Investigation of the Structure of the ν_1 Band of Monochloroacetylene

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The ν_1 band of monochloroacetylene was investigated. The rotational structure of this $\Sigma-\Sigma$ type band was resolved and lines of both $HCCCl^{35}$ and $HCCCl^{37}$ were assigned. The rotational constants of these molecules were obtained both in the ground and the excited state. For the D constant of $HCCCl^{35}$ a value of $(4.8 \pm 1) \times 10^{-8}$ cm^{-1} was obtained from the band. The constant was also computed theoretically and the result was 4.6×10^{-8} cm^{-1}.

The linearity of monohaloacetylene molecules has been confirmed by electron diffraction and microwave measurements[1, 2]. The infrared spectrum of chloroacetylene has first been published by Richardson and Goldstein[2]. Middleton and Sharkey[3] recorded the spectrum of fluoroacetylene. Later Hunt and Wilson[4] studied the spectra of fluoro-, chloro- and bromoacetylenes and assigned all the fundamentals both for hydrogen and deuterated compounds. The rotational constants B of these compounds in the ground state are known from microwave measurements[1, 5] but no works on the rotational structures of the infrared bands of these molecules seem to have been published. Thus the B constants in excited states are mostly unknown. Neither have the centrifugal distortion constants D been measured for all these compounds.

The authors thus decided to try to investigate in detail some infrared bands of these molecules and the work was started with the CH-stretching band ν_1 of HCCCl.

The gas sample was prepared according to the method given by Bashford et al.[6]. The gas was in a 10 cm cell. The pressure, some cm Hg, was not accurately measured. The measurements were carried out using the high resolution grating spectrometer at the University of Oulu[7].

The recorded spectrum clearly showed a central minimum but the exact position of the gap was not, however, quite obvious, because water vapour and especially some impurity in the sample gas caused disturbances just in the centre of the band. In the spectrum two line systems with slightly differing line spacings were easily detected. These were assigned to correspond to the isotopically different molecules $HCCCl^{35}$ and $HCCCl^{37}$, whose abundancies are approximately in the ratio 3 : 1. Nearly 200 lines were measured, all from at least three recordings. Their observed wavenumbers are given in Table 1.

The observed lines of $HCCCl^{35}$ were fitted to a third order polynomial and the result is given in Eq. (1):

$$\nu = 3340.673 + 0.37886\,\mathrm{m} - 3.92 \times 10^{-4}\,\mathrm{m}^2 - 1.9 \times 10^{-7}\,\mathrm{m}^3. \quad (1)$$

This fit is fairly close, the average deviation between an observed and calculated value is less than 0.010 cm^{-1}.

The lines of $HCCCl^{37}$ could not be measured up to so high quantum numbers as in the case of $HCCCl^{35}$. Thus the wavenumbers were now fitted to a second order polynomial given in Eq. (2):

$$\nu = 3340.645 + 0.37078\,\mathrm{m} - 4.14 \times 10^{-4}\,\mathrm{m}^2. \quad (2)$$

The average deviation between an observed and calculated value is about 0.01 cm^{-1}.

The lines placed in parentheses in Table 1 were omitted in the derivation of the polynomials. In these cases the impurity causes perturbances, or the heavier isotopic molecule markedly shifts the lines of $HCCCl^{35}$.

The constants derived from the coefficients of the polynomials (1) and (2) are given in Table 2. The B'' values obtained here agree well with the micro-

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[1] A. A. Westenberg, J. H. Goldstein, and E. Bright Wilson, Jr., J. Chem. Phys. **17**, 1319 [1949].

[2] W. S. Richardson and J. H. Goldstein, J. Chem. Phys. **18**, 1314 [1950].

[3] W. J. Middleton and W. H. Sharkey, J. Am. Chem. Soc. **81**, 803 [1959].

[4] G. R. Hunt and M. K. Wilson, J. Chem. Phys. **34**, 1301 [1961].

[5] J. K. Tyler and J. Sheridan, Trans. Faraday Soc. **59**, 2661 [1963].

[6] L. A. Bashford, H. J. Emeleus, and H.V.A.Briscoe, J. Chem. Soc. **1938**, 1358.

[7] R. Anttila, Ann. Acad. Sci. Fenn. A **VI**, 254 [1967].

J	$P(J)$		$R(J)$	
	$HCCCl^{35}$	$HCCCl^{35}$	$HCCCl^{37}$	$HCCCl^{37}$
0			(41.092)	
1	(40.332)		41.448	
2	—		41.824	
3	39.527		42.189	
4	39.165		—	
5	38.779		42.930	
6	38.408		43.301	
7	38.007		43.669	
8	37.613		44.036	
9	(37.167)		44.405	44.268
10	—		44.777	44.629
11	36.472		(45.159)	44.985
12	36.094		(45.516)	—
13	35.709		45.893	45.750
14	35.316		46.263	46.103
15	34.938		46.623	46.491
16	—		46.995	46.837
17	(34.174)		47.355	47.215
18	33.744	33.868	47.722	47.535
19	33.351	33.472	—	—
20	32.937	33.076	48.448	48.250
21	32.543	32.687	48.805	48.613
22	32.149	32.283	49.178	48.960
23	(31.759)	31.911	49.534	49.307
24	31.369	—	49.887	49.662
25	30.963	31.115	50.247	50.027
26	30.550	30.731	—	
27	30.142	30.339	50.969	
28	29.736	29.940	51.318	
29	29.329	29.563	51.681	
30	(28.934)	29.159	52.042	
31	28.542	—	52.396	

J	$P(J)$		$R(J)$	
	$HCCCl^{35}$	$HCCCl^{37}$	$HCCCl^{35}$	$HCCCl^{37}$
32	28.142	28.347	52.753	
33	27.740	27.956	53.104	
34	27.347	27.552	(53.443)	
35	26.938	27.146	53.803	
36	26.524	26.752	54.159	
37	26.119	26.354	54.503	
38	25.710	25.950	54.853	
39	25.313	25.547	55.185	
40	24.901	25.133	(55.553)	
41	24.497	24.743	(55.872)	
42	24.073	24.344	56.224	
43	23.678	23.938	56.559	
44	23.258	23.533	56.918	
45	22.851	—	57.231	
46	22.427	22.725	57.593	
47	22.014	22.299	57.930	
48	21.590		(58.282)	
49	21.187		(58.542)	
50	20.756		58.943	
51	(20.297)		(59.309)	
52	19.940		—	
53	19.535		59.971	
54	19.096		60.275	
55	18.686		60.620	
56	18.282		(61.026)	
57	17.869		61.302	
58			—	
59			61.951	
60			62.279	
61			62.615	
62			62.931	

Table 1. Observed wavenumbers (cm^{-1} in vacuum) in the ν_1 band of monochloroacetylene. 3300 cm^{-1} should be added to the numbers given.

Constant	$HCCCl^{35}$	$HCCCl^{37}$	Reference
$B''[cm^{-1}]$	0.189606 $0.18963 \pm 5 \times 10^{-5}$	0.185874 $0.18560 \pm 3 \times 10^{-4}$	Microwave measurement[1] Infrared spectrum, this work
$\alpha_1[cm^{-1}]$	$(3.92 \pm 0.05) \times 10^{-4}$	$(4.14 \pm 0.20) \times 10^{-4}$	Infrared spectrum, this work
$D[cm^{-1}]$	$(4.8 \pm 1) \times 10^{-8}$ 4.6×10^{-8}	 4.5×10^{-8}	Infrared spectrum, this work Theor. value, this work

Table 2. Molecular constants of HCCCl.

wave data of WESTENBERG et al.[1]. The centrifugal distortion constant D was also computed theoretically from the formula presented by WILSON[8] and using the force constants and geometrical parameters of HUNT and WILSON[4]. The experimental value is within the limits of error in fairly good agreement with the computed one. No former values seem to exist with which these results could be compared.

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[8] E. B. WILSON, J. Chem. Phys. **27**, 986 [1957].