MICROWAVE SPECTRUM OF TRICHLOROACETONITRILE

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Abstract

The microwave spectra of different isotopic species of trichloro-acetonitrile—$CCl_3{}^{35}CN$, $CCl_2{}^{35}Cl^{37}CN$, $CCl^{35}Cl_2{}^{37}CN$ and $CCl_3{}^{37}CN$—in the region 20,000–40,100 Mc./sec. have been studied both at room temperature and at low temperature. From the measurements of B_0 values of the symmetric tops, assuming the C–C and C–N bond distances, the other two parameters are determined. They are: C–Cl = 1·771 A, C–C–Cl = 108° 52′.

Introduction

The microwave spectrum of CCl_3CN was reported earlier by Zeil and Pfrommer[1] and by Baker, Jenkins, Kenny and Sugden[2]. Zeil and Pfrommer observed the transition J = 6→7 and 8→9 for the $CCl_3{}^{35}$ CN molecule and calculated the C–C bond distance by assuming the other three parameters. The accuracy of their measurement of the lines was reported to be $\pm$ 10 Mc./sec. Baker *et al.*, worked in the region 16,000—27,000 Mc./sec. and reported four lines corresponding to the transitions J = 4→5 to 7→8 of $CCl_3{}^{35}$ CN and also a few lines corresponding to the transition J = 6→7 of the slightly asymmetric top $CCl_2{}^{35}Cl^{37}CN$. The microwave spectra of heavy molecules like CCl_3CN which have low lying vibrational states[3] become complicated as the lines due to the rotational transitions in the excited states will appear with good intensity and also may overlap with the lines in the ground state. As the earlier workers did not consider the possibility of the presence of lines in the excited vibrational states, it appeared that a reinvestigation of the spectrum at room temperature as well as at lower temperature would be necessary to properly identify the lines in the ground state from those in the excited states. The spectrum of other symmetric top

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isotopic species—$CCl_3{}^{37}CN$ was not observed earlier. A determination of the B_0 value of this along with that of $CCl_3{}^{35}CN$ is expected to enable one to determine the molecular parameters more accurately than otherwise. Therefore, a reinvestigation of the microwave spectra of different isotopic species of CCl_3CN was undertaken and the results obtained are reported in this paper.

EXPERIMENTAL METHODS

The sample of CCl_3CN was prepared starting from trichloroacetic acid by the method described by Pierce.[3, 4] It was first distilled under low pressure from the mixture of trichloroamide and phosphorous pentoxide and later fractionally distilled. Before finally using it in the experiments, the sample was further purified by redistillation.

A 100 Kc. Stark Modulation Spectrograph,[5] with a $10\frac{1}{2}$ ft. brass X-band Stark Cell made in the manner described by McAfee, Hughes and Wilson,[6] was used to study the spectra of CCl_3CN. Line frequencies were measured using known appropriate spectral lines as secondary standards, details of measurements being the same as those given elsewhere.[7] The line width and shape were greatly improved by cooling the cell either with freezing mixture or with dry ice. This enables one to distinguish the rotational transitions of the ground state from those of the excited vibrational states.

EXPERIMENTAL RESULTS

The molecule CCl_3CN is a symmetric top having 12 fundamental modes of vibration. The fundamental ν_8 has the frequency 163 cm.$^{-1}$ [3] Therefore, even at room temperature enough molecules can be expected to be in the excited states. At room temperature the lines were quite broad and most
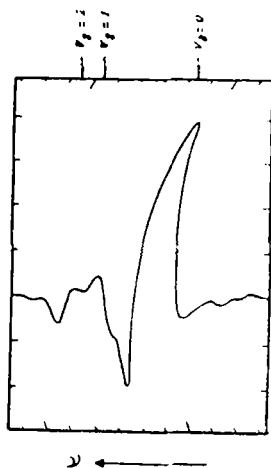

FIG. 1.

of them showed three components, the central one being the most intense. As the cell was cooled, the component on the lower frequency side of the central one became stronger and the one on the higher frequency side became quite weak, sometimes even unobservable. Hence, two of the three lines observed for each transition have been therefore, attributed to the molecules in the excited vibrational states $v_8 = 1$ and $v_8 = 2$. However, when only two components were observed the one on the low frequency side became more intense at low temperature and it was therefore taken as belonging to the molecule in the ground vibrational state while the other was taken as belonging to the molecule in the excited state $v_8 = 1$. The recording of the transition J $= 11 \rightarrow 12$ of $CCl_3{}^{35}CN$ showing the lines corresponding to $v_8 = 0$, $v_8 = 1$ and $v_8 = 2$ is shown in Fig. 1. The frequencies of the lines observed for the ground vibrational state are given in Table I while those for the excited states

TABLE I

Frequencies of the observed transitions in the ground state

Isotope	Transition	Frequency Mc./sec.
$CCl_3{}^{35}CN$	5→6	20,009·2
	6→7	23,343·7
	7→8	26,674·5
	8→9	30,009·2
	9→10	33,346·5
	10→11	36,681·9
	11→12	40,050·0*
$CCl_2{}^{35}Cl^{37}CN$	6→7	23,111·9
	7→8	26,394·8
	8→9	29,695·1
	9→10	32,999·9
	10→11	36,301·8
	11→12	39,600·0*
$CCl^{35}Cl_2{}^{37}CN$	7→8	26,115·9
	8→9	29,400·0*
	9→10	32,650·0*
	10→11	35,900·0*
	11→12	39,150·0*
$CCl_3{}^{37}CN$	7→8	25,818·5
	8→9	29,050·0*
	9→10	32,279·5
	10→11	35,499·4

* Frequencies measured with a cavity wavemeter (± 20 Mc./sec.).

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are given in Table II. The error involved in the measurements is probably around $\pm 1 \cdot 0$ Mc./sec.

TABLE II

Frequencies of the lines observed in the excited states

Isotope	Transition	in $v_8 = 1$ Mc./sec.	in $v_8 = 2$ Mc./sec.
$CCl_3{}^{35}CN$	5→6	20,017·1	20,028·9
	6→7	23,353·2	..
	7→8	26,691·9	26,705·4
	8→9	30,027·4	30,035·0
	9→10	33,363·7	..
	10→11	36,701·7	..
$CCl_2{}^{35}Cl^{37}CN$	6→7	23,127·3	••
	7→8	26,426·0	..
	10→11	36,335·2	..
$CCl^{35}Cl_2{}^{37}CN$ ..	7→8	26,142·3	..

Baker et al.,[2] reported lines at 22914, 22992, 23055 and 23138 Mc./sec. and an unresolved group between 23080 and 23120 Mc./sec. which they attributed to sets of different asymmetric top transitions of the molecule $CCl_2{}^{35}Cl^{37}CN$ for J = 6→7. The first four of these were not observed in the present experiments. An unresolved group between 23090 and 23135 Mc./sec. was observed, which is probably the same as the one between 23080 and 23120 Mc./sec. reported by Baker et al. This group appeared to have two broad envelopes, each of which probably have a number of unresolved lines. The maxima of these are at 23112 and 23127 Mc./sec. The first one became more intense than the second at low temperature. Similar results were obtained for other transitions of $CCl_2{}^{35}Cl^{37}CN$ and also of $CCl^{35}Cl_2{}^{37}CN$. The envelope having the maximum intensity at low temperature is taken as the one belonging to the molecule in the ground state while the other is taken as the one belonging to the excited state. The results obtained for these molecules are also included in Tables I and II.

The rotational constants B_0 for the molecules $CCl_3{}^{35}CN$ and $CCl_3{}^{37}CN$ have been obtained from the simple equation $\nu = 2\,B_0\,(J + 1)$ as the centrifugal stretching constants D_J and D_{JK} can be assumed to be zero since their effect on the spectra could not be observed for the lines measured. The B_0 values are given in Table III.

TABLE III

Rotational Constants and $I°_b$ Values

Isotope	B_0 (obs.) Mc./sec.	B_0 (cal.) Mc./sec.	$I°_b$ (obs.) amu A^2	$I°_b$ (cal.) amu A^2
$CCl_3{}^{35}CN$	$1,667\cdot3 \pm 0\cdot2$	$1,667\cdot6$	$303\cdot17$	$303\cdot11$
$CCl_3{}^{37}CN$	$1,613\cdot8 \pm 0\cdot2$	$1,614\cdot1$	$313\cdot22$	$313\cdot15$

MOLECULAR STRUCTURE

Zeil and Pfrommer,[1] assuming the three parameters C–Cl, C–N and angle C–C–Cl, gave the value of C–C as $1\cdot47$ A. Baker *et al.*,[2] with the B value of $CCl_3{}^{35}CN$, the computed values of A,B, C for the $CCl_2{}^{35}Cl^{32}$ and the assumed distance of C–N suggested the structure as C–N = ($1\cdot158$ A), C–C = $1\cdot46$ A, C–Cl = $1\cdot77$ A and angle Cl–C–Cl = $109°$ 56'. The structure had also been determined by thermodynamic[8] and electron diffraction[9] methods.

TABLE IV

Molecular Structure

	C–Cl (A)	C–C–Cl	C–C (A)	C–N (A)	Ref.
This study ..	$1\cdot771$	$108°\ 52'$	$(1\cdot46)$	$(1\cdot158)$	..
Zeil *et al.* ..	$(1\cdot767)$	$(110°\ 24')^*$	$1\cdot47$	$(1\cdot158)$	1
Baker *et al.* ..	$(1\cdot77)$	$109°\ 56'{}^*$	$1\cdot46$	$(1\cdot158)$	2
Janz *et al.* ..	$1\cdot761$	$112°$	$1\cdot48$	$(1\cdot158)$	8
Rao, C. N. R...	$1\cdot76_5$	$109°\ 30'$	$1\cdot46_5$	$1\cdot16_5$	9

* This angle refers to Cl–C–Cl.
The parameters given in brackets are the assumed values.

As only two B_0 values for the symmetric top species were measured and as the asymmetric top lines were not resolved, it was necessary to assume two parameters to determine the complete structure of this molecule. As the isotopic species studied involve only the substitution of chlorine isotopes, it was felt better to assume the bond distances of C–C and C–N to determine the other two—C–Cl and angle C–C–Cl. The C–N bond distance was taken to be $1\cdot158$ A, a value obtained in the case of similar molecules,[10, 11] as it is known to be considerably independent of the substitution at the C atom. The C–C distance is assumed to be $1\cdot46$ A as in CH_3CN. With these parameters, the other two were calculated and are given in Table IV along with those obtained by earlier workers. The B_0 values calculated for the symmetric tops $CCl_3{}^{35}CN$ and $CCl_3{}^{37}CN$ from these parameters are included in Table III.

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