3 . \qquad (4)$$

The average deviation between an observed value and a calculated one was even now 0.011 cm^{-1}.

The coefficients of the above polynomial give

$$\begin{aligned} \nu_0 &= 2610.858\ cm^{-1} , \\ B'' = B_0 &= 0.12155\ cm^{-1} , \\ B'' - B' = \alpha_1 &= 3.63 \times 10^{-4}\ cm^{-1} , \\ D &= 2 \times 10^{-8}\ cm^{-1} . \end{aligned}$$

By computing the eigenvalues of the GF matrix derived, using the F matrix of Venkateswarlu and Mathew [12], the difference between the ν_1 vibration frequencies of the isotopic molecules $DCCBr^{79}$ and $DCCBr^{81}$ was estimated to be less than 0.01 cm^{-1}. For this reason, the lines belonging to the isotopically different molecules coinside in the central region of the band, and the perturbations observed there must be due to the overlaping hot bands. In addition, Jones et al. [3] found the difference between the B'' values of the isotopic molecules to be 6.7×10^{-4} cm^{-1}. These considerations give support to the assignment made above and that in the fundamental, the lines due to the isotopically different molecules cannot be measured separately with the resolution used.

Discussion

The rotational analysis of the fundamental ν_1 gives the rotational constants both in the ground and in the exited states. In the case of DCCF the obtained value $B'' = 0.29146$ cm^{-1} agrees well with the result $B'' = 0.291406$ cm^{-1} of Tyler and Sheridan [2].

The average rotational constant of the molecule DCCBr can be calculated to be $B'' = 0.121589$ cm^{-1} using the B values of Jones et al. [3] for isotopically different derivatives. The result $B'' = 0.12155$ cm^{-1} obtained for DCCBr in this work is close to this value.

The values for α_1 derived, 12.40×10^{-4} cm^{-1} and 3.63×10^{-4} cm^{-1} for DCCF and DCCBr, respectively, are reasonable when compared with the values of other monohaloacetylenes [4, 5]. In addition, both are larger than the corresponding constants of the undeuterated compounds.

The centrifugal distortion constants obtained from the ν_1 bands are 12×10^{-8} cm^{-1} and 2×10^{-8} cm^{-1} for DCCF and DCCBr, respectively. These constants were also calculated theoretically from the formula given by Wilson [13] for linear molecules using the bond lengths of Tyler and Sheridan [2] in the former, and the internuclear distances of Jones et al. [3], in the latter case. For both molecules the F matrix elements of Venkateswarlu and Mathew [12] were used. The results 8.7×10^{-8} cm^{-1} and 1.9×10^{-8} cm^{-1}, respectively, are close to the experimental values. The centrifugal constant of DCCF has also been measured by Tyler and Sheridan [2]. Their result

Table 4. Rotational constants of DCCF and DCCBr derived from the analyses of the ν_1 bands.

	ν_0 [cm^{-1}]	B_0 [cm^{-1}]	α_1 [10^{-4} cm^{-1}]	D [10^{-8} cm^{-1}]	Ref.
DCCF	2645.090 ± 0.010	0.29146 ± 0.00007	12.40 ± 0.10	12 ± 4	IR, this work
		0.291403		8.7	MW, Tyler and Sheridan [2]
				8.7	Calc., this work
DCCBr	2610.858 ± 0.010	0.12155 ± 0.00009	3.63 ± 0.10	2 ± 2	IR, this work
		0.121589 *			MW, Jones et al. [3]
				1.9	Calc., this work

* This value has been calculated from the data of Jones et al. [3] for DCCBr, which contains the isotopes of bromine in natural abundance.

$D = 8.7 \times 10^{-8}$ cm^{-1} is also consistent with the D constant obtained for fluoroacetylene in this work.

The values $D = 12 \times 10^{-8}$ cm^{-1} and $\alpha_1 = 12.2 \times 10^{-4}$ cm^{-1} derived from the analysis of the hot band $\nu_1 + \nu_5 - \nu_5$ are compatible with the results from the fundamental ν_1. On the contrary, the rotational constant $B_5 = 0.2918$ cm^{-1} obtained is not in good agreement with the value $B_5 = 0.29222$ cm^{-1} calculated from the data of Tyler and Sheridan [2] and it cannot be made better by changing the numbering in the band. The difference between these B values is probably due to the small number of measured lines. In addition, some of the lines may be blended with other absorptions.

The results from the analyses of the C-D vibration bands are given in Table 4.

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