Die Berechnung erfolgte in folgenden Schritten:

a) Numerische Berechnung der Integrale. Die einfacheren wurden mit Bibliotheksprogrammen [6, 7] gerechnet, für die Dreizentren-Austausch- und Vierzentrenintegrale wurde ein eigenes Programm entwickelt, es basiert im wesentlichen auf der Berechnungsmethode von HARRIS und MICHELS [8].

b) Berechnung der Faktoren für die Integrale in den Elementen der Energiematrix und Berechnung der verschiedenen Normen-Werte.

c) Zusammenstellung der Energiematrix, Bestimmung der Eigenwerte und Eigenvektoren.

---

[6] N. ALBAT u. N. GRÜN (nicht veröffentlicht).

[7] „Programm für die Berechnung von Dreizentren-Coulomb-Integralen", Programmbibliothek des Rechenzentrums in Darmstadt.

[8] F. F. HARRIS u. H. H. MICHELS, J. Chem. Phys. **45**, 116 [1966].

Application of a New Principle of Assignment to the Infrared Spectrum of 2-Chloroacrylonitrile

F. WINTHER

Institut für Physikalische Chemie der Universität Köln und Abteilung Chemische Physik
Institut für Physikalische Chemie der Universität Kiel

(Z. Naturforsch. **26 a**, 1499—1514 [1971]; received 27 April 1971)

The principle of phase independent anharmonicity constants has been applied to the assignment of the infrared spectra of gaseous and liquid 1-chloro-1-cyanoethylene. The transferability of the anharmonicity constants of 1,1-dichloroethylene and some other objective criteria have also been utilized. An attempt has been made to correct for vibrational resonances and to determine the harmonic frequencies of $H_2C{:}CCl(CN)$.

In an earlier paper [1] it has already been stated that the anharmonicity constants of polyatomic molecules seem to be phase independent within the accuracy of measurement, where no vibrational resonance or Coriolis coupling occurs. This principle has been used in the present investigation as an objective criterion of correct asignment and for the identification of vibrational resonances in the spectrum.

For several applications, it is desirable to know the harmonic frequencies (ω_i) of the normal vibrations. In the past, these frequencies have only been calculated for very few molecules with more than three atoms. However, it seems possible to extend the determination to large molecules provided a sufficient number of combination levels can be observed. Here 163 vibrational levels have been identified, and from these 15 fundamentals (ν_i), 81 anharmonicity constants (x_{ij}), and one vibrational resonance parameter (W_{ijk}) could be obtained. An approximation method had to be used for the reduction of these data to the 15 harmonic frequencies and 120 anharmonicity constants of 2-chloroacrylonitrile.

Before this work had been completed, a paper by LIE and KLABOE [2] on the same molecule appeared. Since LK are mainly dealing with the fundamentals, and because of some discrepancies and questions left open in their paper, it was thought worth while publishing these extended and independent measurements.

Experimental

The infrared spectra were recorded on Perkin-Elmer mod. 125 ($10\,000-400$ cm^{-1}) and Beckman IR-11 ($400-100$ cm^{-1}) spectrometers, calibrated with frequencies from [3] and [4]. The gas phase spectra were investigated with spectral slit widths between 0.3 and 1.5 cm^{-1}, depending upon frequency range and inten-

---

Reprints request to Dr. F. WINTHER, Institut für Physikalische Chemie der Universität Kiel, Abt. Chemische Physik, *D-2300 Kiel*, Olshausenstraße 40—60.

[1] F. WINTHER, Z. Naturforsch. **25 a**, 1912 [1970].

[2] S. B. LIE and P. KLABOE, Spectrochim. Acta **A 26**, 1191 [1970].

[3] I.U.P.A.C. Tables of Wavenumbers for Calibration of Infra-Red Spectrometers, Butterworths, London 1961.

[4] K. N. RAO, C. J. HUMPHREYS, and D. H. RANK, Wavelength Standards in the Infrared, Academic Press, New York 1966.

Table 1. Assignments, negative anharmonicities and observed bands of 2-chloroacrylonitrile. Sym. is the symmetry species of the different levels in the C_{2v} approximation. A_1 and B_1 are in the in-plane vibrations, actually A′, and A_2 and B_2 are the out-of-plane (A″) vibrations. Anharm. ist the *negative* anharmonicity, defined on p. 1509. For difference bands the deviation between the calculated (upper level — fundamental) and observed position is given in brackets. Err. indicates the probable error of measurement. R−ν is the frequency distance between the maximum of the R branch and the band center; R−P and ν−P are defined analogously. Inten. gives the maximum absorbance of liquid bands, between 10 000 and 4700 cm^{-1} for a 10 mm and below 4700 cm^{-1} for a 250 μ layer. $\Delta\nu_{1/2}$ is the halfwidth of bands in the liquid phase. Other abbreviations are: ass. = assumed, min = minimum, unsymm. = unsymmetrical, br = broad, impur. = impurity, and doub. = double. Levels assigned to $H_2C_2\,^{37}ClCN$ are marked with an asterisk, e. g. 2* 7*.

Assignment				Sym.	Gas							Liquid				
ν_i	ν_j	ν_k	ν_l		Anharm. cm^{-1}	Found cm^{-1}	Err. cm^{-1}	Band shape	$R-\nu$ cm^{-1}	$R-P$ cm^{-1}	$\nu-P$ cm^{-1}	Anharm. cm^{-1}	Found cm^{-1}	Err. cm^{-1}	Inten. (10 mm)	Remarks $\Delta\nu_{1/2}$ cm^{-1}
													9758	10		
													9556	10		
1	1	1		B_1								153.9	9228	2	0.03	
													9154	5		
1	1	2		A_1	227.8	9091	5	A/B				229.5	9063.7	1	0.17	
													8953	5		
2	2	2		A_1	240.0	8901	5	A/B				252.8	8863	5	0.25	
						8870	10	A/B					8838	5		
													8765	5		
													8694	5		
													8507	10		
													8244	10		
1	1	12	12	A_1								116.4	7998	10		
1	1	4		A_1								42.2	7816.9	1	0.05	
													7762	5		
													7675	5		
2	2	4		A_1								85.7	7596	5		
1	1	5		A_1								79.8	7547.9	1	0.22	
													7469	5		
2	2	13	13	A_1								72.4	7426.8	1		
2	2	5		A_1								83.2	7367.1	1	0.09	
													7239	5		
1	2	6		A_1								141.1	7190.9	1	0.11	
1	1	7		B_1								46.7	7097.6	1		
													6958	5		
1	2	7		A_1								140.8	6914.8	1	0.12	
													6875	10		
													6839	10		
													6772	3		
1	2	13		B_2								145.7	6731.2	1	0.09	
													6690	10		
													6625	10		
1	1	10		B_1								47.7	6568	2	0.02	
													6547	10		
													6520	10		
													6480	5		
1	1	11		A_1								52.1	6387	3		
4	4	4	4	A_1								57.2	6360.8	1		

Table 1 continued

													6318	5		
1	1			A_1	34.4	6237.4	0.5	B, min	4.2	(17)		38.8	6215.8	1	4.1	
2	4	4		A_1	49.4	6217.2	1	B, min	(7.5)	(12.5)		46.8	6200.8	1		
1	4	12	14	B_1								48.1	6170	10		
1	4	13	13	B_1	11.5	6145	5	A/B				22.8	6131	10		
1	4	5		B_1	15.5	6101.9	0.5	A, Q	6.0	15.0		17.3	6087.6	1		
1	2			B_1	128.6	6054.3	0.5	A, Q	7.5	15.7		131.4	6034.5	0.5	3.4	
2	2			A_1	67.4	6026.6	1	B, min	5.5	12.5		71.2	6006	3		
2	4	5		A_1	49.5	5979.0	1	B, min	8.0	13.0		53.6	5962.6	0.5	≈ 2	
													5935	10		
1	4	6		A_1	11.2	5907.7	1	B, min	5.0	11.5		15.4	5882.5	1		
						5875.4	0.5	A, Q	6.5	16						
						5831.7	1	B/A	5				5826.7	1		
2	4	6		B_1	25.0	5805	5	B/A				26.5	5782.7	1		
													5753	10		
1	6	13	13	A_1								23.1	5692.3	1		
1	5	6		A_1								27.4	5639.1	0.5	0.04	
													5610	5		
													5587	10		
													5542	5		
2	4	7		B_1								26.8	5506	3		
													5472	10		
1	4	13		A_2								13.8	5429	2		
													5385	5		
1	3			A_1								4.7	5356.7	0.5	0.09	
													5310	10		
2	3			B_1								4.8	5267.9	0.5	≈ 0.15	
													5203	3		
1	5	13		B_2	41.3	5171.7	0.3	C ? Q				40.4	5171.0	1	≈ 0.15	
2	6	7		A_1	17.1	5094	3	B/A	6	15		23.0	5071.4	1		
1	5	14		A_2	20.9	5044	2	C ? Q ?				22.8	5034	2		
						5013	5	B/A								
2	4	10		B_1	19.2	4995	5	B/A				21.2	4983	5		
1	12	12		A_1	29.2	4934.5	0.3	A,Q	7.6	13.0		29.5	4957.6	1	≈ 0.3	
						4922	10	B ?					4938	10		
1	7	7		B_1								14.3	4892.4	1		
2	12	12		A_1	19.4	4855.4	1	B, min	6	12		23.4	4875	10		
													4850	5		
													4839	2		
4	4	4		A_1	28.0	4801.4	1	B ? min	4	12		30.9	4782.6	0.5	≈ 0.7	
1	4			B_1	−0.4	4746.1	0.3	A, Q_1	7.5	17		0.6	4731.2	0.5	4.1	16
						4742.9	0.5	Q_2								
						4725.4	0.5	B/A			5.5					
													4666.6	1		
						4665	10									
													4645	5		
2	4			A_1	6.8	4650	10					13.1	4630	2		
1	12	14		B_1	14.3	4592.8	0.3	A, Q_1	6.5	15.0		17.6	4596	2		
						4590.0	0.5	Q_2								

Table 1 continued

		Gas							Liquid				
Assignment ν_i ν_j ν_k ν_l	Sym.	Anharm. cm^{-1}	Found cm^{-1}	Err. cm^{-1}	Band shape	$R - \nu$ cm^{-1}	$R - P$ cm^{-1}	$\nu - P$ cm^{-1}	Anharm. cm^{-1}	Found cm^{-1}	Err. cm^{-1}	Inten. 250μ	Remarks $\Delta\nu_{1/2}$ cm^{-1}
1 13 13	B_1	4.6	4542.1	0.3	A, Q_1	6.0	15.0		12.2	4537.1	0.5	≈ 0.05	23
			4540.0	0.3	Q_2								
			4538.4	0.3	Q_3								
			4536.5	0.5	Q_4								
			4494.1	0.3	Q								
			4489.0	0.3	Q_2								
1 5	B_1	19.6	4488.0	0.3	A, Q_1	8.0	14.8		18.4	4482.0	0.3	0.63	13.0
1 5 13−13	B_1	(−0.3)	4466.6	0.5	Q								
			4464.2	1	Q ?								
			4431	2	B ? min	5				4400.2	0.5	0.006	
1 13 14	A_1	7.6	4391.0	0.5	A, Q	4.5			9.7	4385	3		
			4371	2	B ? min	4				4368	2		
			4354.0	1	B/A, Q ?					4348.8	1	≈ 0.003	
1 6	A_1	2.4	4306.7	0.5	B, min	4.5	8.5/11.5		4.9	4288.5	0.3	0.42	14.0
1 14 14	B_1	5.1	4245.4	0.5	B, min	5.5	11		4.3	4235.8	0.5	≈ 0.025	
			4219.1	0.5	Q_2, unsymm.								
2 6	B_1	6.9	4213.3	0.3	(A) Q_1, unsymm.	6.5	≈12		8.1	4196.6	0.5	≈ 0.25	14
										4185	5		
			4182.5	0.5	Q, Br								
										4174	5		
										4163	5		
2 14 14	A_1	6.5	4155.1	0.3	A, Q	7	16		8.9	4142.5	0.5	≈ 0.01	
										4118.4	1		
										4075	2		
1 12	A_2	15.3	4034.5	0.5	C ? Q				10.2	4047	5		
1 7	A_1	2.2	4024.6	0.5	B, min				4.3	4012.7	0.3	0.21	13.5
1 11 13	B_2	10.4	4004.1	0.5	Q								
2 12	B_2	10.9	3950.0	0.3	C, Q	13			10.9	3957.6	0.5	0.05	br
2 7	B_1	3.9	3934.0	0.3	A, Q_1	8.0	13		6.8	3921.5	0.5	0.06	
2* 7*	B_1		3932.2	0.5	Q_2 ?								
4 7 13 13	B_1								12.2	3904	5		
3 4	B_1	9.4	3843	2	B/A, min	6			5.1 }	3833.5	0.5	0.20	15
1 13	B_2	6.1	3835.2	1	C ? Q				4.8 }				
1 8	B_1	−0.1	3796.0	0.5	A, Q	6	15		0.8	3784.7	1	≈ 0.04	
			3794.5	0.5	Q ?								
1* 8*	B_1		3792.7	0.5	Q ?								
2 13	A_2								17.6	3732	5	0.005	
2 8	A_1	2.0	3705	2	B ? min	6	13		1.8	3695	2		
1 14	A_2								4.7	3679	5		
1 9	B_1	−5.0	3657	2	B/A				1.9	3651	5		
3 5	B_1	5.3	3609	3	B/A				4.1	3603.1	1	≈ 0.025	
1 10	A_1	3.0	3490.3	1	B, min	6	13		5.4	3483	2		
4 12 12	A_1	13.4	3424.2	1	B ? min	5.1	(14)		18.3	3446	5		

Table 1 continued

2 10	B_1	5.0	3399.4	0.3	A, Q_1	(7)	(15)	4.5	3395.2	0.5	0.08	
			3397.0	0.3	Q_2							
									3375	5		
									3336	5		
2 15	B_2							2.1	3314.0	1	0.02	
1 11	B_1							−2.2				
									3280	5		
4 4	A_1	10.8	3208.8	0.5	B, min	5.3	12.7	11.1	3197.9	0.5	0.89	12
1	b_1	(0.0)	3135.9	0.2	A, Q	7.0	14.7	(0.0)	3127.3	0.5	5.2	12.5
2	a_1	(0.0)	3047.0	0.3	B, min	5.1	11.5	(0.0)	3038.6	0.5	2.5	11
4 13 13	A_1	4.4	3016.2	0.5	B, min	≈5	≈12	2.2	3024.3	1	1.7	23.5
4 5	A_1	14.5	2967.0	0.3	B, min	4.8	11.5	14.8	2962.8	0.5	1.0	11
3 13	B_2	4.3	2943.7	0.5	Q ? Br			5.1	2940	10		
									2915	5		
3 8	B_1	1.5	2901.1	0.5	A, Q_1	5	14	1.9	2890.4	0.5	≈ 0.07	
			2899.6	0.5	Q ?							
3* 8*	B_1		2896.6	0.5	Q_2							
1−15	A_2	(0.3)	2866.2	1	Q ?							
5 12 14	A_1							5.7	2853.7	1	≈ 0.007	
3 14	A_2	3.3	2796.6	0.3	C, Q_1	≈13		4.2	2786.3	0.5		
			2792.0	0.3	Q_2							
			2790.3	0.5	Q ? Br							
4 6	B_1	6.9	2776.1	0.3	A, Q_1	6.0	14	8.1	2762.5	0.3	≈ 0.4	≈ 13
			2773.9	0.3	Q_2							
			2749.4	1	R ? Q ? Br, impur. ?							
									2733	5		
			2727.1	0.5	B, min	5.7	11.8		2710.5	0.5	≈ 0.025	
									2680.0	1	≈ 0.013	
									2660.7	1		
									2615	5		
3 10	A_1	5.3	2594.7	1	B, min	6	12	5.6	2589.6	0.3	0.025	
									2570	5		
5 6	B_1	−0.1	2545	2	A/B ?			2.9	2536.3	0.5	≈ 0.025	
4 12	B_2							−1.9				
3 15	A_2	3.3	2508.7	0.3	C, Q_1, sharp			4.4	2507.2	0.5		
			2507.4	0.3	Q_2, sharp							
			2505.8	0.3	C/A, Q_1, Br							
			2503.6	0.3	Q_2							
4 7	B_1	5.2	2495.5	0.2	A, Q_1	≈6.5	≈15	6.4	2487.8	0.3	≈ 0.15	
4* 7*	B_1		2494.1	0.3	Q_2							
1−13	B_2	(−0.3)	2430.8	0.2	C, Q, unsymm.							
3 11	B_1	4.2	2411.6	0.3	A/B, Q ?	4.5	12	5.6	2413.0	0.3	0.11	15
			2410.7	1	min							
			2391.9	0.5	Q ? Br							
									2370	5		
6 6	A_1							5.8	2326.4	1		
									2306	5		
			2271.7	1	B/A, R_1							
			2268.6	1	R_2/Q ? Br							
4 8	A_1	3.8	2266	2	Ass. band center	(6)		2.9	2259.8	0.5	≈ 0.4	≈ 10
5 7	B_1	0.6	2262	2	Ass. band center	(8)		3.0				

Table 1 continued

		Gas							Liquid				
Assignment ν_i ν_j ν_k ν_l	Sym.	Anharm. cm^{-1}	Found cm^{-1}	Err. cm^{-1}	Band shape	$R-\nu$ cm^{-1}	$R-P$ cm^{-1}	$\nu-P$ cm^{-1}	Anharm. cm^{-1}	Found cm^{-1}	Err. cm^{-1}	Inten. 250μ	Remarks $\Delta\nu_{1/2}$ cm^{-1}
3	b_1	(0.0)	2242.6	0.2	A, Q_1	5.2	14.5		(0.0)	2234.1	0.3	3.5	7.5
			2240.4	0.3	Q_2								
3 15−15	B_1	(0.3)	2239.0	0.3	Q_3, unsymm.								
			2237.2	0.5	Q_4								
										2207.5	1		
6 8 10	A_1	−0.9	2191.5	0.5	A ? Q				3.0	2182.4	0.3	0.05	
4 14	B_2	2.0	2165.1	0.2	C ? Q_1				2.0	2158.9	0.5	0.015	
			2164.3	0.5	Q ?								
			2162.7	0.3	Q_2								
4 9	A_1								−1.4	2131.5	1		
2−12	B_2	(−0.4)	2133.5	0.3	Q, Br, unsymm.				(2.7)	2106	5		
			2100.5	1	Q ? Br								
										2090.0	0.5		
6 7	A_1	3.8	2060.3	0.5	B, min	4.8	11.5		8.4	2047.4	0.3	0.10	16
3−11	B_1								(2.2)				
7 14 14	B_1								8.0	1994.5	1	0.005	
4 10	B_1	4.7	1962.5	1	A, Q	6	13		7.8	1957.8	0.5	0.03	
5 9	A_1								5.7	1893	5		
6 13	B_2	−5.5	1884.1	0.5	C ? Q				−3.9	1881	2		
4 15	B_2	3.2	1876.0	0.5	C ? Q				1.0				
12 12	A_1	−2.8	1830.6	0.5	B, min	6.0	12.0		−3.7	1863.5	1	0.90	54
										1846	5		
6 8	B_1								4.3	1820	5		
			1807	2	R/P ?								
4 11	A_1								2.0	1787	5	0.13	
7 7	A_1	−2.2	1784.0	0.5	B ? min	6.5	13		1.3	1778.1	1		
5 10	B_1								3.1	1731.1	0.5	0.07	
			1719	5	A/B								
			1623	5	R ?								
12 13	B_1	4.3	1615	5	Ass. band center	(8)			−4.1	1645	10		
4	a_1	(0.0)	1609.8	0.3	B, min	5.5	12.5		(0.0)	1604.5	0.3	24	8 unsymm.
7 8	B_1	1.0	1549.9	0.3	Q, doub.				2.1	1545.8	1		
6 10	A_1								6.1	1521.1	1	≈ 0.02	
12 14	A_1	−1.9	1473.1	0.3	B/A, Q	6.5	13.8		−2.5	1488.8	0.5	0.14	18
13 13	A_1	−9.4	1420.2	0.5	B/A, Q	4.5	12.9		0.1	1421.9	1	≈ 0.9	27
5	a_1	(0.0)	1371.7	0.3	B/A, Q	5.5	12.6		(0.0)	1373.1	0.3	5.7	
6 11	B_1	1.4	1345	2	Q ?				5.6	1345	5		
			1323.1	0.3	Q								
8 8	A_1	1.5	1318.5	0.2	A, Q_1	6	13.5		1.6	1314.8	0.5	≈ 0.13	
			1315.5	0.2	Q								
			1314.0	0.3	Q								
8* 8*	A_1		1312.0	0.2	Q_2								
			1308.9	0.5	Q ?								

Table 1 continued

13 14	B_1	1.3	1261.4	0.2	A/C, Q_1	7 ?			3.2	1264.2	1		
			1258.8	0.3	Q								
7 10	A_1	3.3	1245.0	0.2	A ? Q_1	≈6.5			4.8	1246.0	0.5		
			1235.8	0.3	Q								
8 14	B_2	0.3	1217.0	0.3	A/C, Q_1								
8* 14*	B_2		1213.4	0.5	Q, Br								
12 15	A_1	−0.4	1183.7	0.3	Q ? Br				−2.6	1210	5		
8 9	A_1	−6.4	1182.5	0.1	A/C, Q, Br				−2.2	1186	3		
			1179.7	0.3	Q ? Br								
6 13−13	B_1	(0.1)	1178.6	0.2	Q								
			1174.5	0.5	Q ?								
			1174.0	0.1	Q_2								
6	b_1	(0.0)	1173.2	0.1	A, Q_1	6.5	13.5		(0.0)	1166.1	0.3	36	10.5
			1172.3	0.2	Q								
			1171.3	0.1	Q, Br								
4 15−13	B_1	(0.2)	1170.4	0.2	Q, unsymm.								
			1168.5	0.5	Q ?								
13 13−15	B_2								(1.9)	1142.5	1		
14 14	A_1	2.1	1112.5	0.2	A, Q	5.3	14.6		2.5	1110.3	0.3	3.5	10.0
9 14	B_2	− 2.6	1076.0	0.5	Q				−4.0	1086	5		
4−14	B_2	(−2.1)	1054.6	0.5	Q, Br, unsymm.				−1.9	1050.0	0.5		
			1046.9	0.2	Q								
9 10 11	B_1	7.4	1039.3	0.2	A ? Q_1	7			−2.8	1074	3		
9 9	A_1	−0.5	1032.7	0.3	Q ? Br				1.2	1050.0	0.5	≈ 0.15	
			1025.3	1	R ?								
			1017.9	0.5	A ? Q_1 ? Br								
8 10	B_1	3.6	1013.8	0.3	Q				4.6	1014.7	1		
			1008.2	1	P ?								
13 15	B_1	1.8	973.0	0.2	A, Q	7.1	15.7		2.3	986.2	1		
			918.4	0.1	Q								
12 12−12	B_2	(−0.2)	916.9	0.3	Q ?								
12 14−14	B_2	(−0.5)	916.3	0.1	Q_2								
12 15−15	B_2	(−0.6)	914.9	0.3	Q ?								
12	b_2	(0.0)	913.9	0.1	C, Q_1	9.5	≈ 21		(0.0)	929.9	0.5	18	23 unsymm.
			911.9	0.1	Q								
12 13−13	B_2	(1.7)	907.9	0.1	Q_3								
			895.7	0.2	Q								
			893.9	0.1	Q_2								
			892.5	0.1	Q_3								
7	b_1	(0.0)	890.9	0.1	A, Q_1			6.0	(0.0)	889.7	0.3	≈ 12	8.0
7 8−8 & 7*	B_1	(0.5)	889.4	0.1	Q								
13 13−14	B_2	(0.5)	862.4	0.3	C ? Q, unsymm., doub. ?								
8 11	A_1	0.2	833.0	0.5	Q ?				−0.6	843.3	1		Raman
			830.2	0.5	R/Q ?								
14 15	A_1	1.7	825.0	0.3	A, Q_1	5	13		1.8	832.1	0.3	≈ 0.8	11
6−10	A_1								(−2.0)	807	5		
13	a_2	(0.0)	705.4	0.3	Q								
			702.5	0.3	Q								

Table 1 continued

Assigment ν_i ν_j ν_k ν_l	Sym.	Gas Anharm. cm^{-1}	Found cm^{-1}	Err. cm^{-1}	Band Shape	$R-\nu$ cm^{-1}	$R-P$ cm^{-1}	$\nu-P$ cm^{-1}	Liquid Anharm. cm^{-1}	Found cm^{-1}	Err. cm^{-1}	Inten. (250 μ)	Remarks $\Delta\nu_{1/2}$ cm^{-1}
			693.3	0.3	Q								
			691.6	0.1	Q								
			690.0	0.3	Q ?								
9 11	A_1	0.2	689.1	0.1	A, Q_1	7.7			3.2	706.9	0.5	$\approx$ 0.7	15
			684.9	0.5	Q								
			662.3	0.2	Q								
8	a_1	(0.0)	660.0	0.1	A, Q_1	5.7	13.7		(0.0)	658.2	0.5	15	9.5
			658.6	0.1	Q_2								
8*	a_1		656.8	0.2	Q, Br								
			655.4	0.5	Q ?								
			616.2	0.1	Q_2								
6−14	A_2	(0.5)	615.4	0.1	C ? Q_1	$\approx$10	$\approx$22		(0.8)	608.9	1	$\approx$ 0.07	
			614.1	0.5	Q ?								
9 14−9	B_2	(0.0)	559.9	0.2	Q								
14	b_2	(0.0)	557.3	0.1	C, Q_1	$\approx$7	$\approx$23		(0.0)	556.4	0.3	11	6.0
14 15−15	B_2	(−0.4)	556.0	0.1	Q_2								
13 14−13	B_2	(0.0)											
14 14−14	B_2	(0.2)	555.0	0.1	Q_3								
			553.8	0.2	Q ?								
			552.9	0.5	Q ?								
			545.2	0.5	Q ?								
10 11	B_1								0.6	545	2		
15 15	A_1	0.7	538.1	0.3	Q								
9	a_1	(0.0)	516.1	0.3	B, min	$\approx$6	$\approx$12		(0.0)	525.6	0.3	$\approx$ 4	8.5
8−11	A_1								(−1.6)	475.3	1	$\approx$ 0.035	
13−15	B_1									433.3	1	0.015	
10	b_1	(0.0)	357.4	0.5	A, Q	7	15		(0.0)	361.1	1	$\approx$ 0.1	$\approx$15
			354.8	0.3	Q								
9−11	A_1								(−0.4)	341.5	0.5	$\approx$ 0.08	
			271.0	1	Q ?								
15	b_2	(0.0)	269.4	0.2	C, Q_1, unsymm.	$\approx$10	$\approx$20		(1.2)	276.3	0.5	2.2	8.5
11	a_1	(0.0)	173.2	0.5	B, min	6.3	12.3		(−1.3)	185.8	1	4	12 (in n-C_7H_{16})

sity of the absorption. The recording temperatures were: $45 \pm 5°$ (gas, P.-E.), $35 \pm 5°$ (gas and liq., B.), and 20 ± 3 °C (liq., P.-E.). The purity of the samples used was better than 98% as tested on a 50 m, 0.25 mm$^{\varnothing}$ capillary column coated with silicone rubber OV 17; FID detector.

To obtain a high accuracy in the frequency determinations the following method was used: In the case of liquid bands or R, Q, and P branches in the gas phase, the curve of band centers was extrapolated through the absorption curve to give the point of maximum absorption and the band frequency. For B bands a corresponding method was used in determining the frequency of the central minimum. The probable errors given in Table 1 refer to the accuracy of this determination and do not include the systematic error that the band origin does not coincide with e. g. the maximum of a Q branch. As far as it could be checked, the systematic frequency errors seem to be of the same order of magnitude as the experimental ones. This seems to be reasonable because most Q-branches of 2-chloroacrylonitrile have half widths less than 0.5 cm^{-1}.

Fundamentals

ν_{11} was not assigned with confidence by LK [2] because of the rather high polarization ratio of the Raman line at 185 cm^{-1} and the lack of an infrared gas phase contour. Figure 2 confirms that the intense band near 175 cm^{-1} is of B type. Its gas-liquid shift is strongly negative as presumed by LK, and this behaviour corroborates their assignment of $\nu_9 + \nu_{11}$. The Fermi resonance between this band and ν_8 has already been treated in [1].

The missing C:C torsion ν_{13} is expected near $\nu_9 + \nu_{11}$, and an attempt was made to detect this fundamental by utilizing the frequency lowering of $\nu_9 + \nu_{11}$ upon dilution of the liquid with cyclohexane. However, no additional bands were detected between 750 and 670 cm^{-1} in solutions of decreasing 2-chloroacrylonitrile concentration, meaning that ν_{13} must either be very weak in the infrared spectrum or lie outside this range, because its frequency shift between liquid and solution should be very small [5].

There is a close analogy between the spectra of 1,1-dihalogenethylenes [5] and that of 2-chloroacrylonitrile, apart from some vibrational resonances and the vibrations of the $-$CN group. Prominent combination bands, containing ν_{13} are thus expected to be (H_2C_2ClCN notation): $\nu_1 + \nu_2 + \nu_{13}$, $\nu_1 + 2\,\nu_{13}$ (Fermi resonance with $\nu_1 + \nu_5$), $\nu_1 + \nu_{13}$, $\nu_4 + 2\,\nu_{13}$, $\nu_1 - \nu_{13}$, $\nu_{12} + \nu_{13}$, $2\,\nu_{13}$ (Fermi resonance with ν_5), and $\nu_{13} + \nu_{14}$ (Fermi resonance with ν_6). To determine the frequency of ν_{13} from these combinations, the best point of attack seems to be $\nu_1 - \nu_{13}$. ν_{13} may be calculated exactly from this band, which should be of C type and occur at $3136 - (\approx 700) \approx 2436$ cm^{-1}, assuming an approximate C:C torsion frequency of 700 cm^{-1}. Indeed, the only C band within ± 40 cm^{-1} of 2436 cm^{-1} is found at 2430.8 cm^{-1}, yielding $\nu_{13} = 705.1$ cm^{-1} (see Fig. 7).

A careful examination of the gas phase infrared spectrum (Fig. 3) revealed a small Q branch at

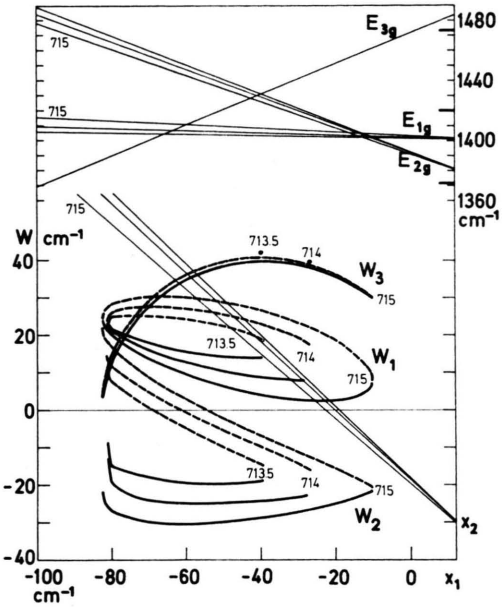

Fig. 1. The resonance triad $\nu_5 \rightarrow 2\,\nu_{13} \rightarrow \nu_{12} + \nu_{14}$, calculated for three different values of $\nu_{13\,l}$. $W_1 = |W|_{5\cdot 12\cdot 14}$, $W_2 = |W|_{5\cdot 13\cdot 13}$, $W_3 = |W|_{12\cdot 13\cdot 13\cdot 14}$. The two sets of W values are given as full and dotted curves, each defining one possible sign combination. Only the right extremal points of the W_3 curves for $\nu_{13\,l} = 713.5$ and 714 cm^{-1} have been drawn, because the curves almost coincide with the one for $\nu_{13\,l} = 715$ cm^{-1}. $x_1 = 2x_{12\cdot 14}$, $x_2 = 2x_{13\cdot 13}$, $E_1 = \nu_5$, $E_2 = 2\nu_{13}$, $E_3 = \nu_{12} + \nu_{14}$ (unperturbed). The three observed levels are shown as heavy lines on the right.

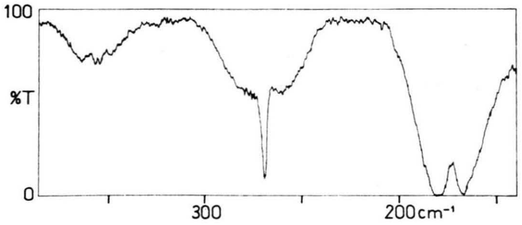

Fig. 2. Gas. $p \approx 45$ mm Hg, 1 m, Δ (spectral slit width) $= 1.3 - 2$ cm^{-1}.

---

[5] F. WINTHER, Dissertation, Köln 1969.

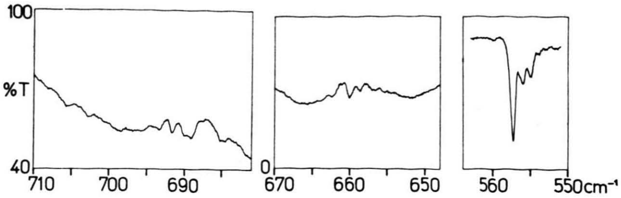

Fig. 3. Gas. $p < 50$ mm Hg, 10 cm, $\Delta = 0.5$, 0.5, and 0.4 cm^{-1}.

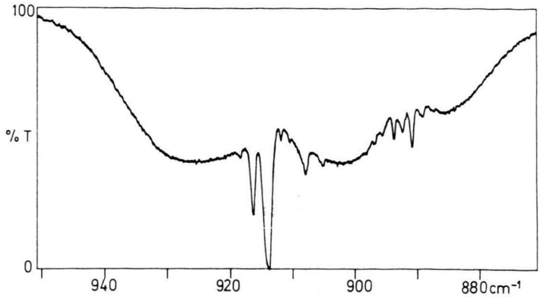

Fig. 4. Gas. $p \approx 50$ mm Hg, 10 cm, $\Delta = 0.3$ cm^{-1}.

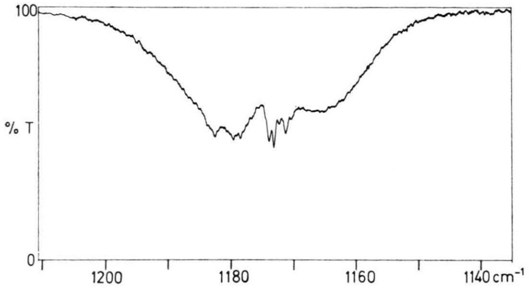

Fig. 5. Gas. $p \approx 20$ mm Hg, 10 cm, $\Delta = 0.3$ cm^{-1}.

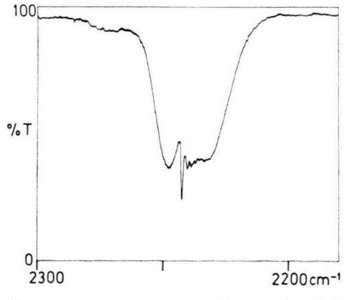

Fig. 6. Gas. $p \approx 35$ mm Hg, 1 m, $\Delta = 0.6$ cm^{-1}.

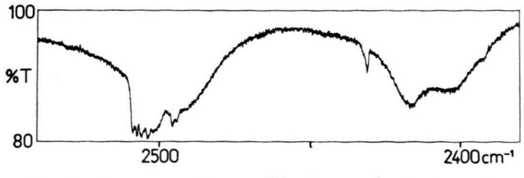

Fig. 7. Gas. $p \approx 65$ mm Hg, 1 m, $\Delta = 0.6$ cm^{-1}.

705.4 cm^{-1}, probably belonging to ν_{13}, but it has not been possible to obtain any reliable frequency for the liquid phase. $\nu_9 + \nu_{11}$ is found at 710 cm^{-1} in the Raman spectrum[2] but at 707 cm^{-1} in the infrared spectrum of the liquid. This difference indicates that some intensity of the Raman line may be due to ν_{13}, and an approximate liquid frequency of 711 cm^{-1} has been adopted for ν_{13} in this work. It seems promising to investigate the Raman spectrum of a hydrocarbon solution of 2-chloroacrylonitrile, where the solvent shifts should facilitate the separation of ν_{13} and $\nu_9 + \nu_{11}$.

Several difference bands have been identified in the infrared spectrum, and in principle it would have been possible to correct the fndamental frequencies slightly by means of these bands. Because most corrections are of the same magnitude as the experimental errors, such corrections have just been made for the liquid frequencies of ν_{11} and ν_{15}. LK give a Raman frequency of 280 cm^{-1} for ν_{15}, whereas the infrared spectrum of the liquid yields 276.3 cm^{-1}. From ν_{13}—$\nu_{15} = 433.3$ cm^{-1} and the adopted frequency $\nu_{13} = 711.0$ cm^{-1} is found $\nu_{15} = 277.7$ cm^{-1}. These (inconsistent) values are combined to give $\nu_1 = 277.5$ cm^{-1} as probable value. Similarly, ν_{11} is corrected to 184.5 cm^{-1} from the Raman measurement[2], ν_8—ν_{11}, and $\nu_9 - \nu_{11}$.

The frequency of ν_{10} is ill defined in the gas phase because of two equally weak Q branches and in the liquid because the Raman and the infrared frequencies differ 3 cm^{-1}. However, it has not been possible to correct ν_{10} from difference band measurements. The reason for the discrepancies in the liquid phase frequencies is not certainly known, but it may be different hot band patterns of infrared and Raman bands or the lacking correction of the infrared band shapes for changes in the refractive index across the band. In the case of ν_{10} part of the frequency difference may be due to the two isotopic species present, because the spectral slit widths of the infrared and the Raman spectrometer were different.

Four fundamentals ν_7, ν_8, ν_9, and ν_{10} are expected to show splittings > 1 cm^{-1} due to the natural abundance of 25% $H_2C_2\,^{37}Cl(CN)$ in 2-chloroacrylonitrile[5, 6]. The detection is complicated by numerous hot bands near the fundamental frequencies and near many combinations. For ν_8 an isotopic splitting of 3.3 cm^{-1} may be deduced from

---

[6] H. Hunziker and Hs. H. Günthard, Spectrochim. Acta **21**, 51 [1965].

ν_8 (3.2 ± 0.3 cm^{-1}), $\nu_8 + \nu_{14}$ (3.6 ± 0.8 cm^{-1}), $2\,\nu_8$ (6.5 ± 0.4 cm^{-1}), $\nu_3 + \nu_8$ (4.5 ± 1 cm^{-1}) and $\nu_1 + \nu_8$ (3.3 ± 1 cm^{-1}). Each of the assignments $\nu_8(^{37}\mathrm{Cl})$ and $2\,\nu_8(^{37}\mathrm{Cl})$ is confirmed by one hot transition having the same frequency distance from the main Q branch as analogous difference bands from $\nu_8(^{35}\mathrm{Cl})$ and $2\,\nu_8(^{35}\mathrm{Cl})$. This equivalence is anticipated because the anharmonicity constants of the two isotopic species will be very nearly identical.

ν_7 and two of its combination bands, $\nu_4 + \nu_7$ and $\nu_2 + \nu_7$, have secondary Q branches 1.5 ± 0.2, 1.4 ± 0.5, and 1.8 ± 0.8 cm^{-1} lower than Q_1. Thus an isotope shift of 1.5 cm^{-1} may be adopted for ν_7, but it bases upon rather limited evidence. No confirmed splittings could be obtained for ν_9 and ν_{10}, mainly because of the weakness in the gas phase of useful combination bands of A or C type. The suggestion of LK [2] that ν_6, ν_{12}, and ν_{14} might show isotopic splitting at a resolution of ≈ 0.5 cm^{-1} is not realistic, since a maximum separation of ≈ 0.2 cm^{-1} is expected for these bands [6].

The low intensity of ν_1 and ν_2 in the gas phase spectrum, equalling that of their first overtones should be noticed. In the liquid ν_1 and ν_2 have almost the same intensity as ν_5 and ν_3, respectively. Similarly, $\nu_a(\mathrm{CH_2})$ (here ν_1) of the 1,1-dihalogenethylenes [5] is too weak even to be detected in the gas phase. (Compare 4, p. 1511.) The intensity and halfwidth determinations of ν_2 and $\nu_4 + 2\,\nu_{13}$ in the liquid spectrum were made on bands, graphically separated under the assumption that both absorptions are symmetrical and not overlapped by further bands.

Vibrational Resonances

Several vibrational resonances are found in the spectrum of 2-chloroacrylonitrile. They are generally characterized by gas and liquid phase anharmonicities (x_g, x_l) differing more than expected from the accuracy of measurement, or a combination band of unusually high intensity (e. g. $\nu_4 + 2\,\nu_{13}$) may indicate the presence of a vibrational resonance. The anharmonicity is defined as

$$\sum_{i=1}^{n} \sum_{j \geqq i}^{n} x_{ij} (v_i + 1/2)\,(v_j + 1/2)$$

for a non-degenerate combination level, where n is the number of fundamentals, x_{ij} the anharmonicity constants, and v the vibrational quantum numbers.

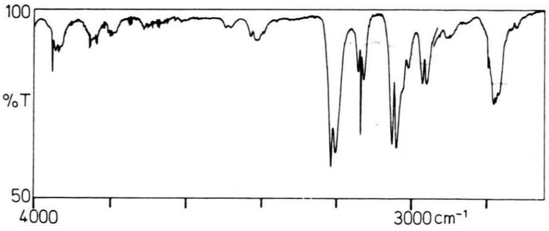

Fig. 8. Gas. $p \approx 65$ mm Hg, 1 m, $\Delta = 0.5 - 1.5$ cm^{-1}.

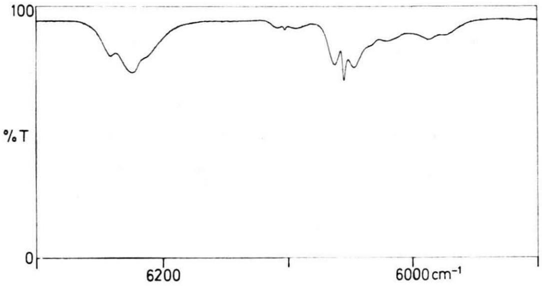

Fig. 10. Gas. $p \approx 65$ mm Hg, 1 m, $\Delta = 0.5$ cm^{-1}.

One prominent resonance, $\nu_8 \rightarrow \nu_9 + \nu_{10}$ has already been dealt with in a previous paper. Due to the slightly different ν_{11l} frequency used here, the unperturbed levels for the gas phase change to the

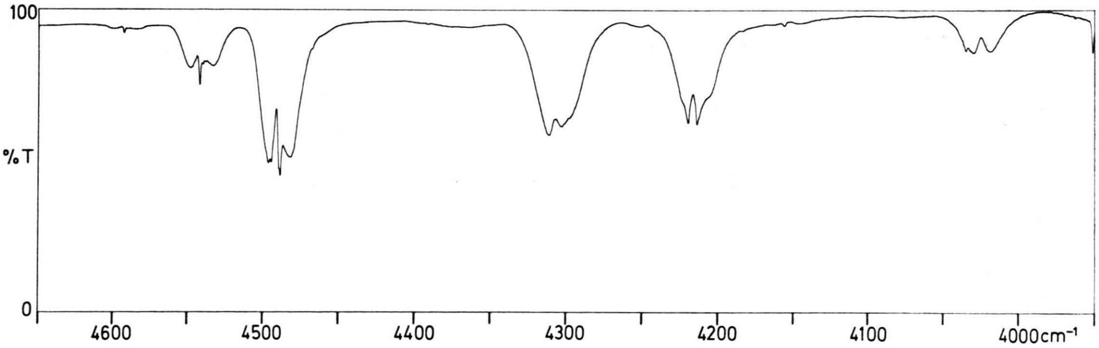

Fig. 9. Gas. $p \approx 65$ mm Hg, 1 m, $\Delta = 0.3 - 0.5$ cm^{-1}.

following frequencies (mean values of the gas-liquid and gas-solution calculation): $\nu_9 + \nu_{11} = 682.6$, $\nu_8 = 666.5$, $2\,x_{9.11} = -6.7$, $|W_{8.9.11}| = 12.1\ \text{cm}^{-1}$.

It seems likely that $\nu_8 + \nu_{10}$ and $\nu_9 + \nu_{10} + \nu_{11}$ (see Table 1) are perturbed by the same resonance, but the assignment of these bands is uncertain due to complicated gas phase contours. The frequencies of other combinations $\nu_i + \nu_8$ may be displaced by analogous resonances, but no components of the type $\nu_i + \nu_9 + \nu_{11}$ have been detected.

ν_6 seems to be influenced by some vibrational resonance or Coriolis coupling, particularly because $\nu_1 + \nu_6$ and $\nu_2 + \nu_6$ show phase dependent anharmonicities and heavily distorted bands shapes in the gas phase, where also the R branch of the fundamental is irregular (Figs. 9 and 5). The most probable interacting frequency is $\nu_8 + \nu_9$, but also $2\,\nu_{14}$ or $\nu_{12} + \nu_{15}$ are possible. In the C_{2v} approximation these combinations belong to the A_1 species, whereas ν_6 is of b_1 symmetry, but strictly speaking, all transitions are of A′ (a′) type. This means that both interactions are possible. The frequency shift of ν_6 seems to be less than $5\ \text{cm}^{-1}$ and has not been corrected for.

A strong Fermi resonance is found between ν_5 and $2\,\nu_{13}$, probably also including $\nu_{12} + \nu_{14}$. Since the exact frequency of ν_{13} in the liquid is unknown, it has not been possible to correct ν_5 for the influence of this resonance. If it is assumed that

$$W_{5.12.14} = W_{12.13.13.14} = 0$$

a calculation by means of the method given in [1] can be made. Curves of the same shape as those of Fig. 2 of [1] are obtained with $|W_{5.13.13}|$ imaginary in a small intervall near $\nu_{13l} = 706.2\ \text{cm}^{-1}$ and else between 22 and $24\ \text{cm}^{-1}$. For $\nu_{13l} = 711\ \text{cm}^{-1}$ the following values are obtained: $\nu_{5g} = 1400.4$, $2\nu_{13g} = 1391.5$, $\nu_{5l} = 1392.3$, $2\nu_{13l} = 1402.7$, $2x_{13.13} = -19.3\ \text{cm}^{-1}$.

If resonances with $\nu_{12} + \nu_{14}$ are assumed, the picture given as Fig. 1 emerges. For $\nu_{13l} \leqq 713.5\ \text{cm}^{-1}$ no solutions exist, and this makes any further discussion somewhat hypothetical. The anharmonicity of $\nu_{12} + \nu_{14}$ is known from several 1,1-dihalogenethylenes to be numerically small [5]. This means that the right side of Fig. 1 should contain the possible solutions. A resulting value of $\nu_{13l} = 714 - 716\ \text{cm}^{-1}$ seems unreasonably high, because it involves $\nu_{15l} = 281 - 283\ \text{cm}^{-1}$ (from $\nu_{13} - \nu_{15}$), and because ν_{13} might then have been observed in the Raman spectrum in spite of the overlapping $\nu_9 + \nu_{11}$.

The difficulties of the ν_5 resonance system are repeated in the $\nu_1 + \nu_5 \rightarrow \nu_1 + 2\nu_{13} \rightarrow \nu_1 + \nu_{12} + \nu_{14}$ triad. If just the $\nu_1 + \nu_5 \rightarrow \nu_1 + 2\nu_{13}$ resonance is considered, $|W_{5.13.13}| = 27\ \text{cm}^{-1}$ is found rather independent of the chosen frequency of ν_{13l}. An additional resonance triad $\nu_2 \rightarrow \nu_4 + 2\nu_{13} \rightarrow \nu_4 + \nu_5$ is observed at about $3000\ \text{cm}^{-1}$, and calculations with some trial values of ν_{5g} and ν_{5l} obtained from Table 2 show that solutions exist for $\nu_{13l} \geqq 714\ \text{cm}^{-1}$, but as outlined above such frequencies cannot be accepted.

Further vibrational resonances are found in the region of $2\nu(\text{CH})$ and $3\nu(\text{CH})$. However, the phase shifts of the anharmonicities are too small to make any calculation appropriate. Moreover, it is not certain that all participating bands are resolved. The most clear cut example is the resonance between $2\nu_1$ and $\nu_2 + 2\nu_4$, which is also found regularly in the spectra of the 1,1-dihalogenethylenes [5].

Combination Bands

Table 1 gives all observed frequencies together with other data relevant to the assignment. Apart from the main principle of phase independent anharmonicities, a number of other conditions have been imposed upon the assignment of the combina-

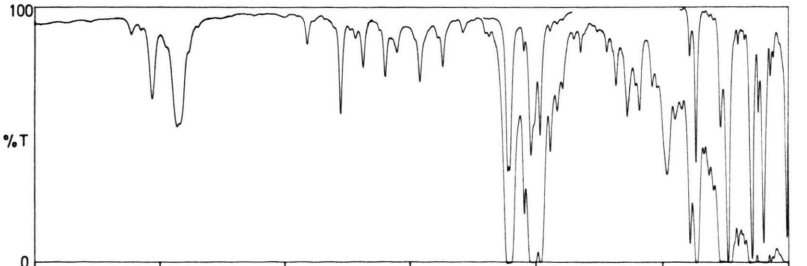

Fig. 11. Liquid. 10 and 1 mm, $\Delta = 2 - 0.5\ \text{cm}^{-1}$.

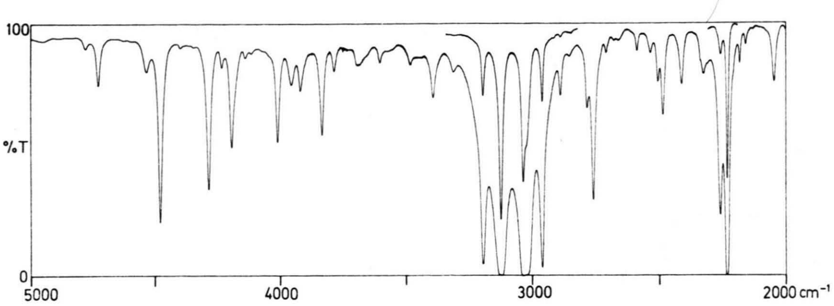

Fig. 12. Liquid. 246 and 28 μ, $\Delta = 0.3 - 1$ cm^{-1}.

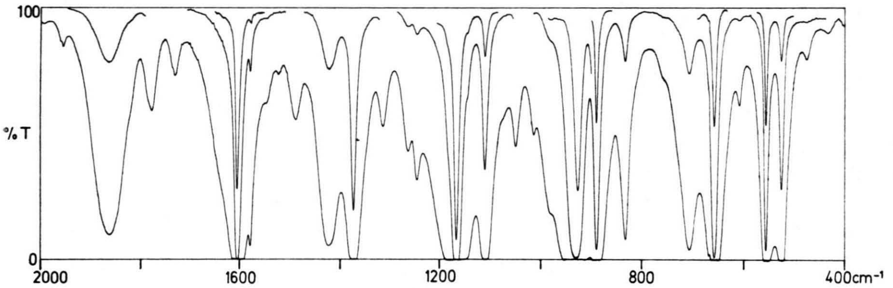

Fig. 13. Liquid. 246, 28 μ, solution in $H_2C_2Cl_2$ (1700 – 900 and 600 – 400 cm^{-1}) and solution in CCl_4 (different concentration; 900 – 600 cm^{-1}). $\Delta = 1 - 3$ cm^{-1}.

tion bands. These conditions are given below. Some are widely used in the literature but usually without being stated explicitly.

1. The anharmonicities and, to a lesser extent, the intensities of analogous combination bands of closely related substances are equal (Compare [7]). – Especially the assignment of ternary combinations above 4500 cm^{-1} was facilitated by comparison with the spectrum of 1,1-dichloroethylene [5, 8]. The assignment for this substance could be supported by band shape determinations in the gas phase spectrum thanks to its larger vapour pressure. Table 2 shows the degree of agreement obtained. The anharmonicities given are from some bands of high intensity, they have not been selected to give unusually good agreement. No resonance corrections have been applied, and the frequency numbering is that of 2-chloroacrylonitrile.

Table 2. Anharmonicities of some combination bands of 2-chloroacrylonitrile and 1,1-dichloroethylene.

$-x_1$ (cm^{-1})	$H_2C:CCl(CN)$	$H_2C:CCl_2$
$3\,\nu_1$	154	155
$2\,\nu_1 + \nu_2$	229	224
$3\,\nu_2$	253	243
$2\,\nu_1 + \nu_4$	42	47
$2\,\nu_1 + \nu_5$	80	76
$2\,\nu_1 + \nu_7$	47	48
$\nu_1 + \nu_2 + \nu_{13}$	146	137
$2\,\nu_1 + \nu_{10}$	48	46
$2\,\nu_1$	39	43
$\nu_1 + \nu_2$	131	121
$\nu_2 + \nu_4 + \nu_5$	54	46
$\nu_1 + 2\,\nu_{12}$	29	27
$\nu_1 + \nu_4$	1	1
$\nu_1 + \nu_5$	18	18

2. The band shapes in the gas phase spectrum of a slightly asymmetrical molecule agree closely with those of a corresponding symmetrical molecule (in itself being an asymmetric top). Symmetry species of and selection rules for combination bands may be calculated as if the molecular symmetry were higher than it actually is. – The 2-chloroacrylonitrile molecule has been treated here as belonging to the C_{2v} symmetry group. LK [2] have also mentioned this point.

3. The assignment of the combination bands of one member of a homologous series of compounds (not including atoms from the first row of the periodic table) must fit through the whole series. – This condition has only been applied indirectly by using it to check the assignment of 1,1-dichloroethylene connected to the 2-chloroacrylonitrile spectrum by principle 1.

4. The relative band intensities in the gas and liquid phase are of equal order of magnitude. Notable exceptions to this rule are known among fundamen-

---

[7] D. Papoušek, Coll. Czech. Chem. Commun. **29**, 2277 [1964].

[8] F. Winther, unpublished results.

Table 3. Comparison of anharmonicity constants from different levels. $x_{2.5}$, $x_{2.14}$, $x_{4.13}$, $x_{5.12}$, $x_{5.13}$, $x_{5.14}$, $x_{7.14}$, and $x_{11.13}$ were also calculated from ternary combination bands.

x_{ij} cm^{-1}	From $\nu_i + \nu_j$	x_{ij}	From level	x_{ij}	From level	x_{ij}	From level	x_{ij}	From level
$x_{1.1}$	-18 ± 2	-21 ± 3	1.1.10	-21 ± 2	1.1.7	-21 ± 1	1.1.4	-26 ± 1	1.1.1
$x_{1.2}$	-65 ± 1	-55 ± 2	1.1.2						
$x_{1.5}$	-9.5 ± 0.5	-12 ± 2	1.1.5						
$x_{1.6}$	-1.9 ± 1	-2 ± 2	1.2.6	-3.0 ± 1	1.4.6				
$x_{1.11}$	2 ± 2	-4 ± 2	1.1.11						
$x_{1.14}$	-3 ± 3	0.0 ± 1	1.13.14	-0.7 ± 0.5	1.14.14	-1 ± 2	1.12.14		
$x_{2.2}$	-41 ± 2	-34 ± 1	2.2.2						
$x_{2.4}$	-6.5 ± 1	-5 ± 3	2.4.10	-5.8 ± 1	2.4.6	-5 ± 2	2.2.4		
$x_{2.6}$	-3.7 ± 0.5	-6 ± 2	2.6.7						
$x_{2.7}$	-3 ± 1	-4 ± 2	1.2.7	-4 ± 2	2.4.7				
$x_{2.13}$	-9 ± 3	-5 ± 2	1.2.13						
$x_{4.4}$	-5.5 ± 0.3	-5.0 ± 0.5	4.4.4	-4.8 ± 0.5	4.4.4.4				
$x_{4.12}$	-1 ± 3	-4.7 ± 0.5	4.12.12						
$x_{5.6}$	0 ± 2	-2 ± 2	1.5.6						
$x_{7.7}$	0 ± 2	-4 ± 2	1.7.7						
$x_{12.12}$	1.5 ± 0.3	0 ± 2	2.12.12	-1.2 ± 1	1.12.12				

tals, e. g. $\nu_a(CH_2)$ in methylene and vinylidene chloride, so that it should not be applied uncritically.

5. The vapour-liquid shift of a band is generally small ($\approx 0.5\%$) and positive. – Exceptions such as ν_{11} of 2-chloroacrylonitrile having a 5% negative frequency shift may be found, however. For statistical reasons such exceptions become infrequent in combination bands of higher order.

6. In special cases, the half widths of bands in the spectrum of the liquid may provide additional evidence for some assignment. – Examples of general character are ν_{12} and $2\nu_{12}$ [H_2C:CCl(CN) numbering] [9]. Similarly, bands of the $2\nu_{13}$ series show unusually large half widths of 27 cm^{-1} ($2\nu_{13}$), 23.5 cm^{-1} ($\nu_4 + 2\nu_{13}$), and 23 cm^{-1} ($\nu_1 + 2\nu_{13}$).

7. The frequency combination of lowest possible order fullfilling all criteria was accepted as correct assignment. To this purpose all binary and ternary combinations were calculated and compared with the measured bands. Where a Fermi resonance between a fundamental and some combination frequency was known or suspected, ternary and quaternary bands were also calculated using the resonance partner as a pseudo-fundamental.

Table 4. Anharmonicity constants

	x_{ij} cm^{-1}	i						
		1	2	3	4	5	6	7
j	1	-21 ± 2	-60 ± 5	-2.4 ± 1	0.0 ± 0.3	-11 ± 2	-2.0 ± 1	-1.6 ± 1.5
	2		-36 ± 3	-2.5 ± 0.5	-6.0 ± 1	-5 ± 2	-4 ± 2	-3.0 ± 1
	3				-5 ± 2	-2.1 ± 0.5		
	4				-5.2 ± 0.3	R	-3.7 ± 0.5	-2.8 ± 0.3
	5						-1 ± 2	-1.0 ± 1
	6						-2.9 ± 1	-2.0 ± 1
	7							-2 ± 2
	8							
	9							
	10							
	11							
	12							
	13							
	14							
	15							

* Corrected for Fermi resonance. R: Could not be determined because of vibrational resonance.

---

[9] D. B. Cunliffe-Jones, Spectrochim. Acta **21**, 245 [1965].

The principles given above, especially $x_g \approx x_l$ are suited for programming thus making a computer assignment of the very high number of combination bands of larger polyatomic molecules feasible. Work in this direction is in progress.

Discussion

The reasons for the assignments of Table 1 have been stated, but a few interesting points deserve a more detailed comment. First, some disagreements between this work and that of LK[2] should be discussed. The assignment of the 1420 cm^{-1} band to $\nu_7+\nu_9$ is considered improbable, because the symmetry species of $\nu_7+\nu_9$ in the C_{2v} approximation is B_1. This should give a rather weak resonance with ν_5 and a band in the gas phase of pure A type with a strong Q branch. Two other reasons have already been mentioned: The analogy with $H_2C{:}CCl_2$ and the large halfwidth of the band in the liquid.

The other combination bands of ν_{13} listed on p. 1507 were easily identified with the exception of $\nu_{12}+\nu_{13}$, which is heavily overlapped by ν_4. $\nu_4+2\nu_{13}$ is seen clearly in the Raman spectrum of LK, but it is not given in their frequency list, where also $\nu_1+2\nu_{13}$, $\nu_{13}+\nu_{14}$, and $\nu_{13}+\nu_{15}$ were left unassigned. The straightforward assignment of so many combination frequencies gives additional evidence of the correct identification of ν_{13}.

LK assumed bands at 609 and 342 cm^{-1} to be due to impurities. No indication of this could be obtained, and both absorptions are readily explained as difference bands. The combination $\nu_8+\nu_{12}$ (A_2) was assigned by LK to a band at 1579 cm^{-1} (here: 1578.4 ± 0.5 cm^{-1}), but this is probably ν(C:C) of an impurity. A few other frequencies of Table 1 may also be spurious. On the other hand, the spectrum of the liquid should be complete between approximately 8000 and 400 cm^{-1} in the sense that no further absorptions may be detected.

The absorbance of a band in the liquid phase is just a rough indication of its intensity because of differing band shapes and band widths. To improve the intensity data of Table 1, the halfwidths ($\Delta\nu_{1/2}$) of the fundamentals and some of the stronger combination bands were measured and listed in Table 1. It is seen that $\Delta\nu_{1/2}$ of the fundamentals are generally smaller than $\Delta\nu_{1/2}$ of the combination bands and that only combinations of ν_{12} and ν_{13} have $\Delta\nu_{1/2} > 16$ cm^{-1}.

$\nu_8+\nu_{11}$ was not observed in the infrared liquid phase spectrum because of its weakness and serious overlapping from $\nu_{14}+\nu_{15}$ and ν_7, but it was found in a Raman spectrum, obtained through the courtesy of Coderg, Paris. Incidentally, this spectrum confirms the one of LK apart from a few additional very weak bands, which have not been listed in Table 1.

Numerous secondary Q branches in the gas phase could be assigned to hot bands of the type $\nu_i+\nu_j-\nu_j$. The identification was mainly based

of 2-chloroacrylonitrile.

i							
8	9	10	11	12	13	14	15
0.0 ± 0.3	2.5 ± 1	− 1.8 ± 0.5	1 ± 1	− 7.6 ± 0.5	− 3.0 ± 1	− 0.5 ± 0.5	
− 1.0 ± 1		− 2.4 ± 0.3		− 5.5 ± 0.3	− 8 ± 2	− 1.5 ± 1	− 1.0 ± 1
− 0.9 ± 0.3		− 2.8 ± 0.3	− 2.4 ± 0.5		− 2.2 ± 0.5	− 1.8 ± 0.3	− 1.9 ± 0.3
− 1.5 ± 1	0.7 ± 1	− 3.7 ± 0.5	− 1 ± 3	− 4.7 ± 1	− 4 ± 3	− 1.0 ± 0.3	− 1.5 ± 0.5
	− 3 ± 3	− 1.6 ± 0.5		− 2 ± 2	− 8 ± 2	− 2 ± 2	
− 2 ± 3		− 3.0 ± 1	− 0.7 ± 1		− 2.5 ± 0.5		
− 0.6 ± 0.3		− 1.8 ± 0.5				− 1.6 ± 1	
− 0.8 ± 0.3	− 1 ± 2	− 1.9 ± 0.5	0.0 ± 0.3			− 0.2 ± 0.5	
	− 0.1 ± 0.5		− 3.3 ± 0.5*			1.3 ± 0.5	
			0 ± 2				
					− 3 ± 2		
				1.5 ± 0.3	− 1 ± 3	1.1 ± 0.5	0.2 ± 0.5
					R	− 0.8 ± 0.5	− 0.9 ± 0.3
						− 1.1 ± 0.3	− 0.9 ± 0.3
							− 0.3 ± 0.5

upon the difference $[\nu_i+\nu_j]-[\nu_i+\nu_j-\nu_j]$, which must be ν_j within the accuracy of measurement. The intensity of $\nu_i+\nu_j-\nu_j$ should be proportional to $\exp\{-\nu_j\}$ at constant temperature, but this relation is not quite reliable, probably because of vibrational resonance between $\nu_i+\nu_j-\nu_j$ and ν_i. These bands often have a frequency difference close to zero. However, an upper limit of $\approx 1200\ \mathrm{cm}^{-1}$ for ν_j may be adopted for all types of difference bands at 45 °C.

Table 1 lists only hot bands whose upper level has been identified, but a less certain possibility of determining unobserved $\nu_i+\nu_j$ levels (or higher combinations) is from two pairs of bands with identical frequency difference:

$$[\nu_i+\nu_j-\nu_j]-\nu_i=[\nu_i+\nu_j-\nu_i]-\nu_j\quad(=2x_{ij}).$$

Even more uncertain, but eventually useful for approximate determination of harmonic frequencies, is the assumption that all bands within $\approx 10\ \mathrm{cm}^{-1}$ of a fundamental ν_i are of the type $\nu_i+\nu_j-\nu_j$. From these levels x_{ij} with unknown j may be deduced. This approximation becomes worse, the more low frequent fundamentals a compound has, because bands of the type $\nu_i+\nu_j+\nu_k-(\nu_j+\nu_k)$ will also occur.

Anharmonicity Constants and Harmonic Frequencies

For the calculation of the 120 anharmonicity constants x_{ij} of 2-chloroacrylonitrile the following method was adopted: First the weighted mean of the gas and liquid anharmonicities of all observed binary combinations was determined. Where only one phase had been measured, the probable error was approximately doubled. The results were used to calculate further anharmonicity constants from the ternary combination bands. The x_{ij} values from these are less certain because also systematic errors of the fundamental frequencies are added in the calculation, but Table 3 shows that in most cases a satisfactory accordance is obtained between the constants determined from different levels.

Some systematic errors due to vibrational resonances may remain for constants involving the fundamentals ν_2, ν_5, or ν_8. Generally however, a resonance will be repeated for levels of the form $\nu_k+\Sigma\nu_i$ $(k=2,\ 5,\ \text{or}\ 8)$. This means that approximately equal resonance shifts of ν_k and $\nu_k+\Sigma\nu_i$ are compensating each other, so that the directly calculated anharmonicity of a $\nu_k+\Sigma\nu_i$ level will be almost correct in spite of the perturbation of the individual levels. This consideration is of course not valid for complex resonances such as

$$\nu_2\rightarrow\nu_4+2\nu_{13}\rightarrow\nu_4+\nu_5\,.$$

A total of 81 anharmonicity constants have been summarized in Table 4. The missing anharmonicity constants were obtained as averages of the known x_{ij} values within three groups of constants: 1. Those of the $a'\otimes a'$ combinations, excluding $x_{1.1}$, $x_{1.2}$, and $x_{2.2}$. 2. Those of the $a'\otimes a''$ and 3. those of the $a''\otimes a''$ combinations. Averages of -2.0_9, -2.6_0, and $-0.2_4\ \mathrm{cm}^{-1}$ were found and substituted for unknown anharmonicity constants within the respective groups. The harmonic frequencies given in Table 5 were now calculated from the expression

$$\omega_i=\nu_i-2x_{ii}-\sum_{j\neq i}x_{ij}\,.$$

It is rather difficult to estimate the accuracy of the harmonic frequencies, particularly because of the uncertainty involved through the unknown anharmonicity constants. The frequencies may roughly be divided into three groups of decreasing reliability:

1. ω_1, ω_2, ω_4, ω_{14}.
2. ω_3, ω_6, ω_8, ω_{13}.
3. ω_5, ω_7, ω_9, ω_{10}, ω_{11}, ω_{12}, ω_{15}.

The best frequencies are probably accurate to about $\pm 5\ \mathrm{cm}^{-1}$.

Table 5. Approximate harmonic frequencies (gas phase) for 2-chloroacrylonitrile.

ω_i	cm^{-1}
1	3222
2	3171 *
3	2263
4	1638
5	1399 *
6	1193
7	909
8	678†
9	527
10	377
11	189
12	930
13	725
14	569
15	283

* ω_2 should be corrected by 0 to $-10\ \mathrm{cm}^{-1}$ and ω_5 by $+10$ to $+25\ \mathrm{cm}^{-1}$ because of vibrational resonance.

† Corrected for Fermi resonance.

Acknowledgements

The Chemische Fabrik Münzing & Co. is thanked for a sample of 2-chloroacrylonitrile and the Deutsche Forschungsgemeinschaft for generous financial support.