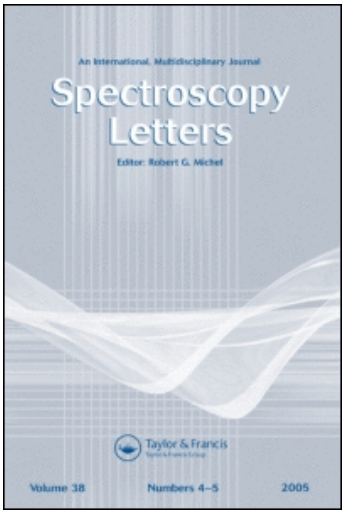

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The Infrared Spectrum of Solid Chlorotrifluoromethane

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THE INFRARED SPECTRUM OF SOLID CHLOROTRIFLUOROMETHANE

Key Words: Infrared spectroscopy, chlorotrifluoromethane

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ABSTRACT

The Infrared spectrum of solid chlorotrifluoromethane (CF_3Cl) has been studied and compared with that of matrix-isolated CF_3Cl. Crystal field splitting patterns of the strongest modes ν_1 and ν_4 suggest the crystal structure to be orthorhombic with a C_{2v} factor group and two molecules per unit cell located on C_s sites.

I. INTRODUCTION

Plastic crystals have in recent years played a prominent role as models for metallic solidification.[1-4] One of the often desired

properties for such model materials is the development of a rough, crystallograhically insignificant growth interface during solidification. In most metals, a rough solidification interface develops because the surface free energy is minimum when about half the surface sites are occupied with new atoms on an advancing interface. Since their basic units are atomic, pure solidifying metals generally retain much of their liquid phase structure and grow with low entropies of fusion and may not develop crystallograhic faces at the growth interface. They generally form close-packed crystals of the high symmetry cubic class, consistent with few orientational constraints on atomic units.[5]

"Spherically" symmetrical molecules with a central carbon atom tetrahedrally bonded to other groups are among the plastic crystal compound types which are believed to behave as "spherical" units (as metallic units) despite having permanent dipole moments in some cases. Dielectric constant measurements for such molecules suggest that at the freezing temperature these compounds tend to form cubic crystals which transform to lower symmetries at low temperatures.[6] At higher temperatures, there is presumably sufficient free rotation, librationally hindered, which allows enough random mobility for high solid phase entropy and isotropy consistent with cubic packing. The lattice change to anisotropic packing is a result of dipole-induced molecular alignment as the temperature becomes sufficiently low to lose librational energy.

In the above sense, chlorotrifluoromethane (CF_3Cl) is a "spherically" symmetrical molecule and has a permanent dipole moment. The intermolecular dynamics of the molecule has been studied by observing the far infrared features of gaseous CF_3Cl under pressure

and in the liquid phase.[7] The studies concluded that in the compressed gas phase and even in the liquid, the molecular dynamics are those of almost free rotation. Although the latter study is on the gaseous side of the liquid phase, when coupled with the earlier dielectric studies on "symmetrical" tetrahedral molecules,[6] it supports the notion that a high degree of librational freedom may exist for CF_3Cl at the freezing point. We may expect, in fact, to observe a cubic structure predicted for this type of molecule just below the freezing point.

Chlorotrifluoromethane has the point group symmetry of C_{3v} and exhibits three A_1-type vibrations (ν_1, ν_2, ν_3) and three E-type vibrations (ν_4, ν_5, ν_6), all of which are infrared active. The infrared spectra for CF_3Cl have been extensively studied.[8-21] The Raman spectra for the gaseous and liquid CF_3Cl have also been reported.[21-26] However, all of the IR studies were on the vapor phase CF_3Cl except one using Ne and Kr matrices.[15] There is no IR study on solid CF_3Cl. In this work, we study the IR spectra of the solid phase CF_3Cl as well as the matrix isolated CF_3Cl to obtain the crystal structure of solid CF_3Cl.

II. EXPERIMENTAL

Chlorotrifluoromethane (Freon-13) with 99% purity (Matheson) was purified by removing non-condensable gases with liquid nitrogen (77 K) and the condensable materials with an isopentane/N_2 slush (113 K). Matrix gases, argon (99.9%), nitrogen (99.9%), carbon dioxide (99.9%), and sulfur hexafluoride (99.9%), from Matheson, were used without further purification.

Samples for matrix isolation studies are prepared by first pumping the vacuum line to at least 7 x 10^{-5} torr. Vacuum line is

TABLE 1

Observed infrared frequencies (in cm^{-1}) for gaseous and solid CF_3Cl and their assignments

Gas		Solid		Assignment
2430	m	2400	m	$2\nu_4$
2320	s	2280	m	$\nu_1 + \nu_4$
2222	vvw	-		$2\nu_1$
2000	m	1960	m	$\nu_2 + \nu_4$
-		1905	w	-
1890	w	1860	m	$\nu_1 + \nu_2$
1790	vvw	1790	vw	$\nu_4 + \nu_5$
		1780	vw	
		1745	vw	
-		1630 -1645	w	$\nu_1 + \nu_5$
1588	vw	1575	vw	$\nu_1 + \nu_3$
1580	vw	1570	vw	$\nu_4 + \nu_6$
-		1555	w	$2\nu_2$
1445	vw	1445	vw	$\nu_1 + \nu_6$
		1440	vw	
		1435	vw	$(\nu_4 + 220)$?
		1430	vw	
		1420	vw	
-		1385	vw	$(\nu_1 + 280)$?
1340	w	1340	s	$\nu_2 + \nu_5$
-		1280	m	$2\nu_6 + \nu_5$
1260	s	1255	s	$\nu_2 + \nu_3$
1212 vs, 1184 w		1215	s	$\nu_4(A_1)$, asym. C-F stretch
		1208	vs	$\nu_4(B_2)$, asym. C-F stretch
		1200	s	$\nu_4(B_1)$, asym. C-F stretch

s-strong, m-medium, w-weak, v-very, asym.-asymmetric, sym.-symmetric

TABLE 1 (continued)

Gas	Solid		Assignment
1130 s	1128	vw	$\nu_2 + \nu_6$
1130 s	1120	m	$2\nu_5$
1105 vs, 1078 vw	1100	vs	$\nu_1(B_2)$, sym. C-F stretch
	1095	s	$\nu_1(A_1)$, sym. C-F stretch
1065 vw	1065	m	$\nu_3 + \nu_5$
955 w	955	m	$2\nu_3$
-	940	w	-
915 w	910	w	$\nu_5 + \nu_6$
-	825	vw	$\nu_3 + \nu_6$
781 m	781	s	ν_2, sym. C-Cl stretch
-	700	vvw	$2\nu_6$
563 w	563	m	ν_5, asym. FCF bending
480 vw	478	w	ν_3, asym. CF_3 deformation
-	385	vw	-
-	375	vw	-
-	365	vw	-
350 vvw	350	w	ν_6, asym. FCCl bending
-	340	vw	-
-	330	vw	-
-	320	vvw	-
-	280	w	-
-	245	w	-
-	220	w	-

s-strong, m-medium, w-weak, v-very, asym.-asymmetric, sym.-symmetric

flushed with active material CF_3Cl two or three times. The active material is then trapped with liquid nitrogen. Purified sample is isolated from the system and required matrix gases are introduced to prepare various M/A (matrix material to active material) ratios. Mixtures are allowed to reach equilibrium. The sample of a given M/A ratio is deposited on the CsI cold window which is maintained at 10 K by a "displex" (Air Products) closed-cycle helium refrigerator. Deposition rates are controlled by micrometering valves and are typically about 0.5 micromole/min. Pure CF_3Cl is deposited in the same manner but at a slower rates. Spectral observation of prepared samples are made on a Beckman 4250X infrared spectrometer. Resolution is better than 0.5 cm^{-1} at 1000 cm^{-1}.

III. RESULTS AND DISCUSSION

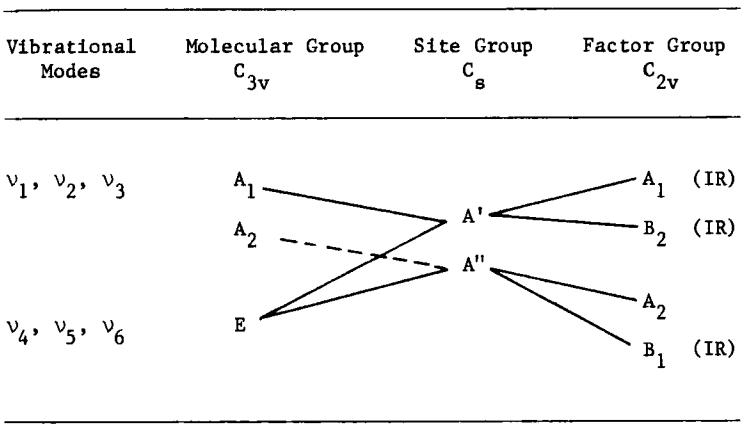
The observed IR frequencies for gaseous and solid CF_3Cl are tabulated in Table 1 together with their assignments. Our gas phase IR observations agree with those reported previously[10,14] and are used for comparison with the solid IR spectrum. Most of the IR bands observed in the gas phase are also observed in the solid phase. However, there are some noticeable differences in both the intensities and the spectral features. The liquid Raman work of Kahovec and Wagner[22] indicated that there is no activity below 350 cm^{-1}, the lowest frequency fundamental, ν_6. The solid state IR spectrum, however, shows several peaks in the region 220-340 cm^{-1}. We did not scan the spectral region below 200 cm^{-1}. The low frequency bands in the region 220-340 cm^{-1} are most probably associated with the lattice vibrations of crystalline CF_3Cl.

The most significant differences between the gaseous and solid state spectra of CF_3Cl are the splittings in the solid state of the strongest features, ν_1 and ν_4. In the gaseous spectrum, the ν_1 mode due to symmetric ^{12}C-F stretch was observed at 1105 cm^{-1}. A very weak satellite peak was observed at 1078 cm^{-1} which was assigned to the symmetric ^{13}C-F stretch,[15] due to the natural occurrence of the carbon isotopes. In the solid state, the 1105-cm^{-1} band was split into two strong bands at 1095 and 1100 cm^{-1}. The ν_4 mode, due to the asymmetric stretch of ^{12}C-F, was observed at 1212 cm^{-1} in the gas phase. The corresponding ^{13}C-F stretch was at 1184 cm^{-1}. In the solid state, the 1212-cm^{-1} band was split into a set of three strong bands at 1200, 1208, and 1215 cm^{-1}. Also, the 1455-cm^{-1} band, assigned to $\nu_1 + \nu_6$ in the gas phase, containing at least five maxima with its band center shifted to the lower frequency side (1435 cm^{-1}). Some of these bands may be due to the combinations of the ν_4 mode and the lattice modes. A weak absorption band occurring in the pure condensed phase at 1388 cm^{-1} is absent in both the gaseous and matrix-isolated spectra, which is assigned to $\nu_1 + 280$.

The splittings of fundamentals observed in the low temperature spectrum of a pure sample should be attributable to the effects of the crystal field. Additional bands may be due to combinations of internal molecular modes with external lattice modes.[27,28] The crystal field splitting patterns of the ν_1 and ν_4 modes can be rationalized using the site symmetry and factor group from previous works on C_{3v}-type molecules.[29,30] The factor group is taken as C_{2v} whereas the site symmetry is C_s. The correlation diagram in Table 2 demonstrates the predicted splitting patterns of the symmetric (ν_1, ν_2, ν_3) and antisymmetric (ν_4, ν_5, ν_6) modes.

TABLE 2

Correlation between point groups and the expected splitting patterns of vibrational modes



The C_{3v} symmetric modes on C_s sites are split into two infrared active absorptions by the unit cell group (C_{2v}) having A_1 and B_2 symmetry. There is no A_2 fundamental vibration. The doubly degenerate E species is separated into its two components, A' and A'', by site group symmetry. Each of these, in turn, is split into A_1, B_2 and A_2 , B_1 type vibrations, respectively. Thus, for the symmetric modes, four absorbances arise of which three are infrared active. The condensed phase spectrum should reveal the symmetric modes split into doublets, and the asymmetric modes into triplets. It has been noted that such splitting patterns cannot be observed in the infrared unless the dipole moment change is large for the mode in question. It is apparent that in this study that ν_1 and ν_4, the strongest features in the spectrum, are the only ones split by the crystal field. The splitting patterns are as predicted by the presumed structure.

In the presence of isolation matrices (Ar, N_2, CO_2, SF_6), the splitting patterns of both ν_1 and ν_4 modes are not observed as in the solid spectra. In particular, in experiments where argon was used as matrix, an interesting observation was made when the mixture was heated to beyond the boiling point of argon (87 K). Upon heating the mixture, the ν_1 and ν_4 modes remain unchanged, except for little intensity variation, until the temperature exceeds 87 K but below 93 K (the melting point of CF_3Cl). At that temperature range, the ν_4 mode splits into A_1, B_1 and B_2 components and the ν_1 mode splits into A_1 and B_2 components. As the boiling point of argon is reached, the argon matrix is removed, the neighboring CF_3Cl molecules feel the presence of each other and hence the crystal field effect.

Several investigations[29-31] have demonstrated that C_{3v}-type molecules cannot have higher crystal symmetry than orthorhombic structure. The present work on the IR spectra of solid CF_3Cl and Ar matrix isolated CF_3Cl has provided evidence of intermolecular dynamics of CF_3Cl below the liquid-solid phase transition temperature. The observed splittings of the fundamental vibrational modes by the crystal field suggest that the crystal class is orthorhombic just below the freezing point, and not cubic as suggested for plastic crystals, which thus implies strong constraints by dipolar interaction.

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