

## The i.r. and Raman spectra of solid trichloroacetonitrile

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**Abstract**—The i.r. and Raman spectra of polycrystalline films of  $\text{CCl}_3\text{CN}$  have been recorded at liquid nitrogen temperature. Chlorine isotope splitting has been resolved for the  $\nu_2$  fundamental and crystal splittings have been observed for five of the fundamentals. A possible crystal structure is discussed. Raman wavenumbers and depolarization ratios are included for liquid  $\text{CCl}_3\text{CN}$ .

### INTRODUCTION

Infrared spectra of gaseous and liquid  $\text{CCl}_3\text{CN}$  and the Raman spectrum of the liquid have been published previously [1, 2]. In this older work the i.r. spectrum only extended to  $475\text{ cm}^{-1}$ . However, four of the eight fundamentals ( $\nu_4$ ,  $\nu_6$ ,  $\nu_7$  and  $\nu_8$ ) occur at lower wavenumbers. Three of these ( $\nu_4$ ,  $\nu_7$  and  $\nu_8$ ) were observed in the Raman spectrum by WAIT and JANZ [1]. These workers estimated  $\nu_6$  to be  $350\text{ cm}^{-1}$  from combination bands in the i.r., whereas EDGELE and ULTEE [2] assigned a very weak Raman line at  $388\text{ cm}^{-1}$  to  $\nu_6$ . Only qualitative depolarization measurements were made on the Raman lines and some of these were uncertain [1, 2].

Our main interest in  $\text{CCl}_3\text{CN}$  is in solid state i.r. and Raman spectra and gas phase i.r. spectra. No previous solid state spectra of  $\text{CCl}_3\text{CN}$  have been reported and the crystal structure is not known. Preliminary work on the gas phase i.r. spectrum indicated that few of the interesting features observed for  $\text{CF}_3\text{CN}$  [3, 4] were present in the spectrum of  $\text{CCl}_3\text{CN}$ .

We have recently studied the solid state vibrational spectra of  $\text{CCl}_3\text{H}$  [5] and  $\text{CCl}_3\text{F}$  [6, 7] and observed splittings of fundamentals, which were attributed to both crystal and chlorine isotope effects. Chloroform is known to have an orthorhombic crystal structure [8] and the reported vibrational spectra are consistent with this structure [5, 9, 10]. From i.r. and Raman spectra of solid  $\text{CF}_3\text{CN}$  [11], a possible crystal

structure was deduced from splittings of fundamentals. In this paper we extend previous work on analogous compounds to solid  $\text{CCl}_3\text{CN}$ . In addition, we report here extended i.r. measurements of liquid  $\text{CCl}_3\text{CN}$  and depolarization ratios for the Raman lines of the liquid.

### EXPERIMENTAL

Research grade  $\text{CCl}_3\text{CN}$  was obtained from The Aldrich Chemical Company. No impurities were detected in the spectra and apart from outgassing on a vacuum line, the material was used without further purification.

The infrared spectra were recorded on both Perkin-Elmer E14 single beam double-pass and Perkin-Elmer model 180 double beam grating spectrophotometers. The instruments were thoroughly flushed with dry nitrogen gas to remove atmospheric  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . The spectral slit width used varied from  $1.0$  to  $2.0\text{ cm}^{-1}$ . The instruments were calibrated with suitable standards [12] and the frequencies given in Table 1 are believed to be accurate to within  $\pm 1.0\text{ cm}^{-1}$ .

A conventional low temperature liquid nitrogen cell was used and the sampling method employed is similar to that described for  $\text{CF}_3\text{CN}$  [5]. Very careful annealing of the deposited films was necessary to obtain reproducible results. Spectra obtained from initial deposits usually showed less structure than they did after annealing.

The Raman spectra were recorded on a Cary 82 spectrophotometer at the University of Queensland. Spectra were excited by the  $5145\text{ \AA}$  line of a C.R.L. model 52 Argon ion laser. The cryostat used was an Oxford instruments, CF100 liquid transfer cryostat. Calibration was made using known wavelengths of argon ion emission lines from the laser [13].

Table 1. Raman and i.r. wavenumbers ( $\text{cm}^{-1}$ )<sup>a</sup> in the regions of the fundamentals of liquid and solid  $\text{CCl}_3\text{CN}$ 

Mode	Infrared		Raman		Assignments
	Liquid	Solid	Liquid <sup>b</sup>	Solid	
$\nu_1(A_1)$	2251 s	2251.5 s	2249.5 vs (0.10)	2249.5 vs	C≡N str.
	--	--	--	2222 vw	C≡ <sup>15</sup> N str.
	--	--	--	2198 vw	<sup>13</sup> C≡N str.
$\nu_2(A_1)$	1028 vs	1025.5 vs	1028.0 w (0.02)	1025.9 w	C-C str.
	--	1018.0 w	--	--	<sup>13</sup> C-C str.
	490 s	496.0 vs,b	487.8 vs (0.02)	487.5 s	C <sup>35</sup> Cl <sub>3</sub> CN str.
$\nu_3(A_1)$	--	--	484.8 vs (0.02)	484.5 m	C <sup>35</sup> Cl <sub>2</sub> <sup>37</sup> ClCN orientation splitting
	--	--	--	483.6 m	
	--	--	--	481.2 m	C <sup>35</sup> Cl <sup>37</sup> Cl <sub>2</sub> CN orientation splitting
	--	--	--	480.0 sh	
	--	--	--	478.0 w	C <sup>37</sup> Cl <sub>3</sub> CN str.
	--	--	--	--	--
$\nu_4(A_1)$	318 w	318.0 w	316.5 m (0.34)	318.9 m	CCl <sub>3</sub> def.
	--	--	--	792.6 m	CCl <sub>3</sub> str.
	--	--	--	789.4 s	site and unit cell splitting
$\nu_5(E)$	787 vs	791.7 vs	789.0 m (0.79)	786.9 s	
	--	784.6 w	--	785.4 m	
$\nu_6(E)$	334 wsh	360.0 vw	--	--	CCl <sub>3</sub> def.
$\nu_7(E)$	262 s	265.0 m	262.0 s (0.78)	263.6 w	CCl <sub>3</sub> rock
	--	--	--	181.6 w	C-C≡N def. site and
	--	--	--	173.9 m	
$\nu_8(E)$	156 s	--	160.5 s (0.80)	164.8 s	unit cell splitting
	--	--	--	156.0 s	

<sup>a</sup> v = very, s = strong, m = medium, w = weak, sh = shoulder, b = broad

<sup>b</sup> depolarization ratios are given in brackets

### RESULTS AND DISCUSSION

To indicate relative intensities of the bands, i.r. and Raman survey spectra of solid  $\text{CCl}_3\text{CN}$  are shown in Figs. 1 and 2. Figure 3 shows the far i.r. spectrum of liquid  $\text{CCl}_3\text{CN}$ . Some details of the i.r. and Raman spectra of fundamentals and other features are seen in Figs. 4, 5 and 6. Table 1 lists the observed wavenumbers, Raman depolarization ratios and assignments in the regions of the fundamentals and Table 2 gives the wave-numbers of overtone and combination bands.

Frequency shifts in passing from liquid to solid states are very small. However, five of the fundamentals and several combinations and overtones are observed to split into multiplets. In

addition to the chlorine isotope splitting discussed below, the  $a_1$  modes might be split by vibrational coupling if there are two or more molecules in the unit cell. The  $e$  modes on the other hand, might show both site and unit cell components.

#### Isotope splitting

The relative abundances and symmetries of the four chlorine isotopic  $\text{CCl}_3\text{CN}$  molecules are:  $\text{C}^{35}\text{Cl}_3\text{CN}$  42.8% ( $C_{3v}$ ),  $\text{C}^{35}\text{Cl}_2^{37}\text{ClCN}$  41.9% ( $C_s$ ),  $\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{CN}$  13.9% ( $C_s$ ) and  $\text{C}^{37}\text{Cl}_3\text{CN}$  1.5% ( $C_{3v}$ ). Chlorine isotope splitting is responsible for some of the observed fine structure associated with the  $\nu_3$  fundamental, the overtone  $2\nu_3$  and the combinations  $\nu_3 + \nu_4$  and  $\nu_3 + \nu_7$ .

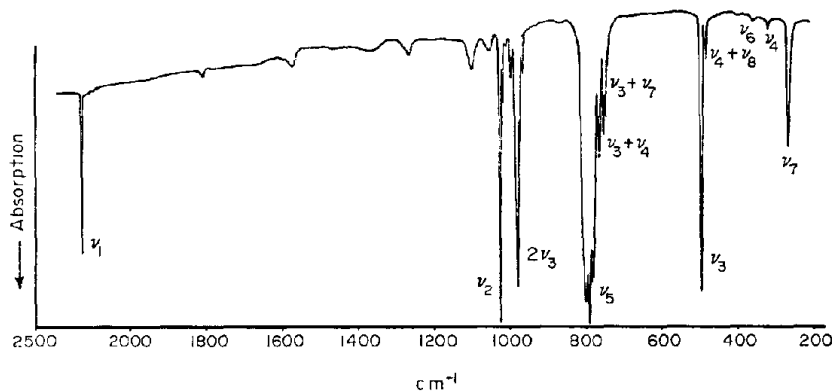


Fig. 1. An i.r. survey spectrum of solid  $\text{CCl}_3\text{CN}$  at 77 K. The spectral slit width was  $3 \text{ cm}^{-1}$ .

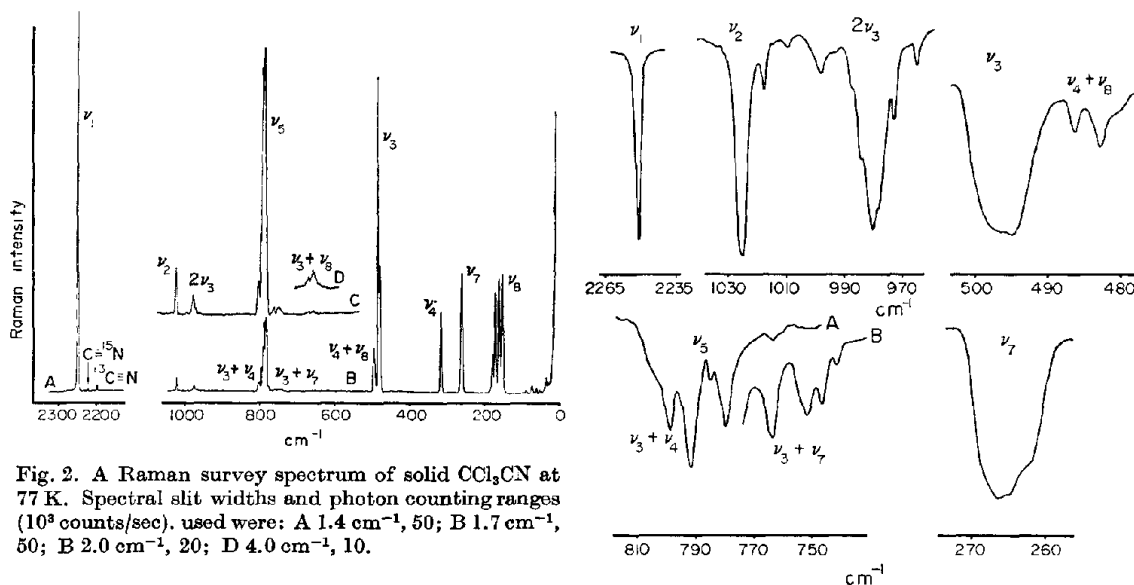


Fig. 2. A Raman survey spectrum of solid  $\text{CCl}_3\text{CN}$  at 77 K. Spectral slit widths and photon counting ranges ( $10^3$  counts/sec) used were: A  $1.4 \text{ cm}^{-1}$ , 50; B  $1.7 \text{ cm}^{-1}$ , 50; B  $2.0 \text{ cm}^{-1}$ , 20; D  $4.0 \text{ cm}^{-1}$ , 10.

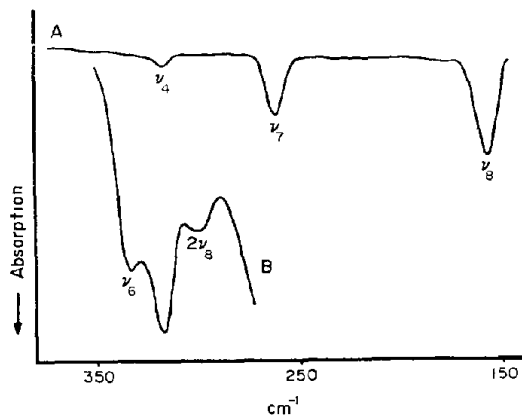


Fig. 3. The far i.r. spectrum of liquid  $\text{CCl}_3\text{CN}$  at  $35^\circ\text{C}$  in polyethylene cells. A  $0.1 \text{ mm}$  and A  $1.0 \text{ mm}$  path-length.

Fig. 4. Details of some i.r. bands of solid  $\text{CCl}_3\text{CN}$  at 77 K. Trace A was obtained from a very thin film, trace B from a thick film. A medium thick film was used for  $\nu_7$  and thin films for the other bands.

The magnitudes of the splittings due to chlorine isotopic molecules were predicted by means of a normal coordinate analysis. The Wilson FG matrix method [14] was used and an initial valence force field, including a few interaction constants, was obtained for  $\text{CCl}_3\text{CN}$  from reference [1]. The force field was refined using a computer program written by SCHACHTSCHNEIDER [15] and modified by BROOKS [16]. The following structural parameters were taken from the electron diffraction study of LIVINGSTON *et al.* (17):  $\text{C}-\text{N} = 1.165 \text{ \AA}$ ,

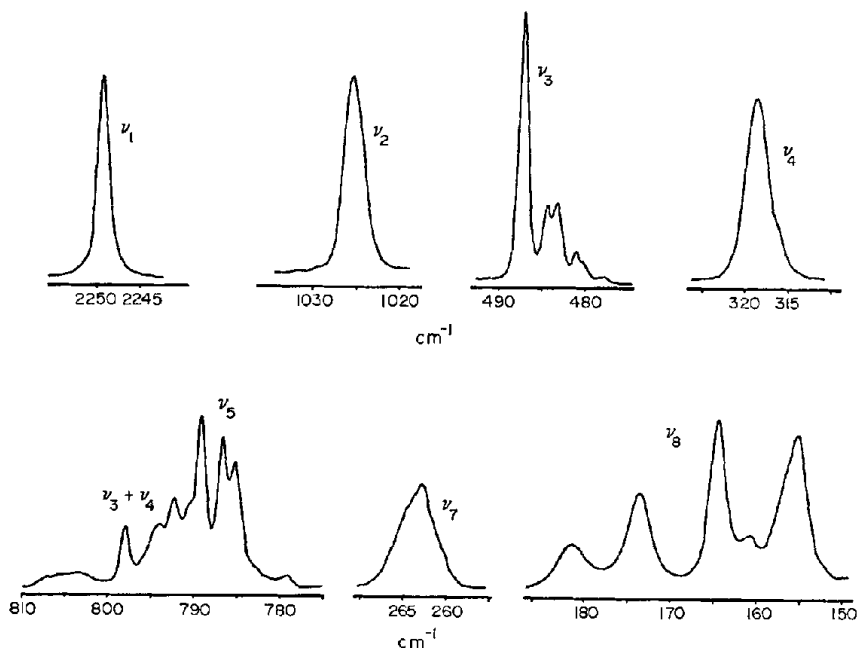


Fig. 5. Details of some Raman bands of solid  $\text{CCl}_3\text{CN}$  at 77 K. Spectral slit widths and photon counting ranges (counts/sec.) used were:  $\nu_1$   $0.6 \text{ cm}^{-1}$ , 5000;  $\nu_2$   $1.0 \text{ cm}^{-1}$ , 2000;  $\nu_3$   $0.5 \text{ cm}^{-1}$ , 5000;  $\nu_4$   $0.5 \text{ cm}^{-1}$ , 1000;  $\nu_5/\nu_3 + \nu_4$   $0.5 \text{ cm}^{-1}$ , 2000;  $\nu_7$   $0.5 \text{ cm}^{-1}$ , 1000 and  $\nu_8$   $0.4 \text{ cm}^{-1}$ , 500.

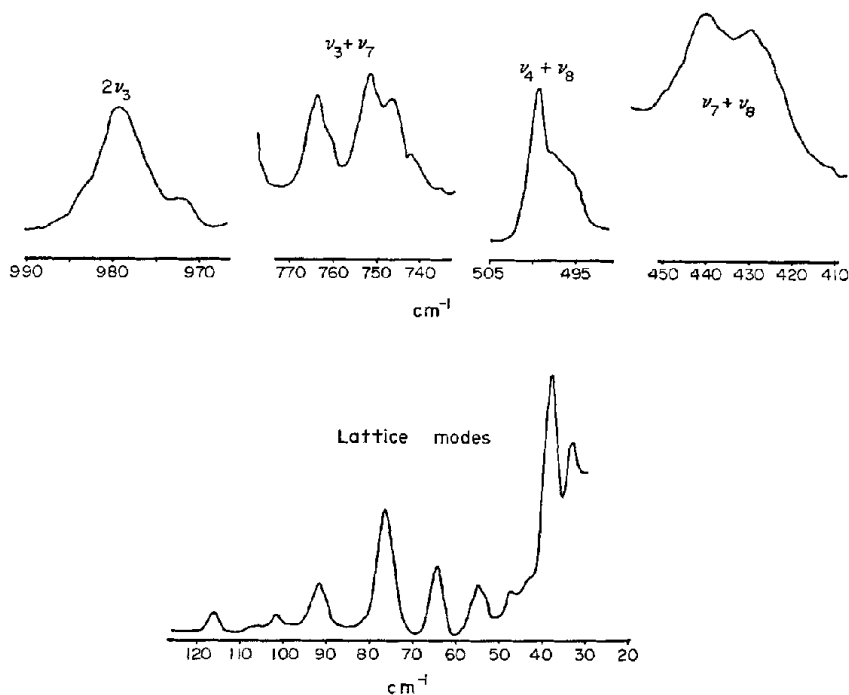


Fig. 6. Some overtone and combination bands and the lattice mode region of the Raman spectrum of solid  $\text{CCl}_3\text{CN}$  at 77 K. Spectral slit widths and photon counting ranges (counts/sec.) used were:  $2\nu_3$   $1.0 \text{ cm}^{-1}$ , 1000;  $\nu_3 + \nu_7$   $2.0 \text{ cm}^{-1}$ , 1500;  $\nu_4 + \nu_8$   $0.75 \text{ cm}^{-1}$ , 2000;  $\nu_7 + \nu_8$   $4.0 \text{ cm}^{-1}$ , 2000 and for the lattice mode region  $2.0 \text{ cm}^{-1}$ , 5000.

Table 2. Wavenumbers ( $\text{cm}^{-1}$ ) of some overtone and combination bands observed<sup>a</sup> in the Raman and i.r. spectra of solid  $\text{CCl}_3\text{CN}$ 

Raman	Infrared	Assignment
---	1805.0 vw	$\nu_2 + \nu_5$ (E)
---	1575.0 vw	$2\nu_5$ ( $A_1 + A_2 + E$ )
---	1265.0 vw	$\nu_3 + \nu_5$ (E)
---	1098.0 w	$\nu_4 + \nu_5$ (E)
---	1046.0 vw	$\nu_5 + \nu_7$ ( $A_1 + A_2 + E$ )
---	1009.5 vw	?
996.2 w,b	998.3 w	?
983.0 sh 979.3 s 972.7 w,b	~ 984.0 sh 980.5 vs 973.0 m	} $2\nu_3$ ( $A_1$ )
---	965.0 w	?
~ 805.0 w,b	~ 805.0 sh	?
798.2 m ~ 794.0 w 790.5 sh	798.7 s --- ---	} $\nu_3 + \nu_4$ ( $A_1$ )
779.5 vw	779.5 s	?
764.2 m ~ 762.0 sh 752.0 m 746.6 m 741.5 w 736.0 vw	764.0 m --- 751.8 m 746.4 m 741.3 w ---	} $\nu_3 + \nu_7$ (E)
672.0 vw 658.0 w	--- ---	} $\nu_3 + \nu_8$ (E)
499.7 s 497.0 sh --- ---	--- --- 486.3 w 482.7 m	} $\nu_4 + \nu_8$ (E)
440.5 vw 430.7 vw	--- ---	} $\nu_7 + \nu_8$ ( $A_1 + A_2 + E$ )
---	302.0 vw <sup>b</sup>	$2\nu_8$ ( $A_1 + A_2 + E$ )
161.2 sh	---	---

<sup>a</sup> For comparison of relative intensities within this table, the symbols: v = very, s = strong, m = medium and w = weak, are used. With the exception of  $2\nu_3$  these intensities are generally an order of magnitude weaker than those of Table 1.

<sup>b</sup> Observed in the spectrum of liquid  $\text{CCl}_3\text{CN}$ .

$\text{C}-\text{C} = 1.465 \text{ \AA}$ ,  $\text{C}-\text{Cl} = 1.765 \text{ \AA}$  and  $\text{CCl} = 109.5^\circ$ .

A reasonable fit was obtained between observed (liquid phase) wavenumbers and those calculated using an atomic weight of chlorine of 35.45. The same force constants were then used to calculate

the wavenumbers of the four chlorine isotopic molecules using atomic weights of 35.00 and 37.00. No splitting was predicted for  $\nu_1$  and  $\nu_2$  and the calculated separations between isotopic components of  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$ ,  $\nu_6$ ,  $\nu_7$  and  $\nu_8$  were 3.0, 1.5-1.9, 0.6, 0.6, 1.0-1.8 and  $0.6 \text{ cm}^{-1}$  respectively. From

these calculations it was expected that isotopic structure might be resolvable for  $\nu_3$ ,  $\nu_4$  and  $\nu_7$ . However it appears that isotopic splitting is only observed for  $\nu_3$ ,  $2\nu_3$  and some combinations involving this fundamental.

The relative abundances of  $^{12}\text{CCl}_3^{12}\text{CN}$ ,  $^{13}\text{CCl}_3^{12}\text{CN}$  and  $^{12}\text{CCl}_3^{13}\text{CN}$  are: 97.8%, 1.1% and 1.1% respectively. It is expected that  $\nu_2$  of  $\text{CCl}_3\text{CN}$  will be appreciably shifted in the molecules containing  $^{13}\text{C}$  and the intensity should be about 2% of the light molecule. The weak peak at  $1018\text{ cm}^{-1}$  in the i.r. spectrum, (Fig. 4), could be due to  $\nu_2$  of the two  $^{13}\text{C}$  isotopic molecules\*.

In the  $\text{C}\equiv\text{N}$  stretching region two isotopic satellites are possible due to  $\text{C}\equiv^{15}\text{N}$  and  $^{13}\text{C}\equiv\text{N}$ . The relative abundances are 0.4% and 1.1% and a diatomic molecule model, predicts shifts of 35 and  $50\text{ cm}^{-1}$  respectively. The two very weak Raman lines at  $2222$  and  $2198\text{ cm}^{-1}$ , (Fig. 2), are assigned to  $\nu_1$  of the two heavy isotopic molecules.

#### *A<sub>1</sub> fundamentals*

The  $\text{C}\equiv\text{N}$  and  $\text{C}-\text{C}$  stretching modes  $\nu_1$  and  $\nu_2$ , and the symmetric  $\text{CCl}_3$  deformation  $\nu_4$  all appear as single peaks in both i.r. and Raman spectra. A weak peak on the low wavenumber side of  $\nu_2$  in the i.r. spectrum, (see Fig. 4) is probably due to  $^{13}\text{C}$  isotopic molecules.

Both i.r. and Raman spectra of the symmetric  $\text{CCl}_3$  stretching mode  $\nu_3$  are complicated. The i.r. spectrum shows a strong broad peak centered at  $496\text{ cm}^{-1}$  with unresolved structure and a weak doublet on the low wavenumber side. A Raman band centered at  $487.5\text{ cm}^{-1}$  contains at least eight features, some of which are shoulders. This fundamental should have well resolved chlorine isotopic structure. In addition, absorption or scattering arising from the combination  $\nu_4 + \nu_8$  is expected from  $475$  to  $500\text{ cm}^{-1}$ . The resulting i.r. and Raman bands are difficult to identify. If the Raman scattering observed near  $495\text{ cm}^{-1}$  is attributed to components of  $\nu_4 + \nu_8$ , a pattern remains which can be recognized as a chlorine isotope quartet similar to that observed for  $\text{CCl}_3\text{F}$  [6] and  $\text{CCl}_3\text{H}$  [5]. However, in the present case, the peaks due to the  $\text{C}^{35}\text{Cl}_2^{37}\text{ClCN}$  and  $\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{CN}$  molecules are split into doublets, which can be explained as an orientational field effect as follows†. If the  $\text{CCl}_3\text{CN}$  molecules

occupy  $C_s$  sites in the crystal and the plane of symmetry contains one of the  $\text{C}-\text{Cl}$  bonds, then the orientations shown in Fig. 7 are possible.

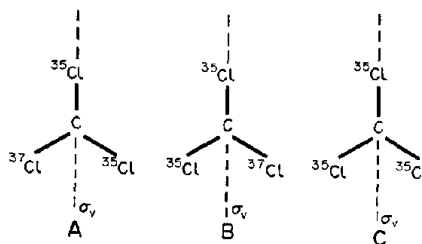


Fig. 7. Possible orientations of  $\text{C}^{35}\text{Cl}_2^{37}\text{ClCN}$  and  $\text{C}^{35}\text{Cl}_3\text{CN}$  molecules on  $C_s$  sites.

A mixed isotopic molecule such as  $\text{C}^{35}\text{Cl}_2^{37}\text{ClCN}$  can have two non-equivalent orientations *A* and *B* with respect to the site symmetry. This applies equally to  $\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{CN}$  but not to  $\text{C}^{35}\text{Cl}_3\text{CN}$  or  $\text{C}^{37}\text{Cl}_3\text{CN}$  which have a unique orientation *C*.

The broad band observed for  $\nu_3$  in the i.r. extends from  $490$  to above  $500\text{ cm}^{-1}$ . The band undoubtedly contains several components, but attempts to resolve these components were unsuccessful, even using spectral slit widths as small as  $0.5\text{ cm}^{-1}$ . This may be due to the difficulty in obtaining a properly annealed sample. This problem is difficult to avoid in the sampling method used to study i.r. spectra of thin films. The films are deposited from the gas phase onto a CsI window, which has poor heat conduction properties. Annealing is less of a problem in Raman studies, because the deposit is made directly onto a metal surface.

#### *E fundamentals*

Of the four degenerate vibrations of solid  $\text{CCl}_3\text{CN}$  only  $\nu_5$ ,  $\nu_7$  and  $\nu_8$  were observed in the Raman spectrum. The lowest frequency fundamental  $\nu_8$  was not observed in the i.r. spectrum of the solid, but a band was seen in the liquid phase spectrum at  $156\text{ cm}^{-1}$ , using a polyethylene cell.

The antisymmetric  $\text{CCl}_3$  stretching mode  $\nu_5$  shows considerable structure in both i.r. and Raman spectra. The region is complicated by two combinations  $\nu_3 + \nu_7$  and  $\nu_3 + \nu_4$ . Chlorine isotope structure is difficult to identify, but it might account for part of the structure of the Raman band. However, it is apparent that crystal splittings are present with possibly four Raman and three i.r. active components.

The  $\text{CCl}_3$  deformation  $\nu_6$  is assigned to a very weak peak at  $360\text{ cm}^{-1}$  in the i.r. spectrum of the solid, while a shoulder on the high wavenumber

\* The natural abundance of  $^{13}\text{CCl}_3^{13}\text{CN}$  is negligibly small (0.01%).

† We are grateful to a referee for suggesting this explanation of the observed splitting of two components of  $\nu_3$ .

side of  $\nu_4$  in the liquid phase spectrum, (see Fig. 3), may also be due to  $\nu_6$ . However, there is a difference of  $26\text{ cm}^{-1}$  between these liquid and solid phase absorptions, which seems to be unreasonably large. The location of  $\nu_6$  remains uncertain for the present.

The  $\text{CCl}_3$  rock  $\nu_7$  gives rise to a fairly broad band in the i.r. spectrum of solid  $\text{CCl}_3\text{CN}$ . The three shoulders seen in Fig. 4 for this band may well be due to unresolved chlorine isotope structure. The Raman band is also broad and asymmetric.

The C—CN deformation  $\nu_8$  gives rise to a Raman band very similar to that of  $\text{CF}_3\text{CN}$  [11]. Four widely separated components are found in the spectra of both molecules. There is an additional weak shoulder in the  $\text{CCl}_3\text{CN}$  case, but this could be a lattice mode. The observed splittings must be due to both site and correlation field components in the crystal.

#### External modes

In Fig. 6, nine clearly resolved peaks are seen in the Raman spectrum of solid  $\text{CCl}_3\text{CN}$  between  $30$  and  $120\text{ cm}^{-1}$ . The wavenumbers and relative intensities are:  $33.3\text{ m}$ ,  $38.2\text{ s}$ ,  $47.3\text{ w}$ ,  $55.0\text{ m}$ ,  $64.7\text{ m}$ ,  $76.7\text{ s}$ ,  $92.3\text{ m}$ ,  $102.2\text{ w}$  and  $117.3\text{ w}$ . Two weak shoulders are also evident at  $43.4$  and near  $108\text{ cm}^{-1}$ . The relative intensities of these lattice modes can be compared with the intensities of the internal modes in Fig. 2, where it is seen that the external vibrations are quite weak.

#### Overtones and combinations

A large number of weaker features in the i.r. and Raman spectra of solid  $\text{CCl}_3\text{CN}$  can be assigned to overtones and combinations. The overtone  $2\nu_3$  is very strong in the i.r. due to Fermi resonance with  $\nu_2$ . The fundamental  $\nu_2$  is weak in the Raman spectrum, so that  $2\nu_3$  is also weak in the Raman. Several combinations involving  $\nu_3$  are observed in both i.r. and Raman spectra. Of these,  $\nu_3 + \nu_4$ , and  $\nu_3 + \nu_7$  as well as  $2\nu_3$ , have fairly complex bands, part of which may be due to chlorine isotope structure. The combination  $\nu_3 + \nu_7$  consists of two groups of bands, the lower wavenumber groupings (see Figs. 4 and 6) have the intensities and separations expected for the four isotopic  $\text{CCl}_3\text{CN}$  molecules.

Three combinations involving  $\nu_8$  have been identified from the large separations between their components. For  $\nu_3 + \nu_8$  and  $\nu_7 + \nu_8$  two components are observed in each case with splittings of  $14$  and  $9.8\text{ cm}^{-1}$  respectively. The approximate wavenumbers expected for the com-

ponents of  $\nu_4 + \nu_8$  can be estimated from the Raman wavenumbers of the fundamentals to be  $500$ ,  $493$ ,  $484$  and  $475\text{ cm}^{-1}$ . In the Raman spectrum a line at  $499.7\text{ cm}^{-1}$  is observed with a shoulder at about  $497.0\text{ cm}^{-1}$ . A doublet is observed at  $486.3$  and  $482.7\text{ cm}^{-1}$  in the i.r. on the low wave number side of the  $\nu_5$  fundamental. All of these features are probably components of the combination  $\nu_4 + \nu_8$ .

#### Crystal structure

There is not sufficient evidence to draw any definite conclusions concerning the crystal structure. However, it is not unreasonable to expect that  $\text{CCl}_3\text{CN}$  will crystallize with an orthorhombic structure similar to that of the related tetrahedral  $C_{3v}$  molecules  $\text{CCl}_3\text{H}$  [5],  $\text{CCl}_3\text{F}$  [6, 7] and  $\text{CF}_3\text{CN}$  [11]. The doublet splittings of the  $\nu_3$  bands of  $\text{C}^{35}\text{Cl}_2\text{C}^{37}\text{ClCN}$  and  $\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{CN}$  is good evidence for a  $C_s$  site and if the unit cell symmetry is  $C_{2v}$  or  $D_{2h}$ , then those non-degenerate fundamentals which do not show chlorine isotope splitting can split into two or four components by correlation field splitting. In each case two would be i.r. and two Raman active. On the other hand, the degenerate modes can split into four or eight components, three being i.r. active and four active in the Raman for either structure. Correlations between the various symmetry species of  $C_{3v}$ ,  $C_s$  and  $C_{2v}$  or  $D_{2h}$  are shown in Table 3. While non-coincidence of wavenumbers of components in i.r. and Raman spectra would indicate the  $D_{2h}$  unit cell group, coincidence would not rule out this possibility.

The only evidence of crystal effects for the non-degenerate fundamentals is the splitting of two of the chlorine isotopic lines of  $\nu_3$  in the Raman spectrum (see Fig. 5 and Table 1). As discussed above, this may be due to an orientational effect which produces an apparent site splitting of the non-degenerate modes of the partially substituted isotopic molecules. On the other hand, both  $\nu_5$  and  $\nu_8$  show four crystal components in the Raman while the i.r. band for  $\nu_5$  has three. It would have been useful to observe the i.r. band for  $\nu_8$ , but experimental limitations prevented this.

For the combinations of site and unit cell symmetries discussed above, there will be more than one molecule per unit cell. If there were two molecules per unit cell, (e.g.,  $C_s$  site,  $C_{2v}$  unit cell), we would expect nine Raman active external modes. For a  $D_{2h}$  factor group and a  $C_s$  site there would be four molecules per unit cell. Of the 21 optical lattice modes 12 would be Raman active

Table 3. A correlation table for the point groups involved in two possible crystal structures for solid  $\text{CCl}_3\text{CN}$ 

Molecule group	A possible site group	Two possible unit cell groups	
$C_{3v}$	$C_s$	$C_{2v}$	$D_{2h}$
$A_1$	$A'$	$A_1$ (IR, R)	$A_g$ (R) $B_{1u}$ (IR)
$E$		$B_1$ (IR, R)	$B_{2g}$ (R) $B_{3u}$ (IR)
	$A''$	$A_2$ (-, R)	$B_{1g}$ (R) $A_u$ (-)
		$B_2$ (IR, R)	$B_{3g}$ (R) $B_{2u}$ (IR)

under any of the 28  $D_{2h}$  space groups. A total of eleven features were observed in the lattice mode region of the Raman spectrum (see Fig. 6). However, we were unable to record the spectrum below about  $25\text{ cm}^{-1}$ , because of strong scattering of the Rayleigh line so that it is possible that additional optical lattice modes have not been observed.

### CONCLUSIONS

Solid state i.r. and Raman spectra of  $\text{CCl}_3\text{CN}$  have been recorded for the first time. Many of the fundamentals, as well as overtones and combinations give rise to complex bands. The observed splittings are due to both chlorine isotope and crystal components. The splittings of degenerate modes indicate a lowering of symmetry in the crystal and the doubling of the  $\nu_3$  lines of  $\text{C}^{35}\text{Cl}_2^{37}\text{ClCN}$  and  $\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{CN}$  in the Raman spectrum may be due to an orientation effect resulting from a  $C_s$  site. The observation of eleven lattice modes in the Raman spectrum shows that there must be more than one molecule in the unit cell. The evidence is insufficient to draw any definite conclusions concerning the crystal structure, but an orthorhombic structure is not ruled out.

The laser Raman spectrum of liquid  $\text{CCl}_3\text{CN}$  has been recorded for the first time and depolarization ratios measured for the fundamentals. The i.r. spectrum has been extended to  $150\text{ cm}^{-1}$  and

three of the low frequency fundamentals  $\nu_4$ ,  $\nu_7$  and  $\nu_8$  have been observed. However, the degenerate  $\text{CCl}_3$  deformation mode  $\nu_6$  is extremely weak and was not observed in the Raman spectrum. Very weak absorptions at  $360$  and  $334\text{ cm}^{-1}$  in the solid and liquid phase i.r. spectrum might be due to  $\nu_6$ , but unfortunately  $+26\text{ cm}^{-1}$  is an unreasonably large wavenumber shift between liquid and solid, so that the frequency of  $\nu_6$  remains uncertain.

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