Investigation of the ν_1 and $2\nu_1$ Infrared Bands of Monofluoracetylene

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(Z. Naturforsch. **26 a**, 1847—1851 [1971]; received 25 May 1971)

The rotational structures of the ν_1 and $2\nu_1$ infrared bands of monofluoroacetylene were investigated. The values $B_0 = 0.32374 \pm 0.00005$ cm^{-1} and 0.32372 ± 0.00010 cm^{-1}, respectively, were obtained. In addition, the analysis of the fundamental gave $\alpha_1 = (6.85 \pm 0.15) \times 10^{-4}$ cm^{-1} and $D_0 = (15 \pm 3) \times 10^{-8}$ cm^{-1}. Theoretically, the centrifugal disortion constant was computed to be 13×10^{-8} cm^{-1}. The hot bands accompanying the fundamental were also studied.

Introduction

The microwave spectra of different isotopic forms of HCCF have been measured by TYLER and SHERIDAN [1]. These measurements give for the rotational constant of HCCF in the ground state, a value of $B_0 = 9706.19$ MHz corresponding to $B_0 = 0.323764$ cm^{-1}. The centrifugal distortion constant D has been evaluated to be $3{,}_6$ kHz, i. e. 12×10^{-8} cm^{-1}. In addition the constants α for the low lying fundamentals ν_4 and ν_5 have been obtained.

The infrared spectrum of monofluoroacetylene with the assignment of the fundamentals has been published by HUNT and WILSON [2]. Recently REICHMAN et al. [3] have studied the rotational structure of several infrared bands and obtained the value of the rotational constant B for different excited vibrational states. The aim of the present work was to study the $\mathrm{C-H}$ stretching vibration band ν_1, together with its overtone, to get more accurate vibrational data and to measure the rotational constant in the corresponding vibrational states. This work also completes our recent series on the $\mathrm{C-H}$ stretching bands of other monohaloacetylenes [4, 5].

Experimental

The sample gas was prepared according to the method of VIEHE and FRANCHIMONT [6]. Slight amounts of acetylene remained in the sample as an impurity.

The path lengths used were 10 cm for the fundamental and 20 cm for the overtone. Different pressures, some tens of mm Hg, were used according to the absorption when measuring the fundamental and the accompanying hot bands. In the case of the overtone, the pressure was about 100 mm Hg. The pressure of HCCF changed to some extent due to polymerization, although the sample remained usable for a few weeks.

The spectra were recorded using the grating spectrometer at the University of Oulu [7]. The wavenumbers were derived by interpolating between noble gas emission lines with the aid of an interferometric scale. All the lines were measured using several recordings.

Results

The ν_1 Band

The general appearance of the absorption around 3355 cm^{-1} clearly corresponds to that of a $\Sigma-\Sigma$ type band of a linear molecule. A recording is given in Fig. 1. The central gap is obscured by overlapping hot bands but by recording the spectrum at very low pressure the origin was easy to locate. The assignment of the main band ν_1 is relatively clear.

The observed frequencies are given in Table 1. They were treated graphically and also fitted by least squares to the fourth order polynomial

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

where the letters have their usual meaning.

The result was

$$\nu = 3356.966 + 0.64680\, m - 6.845 \times 10^{-4}\, m^2 - 5.49 \times 10^{-7}\, m^3 + 1.6 \times 10^{-8}\, m^4. \qquad (2)$$

The average deviation between an observed value and one from (2) is 0.017 cm^{-1}. The coefficients

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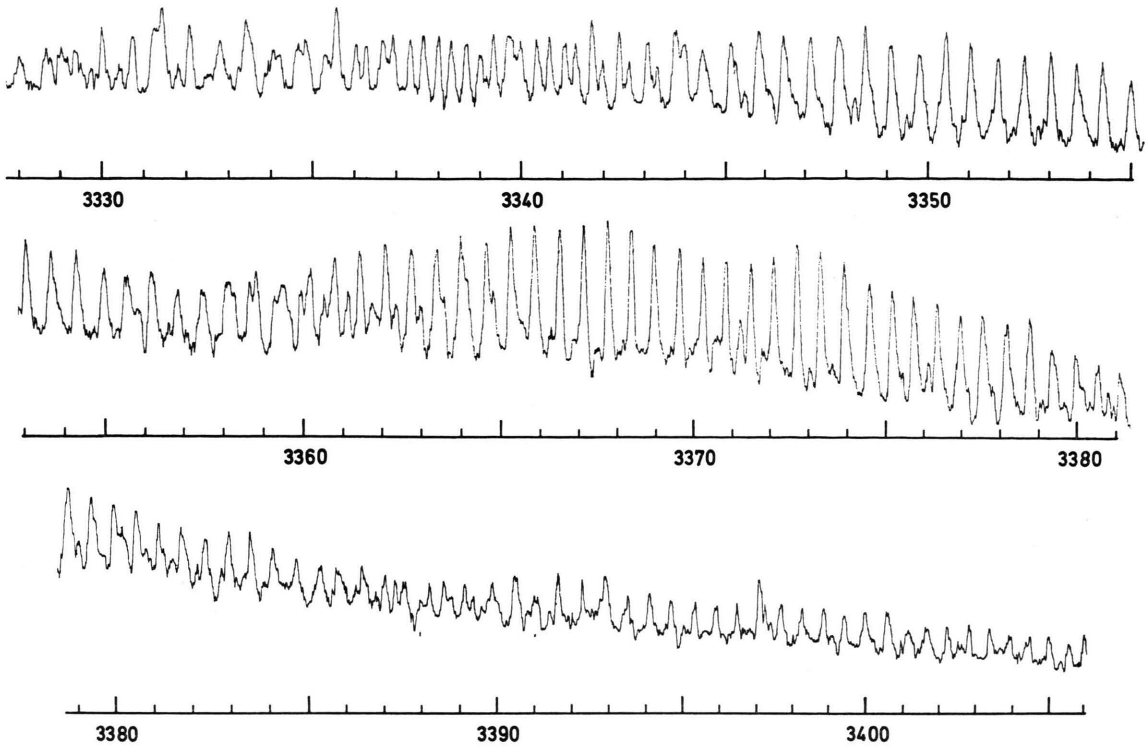

Fig. 1. The absorption of HCCF between 3328 and 3406 cm^{-1}. Acetylene impurity lines are clearly discernible between 3330 and 3345 cm^{-1} and water vapour absorptions especially at about 3393 and 3397 cm^{-1}.

of the polynomial (2) give

$$\begin{aligned}\nu_0 &= 3356.97\ \mathrm{cm}^{-1},\\ B'' = B_0 &= 0.32374\ \mathrm{cm}^{-1},\\ B'' - B' = \alpha_1 &= 6.85\times10^{-4}\ \mathrm{cm}^{-1},\\ D'' &= 15\times10^{-8}\ \mathrm{cm}^{1}.\end{aligned}$$

The hot bands accompanying the main absorption are more difficult to interpret and assign. On the low frequency side of ν_1, another band can be seen in Figure 1. Its intensity between 3335 and 3340 cm^{-1}, where both the bands are well resolved, is approximately the same as that of the main band. This strongest hot band was assigned to $\nu_1+\nu_5-\nu_5$. According to the Boltzmann factor, the intensity of this band ought to be 33% of that of the main band. The observed relative intensity seems to be greater than this calculated ratio implies. The same fact was found also by Reichman et al.[3] in the case of the ν_3 fundamental. The relatively strong absorptions around the central gap of the main band must be due to hot bands and they have been assigned to $\nu_1+\nu_5-\nu_5$. The origin of this band could not be located quite unambiguously, because the weak Q branch of this π-π type band was not found. According to the general appearance of the band, the origin was obtained approximately and the final assignment was made so that the rotational constant of the lower state was in agreement with the results of the microwave measurements[1]. Some experiments were also performed by changing the temperature, although only within some tens of degrees. The results supported the assignments.

The observed wavenumbers of the lines assigned to $\nu_1+\nu_5-\nu_5$ are given in Table 2. When fitting the lines by least squares the centrifugal constants were constrained to $D' = D'' = 13\times10^{-8}\ \mathrm{cm}^{-1}$. The fit was not very close, the average deviation between an observed and a calculated wavenumber being 0.02 cm^{-1}.

The following results were obtained:

$$\begin{aligned}\nu_0 &= 3347.92\ \mathrm{cm}^{-1},\\ B'' = B_5 &= 0.32462\ \mathrm{cm}^{-1},\\ B'' - B' &= 8.76\times10^{-4}\ \mathrm{cm}^{-1}.\end{aligned}$$

Another line system, which partly overlaps ν_1 and which can be followed, is situated at higher frequencies than the main band. It could not be assigned to any combination originating from the

Table 1. The observed vacuum wavenumbers (cm^{-1}) of the lines in the ν_1 band of monofluoroacetylene. 3300 cm^{-1} should be added to the numbers given. The values placed in parentheses are clearly perturbed by acetylene or water vapour and they have been omitted in the calculations.

J	$P(J)$	$R(J)$	J	$P(J)$	$R(J)$
2		58.856	29	37.650	75.772
3	55.010	59.507	30	36.939	76.373
4	54.362	60.153	31	36.274	76.959
5	53.720	60.791	32	(35.551)	77.557
6	53.069	61.439	33	(34.874)	78.173
7	52.398	62.082	34	(34.154)	78.787
8	51.757	62.721	35	(33.446)	79.395
9	51.105	63.362	36	32.792	79.978
10	50.449	(64.046)	37	32.108	80.562
11	49.791	64.643	38	(31.369)	81.163
12	49.138	65.268	39	30.751	81.744
13	48.464	65.878	40	30.063	82.345
14	47.815	66.511	41	29.377	82.937
15	47.143	67.126	42	28.711	83.530
16	46.474	67.743	43	28.028	84.126
17	45.799	68.373	44	(27.349)	84.721
18	45.132	68.996	45		85.290
19	44.447	69.611	46		85.866
20	43.796	70.238	47		86.455
21	43.085	70.859	48		87.028
22	42.413	71.463	49		87.608
23	41.754	72.074	50		88.197
24	41.073	72.693	51		88.772
25	40.389	73.331	52		89.340
26	(39.778)	73.954	—		—
27	39.012	74.563	62		95.123
28	38.316	75.167	63		95.696
			64		96.249

Table 2. The observed vacuum wavenumbers (cm^{-1}) of the lines in the $\nu_1+\nu_5-\nu_5$ band of monofluoroacetylene. 3300 cm^{-1} should be added to the numbers given.

J	$P(J)$	$R(J)$	J	$P(J)$	$R(J)$
3	45.942		17	36.700	59.338
4	—		18	36.026	—
5	—		19	—	60.542
6	43.987		20	—	61.151
7	43.281		21	—	61.745
8	42.624		22	33.236	62.338
9	41.972		23	32.548	62.948
10	41.334		24	31.861	63.531
11	40.665		25	—	64.143
12	40.003		26	30.461	
13	39.335	56.852	27	29.780	
14	38.676	57.486	28	—	
15	38.007	58.094	29	28.384	
16	37.344	58.710			

ground state. The only assignment that seems possible is $\nu_1+\nu_4-\nu_4$, although the positive anharmonicity becomes remarkable in this case. The intensity of this band ought to be 13% of that of the main band, and the observed intensity does not contradict this value.

The origin of this band is not obvious. It can be located approximately from the band shape but not unambiguously. In the R branch the line system could be followed up to quantum numbers higher than 50, using elevated sample pressure. On the P branch side only few lines could be measured because this branch is obscured by other absorptions.

The observed wavenumbers, together with the assignment are given in Table 3. The lines were fitted to the polynomial (1) (assuming $D'=D''$) and the result was

$$\nu = 3384.136 + 0.64816\, m - 1.44\times10^{-3}\, m^2 - 6.2\times10^{-7}\, m^3. \qquad (3)$$

The average deviation between an observed and calculated value is 0.009 cm^{-1}. The coefficients of the polynomial (3) give

$$\nu_0 = 3384.14 \text{ cm}^{-1},$$
$$B'' = B_4 = 0.32480 \text{ cm}^{-1},$$
$$B'' - B' = 14.4\times10^{-4} \text{ cm}^{-1},$$
$$D = 16\times10^{-8} \text{ cm}^{-1}.$$

Table 3. The observed vacuum wavenumbers (cm^{-1}) of the lines assigned to the hot band $\nu_1+\nu_4-\nu_4$ of monofluoroacetylene. 3000 cm^{-1} should be added to the numbers given. The lines in parentheses are someway perturbed and have not been used in calculations.

J	$P(J)$	$R(J)$	J	$R(J)$
3	382.179	386.733	30	402.824
4	381.522	387.376	31	403.392
5	380.871	387.999	32	403.941
6	—	388.601	33	404.496
7	—	389.219	34	405.033
8	—	(389.874)	35	405.586
9	—	(390.474)	36	406.125
10	—	391.085	37	406.664
11	—	391.689	38	407.205
12	376.164	392.315	39	407.737
13	—	(392.913)	40	408.262
14	—	(393.516)	41	408.789
15	—	(394.117)	42	409.303
16	—	394.719	43	409.829
17	372.693	395.318	44	410.342
18	—	395.911	45	410.853
19	371.274	396.509	46	411.364
20	370.614	—	47	411.867
21	369.900	397.707	48	412.367
22		398.295	49	412.881
23		398.869	50	413.372
24		399.436	51	413.870
25		400.005	52	414.363
26		400.582	53	414.844
27		401.136	54	415.337
28		401.707	55	415.809
29		402.259	56	416.307
			57	416.778

Some absorptions in Fig. 1, which are not due to impurities, have remained unassigned. It is believed that they are either blended lines due to the treated bands or that they are due to other hot bands such as $\nu_1 + 2\,\nu_5 - 2\,\nu_5$ in some cases.

The wavenumbers in all the tables have been uniformly given to three decimal places. In some regions where the lines are blended this is more than sufficient as also the poorness of the fit implies.

The $2\,\nu_1$ Band

In the $2\,\nu_1$ band around 6600 cm^{-1} the origin could be easily and unambiguously located. Some rotational lines especially in the R branch were masked by acetylene impurity absorptions but the assignment remained quite straightforward. However, the band is clearly perturbed at high J values. The perturbation becomes very striking above $J' = 34$. In Table 4, the measured wavenumbers of the lines up to $J' = 33$ are given. These apparently unperturbed lines were fitted to the polynomial (1) by assuming $D' = D''$. The result was

$$\nu = 6599.288 + 0.64515\,m - 2.29 \times 10^{-3}\,m^2 - 6.6 \times 10^{-8}\,m^3. \quad (4)$$

Table 4. The observed vacuum wavenumbers (cm^{-1}) of the lines in the $2\,\nu_1$ band of monofluoroacetylene. 6000 cm^{-1} should be added to the numbers given.

J	$P(J)$	$R(J)$	J	$P(J)$	$R(J)$
1	598.617	600.608	18	586.905	610.710
2	—	601.212	19	586.222	611.265
3	597.348	—	20	585.462	611.805
4	596.677	602.478	21	—	612.367
5	(596.032)	603.090	22	583.981	612.908
6	595.312	603.685	23	583.233	613.445
7	594.647	604.317	24	—	613.978
8	593.997	604.934	25	581.731	614.512
9	593.302	605.504	26	580.943	615.011
10	(592.540)	606.114	27	580.193	615.559
11	591.911	606.724	28	579.408	616.072
12	591.200	607.280	29	—	616.585
13	—	607.860	30	577.883	617.085
14	589.825	(608.466)	31	577.105	617.600
15	589.901	609.020	32	—	618.114
16	588.383	609.585	33	575.536	—
17	587.665	610.145	34	(574.760)	

The average deviation between an observed value and a calculated one was 0.013 cm^{-1}. The coefficients of this polynomial give

$$B'' = 0.32372\ \text{cm}^{-1},$$
$$B'' - B' = 22.9 \times 10^{-4}\ \text{cm}^{-1},$$
$$D = 2 \times 10^{-8}\ \text{cm}^{-1}.$$

Also this band was overlapped by a hot band which obviously starts from the level ν_5. The relative intensity of the hot band was now, however, lower than in the case of the fundamental ν_1. Only very few lines were measured and no analysis of them was performed. On the high frequency side the overtone $2\,\nu_1$ was partly overlapped by a band whose origin is around 6645 cm^{-1}. Its distance from the origin of $2\,\nu_1$ is approximately twice that between $\nu_1 + \nu_4 - \nu_4$ and ν_1 and thus it was assigned to $2\,\nu_1 + \nu_4 - \nu_4$, but it was not analyzed in detail.

Discussion

The rotational analysis of the fundamental ν_1 and the overtone $2\,\nu_1$ both ought to give the rotational constant in the ground state B_0 and also the constant α_1 which describes the change in B value due to the ν_1 vibration. The values obtained $B'' = 0.32374\ \text{cm}^{-1}$ (ν_1) and $B'' = 0.32372\ \text{cm}^{-1}$ ($2\,\nu_1$) are in excellent agreement both with each other and with the microwave value[1] 0.323764 cm^{-1}. The results for α_1 on the other hand are contradictory. The fundamental gives $6.85 \times 10^{-4}\ \text{cm}^{-1}$ but the overtone gives $B'' - B' = 2.29 \times 10^{-3}\ \text{cm}^{-1}$ corresponding to $\alpha_1 = 11.4 \times 10^{-4}\ \text{cm}^{-1}$. Since the latter band was clearly perturbed the value from the fundamental is considered more reliable. This value $6.85 \times 10^{-4}\ \text{cm}^{-1}$ seems also to be more consistent with the results obtained for α_1 in case of other monohaloacetylenes[4, 5].

Both the bands also give D. The result $15 \times 10^{-8}\ \text{cm}^{-1}$ from the fundamental is in agreement both with the microwave value $(12 \pm 2) \times 10^{-8}\ \text{cm}^{-1}$ of TYLER and SHERIDAN[1] and with $14 \times 10^{-8}\ \text{cm}^{-1}$ obtained by REICHMAN et al.[3] from the analysis of the ν_3 fundamental. Because only lines corresponding to low J values were available in the case of the overtone, the result then remained very indefinite.

The centrifugal distortion constant D was also calculated from the formula given by WILSON[8]. When using the force constant matrix of VENKATESWARLU and MATHEW[9] the result $D = 13 \times 10^{-8}\ \text{cm}^{-1}$ was obtained. The above experimental values are well in agreement with this calculated one.

The analysis of the hot band $\nu_1 + \nu_5 - \nu_5$ ought to give $B'' = B_5$ and $B'' - B' = \alpha_1$. The result

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$B'' = 0.32462\ \mathrm{cm}^{-1}$ was obtained above. On the other hand, the data of TYLER and SHERIDAN[1] lead to $B_5 = 0.32468\ \mathrm{cm}^{-1}$. The close agreement between these values supports the performed assignment. The value $B'' - B' = 8.77 \times 10^{-4}\ \mathrm{cm}^{-1}$ is not, however, satisfactorily consistent with α_1 from the fundamental. It is believed that this is an expression of a resonance interaction between the $\nu_1 + \nu_5$ and some other combination level.

When two levels are in Fermi-resonance, the actual values of their rotational constants are linear combinations of the B values of the unperturbed states (cf. e. g. HERZBERG[10]). In view of the observed $B'' - B'$ value, the level perturbing $\nu_1 + \nu_5$ ought to be such that it makes the rotational constant smaller than $B_0 - \alpha_1 - \alpha_5$. According to REICHMAN et al.[3] $\alpha_3 = 12.4 \times 10^{-4}\ \mathrm{cm}^{-1}$. Thus the other level in the Fermi-diad probably contains ν_3. When the unknown α_2 is likely to be positive, the level $\nu_2 + \nu_3 + \nu_5$ seems to fulfill the requirements for the resonance.

The microwave results of TYLER and SHERIDAN[1] lead to $B_4 = 0.32405\ \mathrm{cm}^{-1}$. From the analysis of the band assigned to $\nu_1 + \nu_4 - \nu_4$, $B'' = 0.32480\ \mathrm{cm}^{-1}$ was obtained above. The agreement between these two values is not good and it cannot be made better by changing the assignment in the hot band.

The accuracy of the derived B'' value is diminished by the fact that there are very few observed lines in the P branch and in addition some of these are blended with other absorptions. However, the fit is close and it gives a reasonable D value. The difference $B'' - B' = 14.4 \times 10^{-4}\ \mathrm{cm}^{-1}$ is not in agreement with α_1 from the fundamental. This corresponds to a similar resonance between the $\nu_1 + \nu_4$ and $\nu_2 + \nu_3 + \nu_4$ levels as discussed previously in the case of the hot band $\nu_1 + \nu_5 - \nu_5$.

Table 5. Results from the analysis of the ν_1 and $2\,\nu_1$ bands of HCCF. The calculated value of the D constant as well as the literature values for the B_0 and D constants are also given.

B_0 [cm^{-1}]	$= 0.323764$	Microwaves, TYLER and SHERIDAN[1]
	$= 0.32374 \pm 5 \times 10^{-5}$	ν_1, this work
	$= 0.32372 \pm 10 \times 10^{-5}$	$2\,\nu_1$, this work
α_1 [10^{-4} cm^{-1}]	$= 6.85 \pm 0.15$	ν_1, this work
D_0 [10^{-8} cm^{-1}]	$= 12 \pm 2$	Microwaves, TYLER and SHERIDAN[1]
	$= 15 \pm 3$	ν_1, this work
D [10^{-8} cm^{-1}]	$= 14$	ν_3, REICHMAN et al.[3]
	$= 13$	Calculated, this work
ω_1^0 [cm^{-1}]	$= 3414.29$	this work
X_{11}^0 [cm^{-1}]	$= -57.32$	

In Table 5 results for the rotational constants have been collected. In addition, the computed frequency $\omega_1{}^0$ and the anharmonicity coefficient $X_{11}{}^0$ are given there. The value of $X_{11}{}^0$ is almost equal to those of other monohaloacetylenes[5].

Acknowledgements

The authors are deeply indebted to Mr. H. RUOTSALAINEN, Department of Chemistry, University of Oulu, for the preparation of the sample. They are also grateful to Professor P. TUOMIKOSKI for reading the manuscript.

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