Investigation of the Structure of the ν_5 Band of Monofluoroacetylene

Mikko Huhanantti and Jyrki Kauppinen

Department of Physics, University of Oulu, Oulu, Finland

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The rotational structure of the bending fundamental ν_5 of monofluoroacetylene around 366 cm^{-1} was investigated. The measurements were performed using a Michelson type Fourier spectrometer with a resolution of about 0.05 cm^{-1}. The values $B_0=0.32373$ cm^{-1}, $\alpha_5^-=-6.00\times10^{-4}$ cm^{-1}, $q_5=6.3\times10^{-4}$ cm^{-1} and $D=11.2\times10^{-8}$ cm^{-1} were obtained from the analyses of the P-, Q-, and R-branches. In addition, some hot bands accompanying the fundamental were studied.

Introduction

The low resolution infrared spectrum of monofluoroacetylene and the assignment of the observed vibration bands was first published by Hunt and Wilson[1]. The subsequent infrared investigations[2–4] contain, among other things, the rotational analyses of the fundamentals, except the lowest bending vibration ν_5. The rotational constants of the molecule are well-known from these measurements and from the microwave data of Tyler and Sheridan[5]. The present study was carried out to complete the investigations of the fundamental vibrations with high resolution.

Experimental

The gas sample was prepared using the method of Viehe and Franchimont[6]. The sample was evaporated into a gas cell giving a 100 cm path length. The pressure was about 2 kPa. A small amount of water remained in the cell, and it caused some external lines in the spectrum.

The interferograms were registered by a Michelson type Fourier spectrometer constructed at the Department of Physics[7], and later changed to double-beam operation. The Fourier transforms were calculated using programs also written in this laboratory[8]. The resolution of the spectrum was about 0.05 cm^{-1}, except in those calculations where apodization was used. The latter recordings were, however, only used to make sure of some weak lines.

The accuracy of the measurements was tested by some pure rotational lines of water, which appeared at the low frequency end of the spectrum, and were not blended by other absorptions. The comparison of the measured line positions with the values obtained on the basis of the energy levels, reported by Flaud and Camy-Peyret[9], indicated a systematic deviation of 0.005 cm^{-1}. This difference was calculated to be due to a small phase error in our interferograms, and a proper correction was made for all the frequencies given in this work.

Spectrum

The ν_5 Band

The recording over the region of ν_5 is given in Fig. 1, where a typical $\Pi \leftarrow \Sigma^+$ type band of a linear molecule can be seen. The strong absorption around 368 cm^{-1} is caused by several Q-branches. The most intense of these at 367 cm^{-1} refers to the bending fundamental ν_5, and the others belong to the accompanying hot bands.

The assignment of the rotational lines in the P- and R-branches was relatively clear. Their frequencies are given in Table 1. Some lines, which are blended by the water vapour absorptions, are placed in parentheses and they have been omitted in the calculations. The other lines were fitted by the least squares to the fourth order polynomial

$$\begin{aligned}\nu = \nu_0 &- (B'+D') + (B'+B''+2\,D')\,m \\ &+ (B'-B''+D'+D'')\,m^2 - 2\,(D'+D'')\,m^3 \\ &- (D'-D'')\,m^4\,, \qquad (1)\end{aligned}$$

where the letters have their usual meaning[10], and the constant $B'=B_5^-$ refers to the lower l-state. The fitting resulted in the polynomial

$$\begin{aligned}\nu = 366.314 &+ 0.64806\,m + 6.00\times10^{-4}\,m^2 \\ &- 4.5\times10^{-7}\,m^3 - 2\times10^{-9}\,m^4\,. \qquad (2)\end{aligned}$$

The fit is close and the average deviation between an observed and a calculated value is only 0.003 cm^{-1}.

The coefficients of the polynomial (2) give

$$\begin{aligned}\nu_0 &= 366.638\ \text{cm}^{-1}\,,\\ B'' = B_0 &= 0.32373\ \text{cm}^{-1}\,,\\ B''-B' = \alpha_5^- &= -6.00\times10^{-4}\ \text{cm}^{-1}\,,\\ D &= 11.2\times10^{-8}\ \text{cm}^{-1}\,.\end{aligned}$$

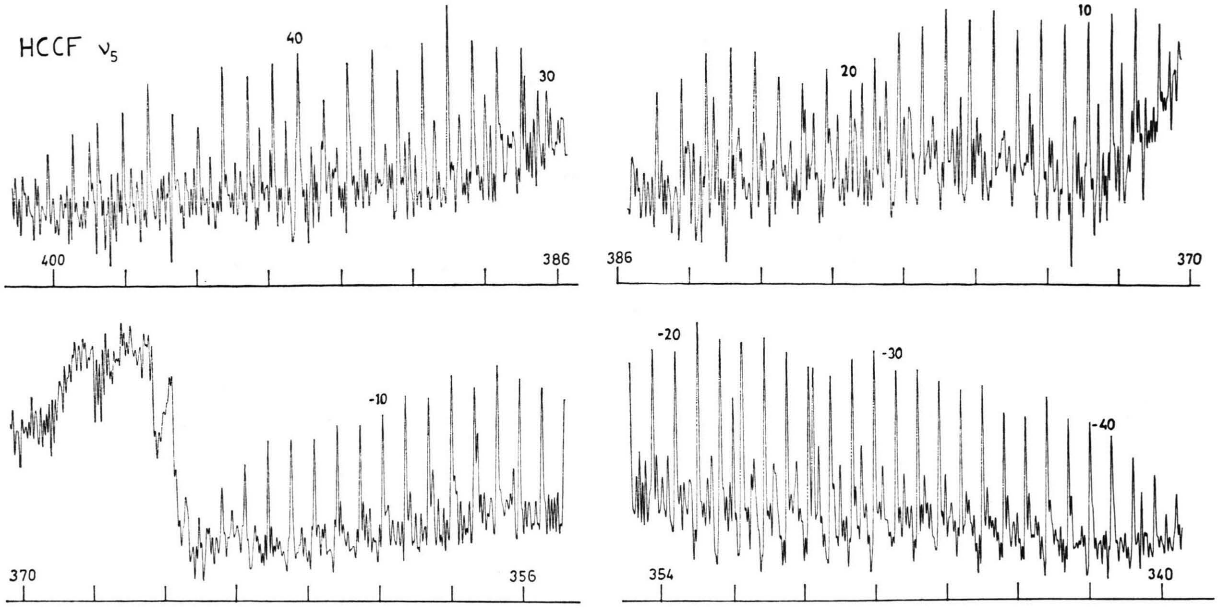

Fig. 1. A recording over the fundamental ν_5 from 340 cm^{-1} to 400 cm^{-1}. The resolution is about 0.05 cm^{-1}. The intensities are in arbitrary units and they are not comparable over the borders of the different parts. The numbers above the lines are *m* values.

Table 1. The line positions (cm^{-1}) in the ν_5 band of HCCF.

J	*P(J)*	*R(J)*	*J*	*P(J)*	*R(J)*
2	365.018	—	29	348.037	386.282
3	64.378	—	30	47.427	86.966
4	63.731	—	31	46.818	87.650
5	63.085	—	32	46.206	88.335
6	62.445	370.884	33	45.594	89.019
7	61.810	71.534	34	44.989	89.705
8	61.168	72.199	35	44.384	90.402
9	60.529	72.849	36	43.781	91.093
10	59.893	73.515	37	(43.182)	91.780
11	59.259	74.173	38	42.578	92.461
12	58.623	74.838	39	41.975	93.165
13	57.990	75.509	40	41.366	93.855
14	57.359	76.169	41	40.772	94.551
15	56.723	76.834	42	40.178	95.249
16	56.103	77.501	43	39.585	95.936
17	55.485	78.163	44	38.992	96.641
18	54.859	78.842	45	38.400	—
19	(54.230)	79.513	46	37.805	98.042
20	53.598	80.186	47	37.219	98.746
21	52.973	80.860	48	36.628	99.444
22	52.347	81.525	49	36.037	400.150
23	51.738	82.208	50	35.451	00.860
24	51.115	82.884	51	34.861	01.554
25	50.490	83.565	52	34.290	02.249
26	49.874	84.240	53	33.705	02.964
27	49.257	(84.921)	54	33.123	
28	48.646	(85.601)			

At the higher frequency side of the Q-branch maximum in Fig. 1, many resolved lines can be observed. These lines are interpreted as the rotational structure of the Q-branch, which is resolved when the quantum number *J* is sufficiently high.

The frequencies of the lines in the Q-branch can be represented by the polynomial [10]

$$\nu = \nu_0 - B' + (B' - B'')J(J+1)\,, \qquad (3)$$

where the effect of centrifugal distortion is neglected and the rotational constant $B' = B_5^{\,+}$ now refers to the upper l-state.

The wavenumbers of the lines assigned to the Q-branch are given in Table 2. The numbering of the lines was carried out so that the value for ν_0 derived from the polynomial (2) and that from the

Table 2. The line positions (cm^{-1}) in the *Q*-branch of the ν_5 band.

J	*Q(J)*	*J*	*Q(J)*
27	367.264	39	368.254
28	67.335	40	68.346
29	67.400	41	—
30	67.476	42	—
31	67.550	43	68.642
32	67.622	44	68.770
33	67.712	45	68.881
34	67.802	46	68.981
35	67.876	47	69.127
36	67.973	48	—
—		49	69.352

analysis of the Q-branch were in the best possible accordance with each other. The frequencies were then fitted versus $J(J+1)$ by the least squares. The result was

$$\nu = 366.329 + 12.32 \times 10^{-4} J(J+1)\,. \qquad (4)$$

The average deviation between an observed value and one from (4) was $0.005\ \mathrm{cm}^{-1}$. The above polynomial gives $B_5{}^+ - B_0 = 12.32 \times 10^{-4}\ \mathrm{cm}^{-1}$. The changing of the numbering of the rotational lines by one unit in one direction or another has an effect of the order of $0.3 \times 10^{-4}\ \mathrm{cm}^{-1}$ on this value. On the other hand, the microwave results [5] give a value of $12.40 \times 10^{-4}\ \mathrm{cm}^{-1}$ for this difference, confirming thus the numbering selected.

Hot Bands

The main band is accompanied by many hot bands. The strongest of these are the components $\Delta \leftarrow \Pi$ and $\Sigma^+ \leftarrow \Pi$ of the $2\nu_5 - \nu_5$ band. These transitions are perpendicular and they both have a strong Q-branch. They are situated around 368 cm^{-1} and 366 cm^{-1}, respectively.

The relative intensities of the transitions $\Delta \leftarrow \Pi$ and $\Sigma^+ \leftarrow \Pi$ can be calculated to be 67% and 34% of the intensity of the main band. These results agree well with the intensities of the Q-branches observed in the spectrum. In the $\Delta \leftarrow \Pi$ transition the splitting due to the l-type doubling could be resolved in the P- and R-branches and therefore the intensity of the lines in these branches is only half of that calculated above.

In the case of the $\Delta \leftarrow \Pi$ transition the two component bands are designated as dd- or cc-components, depending on whether the transition $\Delta J = \pm 1$ take place between the upper levels of the l-doublets or between the lower levels of the l-doublets of the rotational states. The line system in the P- and R-branches of the dd-component was clear and it could be followed up to quantum numbers of about 40. To the cc-component, however, less lines could be assigned, because more lines were blended or hidden behind the lines of the ν_5 band. The assignment of the rotational lines was selected on the basis of the prominent Q-branch. The observed wavenumbers are given in Table 3, where the lines marked with an asterisk have been assigned to both components.

The frequencies of the lines in the P- and R-branches of the hot bands can be given by

$$\nu = \nu_0 + B'' l''^2 - B' l'^2 + (B' + B'')m + (B' - B'')m^2 - 2(D' - D'')m^3 - (D' - D'')m^4\,, \qquad (5)$$

provided that the energy expansion in powers of $J(J+1)$ is valid. In addition, the effect of centrifugal distortion is neglected in the second and lower order terms. The fitting of the lines from Table 3 to the above polynomial gives for the dd-component

$$\nu = 367.980 + 0.65030\, m + 5.93 \times 10^{-4} m^2 - 2.9 \times 10^{-7} m^3 - 0.9 \times 10^{-8} m^4 \qquad (6)$$

and for the cc-component

$$\nu = 367.979 + 0.64983\, m + 12.68 \times 10^{-4} m^2 - 9.9 \times 10^{-7} m^3 - 3.6 \times 10^{-8} m^4\,. \qquad (7)$$

The average deviation between an observed and a calculated value was $0.006\ \mathrm{cm}^{-1}$ in the former fit and $0.010\ \mathrm{cm}^{-1}$ in the latter.

The coefficients of the polynomial (6) give

$$B'' = B_5{}^+ = 0.3249\ \mathrm{cm}^{-1}\,,$$
$$B' - B'' = 5.93 \times 10^{-4}\ \mathrm{cm}^{-1}\,,$$

and those of the polynomial (7)

$$B'' = B_5{}^- = 0.3243\ \mathrm{cm}^{-1}\,,$$
$$B' - B'' = 12.68 \times 10^{-4}\ \mathrm{cm}^{-1}\,.$$

The analysis of the $\Sigma^+ \leftarrow \Pi$ band was carried out as above. The lines were at low quantum numbers blended and the fit of the apparently unperturbed lines from Table 3 leads to

$$\nu = 365.766 + 0.64973\, m + 11.25 \times 10^{-4} m^2 - 4.5 \times 10^{-7} m^3 - 1.05 \times 10^{-7} m^4\,. \qquad (8)$$

The average deviation between an observed value and one from (8) was now $0.008\ \mathrm{cm}^{-1}$.

The coefficients of the above polynomial give

$$B'' = B_5{}^- = 0.3243\ \mathrm{cm}^{-1}\,,$$
$$B' - B'' = 11.25 \times 10^{-4}\ \mathrm{cm}^{-1}\,.$$

In the polynomial (5) the effect of l-type resonance, studied by Amat and Nielsen [11], has been neglected. This perturbation is evident from the appropriate combination relations shown in Figure 2. The effects are similar to those observed earlier e. g. in the spectrum of acetylene [12], but smaller.

Table 3. The line positions (cm^{-1}) in the components of the $2\nu_5-\nu_5$ band of HCCF.

	$\Delta \leftarrow \Pi$				$\Sigma^+ \leftarrow \Pi$	
J	$P_{dd}(J)$	$R_{dd}(J)$	$P_{cc}(J)$	$R_{cc}(J)$	$P(J)$	$R(J)$
3	—	370.606 *	—	370.606 *	—	—
4	—	71.257 *	—	71.257 *	—	—
5	364.741 *	71.915 *	364.741 *	71.915 *	—	—
6	64.090	72.573 *	—	72.573 *	—	—
7	63.461	73.220	—	—	—	—
8	—	—	—	73.942	—	—
9	62.158	—	62.246	—	—	—
10	61.526	75.202	61.608	75.269	—	—
11	60.880	75.878	60.990	75.962	358.755	373.719
12	60.254	76.528	60.365	76.644	58.123	74.404
13	59.622	—	59.744	77.321	57.505	75.073
14	58.987	—	59.134	77.988	56.893	75.746
15	58.357	—	—	78.689	56.271	76.428
16	57.736	—	57.913	79.391	55.653	77.135
17	57.097	—	—	80.093	55.049	—
18	56.476	—	—	80.788	54.428	78.510
19	55.838	81.218	—	—	53.820	79.197
20	55.214	81.902	—	—	53.205	79.885
21	—	82.573	—	—	52.598	80.565
22	53.967	83.245	54.314	—	—	—
23	53.362	83.922	—	—	—	81.965
24	52.725	84.604	—	—	50.794	82.666
25	52.097	85.278	—	—	—	83.369
26	51.487	85.958	51.932	86.395	49.603	84.075
27	50.852	86.635	—	87.128	49.001	—
28	—	87.308	—	87.843	48.397	85.471
29	—	87.990	—		47.798	86.168
30	—	88.698	—		47.202	86.884
31	—	89.388	—		46.622	87.581
32	—	90.082	48.486		46.012	88.285
33	—	90.755	47.901		45.443	
34	46.542	91.438	47.316		44.859	
35	45.939	92.124	—		44.279	
36	45.348	—	—		43.685	
37	44.720	93.499	45.672		43.089	
38	44.130	94.218	45.079		42.504	
39	43.514	94.910	—		41.920	
40	42.915		44.013			
41			43.422			

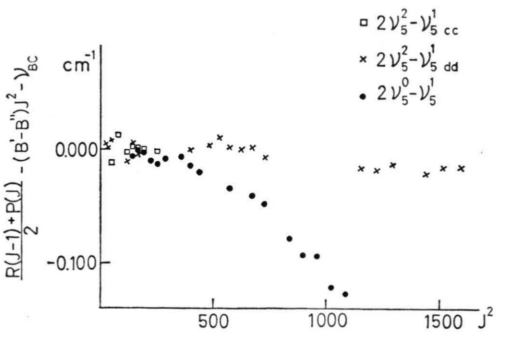

Fig. 2. Effects of perturbations in the hot bands.

Results and Discussion

In a $\Pi \leftarrow \Sigma^+$ band of a linear molecule the transitions $\Delta J = \pm 1$ from the ground state always lead to the lower component of the one-doublet in the upper state. Thus the determination of the rotational constants from the P- and R-branches using polynomial (1) gives the value for the ground state rotational constant, and the second order coefficient gives the value $B_5^- - B_0 = -\alpha_5^-$. In the case of the Q-branch the transition $\Delta J = 0$ is to the upper component of the one-doublet in the excited state, and the coefficient $B' - B''$ in (3) gives the difference $B_5^+ - B_0$. It is therefore possible to determine the l-type doubling constant $q_5 = B_5^+ - B_5^-$ from the rotational analyses of the P-, Q-, and R-branches.

The polynomial (2) gives a value $B_0 = 0.32373$ cm^{-1} for the rotational constant in the ground state. This result is close to the value $B_0 = 0.323764$

cm^{-1} obtained by Tyler and Sheridan[5]. The second order coefficients of the polynomials (2) and (4) give $B_5^- - B_0 = 6.00 \times 10^{-4}\,\text{cm}^{-1}$ and $B_5^+ - B_0 = 12.32 \times 10^{-4}\,\text{cm}^{-\cdot}$. These results lead to the l-type doubling constant $q_5 = 6.3 \times 10^{-4}\,\text{cm}^{-1}$, which is in good agreement with the value $q_5 = 6.37 \times 10^{-4}\,\text{cm}^{-1}$ from the microwave data[5].

The value for the centrifugal distortion constant D has been obtained in several works, and the values derived from the rotation-vibration bands[2-4] and the microwave result[5] $D = 12 \times 10^{-8}\,\text{cm}^{-1}$ are generally consistent with each other. The value $D = 11.2 \times 10^{-8}\,\text{cm}^{-1}$ now obtained from (2) has an error limit closer than the previous values.

The effect of the above l-type resonance on the rotational constants B is small. Thus from the analyses of the hot bands both B_5^+ and B_5^- are obtained. The values derived from the polynomials (7) and (8) both are $B_5^- = 0.3243\,\text{cm}^{-1}$, and the polynomial (6) yields $B_5^+ = 0.3249\,\text{cm}^{-1}$. The corresponding literature values[5] are $B_5^- = 0.32437\,\text{cm}^{-1}$ and $B_5^+ = 0.32500\,\text{cm}^{-1}$.

Theoretically the splitting in the Δ state $2\,\nu_5^{\pm 2}$ is small[13]. The experimental B'-values derived from (6) and (7) are almost equal. The same fact can also be seen from the second order coefficients. They are near to the values $6.04 \times 10^{-4}\,\text{cm}^{-1}$ and $12.40 \times 10^{-4}\,\text{cm}^{-1}$, which can be derived for $-(\alpha_5 + \frac{1}{2} q_5)$ and for $-(\alpha_5 - \frac{1}{2} q_5)$.

On the basis of the band origins obtained it is possible to determine the vibrational constants ω_5^0, x_{55}^0, and g_{55}. The values derived are $\omega_5^0 = 365.48\,\text{cm}^{-1}$, $x_{55}^0 = 0.28\,\text{cm}^{-1}$ and $g_{55} = 0.88\,\text{cm}^{-1}$.

The results from theotational analyses of the ν_5 band have been collected in Table 4.

Table 4. Rotational constants of HCCF derived from the analysis of the ν_5 band.

		This work		Microwaves[5]
B_0	[cm^{-1}]	0.32373	±0.00006	0.323764
α_5^-	[10^{-4} cm^{-1}]	−6.00	±0.07	−6.04
D	[10^{-8} cm^{-1}]	11.2	±1.0	12±2
q_5	[10^{-4} cm^{-1}]	6.3	±0.2	6.37

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