Microwave Spectrum of Chloroacetylene in Ground and Excited Vibrational States

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The microwave spectrum of chloroacetylene in the ground and excited states has been investigated in the frequency range 15 to 306 GHz. Ground state rotational and nuclear quadrupole coupling constants for twelve isotopic species of chloroacetylene and accurate distortion constants were determined for two of these. The data allowed the r_s-structure of chloroacetylene to be reconsidered and the internal consistency of this method of structure determination to be checked. Rotational spectra in five vibrationally excited states, with energy up to 700 cm^{-1} were observed for four different isotopic species and spectroscopic constants for these states were derived.

Introduction

Linear molecules have been, because of their relative simplicity, the subject of many detailed theoretical and experimental studies over many years. Most of this work has concentrated on the relatively frequently occurring linear triatomic molecules. Relatively few linear molecules containing four atoms exist and acetylene and its halogenated compounds form the major part of this small group. The detailed analysis of the infrared and microwave spectra of the linear molecule HCNO (e.g. [1, 2]) which exhibits non-linear characteristics in excited vibrational states, has been carried out over a number of years. With this example of a linear molecule behaving in an anomalous fashion it is obviously desirable to obtain data on "well-behaved" linear molecules for comparison. The results of a study of the microwave spectrum of bromacetylene have already been reported [3] and more detailed work on fluoracetylene will be presented shortly [4]. The present paper is concerned with the results obtained for chloracetylene [3b].

Although two reports of measurements of the ground state microwave spectrum of chloroacetylene have been made [5, 6] no distortion constants or excited vibrational state constants have been given. The r_s-structure of chloroacetylene was calculated [6] on the basis of the rotational constants of two ^{13}C-species, determined by the measurement of a single hyperfine component of each species. As was the case with bromoacetylene [3] it was possible to determine rotation constants for twelve isotopically different species of chloroacetylene. This data set allows the interatomic distances to be determined several times independently. Spectra in five vibrationally excited states up to 750 cm^{-1} were measured for four isotopic species of chloroacetylene.

Experimental

The sample of chloroacetylene was prepared by a standard method [7] and purified by fractional distillation. A deuterated sample was produced by direct exchange with slightly alkaline D_2O.

Spectra up to a frequency of 35 GHz were measured on a conventional, 100 kHz modulated Stark spectrometer, using free-run klystrons and oscilloscope display. Most measurements were made at $-78\,°C$, but spectra of the excited states near 700 cm^{-1} were observed at room temperature. Measurements up to 306 GHz were carried out by harmonic generation of a fundamental frequency provided by OKI 30V11 and 35V11 klystrons, using Gordy type [8] run-in generators and detectors.

Absorption lines were observed using either video or source modulation at a frequency of 5 kHz. The cell used was a metre long section of WR(19) (4.79×2.397 mm) waveguide, which could be cooled to $-78\,°C$.

Results

a) Ground State and Molecular Structure

Measurements of ground state transitions $J \rightarrow (J+1)$ were made of the ^{12}C isotopic species

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with ^{35}Cl and ^{37}Cl with J values up to 26 and 23 respectively. The hyperfine splitting produced by the chlorine quadrupole nucleus decreased with increasing J so that for transitions with $J \geqq 8$ only a single line was observed. The frequencies measured are shown in Table A1 of the appendix, and these were adequately fit by the usual expression for a semi-rigid linear molecule (i.e. constants B_0 and D determined). Two hyperfine components of the $J = 2 \rightarrow 3$ rotation transition were measured for the eight possible ^{13}C-species of H and D chloroacetylene. The frequencies obtained are shown in Table A2. The constants determined for twelve isotopic species of chloroacetylene are shown in Table 1, where some constants from the earlier work [5] are included for completion.

Table A1. Ground state.

$J \rightarrow (J+1)$	$HCC^{35}Cl$	$HCC^{37}Cl$
$4 \rightarrow 5$	56 841.85 56 840.47	
$7 \rightarrow 8$	90 944.76 90 944.03	89 154.90
$8 \rightarrow 9$	102 311.78	100 298.46
$9 \rightarrow 10$	113 678.73	—
$10 \rightarrow 11$	125 045.27	122 584.73
$11 \rightarrow 12$	136 411.48	133 727.33
$14 \rightarrow 15$	170 507.66	167 152.63
$15 \rightarrow 16$	—	178 293.34
$17 \rightarrow 18$	204 599.33	200 573.66
$20 \rightarrow 21$	238 685.83	233 989.35
$23 \rightarrow 24$	272 765.40	267 399.25
$26 \rightarrow 27$	306 838.24	—

Table A2. ^{13}C-Species.

Species	$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$	$3/2 \rightarrow 5/2$ $1/2 \rightarrow 3/2$	Centre
$H-{}^{12}C\equiv{}^{13}C-{}^{35}Cl$	33 934.03 [a]	33 929.11	33 933.08
$H-{}^{13}C\equiv{}^{12}C-{}^{35}Cl$	32 819.27 [b]	32 814.35	32 818.33
$H-{}^{12}C\equiv{}^{13}C-{}^{37}Cl$	33 253.96	33 250.10	33 253.22
$H-{}^{13}C\equiv{}^{12}C-{}^{37}Cl$	32 157.03	32 153.15	32 156.28
$D-{}^{12}C\equiv{}^{13}C-{}^{35}Cl$	30 999.04	30 994.12	30 998.10
$D-{}^{13}C\equiv{}^{12}C-{}^{35}Cl$	30 100.57	30 095.62	30 099.62
$D-{}^{12}C\equiv{}^{13}C-{}^{37}Cl$	30 374.45	30 370.65	30 373.71
$D-{}^{13}C\equiv{}^{12}C-{}^{37}Cl$	29 489.02	29 485.16	29 488.28

Previously measured Ref. [6].
[a] = 33 934.10, [b] = 32 819.35.

In order to determine the r_s-structure [9] of chloroacetylene a minimum of four moments of inertia are required. This minimum requirement has already been reached [6], but with the present data it is possible to calculate four independent C≡C bond lengths and two independent C—H and C—Cl bond lengths, so that one can check the internal consistency of this procedure. The results of such a calculation are shown in Table 2, from which the following average values of the bond lengths are given; H—C = 1.0550 Å, C≡C = 1.2033 Å and C—Cl = 1.6368 Å. The internal consistency is better than 0.0005 Å with respect to these average values, which are probably close to the equilibrium values.

Table 1. Rotation constants and moments of Inertia.

	B_0 (MHz)	I_0 [b]	eqQ (MHz)
$H-{}^{12}C\equiv{}^{12}C-{}^{35}Cl$	5684.216 (5)	88.9086	79.67 [a]
$H-{}^{12}C\equiv{}^{12}C-{}^{37}Cl$	5572.355 (5)	90.6934	62.75 [a]
$H-{}^{12}C\equiv{}^{13}C-{}^{35}Cl$	5655.54 (3)	89.3594	79.4 (5)
$H-{}^{13}C\equiv{}^{12}C-{}^{35}Cl$	5469.75 (3)	92.3947	79.5 (5)
$H-{}^{12}C\equiv{}^{13}C-{}^{37}Cl$	5542.23 (3)	91.1864	62.3 (5)
$H-{}^{13}C\equiv{}^{12}C-{}^{37}Cl$	5359.40 (3)	94.2971	62.6 (5)
$D-{}^{12}C\equiv{}^{12}C-{}^{35}Cl$	5187.01 [a]	97.4311	79.66 [a]
$D-{}^{12}C\equiv{}^{12}C-{}^{37}Cl$	5084.24 [a]	99.4005	63.12 [a]
$D-{}^{12}C\equiv{}^{13}C-{}^{35}Cl$	5166.38 (3)	97.8201	79.5 (5)
$D-{}^{13}C\equiv{}^{12}C-{}^{37}Cl$	5016.63 (3)	100.7401	79.9 (5)
$D-{}^{12}C\equiv{}^{13}C-{}^{35}Cl$	5062.31 (3)	99.8311	62.0 (5)
$D-{}^{13}C\equiv{}^{12}C-{}^{37}Cl$	4914.74 (3)	102.8286	62.3 (5)

[a] from Ref. [5].
[b] conversion factor 5.05376×10^5 MHz a.m.u. Å^2.

Table 2. Interatomic Distances.

Parent species	C—Cl	C≡C	C—H
$H-{}^{12}C\equiv{}^{12}C-{}^{35}Cl$	1.6368	1.2036	1.0550
$H-{}^{12}C\equiv{}^{12}C-{}^{37}Cl$	1.6368	1.2038	1.0549
$D-{}^{12}C\equiv{}^{12}C-{}^{35}Cl$	1.6369	1.2032	1.0550
$D-{}^{12}C\equiv{}^{12}C-{}^{37}Cl$	1.6369	1.2028	1.0549

b) Excited-Vibration States

A linear molecule with four atoms has five fundamental vibrational modes, and since none of the vibrational states studied involved the modes ν_1 and ν_2 the state under consideration will be designated by only three quantum numbers (V_3, V_4, V_5). Rotational transitions for four isotopic forms of chloroacetylene were measured in states $(0, 0^0, 1^1)$, $(0, 1^1, 0^0)$, $(0, 0^0, 2^{0,2})$, and $(1, 0^0, 0^0)$ which from a conventional infrared study [10] have energies of 326 cm^{-1} (312 cm^{-1}); 604 cm^{-1} (472 cm^{-1}); 652 cm^{-1} (612 cm^{-1}) and 756 cm^{-1} (742 cm^{-1}) respectively. (Values in parenthesis refer to deuterated chloroacetylene).

Table A3. State (0, 0^0, 1^1).

	$HCC^{35}Cl$		$HCC^{37}Cl$		$DCC^{35}Cl$		$DCC^{37}Cl$	
$J = 1 \rightarrow 2$	ν (MHz)	q_{eff}	ν (MHz)	q_{eff}	ν (MHz)	q_{eff}	ν (MHz)	q_{eff}
$5/2 \rightarrow 7/2$	22817.50 22786.81	7.67	22367.33 22337.78	7.39				
$3/2 \rightarrow 5/2$	22797.52 22766.93	7.65	22351.38 22322.45	7.21				
$1/2 \rightarrow 3/2$	22822.93 22791.83	7.77	22371.66 22341.76	7.48				
$5/2 \rightarrow 5/2$	22807.68 22776.88	7.70	22358.92 22330.11	7.20				
$3/2 \rightarrow 3/2$	22704.70 22774.17	7.63	22357.21 22327.83	7.34				
$1/2 \rightarrow 1/2$	22832.71 22801.68	7.76	22378.54 22349.61	7.24				
$5/2 \rightarrow 3/2$ $3/2 \rightarrow 1/2$	22814.55 22783.93	7.66						
$J = 2 \rightarrow 3$								
$7/2 \rightarrow 9/2$ $1/2 \rightarrow 3/2$	34220.82 34175.01	7.64	33546.46 33502.44	7.34	31222.70 31182.93	6.63	30603.05 3064.73	6.39
$5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	34215.75 34170.07	7.61	33542.43 33498.52	7.32	31217.63 31177.89	6.62	30599.15 30560.75	6.40
$7/2 \rightarrow 7/2$	34206.12 34160.12	7.67	33534.92 33490.59	7.39	31207.84 31168.00	6.64	30591.42 30552.95	6.41
$5/2 \rightarrow 5/2$	34222.74 34177.05	7.61	33548.04 33405.06	7.33	31224.50 31184.90	6.60	30604.43 30566.32	6.35
$3/2 \rightarrow 3/2$	34230.50 34184.88	7.60	33554.20 33510.19	7.34	31232.34 31192.75	6.60	30610.65 30572.52	6.36
$J = 7 \rightarrow 8$	91247.6 91125.2	7.652	89333.0 89450.9	7.365				
$J = 8 \rightarrow 9$	102652.6 102515.0	7.642	100631.4 —					
$J = 10 \rightarrow 11$	125461.8 125293.7	7.642	122991.6 122829.8	7.357				
$J = 11 \rightarrow 12$	136865.9 136682.6	7.637						
$J = 14 \rightarrow 15$	171075.5 —							
$J = 17 \rightarrow 18$	— 205005.3							

State (0, 0^0, 1^1)

Each rotational transition within this state is split into a doublet by the well-known l-type doubling effect. For low-J transitions (i.e. $J < 7$) the spectrum is further complicated by each transition being split into quadrupole hyperfine components. The frequencies measured for transitions ranging in J from 1 to 17 are shown in Table A3, which were fit to the expression.

$$\nu = 2(B_V \pm q^0/2)(J+1) - 4D(J+1)[(J+1)^2 - l^2] .$$

The data available (Table A3) was sufficient to determine the three constants B_V, $q_5^{(0)}$ and D for $HCC^{35}Cl$ and $HCC^{37}Cl$, but for $DCC^{35}Cl$ and $DCC^{37}Cl$ where no high frequency measurements were made, the distortion constants determined for the normal hydrogen species were assumed (Table 3). The numbers in parenthesis in Table 3 indicate the estimated errors in units of the last digit. Measurements of transitions with J up to 18 were measured and it appears from the very small, but consistent decrease in $q_5^{(0)}$ with increasing J, that the contribution to the doublet splitting from P^4 terms in the

Table 3. Spectroscopic constants.

State (V_3, V_4, V_5)	eqQ (MHz)	B_v (MHz)	D_v (kHz)	α (MHz)	$q^{(0)}$ (MHz)	$q^{(0)}_{\text{calc}}$ (MHz)
$HCC^{35}Cl$						
$(0, 0^0, 0)$	−79.67 (8)	5684.214 (5)	1.39 (2)	—	—	—
$(0, 0^0, 1^1)$	−79.15 (8)	5699.328 (10)	1.41 (5)	−15.112	7.65 (2)	7.77
$(0, 0^0, 2^2)$	−78.9 (4)	5714.32 (3)	—	−15.05	—	—
$(0, 0^0, 2^0)$	−78.0 (4)	5711.94 (3)	—	−13.86	—	—
$(0. 1^1, 0^0)$	−79.15 (8)	5687.90 (2)	1.38 (8)	− 3.68	4.30 (5)	4.36
$(1, 0^0, 0^0)$	−79.5 (2)	5665.35 (2)	—	18.86	—	—
$HCC^{37}Cl$						
$(0, 0^0, 0^0)$	−62.75 (6)	5572.355 (5)	1.33 (2)	—	—	—
$(0, 0^0, 1^1)$	−62.50 (6)	5587.16 (2)	1.25 (10)	−14.84	7.3 (4)	7.46
$(0, 0^0, 2^2)$	−62.1 (3)	5601.87 (3)	—	−14.76	—	—
$(0, 0^0, 2^0)$	−61.5 (3)	5599.17 (3)	—	−13.40	—	—
$(0, 1^1, 0^0)$	−62.5 (5)	5575.92 (3)	—	− 3.57	4.12 (5)	4.19
$(1, 0^0, 0^0)$	−62.0 (3)	5554.39 (3)	—	17.96	—	—
$DCC^{35}Cl$						
$(0, 0^0, 0^0)$	−79.66 *	5187.01 *	—	—	—	—
$(0, 0^0, 1^1)$	−79.15 (8)	5200.13 (2)	—	−13.12	6.62 (2)	6.50
$(0, 0^0, 2^2)$	−76.3 (4)	5213.19 (3)	—	−13.09	—	—
$(0, 0^0, 2^0)$	−78.3 (4)	5211.59 (3)	—	−12.29	—	—
$(0, 1^1, 0^0)$	−79.1 (4)	5194.00 (2)	—	− 6.99	4.38 (5)	4.58
$(1, 0^0, 0^0)$	−79.9 (4)	5171.72 (3)	—	15.29	—	—
$DCC^{37}Cl$						
$(0, 0^0, 0^0)$	−63.12 *	5084.24 *	—	—	—	—
$(0, 0^0, 1^1)$	−62.25 (6)	5097.06 (2)	—	−12.82	6.38 (3)	6.25
$(0, 0^0, 2^2)$	−60.4 (3)	5109.84 (3)	—	−12.80	—	—
$(0, 0^0, 2^0)$	−61.7 (3)	5108.06 (3)	—	−11.91	—	—
$(0, 1^1, 0^0)$	−62.2 (5)	5091.03 (3)	—	− 6.79	4.25 (5)	4.40
$(1, 0^0, 0^0)$	−62.7 (3)	5069.32 (3)	—	14.92	—	—

* From Ref. [5].

Hamiltonian is probably just within the accuracy of measurement. Inspection of the data in Table A3, shows that a correction term $q_5^{(1)} \simeq 3 \times 10^{-5}$ MHz would account for the observed slight decrease. This value is quite reasonable since it is comparable with the value $q_5^{(1)} = 6.3 \times 10^{-5}$ MHz determined for HCCF [4].

As observed in HCCBr [3], one would also expect a variation in the l-type doublet splitting with hyperfine component to be present. This effect has been ascribed to the bending vibration motion producing an asymmetry in the electric field gradient at the nucleus [11] which produces an F-dependent contribution to the doublet separation, $\Delta\nu_{F_i \to F_j}$, such that:

$$\Delta\nu_{F_i \to F_j} = 2\,q^0\,(J+1) + \eta\,e\,q\,Q\,\{f((J+1), F_j) - f(J, F_i)\}\,.$$

where the asymmetry parameter η describes the deviation of the quadrupole tensor from cylindrical symmetry and $f(J, F)$ is the Casimir function [12]. Thus a plot of $\Delta\nu/2(J+1)$ against the difference in Casimir function for the levels involved should yield a straight line of slope $\eta eqQ/2(J+1)$ and intercept $q^{(0)}$. In chloracetylene the variation of the doublet separation with F is very much smaller than that in bromoacetylene, since eqQ is a factor of seven times smaller in the former than in the latter. This is consistent with the observations on ClCN [13] where also only a very small variation in doublet separation was observed. Indeed in the present study the variation is barely larger than the experimental uncertainty. However as may be seen from inspection of Table A3, for the $J = 2 \to 3$ transition, the transitions $F = 7/2 \to 7/2$, for which the difference in Casimir function has the largest negative value, invariably have the largest value of q_{eff}. For the $F = 3/2 \to 3/2$ transitions, where this difference is positive, the smallest values of q_{eff} were observed. [q_{eff} = doublet separation$/2(J+1)$]. The variation in doublet separation may be adequately explained by a value of $\eta = 0.010 \pm 0.003$, which is very

Table A4. State (0, 1^1, 0^0).

	$HCC^{35}Cl$		$HCC^{37}Cl$		$DCC^{35}Cl$		$DCC^{37}Cl$	
$J = 1 \to 2$	ν (MHz)	q_{eff}	ν (MHz)	q_{eff}	ν (MHz)	q_{eff}	ν (MHz)	q_{eff}
$5/2 \to 7/2$	22765.09 22747.57	4.36						
$3/2 \to 5/2$	22745.17 22727.93	4.31						
$1/2 \to 3/2$	22770.28 22752.39	4.47						
$5/2 \to 5/2$	22755.20 22735.94	4.32						
$3/2 \to 3/2$	22752.39 22734.93	4.37						
$1/2 \to 1/2$	22780.01 22762.81	4.30						
$J = 2 \to 3$								
$7/2 \to 9/2$ $1/2 \to 3/2$	34142.03 34116.44	4.27	33469.40 33444.67	4.12	31179.11 31152.85	4.38	30560.7 30534.98	4.28
$5/2 \to 7/2$ $3/2 \to 5/2$	34137.03 34111.44	4.27	33465.50 33440.78	4.12	31174.09 31147.85	4.37	30556.42 30531.09	4.22
$7/2 \to 7/2$	34127.27 —	—			31164.17 31138.58	4.27	30548.73 —	
$5/2 \to 5/2$	34143.97 34118.57	4.23			— 31154.81	—		
$3/2 \to 3/2$	— 34126.40	—			— 31162.72	—		
$J = 11 \to 12$	136551.0 136448.2	4.28						

Table 4. Results of Fermi resonance analysis.

	B_3^0 (MHz)	a^2	k_{355} (cm^{-1})
$HCC^{35}Cl$	5662.97	0.951	35.2
$HCC^{37}Cl$	5551.69	0.945	37.7
$DCC^{35}Cl$	5170.12	0.962	34.5
$DCC^{37}Cl$	5067.54	0.957	37.0

similar to $\eta = 0.0098 \pm 0.0002$ observed in bromoacetylene [3]. The values of $q_5^{(0)}$ shown in Table 3 are consistent with plots of the type discussed above and with the doublet separations observed in the mm-wave spectrum.

The *l*-type doubling constant $q_j^{(0)}$ is related [14] to the Coriolis coupling constants $\zeta_{ji}^{(x)}$ by;

$$q_j^{(0)} = 2\, B_e^2/\omega_j \{1 + 4 \sum_i (\zeta_{ji}^{(x)})^2\, \omega_j^2/(\omega_i^2 - \omega_j^2)\}$$

where ω_j if the frequency of the mode v_j. The values of $q_5^{(0)}$ calculated using the Coriolis constants of Venkateswarlu and Mathew [15] and the frequencies from the infrared spectrum [10] are shown in Table 3 as $q_{calc}^{(0)}$. As may be seen there is very good agreement (better than 2%) between the experimental and theoretical values for all four isotopic species. Although $q^{(0)}$ is not very strongly dependent on the Coriolis constants, this agreement seems to indicate that they are reasonably good.

State (0, 1^1, 0^0)

The rotational transitions belonging to this state were much less intense than those of the (0, 0^0, 1^1) state, and consequently the complete hyperfine pattern was not always observable (Table A4). Here again a very small variation in q_{eff} with hyperfine component was observed. However in this case the variation was comparable with the uncertainty of measurement and all that may be concluded is that η for v_4 is probably smaller than that for v_5, a conclusion which is in keeping with the calculated vibrational amplitudes for these two modes [10]. The values of $q_4^{(0)}$ given in Table 3 are an average of the observed q_{eff}. As in the case of the lower frequency bending mode the calculated $q_4^{(0)}$ agrees well with that observed, although $q_{calc}^{(0)}$ is consistently higher (from 2 to 5%) than the experimental values.

States $(1, 0^0, 0^0)$, $(0, 0^0, 2^0)$ and $(0, 0^0, 2^2)$

The rotational transitions measured for these states are shown in Tables A5, A6 and A7. The B_v rotational constants obtained for these states if they are simply treated as if they were unperturbed and using the ground state distortion constants are given in Table 3.

	ν_5	ν_4
$HCC^{81}Br$	2.308	3.111
$HCC^{79}Br$	2.299	3.038
$DCC^{81}Br$	2.316	
$DCC^{79}Br$	2.308	
$HCC^{35}Cl$	2.297	2.408
$HCC^{37}Cl$	2.297	2.390
$DCC^{35}Cl$	2.301	2.292
$DCC^{37}Cl$	2.310	2.321
HCCF	2.248	2.372
DCCF	2.232	2.325

Table 5. $q^0\,\omega/B_0{}^2$.

Table A5. State $(1, 0^0, 0^0)$

$J = 2 \to 3$	$HCC^{35}Cl$	$HCC^{37}Cl$	$DCC^{35}Cl$	$DCC^{37}Cl$
$7/2 \to 9/2$ $5/2 \to 7/2$	33992.94	33326.96	31031.15	30416.55
$3/2 \to 5/2$ $1/2 \to 3/2$	33987.95	33323.12	31026.19	30412.67
$7/2 \to 7/2$	33973.02			
$5/2 \to 5/2$	34002.16			

Table A6. State $(0, 0^0, 2^0)$

$7/2 \to 9/2$ $5/2 \to 7/2$	34272.45	33595.61	31270.33	30648.94
$3/2 \to 5/2$ $1/2 \to 3/2$	34267.64	33591.83	31265.48	30645.12
$7/2 \to 7/2$	34252.92			
$5/2 \to 5/2$	34281.60			

Table A7. State $(0, 0^0, 2^2)$

$7/2 \to 9/2$ $7/2 \to 7/2$	34291.38	33615.51	31284.51	30663.18
$5/2 \to 5/2$ $5/2 \to 5/2$	34271.66	33599.99	31265.44	30648.07
$3/2 \to 5/2$ $3/2 \to 3/2$	34285.90	33611.19	31279.09	30659.05
$1/2 \to 3/2$	34305.26	33626.63	31299.43	30674.68

The situation arising in the excited states of a linear molecule has been considered in detail by Winnewisser and Winnewisser [1]. In the second excited state of a degenerate bending mode, in the absence of any other effects the rotational transitions of the two substances with $|l| = 0$ and $|l| = 2$ would not be expected to be coincident, but to be observed at frequencies

$$v(l = 0) = 2(J+1)\,B_\mathrm{v} - 4(J+1)^2 D_\mathrm{v}\,,$$
$$v(l = 2) = 2(J+1)\,\{B_\mathrm{v} + 4\gamma_{ll} + 8\,D_\mathrm{v}\} - 4(J+1)^2 D_\mathrm{v}$$

where γ_{ll} is a rovibrational interaction constant. Thus the $|l| = 0$ and $|l| = 2$ rotational transitions have a frequency separation of $2(J+1)\,(4\gamma_{ll} + 8\,D_\mathrm{v})$. Under these circumstances we can describe the rotational spectrum of the state $(0, 0^0, 2^{0,2})$ in terms of a single rotational constant and a γ_{ll}-dependent splitting. If this is done in the present case, using the ground state distortion constants one arrives at the B constants given in Table 3 for the $(0, 0^0, 2^0)$ state and values of γ_{ll} of 0.593, 0.674, 0.400, and 0.445 MHz for $HCC^{35}Cl$, $HCC^{37}Cl$, $DCC^{35}Cl$ and $DCC^{37}Cl$ respectively. Whilst these constants fit the data available it does not seem likely that the observed separation between the $|l| = 0$ and $|l| = 2$ transitions is entirely due to this source. The γ_{ll} derived for the four isotopic species varies considerably and the effective α-constant calculated for this second excited state (that for $(0, 0^0, 2^0)$ state in Table 3) is unreasonably small compared to that of the first excited state. Additionally the values of γ_{ll} are a factor four or five times larger than those observed in fluoroacetylene [4].

There are two sources of perturbation which may be relevant to the present discussion, l-type resonance and Fermi-resonance. In the former interaction between states $(0, 0^0, 2^0)$ and $(0, 0^0, 2^2)$ occurs via off-diagonal matrix elements of the type

$$\langle V_\mathrm{t}, l_\mathrm{t}\,|H_2'|\,V_\mathrm{t}, l_\mathrm{t} \pm 2\rangle = \langle 2, 0\,|H_2'|\,2, 2\rangle$$

and the transitions identifiable with the $|l| = 0$ state and *one* of the $|l| = 2$ states are mutually perturbed, so that three transitions may be observed, two with $|l| = 2$ and one with $|l| = 0$. Such effects have been studied in HCNO [1] and HCCF [4] and have only marked influence at relatively high J. Since for the transitions under consideration $J = 2$ and no splitting of the $|l| = 2$ transitions was observed, effects arising from l-type resonance may be neglected.

Fermi Resonance

The effects of Fermi resonance are far more likely to be of importance. An interaction occurs between the states $(0, 0^0, 2^0)$ and $(1, 0^0, 0^0)$ via the cubic force constants, in this case k_{355}, producing off-diagonal matrix elements,

$$\langle V_t, l_t, V_t' | H_1' | V_t + 2, l_t, V_t' - 1 \rangle = \langle 0, 0, 1 | H_1' | 2, 0, 0 \rangle$$

where t and t' refer to v_5 and v_3 respectively in this case. Thus the effects of Fermi resonance would be to displace the transitions of the $(0, 0^0, 2^0)$ state relative to those of $(0, 0^0, 2^2)$ by an amount dependent on the magnitude of k_{355} and on the unperturbed energy separation, Δ, between $(0, 0^0, 2^0)$ and $(1, 0^0, 0^0)$. This energy separation, which may be approximately derived from the infrared data [10], is 104 cm^{-1} for the H-species and 118 cm^{-1} for the D-species. Since Δ is relatively large the effects of Fermi resonance would be expected to be small, but nevertheless the different values of Δ for the D- and H-species may well account for the observed differences in separation between the $|l| = 0$ and $|l| = 2$ transitions of the different isotopic species.

In order to be able to treat the Fermi resonance effect properly the contribution from the γ_{ll} constant to the separation between the $|l| = 0$ and $|l| = 2$ transitions should be first of all subtracted. In the present case we have no information over the magnitude of γ_{ll} from other sources, such as from states $(0, 0^0, 3^3)$, $(0, 0^0, 3^1)$, but if we consider this constant to be small we can derive an approximate value for k_{355}. This approximation is definitely not as justifiable as it was in the case of bromoacetylene [3] and the results of such an analysis will be correspondingly less reliable.

The treatment of the effects of Fermi resonance on the rotational spectrum of a linear molecule is to be found in many of the standard texts. Mixing of wavefunctions of the two interstates occurs, so that

$\psi_3' = a\,\psi_3^0 + b\,\psi_5^0$; etc. and $B_3' = a^2 B_3^0 + b^2 B_5^0$; etc. Since $a^2 + b^2 = 1$, $B_3' + B_5' = B_3^0 + B_5^0$,

where primed constants refer to perturbed states. Thus with knowledge of three of these B constants the fourth may be calculated. Under the present circumstances B_3', B_5' and B_5^0 were assumed to be experimentally determined constants (Table 3) of the states $(1, 0^0, 0^0)$, $(0, 0^0, 2^0)$ and $(0, 0^0, 2^2)$ respectively, and the unperturbed B_3^0 constant and the mixing coefficient a^2 may be calculated. Since

$$a^2 = 0.5 + (\Delta/2)\,\{\Delta^2 + 4\,|k_{355}/\sqrt{2}\,|^2\}^{-1/2}$$

where Δ is the unperturbed separation between the interacting states the cubic force constant may be calculated. The results obtained for the four isotopic species of chloroacetylene are shown in Table 4.

Discussion

As may be seen from the expression given earlier for the l-type doubling constant,

$$q_j^{(0)} = A\, B_e^2/\omega_j$$

where

$$A = 2\{1 + 4 \sum_i \zeta_{ji}^{(x)}\, \omega_j/(\omega_i^2 - \omega_j^2)\}\,.$$

The fact that for a linear triatomic molecules the factor A had a more or less constant value of 2.6 led to the approximate relationship $q = 2.6\, B^2/\omega$ being frequently quoted. In the case of the monohaloacetylenes a similar relationship holds, except that A now has a value of approximately 2.3. This is illustrated in Table 5 for both v_4 and v_5 modes of fluoro-, chloro- and bromoacetylene. The only values which deviate substantially from 2.3 are those for v_4 of bromoacetylene and this deviation is explainable [3] as being produced by an accidental resonance. The closeness of the values of A given in Table 5 indicates that the harmonic part of the potential function is similar in all three molecules.

Two ways of treating the frequency separation between the rotational transitions of the states $(0, 0^0, 2^0)$ and $(0, 0^0, 2^2)$ were given. It is probable that neither treatment is completely correct, but from qualitative arguments it appears that the Fermi resonance treatment is to be prefered. This is because the effective α-constant for the second excited state of v_5 in this case, that for the state $(0, 0^0, 2^2)$ in Table 3, is most similar to that of the first excited state of this mode. Also a fairly consistent set of values for k_{355} was produced for the four isotopic species (Table 4) by this method and moreover the average value of k_{355} of 36.1 cm^{-1} is very similar to the 44 cm^{-1} observed in bromoacetylene [3]. Thus we conclude that the actual value of γ_{ll} for chloroacetylene is probably quite small and that the main contribution to the separation between rotational transitions of the states $(0, 0^0, 2^0)$ and $(0, 0^0, 2^2)$ is produced by Fermi resonance.

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