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Pressure and temperature studies of Raman scattering of the molecular crystal sym-$C_6Cl_3F_3$

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Abstract. Earlier experimental results have been considerably strengthened by Raman scattering from crystalline sym-$C_6Cl_3F_3$. Measurements have been made as a function of temperature at ambient pressure, and as a function of pressure at room temperature. Apart from a new first-order phase transition observed at 62 kbar but as yet uncharacterised, the crystal structure maintains the $P6_3/m$ space group symmetry. Anomalies in phonon frequencies and line-widths at 296 K indicate a phase transition, which is 'isostructural' order–disorder. Similar features are seen at 15 kbar, suggesting that the phase transition is of the same nature as that observed at 296 K. The half-width of the phonon associated with dynamic disorder is found by fitting to be $\Gamma_{1/2}(T) = 0.032 + 0.0061\,T + 3400\exp(-\Delta E_a/kT)\ \mathrm{cm}^{-1}$, with $\Delta E_a = 35\ \mathrm{kJ\ mol}^{-1}$. Although in-plane 120° molecular reorientational jumps may play a role, this may not be a major role at room temperature due to a rather high activation energy. The full understanding of the results requires there to be another minor activation process that also obeys A_g symmetry. The variation in the crystal structure parameters and the external mode frequencies with pressure up to 60 kbar is calculated using a 6-exp atom–atom potential with the rigid-body approximation. The molecular orientation changes by only 0.5° between 0 and 60 kbar. The calculated external mode frequencies agree with Raman experiment up to 60 kbar within 5–15%. A molecular dynamics simulation for 300 K indicates a residence time between reorientations greater than 500 ps, giving a quasi-elastic Lorentzian broadening of less than 0.01 cm^{-1}.

1. Introduction

Semi-empirical intermolecular potential functions for carbon and hydrogen have been elaborated in the last two decades [1]. These functions reproduce well the lattice energy and dynamics of both aromatic and aliphatic hydrocarbons. Latterly, attempts have been made to extend this work to molecular crystals containing nitrogen and halogen atoms [2]. Sym-$C_6Cl_3F_3$ (1,3,5-trichloro-2,4,6-trifluorobenzene) furnishes an excellent example of a simple molecular crystal by which the interactions of chlorine and fluorine atoms can be studied, and has therefore received considerable attention in the last few years.

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The crystal structure of sym-$C_6Cl_3F_3$ is hexagonal, $P6_3/m$, with two planar molecules in the unit cell stacked along the *c* axis [3]. This particularly simple symmetry gives rise to phonon eigenvectors (polarisations) for the external modes which are completely determined by symmetry, making this material of special interest since the analysis of its lattice vibrations is particularly simplified.

Constrained x-ray data structure refinement has revealed a significant contribution to the thermal motion at room temperature from the internal molecular vibrations [3]. On the other hand, at low temperatures (5 K), there is evidence from coherent inelastic neutron scattering measurements of phonon dispersion of there being only a weak interaction between the lowest-frequency internal modes and the highest external modes [4]. In consequence, the lattice dynamical calculations based on the rigid-body assumption have satisfactorily reproduced the experimental results at this temperature. Thus a strong temperature dependence of the coupling between internal and external excitations is to be expected, reducing the applicability of the rigid-body approximation at higher temperatures.

Calorimetric studies [5, 6] of sym-$C_6Cl_3F_3$ have revealed a small ($\Delta E = 18\ \mathrm{J\ mol^{-1}}$) anomaly in the heat capacity at $T_c = 296$ K. It has been suggested that this anomaly is caused either by impurities [5] or by a phase transition [6]. More recently, reorientations of the sym-$C_6Cl_3F_3$ molecules around their three-fold axes have been observed by NQR and NMR techniques [7]. According to Nakamura [8], changes in the character of this motion are responsible for the thermal anomaly; a molecule performs 120° jumps within its molecular plane above T_c, while below T_c the motion is a large-amplitude libration. An important conclusion from Nakamura's model is that the crystal symmetry does not change at T_c. Thus it would appear to be a rare case of an 'isostructural' order–disorder phase transition. Our present work is a contribution to the link between the classic soft mode phase transition theory [9] and relaxation phenomena [8, 10].

In the present paper we report Raman scattering measurements of the low-energy excitations in sym-$C_6Cl_3F_3$ crystals as a function of both pressure and temperature. Careful analysis of the spectra has shown anomalous behaviour of the frequencies and line-widths near room temperature at ambient pressure. The same features have also been observed around 15 kbar pressure in experiments at constant temperature. Moreover, drastic changes in the spectra have been found at 62 kbar, suggesting the existence of a new phase transition in the solid.

The anharmonic coupling between internal and external phonons in this material has attracted our attention since the relevant modes are active in Raman scattering. We have been able to use the analysis of the line-shapes to estimate a coupling strength and to investigate its temperature variation.

In lattice dynamics calculations, pressure can be taken into account more fully than temperature. We use the method of Pawley and Mika [11] to model the variation of crystal structure and phonon dispersion with pressure, using the same set of potential parameters as used previously [4]. The results are compared with the measured frequencies under pressure; some preliminary work has been reported in symposia proceedings [12].

2. Group theoretical analysis

The crystals of sym-$C_6Cl_3F_3$ belong to a hexagonal system with space group $P6_3/m$ [3]. Two planar molecules occupy sites of $\bar{6}$ (C_{3h}) symmetry in the primitive cell. Each

Table 1. Unnormalised polarisation vectors of the external modes in $C_6Cl_3F_3$ at the $\Gamma(0, 0, 0)$ point. A right-handed space-fixed cartesian reference frame is used where the x and z axes are along the lattice vectors $\boldsymbol{a}$ and $\boldsymbol{c}$ respectively. The Γ_i notation is due to Kovalev [14] and is included for cross reference to other work.

Mode	T_1	L_1	T_2	L_2	Polarisability tensor components
A_g, Γ_1	0 0 0	0 0 1	0 0 0	0 0 1	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
B_g, Γ_7	0 0 1	0 0 0	0 0 −1	0 0 0	
E_{1g}, Γ_3 and Γ_{11}	0 0 0 0 0 0	1 0 0 0 1 0	0 0 0 0 0 0	1 0 0 0 1 0	α_{yz}, α_{zx}
E_{2g}, Γ_5 and Γ_9	1 0 0 0 1 0	0 0 0 0 0 0	−1 0 0 0 −1 0	0 0 0 0 0 0	$\alpha_{xx} - \alpha_{yy}$, α_{xy}
A_u, Γ_2	0 0 1	0 0 0	0 0 1	0 0 0	
B_u, Γ_8	0 0 0	0 0 1	0 0 0	0 0 −1	
E_{1u}, Γ_4 and Γ_{12}	1 0 0 0 1 0	0 0 0 0 0 0	1 0 0 0 1 0	0 0 0 0 0 0	
E_{2u}, Γ_6 and Γ_{10}	0 0 0 0 0 0	1 0 0 0 1 0	0 0 0 0 0 0	−1 0 0 0 −1 0	

molecule, treated as a rigid body, contributes six degrees of freedom, so in all there are twelve external degrees of freedom and twelve possible branches in the corresponding dispersion curves. At the Γ point there are four doubly degenerate and four singlet modes, with the following representations:

$$\Gamma = A_g + B_g + E_{1g} + E_{2g} + A_u + B_u + E_{1u} + E_{2u}.$$

Modes of Ag, E_{1g} and E_{2g} symmetry are Raman active, but none of the non-zero Γ-point modes is infrared active (A_u and E_{1u} are acoustic modes).

As the crystal structure is exceptionally simple group theoretically, it is possible to describe the polarisation vectors for rigid-body molecular motions at Γ completely using projection operator techniques [13]. The results are presented in table 1. The components of each eigenvector are (from left to right) T_1, L_1, T_2, L_2, that is the translational then the librational components for each molecule in order. From an examination of this table it is possible to describe those modes that are Raman active, as follows. The purely librational A_g mode is a vibrational motion around the three-fold axis, with the principal axis of inertia perpendicular to the molecular plane. The E_{1g} modes are again purely librational, but about any axis perpendicular to the three-fold axis, whereas the E_{2g} modes are translational within the molecular plane. The notation used in table 1 follows Kovalev [14].

3. Experimental procedure

3.1. Details of the experiment

Commercial material was carefully purified by means of repeated zone refining. Large single crystals exhibiting perfect (001) cleavage were grown from the melt by the Bridgman method. A crystalline ingot was cleaved with a razor blade and cut with a wire saw into samples of a parallelepipedal shape. The cut faces were polished using diamond paste. Raman scattering studies at ambient pressure were performed with these samples. The X, Y and Z orthogonal axes system used to label the scattering geometry was chosen with X and Z parallel to the a and c crystallographic directions respectively. A Thor Cryogenics S-500 continuous-flow cryostat was used for the low-temperature experiments. Sample temperatures were monitored to ±1° by a thermocouple attached to the crystal face.

High-pressure experiments were carried out at room temperature using a diamond anvil cell. Powdered material was packed along with a tiny ruby chip into a ≈ 0.3 mm diameter hole spark-etched in an inconel gasket. The applied pressure was estimated from the shift of the ruby fluorescence R lines. Hydrostatic pressure conditions were monitored by checking both the separation of the R_1 and R_2 lines and their half-widths [15]. An argon ion laser operating at 514.5 nm and 200 mW was used as the excitation source. At ambient pressure the right-angle scattering configuration was used, while the high-pressure spectra were recorded in the back-scattering configuration. The scattered light was analysed using a Coderg T800 triple-grating spectrometer with computer-controlled operation and data acquisition.

3.2. *Experimental results*

The complete polarised Raman spectra of crystalline sym-$C_6Cl_3F_3$ at room temperature (293 K) and at ambient pressure are shown in figure 1. Three bands of the lattice modes appear clearly below 100 cm^{-1}. Analysis of the polarisation properties leads to the following assignments. The 34 cm^{-1} band recorded in the $X(YX)Y$, $Y(XX)Z$ and $X(YY)Z$ scattering geometries belongs to E_{2g} symmetry, the 45 cm^{-1} band seen in the $Y(XX)Z$, $X(YY)Z$ and $X(ZZ)Y$ geometries is of A_g symmetry, while the E_{1g} mode appears at 61.5 cm^{-1} in $X(ZY)Z$ and $X(ZX)Y$ spectra. The last mode is also seen in the other scattering geometries because of instrumental depolarisation, as can be deduced from the ratios of the band intensities in the forbidden and allowed polarisations. The depolarisation never exceeds 2%. A broad asymmetric feature at 119 cm^{-1} visible in the $X(ZY)Z$ and $X(ZX)Y$ geometries (i.e. in the E_{1g} spectra) is assigned to the lowest out-of-plane internal vibration [16]. This mode couples to another of the same symmetry, the 61.5 cm^{-1} libration [4], giving rise to the characteristic line-shape distortions [17].

The low-frequency spectra (below 150 cm^{-1}) have been studied from 325 K down to 20 K. The number of the lines, as well as their polarisations, remains unchanged in this temperature range. The only clear variation is the continuous evolution of the line-shape of the 119 cm^{-1} mode down to about 100 K (figure 2). In order to extract an accurate temperature dependence for the phonon frequencies and damping constants, the data have been fitted to Raman response functions which differ in their Bose population factors for the Stokes and anti-Stokes cases,

$$\text{Stokes:}\qquad S(\omega) = R(n(\omega) + 1)\sum_k \chi''_k(\omega)$$

$$\text{anti-Stokes:}\qquad S(\omega) = Rn(\omega)\sum_k \chi''_k(\omega)$$

where $n(\omega) = (\exp(\hbar\omega/kT) - 1)^{-1}$, and R is a normalisation constant. The imaginary part of the complex susceptibility $\chi(\omega)$ for the non-interacting modes is approximated by the expression for a damped harmonic oscillator,

$$\chi''_k(\omega) = \mathrm{Im}(P_k(\omega_k^2 - \omega^2 + \mathrm{i}\omega\Gamma_k)^{-1})$$

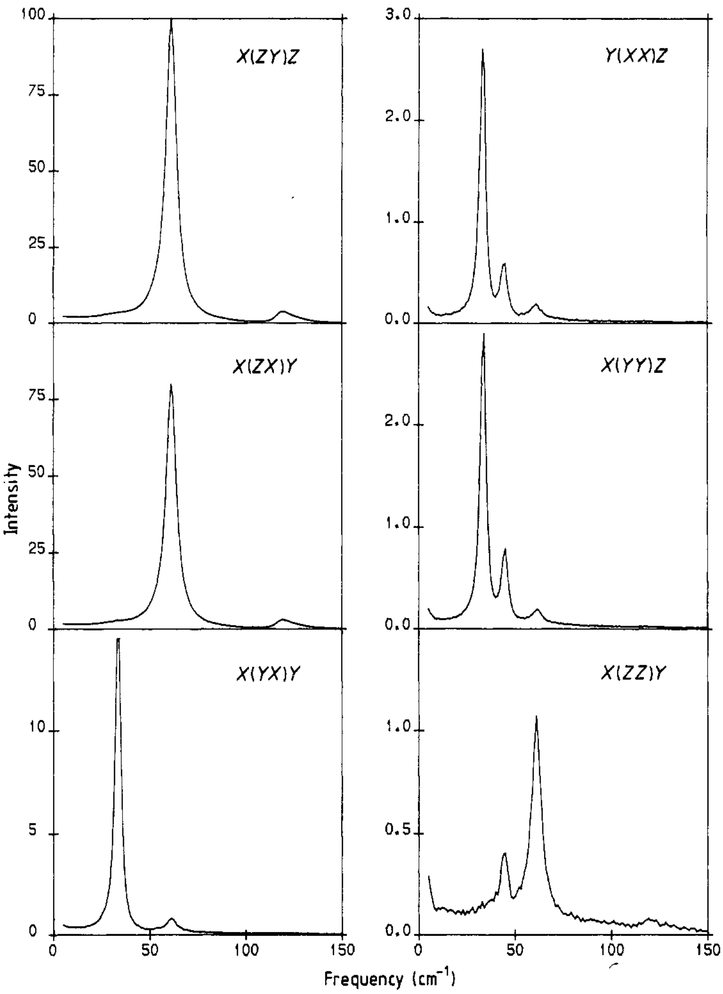

Figure 1. Low-frequency polarised Raman spectra of crystalline $C_6Cl_3F_3$ at ambient temperature and pressure.

where P_k, ω_k and Γ_K describe the strength, frequency and damping of the oscillator; Γ_k corresponds to the full width of the band at half maximum (FWHM). In the case of two coupled modes, $\chi''(\omega)$ is given by [17]

$$\chi''(\omega) = \mathrm{Im}\left(\sum_{k,l} P_k P_l G_{kl}(\omega)\right)$$

where $G_{kl}(\omega)$ are elements of the inverse of the following matrix

$$(\mathbf{G}(\omega))^{-1} = \begin{pmatrix} \omega_1^2 - \omega^2 + \mathrm{i}\omega\Gamma_1 & \Delta^2 + \mathrm{i}\omega\Gamma_{12} \\ \Delta^2 + \mathrm{i}\omega\Gamma_{12} & \omega_2^2 - \omega^2 + \mathrm{i}\omega\Gamma_2 \end{pmatrix}.$$

An arbitrary choice of the real ($\Gamma_{12} = 0$) or imaginary ($\Delta^2 = 0$) coupling terms for the system has to be made in order to determine explicit values for the elements $G_{kl}(\omega)$. In

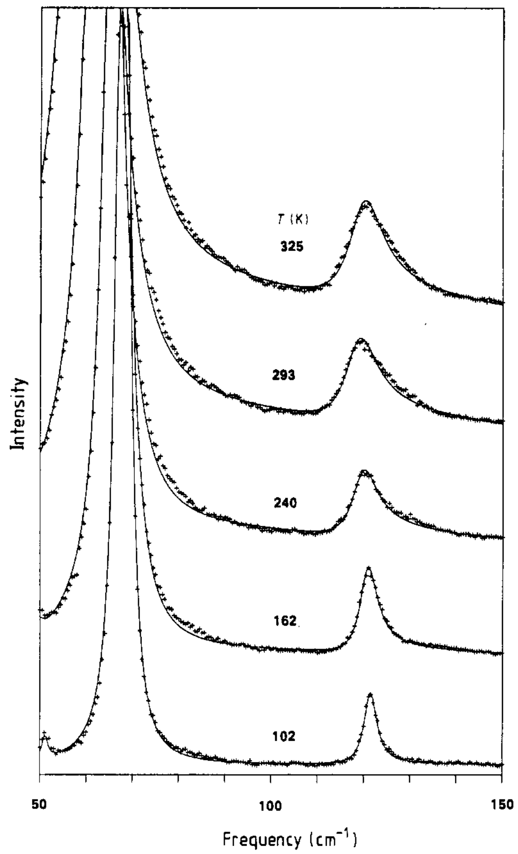

Figure 2. Examples of the E_{1g} spectra in the mode-coupling region recorded at different temperatures. The full curves represent profiles calculated using the coupled mode formalism described in the text.

the present case the experimental line-shapes are well matched only by profiles derived on the assumption of a non-zero imaginary coupling term.

The frequency determination has been done to high accuracy by the simultaneous fitting of the Stokes and anti-Stokes parts of the spectrum recorded in the same scan. This procedure eliminates the error in determining the excitation line used as a reference point to measure the Raman shifts. All the spectra have been analysed without the prior deconvolution of an apparatus function. The temperature variation of the fitted parameters is shown in figures 3 and 4. Lattice mode frequencies vary linearly with T above 140 K, but the gradients of these functions change markedly in the vicinity of T_c = 296 K. Moreover, a small discontinuity of about 0.25 cm^{-1} is observed for the width of the A_g libration at 294 K (figure 3(*b*), note that the error in frequency determination for this mode is about 0.01 cm^{-1}). The variation of the internal mode at 119 cm^{-1} is several times smaller than for the lattice modes, and becomes negligible at room temperature.

The frequency anomalies are accompanied by changes in the variation of the line-widths. The overall variation is a linear broadening of the band up to 296 K, but is distinctly non-linear above this temperature. Only for the internal mode (119 cm^{-1}) is the variation linear over the whole temperature range of the experiments, as shown in

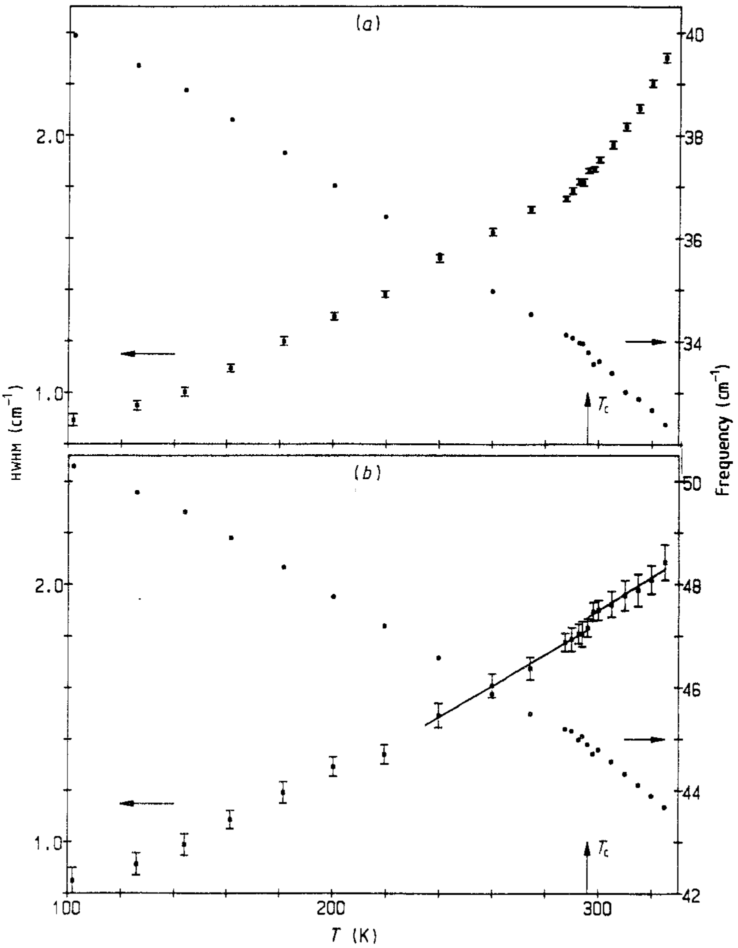

Figure 3. The temperature dependence of the parameters obtained by fitting the damped harmonic oscillator profile to (*a*) the E_{2g} translational mode and (*b*) the A_g librational mode.

figure 4(*b*). The change in the shape of the internal mode line with temperature, as shown in figure 2, implies changes in the coupling strength between this mode and the E_{1g} libration. The variation of the coupling constant Γ_{12} is given in figure 4(*b*), exhibiting a broad maximum around T_c and decreasing linearly as the temperature is reduced, finally approaching zero at around 70 K. From this we deduce that the coupling vanishes below this temperature.

Examples of the unpolarised Raman spectra of sym-$C_6Cl_3F_3$ under pressure are shown in figure 5. The frequency range of the measurements has been extended to 250 cm^{-1} to include the next band of E_{2g} symmetry at 187.3 cm^{-1} which is expected to be a pure internal vibration. As the intensity of the light scattered by the sample in the diamond anvil cell is weak, a long scanning time is necessitated and so only the Stokes part of the spectra has been recorded. This reduces the accuracy of the phonon frequency determination to about ± 0.2 cm^{-1}. Furthermore the poor signal-to-noise ratio has prevented a confident determination of the changes in phonon dampings and couplings.

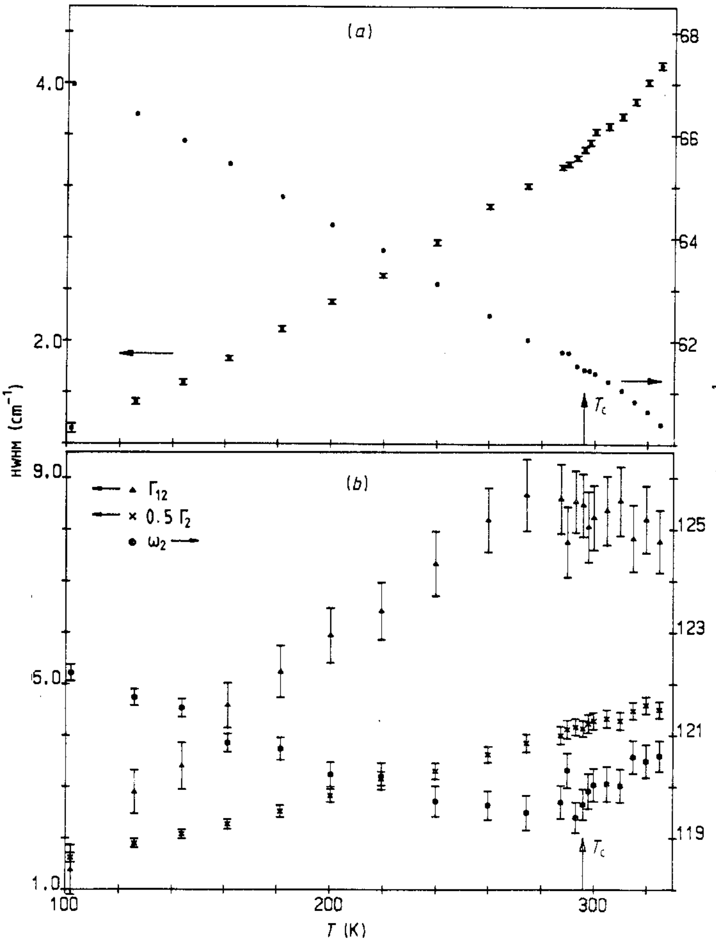

Figure 4. The temperature dependence of the parameters obtained by fitting the coupled mode model to the (*a*) 61 cm^{-1}, and (*b*) 119 cm^{-1} E_{1g} modes in the $X(ZY)Z$ scattering geometry.

The pressure dependencies of the phonon frequencies and intensities measured at room temperature are plotted in figures 6 and 7 respectively. All the lattice modes shift continuously to higher frequencies with increasing pressure up to 62 kbar. However, a distinct change in slope is seen for both functions at 15 kbar, reminiscent of the behaviour of $\omega(T)$ at $T_c = 286$ K. This suggests a common origin for the two anomalies. Bearing in mind that the local temperature of the sample might be a little higher than T_c due to laser heating, one can expect the same type of disorder below 15 kbar as has been found in the high-temperature phase of this material at ambient pressure. The increasing pressure would prevent molecular reorientations at 15 kbar, giving a high-pressure phase from 15 to 62 kbar corresponding to the ambient pressure phase below T_c. A brief examination of figure 7 shows that the pressure variation of the A_g libration intensity occurs mostly up to 15 kbar. This supports the concept of the order–disorder phase transition at this pressure because the influence of the molecular reorientations on the A_g mode has already been established in the temperature studies.

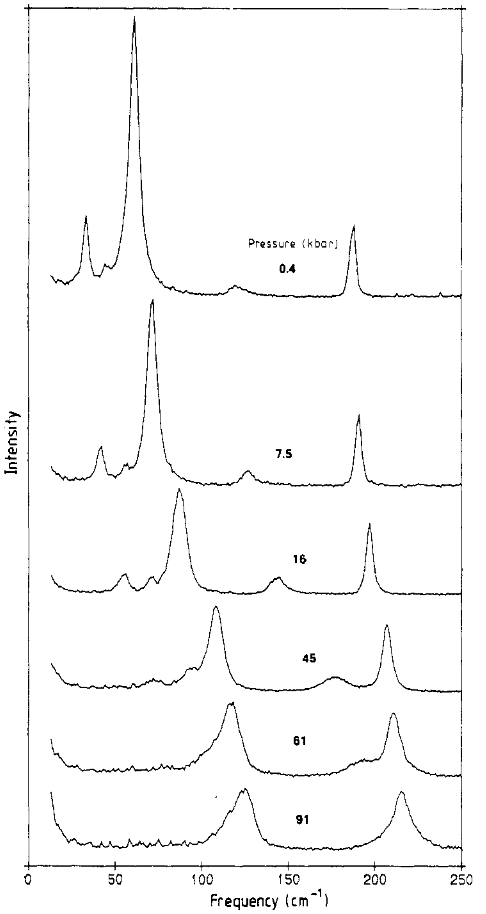

Figure 5. The representative Raman spectra of $C_6Cl_3F_3$ in the low-energy region, recorded at different pressures.

The drastic anomaly that is found at 62 kbar can be attributed to a new structural phase transition. Figures 6 and 7(*c*) show the disappearance of the E_{2g} translational mode at this transition, and at the same point two other lines coalesce into a broad asymmetric band. On analysing this band over a wide pressure range as a superposition of two modes we find a constant difference between the two frequencies and a constant intensity ratio; this supports a possible alternative single-mode interpretation. The E_{1g} internal vibration depends on pressure more like the lattice modes than the next internal vibration at 187.3 cm^{-1}. This indicates that the coupling with the E_{1g} libration remains strong under pressure. Both the phase transitions in this material cause a discontinuous change in the frequency of the E_{1g} internal vibration.

3.3. Discussion of experiments

In the present paper we address several questions of both an experimental and theoretical nature which arose previously during the calorimetric, x-ray and neutron scattering, NQR and NMR studies of crystalline sym-$C_6Cl_3F_3$. Our aim is to make use of the new

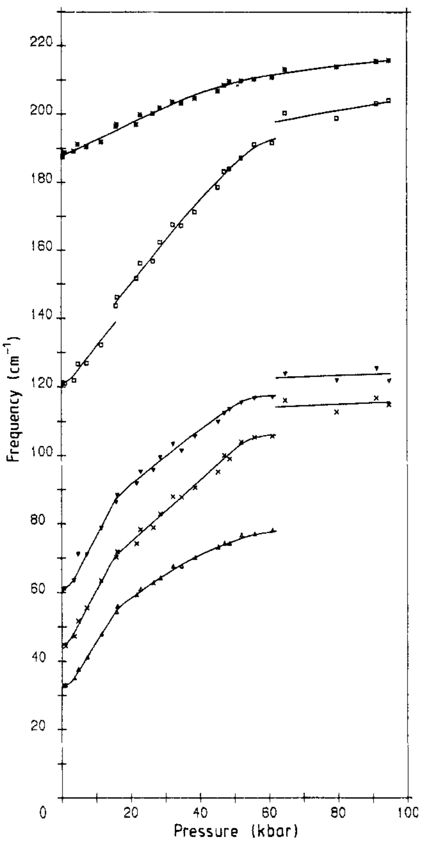

Figure 6. Pressure dependence of the phonon frequencies in $C_6Cl_3F_3$ at room temperature. The full curves are intended as a guide to the eye.

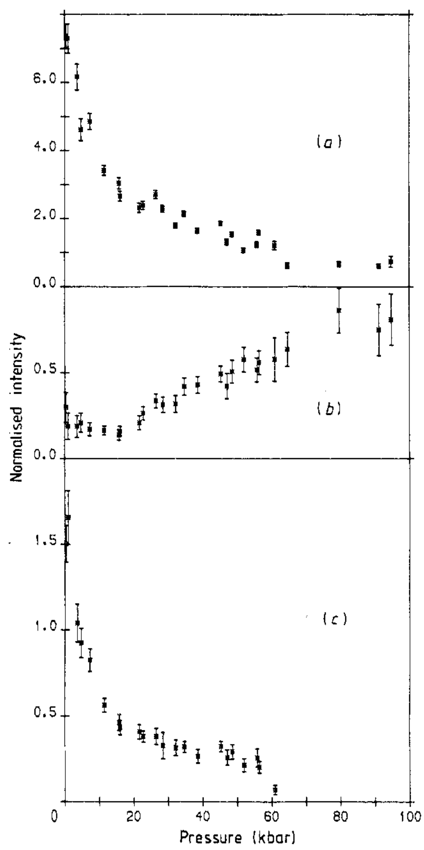

Figure 7. Pressure dependence of the intensities of (*a*) the E_{1g}, (*b*) the A_g, and (*c*) the E_{2g} lattice modes. The intensities are normalised to the intensity of the E_{2g} internal vibration at 187.3 cm^{-1}.

experimental data provided by Raman scattering spectroscopy, a most useful complementary technique to the above since it permits the study of the molecular motions and the effects of symmetry changes associated with phase transitions. First let us briefly summarise the results.

Our studies at ambient pressure are directed towards investigating the possible dynamics and symmetry changes caused by the process that gives the heat capacity anomaly at 296 K. Three lattice modes have been observed and assigned in agreement with the Raman selection rules for the C_{6h} factor group, and as the number of peaks and their polarisations do not change between 11 and 325 K we conclude that the crystal symmetry is invariant through the transition at $T_c = 296$ K. Evidence for isostructural behaviour follows from the fact that there is no symmetry change when the molecules are excited into reorientational jumps about their three-fold symmetry axes. This is consistent with Nakamura's model [8], but it must be recognised that occasional isolated molecular jumps are to be expected well below T_c. The proposed disorder should have no effect on the lattice dynamics as seen by Raman spectroscopy since the phonon frequencies are large compared with the inverse of the relaxation time. Indeed, none of the typical spectral features of disordered systems have been observed, such as broad phonon bands and quasi-elastic scattering. In contrast, the delicate temperature dependent anomalies in the phonon frequencies and damping constants around T_c, and especially the non-linear $\Gamma(T)$ behaviour above T_c suggest the presence of an activation process in the upper phase. We make an attempt to estimate how far the hopping model of Nakamura can be responsible for such phonon damping behaviour. According to Andrade *et al* [10], the half-width of the phonon associated with dynamic disorder characterised by a correlation time $\tau_c = \tau_0 \exp(\Delta E_a/kT)$, is given as

$$\Gamma_{1/2}(T) = a + bT + c\exp(-\Delta E_a/kT)$$

in the $\omega^2\tau_c^2 \gg 1$ limit, where ω is the phonon frequency and ΔE_a is the molecular reorientation activation energy. In the ordered phase this equation reduces to the first two terms, which contribute to the phonon anharmonicity. The full expression has been used to reproduce the half-width variation of the A_g mode using the molecular reorientation activation energy proposed by Nakamura [8]. The half-width of the A_g mode should manifest the largest sensitivity to the reorientational jumps in the disordered phase since the eigenvector of this mode and the jump motion both involve the same generalised coordinate.

The constants a and b have been estimated by fitting the $\Gamma_{1/2}(T)$ function to the experimental data between 240 and 296 K. The value of c has been estimated by assuming that a and b do not vary above T_c, resulting in

$$\Gamma_{1/2}(T) = 0.032 + 0.0061\,T + 3400\exp(-\Delta E_a/kT)\ \mathrm{cm}^{-1}$$

with $\Delta E_a = 35\ \mathrm{kJ\ mol^{-1}}$ [8]. This is shown as a full curve in figure 3(*b*). It is evident that the calculated $\Gamma_{1/2}(T)$ function is too flat to give a totally satisfactory reproduction of the measurements. One can but conclude that the anomalies discovered by Raman spectroscopy are not caused solely by 120° molecular jumps as proposed by Nakamura [8], and that another process of much smaller activation energy must exist. This process must preserve the symmetry of the low-temperature phase, and must vanish below T_c. The similarity between the $\omega(P)$ and $\omega(T)$ dependencies of the lattice modes indicates the same nature of the lattice instability induced by pressure at 15 kbar and temperature at 296 K. However, the phase transition effects are more visible in the $\omega(P)$ variation because pressure produces the larger phonon frequency shifts. The proposed interpretation of the anomaly at 15 kbar leads naturally to the conclusion that the crystal symmetry is $P6_3/m$ up to 63 kbar. The drastic change discovered at this pressure must be a new first-order phase transition, for which our experimental data are insufficient for characterisation.

The mutual anharmonic interaction of the upper external and the lowest internal excitation gives rise to a characteristic anti-resonance line-shape of the latter mode at 119 cm^{-1} in the E_{1g} Raman spectra. The coupled-mode formalism suggests a strong anharmonic coupling at room temperature which becomes negligible below 70 K, giving support to the rigid-body approximation for lattice dynamics at low temperatures. Phonon dispersion curves at 5 K are well reproduced with this approximation, while the increase in coupling with temperature is fully consistent with the observed contribution by the internal motion to the Debye–Waller factor at room temperature [3].

4. Theoretical calculations

4.1. Interatomic potential

The pressure dependence of the structure and dynamics can be calculated [11, 18] if a suitable interatomic potential is available. Though the potential for $C_6Cl_3F_3$ was determined and used earlier [4, 12], the procedure for its determination was not described. This is now briefly done.

In the case of molecular crystals, the intermolecular potential is usually obtained by summing so-called 6-exp potentials over all pairs of non-bonded atoms:

$$V_{kk'}(r) = -A_{kk'}/r^6 + B_{kk'} \exp(-C_{kk'}r) \tag{1}$$

where r is the separation between the atoms k and k' and $A_{kk'}$, $B_{kk'}$, $C_{kk'}$ are adjustable parameters. It has been observed that very dissimilar parameter sets can give an equally good description of structure and dynamics, as for example the dissimilar parameter sets [1] of Kitaigorodskii and Williams. This suggests that the number of independent parameters should be reduced. One common practice is to use combination rules to derive the parameters $A_{kk'}$ etc corresponding to pairs of distinct atoms (k/k'), from the parameters for pairs of like atoms A_{kk} and $A_{k'k'}$. Even with this reduction, the number of parameters is still too large, and it is advisable to make further reductions. Kitaigorodskii and Mirskaya [19] have investigated the following procedure:

$$A_{kk'} = A_0(R_k + R_{k'})^6 \tag{2}$$

$$B_{kk'} = B_0 \tag{3}$$

$$C_{kk'} = C_0/(R_k + R_{k'}) \tag{4}$$

where $A_0 = 0.211$ kcal mol^{-1}, $B_0 = 42000$ kcal mol^{-1}, $C_0 = 13.6/1.1 = 12.364$, and R_k, $R_{k'}$ are close to the van der Waals radii of the atoms. This reduces the number of parameters to $3n$, where n is the number of distinct atomic species forming the molecule, though A_0, B_0 and C_0 could be counted as three more parameters. This has been quite successful for hydrocarbons, for which $R_C = 1.727$ Å and $R_H = 1.272$ Å reproduce the Kitaigorodskii parameters. The assumptions (3) and (4) hve also been successfully used to describe the Born–Mayer repulsive part of the interatomic potential in a number of complex ionic crystals [20], where the R_k were allowed to be free parameters nearly proportional to the crystal ionic radii of the atoms.

In the present case, in describing the structure and dynamics of the molecular crystal $C_6Cl_3F_3$, we found it necessary to modify equation (2) to

$$A_{kk'} = A_0(A_kA_{k'})^{1/2}(R_k + R_{k'})^6 \tag{5}$$

where the A_k are extra parameters. Through a systematic variation of A_k and R_k we found the following set of values which gave the structure and the Raman frequencies in good agreement with low-temperature experiments:

$$A_C = 1 \qquad A_F = A_{Cl} = 2 \qquad R_C = 1.75\ \text{Å} \qquad R_{Cl} = 2.0\ \text{Å} \qquad R_F = 1.5\ \text{Å}.$$

The resulting parameters $A_{kk'}$ etc are given in table 2. The complete phonon dispersion relation as predicted by this set of parameters [12] was found to be in very good agreement with subsequent experimental results [4] at 5 K by coherent neutron inelastic scattering. In comparison, simple modifications to the transferable set of parameters developed by Williams and co-workers [2] overestimated the phonon frequencies usually by about 20–40% [4].

Table 2. Potential parameters used in the structure and dynamical calculations.

Atom pair kk'	$A_{kk'}$ (Å^6 kcal mol^{-1})	$B_{kk'}$ (kcal mol^{-1})	$C_{kk'}$ (Å^{-1})
C C	387.87	42 000	3.532
C F	351.65	42 000	3.804
C Cl	829.82	42 000	3.297
F F	307.64	42 000	4.121
F Cl	775.75	42 000	3.532
Cl Cl	1728.51	42 000	3.091

4.2. Dynamics

For every $C_6Cl_3F_3$ molecule in the crystal there are 36 vibrational coordinates, namely:

(i) rigid-body external motions (3 in and 3 out);
(ii) 18 internal bond-bending motions (9 in and 9 out);
(iii) 12 internal bond-stretching motions (12 in);

where 'in' and 'out' refer to motion in the molecular plane or out of it. Whereas bond stretching gives very high frequencies, some bond-bending modes occur at as low as 121 cm^{-1} in the solid [16], and therefore contribute somewhat to the thermal motion at room temperature. However, there is a band gap between the lowest of these internal modes at 121 cm^{-1} and the highest external mode at 95 cm^{-1} at 11 K. It is therefore understandable that the measured phonon dispersion relation below the band gap at 5 K was found to be in good agreement with the rigid-body calculations [4]; this is similar to the situation found in naphthalene [21]. The coupling of the external and internal coordinates in naphthalene has been studied [22], and similar results may be expected in the present case. We use here the rigid-body approximation for calculating the dynamics up to 60 kbar, and find that all the Raman-active external mode frequencies are in good agreement with the calculations to within 5–15%. We note that the significant coupling between the Raman-active E_{1g} lattice mode and the lowest internal mode above 70 K is necessarily an anharmonic coupling due to phonon–phonon interaction at finite temperatures.

Once the potential function parameters have been chosen, it is straightforward to calculate the structure and dynamics as a function of pressure for zero temperature [11]; the method has also been adopted in more recent work [18]. First the structure is found by minimising the total of the potential and pressure energy (pV) with respect to the structure variables, the lattice parameters and molecular coordinates, keeping the space group symmetry unchanged. The equilibrium structure thus found at any chosen pressure is then used in the harmonic dynamical calculations [23]. The calculations correspond strictly to zero temperature, but we note that the observed [3] change in volume between 0 K and 300 K at $p = 0$ corresponds to that found by calculation for a reduction of pressure by 4 kbar at 0 K.

The results are shown in figure 8, where the variation of the two cell parameters and the bulk modulus are given. The only other structural variable is the molecular orientation about the hexagonal axis, which changed by only 0.5° from 0 to 60 kbar. The pressure variations of the calculated external phonon frequencies at Γ are shown in figure 9. All the frequencies increase with pressure, and are within 5–15% agreement

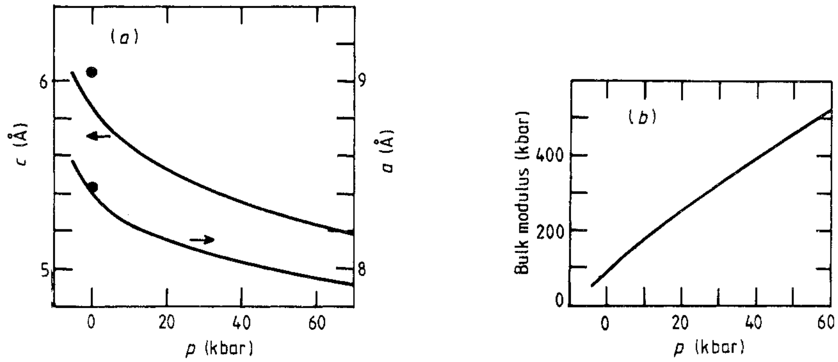

Figure 8. Calculated pressure variation of (a) the unit cell parameters a and c, and (b) the bulk modulus.

with the observations given in figure 6 from 0 to 60 kbar, despite the isostructural phase transition found at 15 kbar. Figure 9 also shows the calculated values of the mode Grüneisen parameters at 0 and 45 kbar. For completeness we also present in figure 10 the calculated acoustic phonon velocities as a function of pressure, which may be compared with Brillouin scattering and ultrasonic measurements. The labels Σ and Λ correspond to the phonons propagating along a^* and c^* respectively.

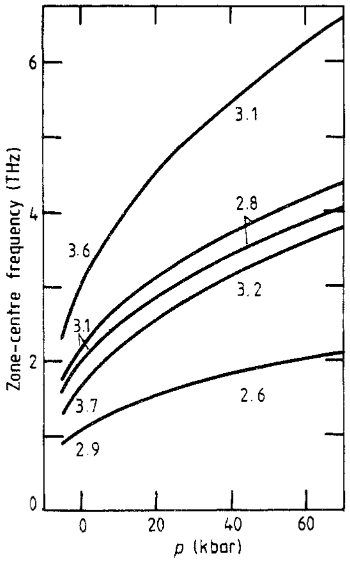

Figure 9. Pressure variation of the calculated external phonon frequencies at the Brillouin zone centre, the Γ point. The mode Grüneisen parameters of different phonon modes at 0 and 45 kbar are indicated. The sequence of the modes in order of increasing frequency is E_{2g}, $A_g + B_u$ (very close pair), E_{2u}, E_{1g} and B_g.

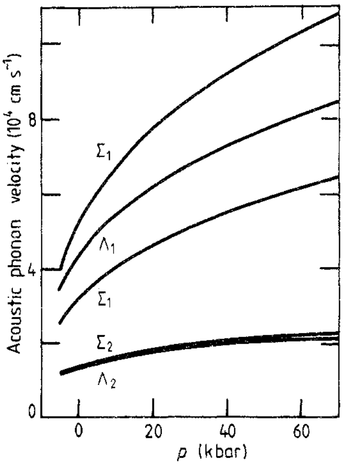

Figure 10. Calculated pressure variation of the acoustic phonon velocities along a^* (Σ) and c^* (Λ) directions. The upper two branches are longitudinal modes, the lower three are transverse modes. The Λ_1 and Σ_2 branches are polarised parallel to the hexagonal axis, the other branches have eigenvectors in the hexagonal plane.

4.3. Molecular dynamics simulation

The effect of finite temperature on the dynamics is best studied by molecular dynamics computer simulation. We focus attention particularly on the possible large-amplitude libration and 120° reorientation of the planar molecule in its plane, as proposed by Nakamura [8] above 296 K. The librational mean square amplitudes, $\langle\theta^2\rangle$, as measured by x-ray diffraction at room temperature [3], are 9.9 and 11.4 deg^2 about the *a* and *c* axes respectively. These values are only slightly larger than the values of 7.3 and 7.8 deg^2 respectively expected from the observed librational phonon frequencies at room temperature. This suggests that the nature of the librational motion is not unusually anharmonic at this temperature. Even the change in the libration frequencies, of about 15% from 11 K to 300 K, is largely due to the implicit anharmonicity, which can be calculated from the observed change in volume [3] arising from thermal expansion and the calculated Grüneisen constants given in figure 9.

We note that the almost dispersion-free nature of the librational phonons as observed by neutron scattering [4] is fully consistent with the model calculations [4, 12], indicating that the libration–libration coupling is negligible. We therefore chose for the molecular dynamics simulation a small macrocell consisting of only 16 molecules. The simulation at 300 K, using a tested program [24], was run for 3000 time-steps of 0.01 ps each, giving 30 ps of simulated time. Only the vibrations about the equilibrium positions were monitored, and no reorientation of any molecule about any axis was observed. This suggests a minimum of 500 ps for the residence time for a molecule between reorientations, corresponding to a quasi-elastic Lorentzian broadening (HWHM) of less than about 0.01 cm^{-1}. The simulation therefore does not support the proposed [8] significant reorientational motion at 300 K. This conclusion is consistent with the large activation energy of 35 kJ mol^{-1} (=4200 K) determined from the phonon half-widths above. We should add, however, that the probability of reorientation would increase if the molecular dynamics sample were larger, and if the flexibility of the molecules were introduced into the simulation. Finally we note that the zero-pressure simulation displayed thermal expansion between 0 and 300 K, approximately 20% higher than observed [3]; this we would expect to decrease for a larger sample of flexible molecules.

5. Conclusion

In this paper we report a detailed investigation of the pressure and temperature dependence of the Raman scattering in $C_6Cl_3F_3$. We have also determined an intermolecular potential, and using this have calculated the structure and dynamics as a function of pressure. The possibility of anomalous molecular reorientation rates has been shown unlikely by molecular dynamics simulations with this potential.

The Raman spectra have been analysed in detail, and anomalies have been found in the intensities, phonon frequencies and line-widths at 296 K at ambient pressure and at 15 kbar at room temperature. Although the flexibility of the molecules and their reorientations could be important, there must be another unidentified activation process of low energy responsible for these anomalies. We also report a new first-order phase transition which needs further investigation by high-pressure x-ray diffraction.

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