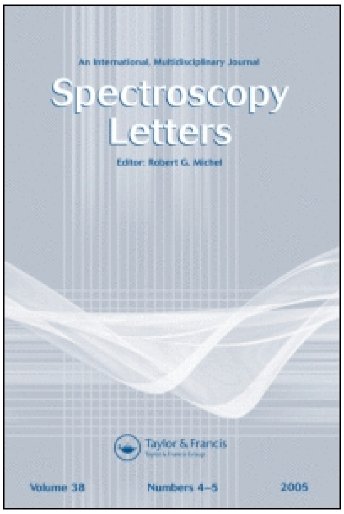

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INFRARED SPECTRA OF BROMOFORM AT HIGH PRESSURES

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ABSTRACT

Infrared spectra in the wavenumber ranges 100–1800 and 2700–4800 cm^{-1} are reported for bromoform samples in diamond anvil cells at ambient temperature and at pressures up to 10 GPa. The freezing pressure is estimated to be 0.13 ± 0.02 GPa. The spectra appear to evolve smoothly and no major discontinuities are detected. The dependence on pressure of eleven peak wavenumbers (five fundamentals and six combinations) is presented. All modes show small percentage increases in wavenumber over this pressure range, except for the degenerate bend, ν_6, which exhibits a 20% increase, suggesting that the equilibrium Br-C-Br angles may be slightly changing with increasing pressure.

Key Words: Infrared spectra; High pressures; Bromoform; Molecular crystals.

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INTRODUCTION

Bromoform, $CHBr_3$, is known to exist in at least three different crystalline phases (1). At ambient pressures, the liquid freezes at 281 K to form the α-phase, shown in Figure 1, which is stable down to 268 K. The molecules are dynamically disordered with their principal axes randomly parallel or anti-parallel to each other. The average symmetry is represented by the space group $P6_3/m$ or C_{6h}^2, with four

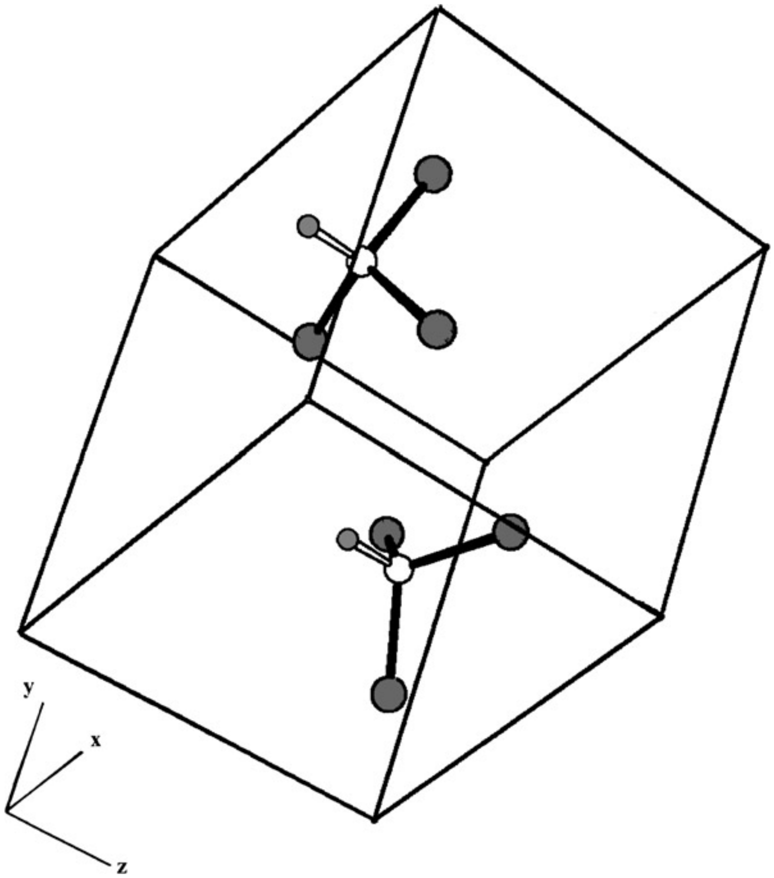

Figure 1. Crystal Structure of Bromoform: α-Phase. The hexagonal unit cell has two dynamically disordered molecules, with their principal axes (C−H bonds) randomly parallel (as shown) or anti-parallel to each other along the crystallographic z-axis. In the ordered β and γ-phases, the two molecules are anti-parallel to one another. Adapted from Ref. 1.

molecules per unit cell, each with an occupancy of 0.5. Rapid cooling of the liquid to liquid nitrogen temperatures produces the metastable γ-phase, in which the dynamical disorder has been frozen out. The structure is now described by the centrosymmetric trigonal space group $P\bar{3}$ or C_{3i}^{1}. The two molecules in the unit cell are anti-parallel, and the arrangement can be considered as comprising bilayers of bromine triangles parallel to the basal plane with hydrogen atoms in the interior. The stable ordered β-phase is obtained either by an irreversible transition from the γ-phase, by annealing at temperatures above 200 K, or by slow cooling of the disordered α-phase. The resulting transformation mainly involves a translational motion of one bilayer relative to its neighbours, with a consequent tilt of the c axis. The space group is now centrosymmetric triclinic, $P\bar{1}$ or C_{i}^{1}, and again contains two anti-parallel molecules.

In addition to a neutron diffraction study (1), these structural phase transitions have also been investigated by Raman and infrared studies of samples at low temperatures (2,3). Group theoretical predictions, based on the known structures, are generally confirmed by the observed spectra. In particular, splittings of some degenerate modes in the low symmetry β-phase are detected. Theoretical analyses of the phase transitions have also been reported (4–5).

At ambient temperatures and elevated pressures, bromoform crystallizes and undergoes two solid state phase transitions, as shown by two independent Raman studies (6,7). The freezing pressure is reported to be 0.1 GPa[6] or 0.33 GPa[7]. Although no direct structural determinations at high pressures have been published, it was deduced from the Raman spectra that the α-phase is first formed and that this transforms to the β-phase at 1.0 GPa[6] or 0.8 GPa[7]. At higher pressures, quoted as 4.2 GPa[6] or 5.15 GPa[7] a second transition to the γ-phase is postulated, but with mixed phases, $\beta + \gamma$, coexisting over an extended pressure range. The pure γ-phase, which is metastable at ambient pressure and low temperature, is thought to become stable at high pressures. However, the observed spectroscopic changes are relatively minor, so that the above interpretations, which agree qualitatively but differ quantitatively, should be regarded as somewhat speculative.

The purpose of the present investigation is to provide confirmation and perhaps clarification of the conclusions reached from the Raman studies, by obtaining infrared spectra of bromoform at ambient temperatures and at pressures up to 10 GPa. To the best of our knowledge, no previous infrared spectra of bromoform at high pressures have been published. Since all three phases are centrosymmetric, the exclusion rule requires that the infrared active modes are distinct from those observed in the Raman studies. In particular, changes in the spectra indicative of phase transformations will be checked, as well as evidence for molecular distortion or perturbation of electronic states at high pressures. The dependence of normal mode wavenumbers on pressure will be determined and used to obtain estimates of changes to principal force constants.

EXPERIMENTAL DETAILS

Liquid bromoform was supplied by J.T. Baker Chemicals and had a stated purity of >99%. Samples were loaded into a diamond anvil cell (DAC) of the piston- cylinder type. This was fitted with type IIa diamonds, which have superior transmission in the mid-infrared region, and an Inconel gasket. The latter was pre-indented by the diamonds to give an initial sample thickness of about .025 mm and then drilled to give a sample diameter of 0.38 mm (volume about 3×10^{-3} mm^3). A few grains of ruby powder were added to the sample chamber to allow in situ measurements of the pressure, using the well-known fluorescence technique (8).

Far-infrared spectra (100–400 cm^{-1}) were recorded with an evacuated Fourier transform spectrometer, equipped with a high pressure mercury lamp as source, Mylar beam divider and silicon bolometric detector, operating at 4.2 K. Radiation was focused on to the DAC, mounted next to the window of the bolometer cryostat, by means of an off-axis ellipsoidal mirror. Spectral resolution was 2 cm^{-1}, and transmittance spectra were obtained by ratioing sample and background transformed interferograms from slow scans, each taking about 15 minutes. Wavenumber accuracy and resolution performance were checked periodically by recording the well- documented spectrum of water vapour.

Mid-infrared spectra (400–4800 cm^{-1}) were obtained using a rapid scan FTIR spectrometer, equipped with a potassium bromide beam divider, water-cooled globar source, air-bearing mirror movement and pyroelectric (DTGS) detector. The instrument was continuously purged to eliminate water vapour and carbon dioxide. Polished brass coned light-pipes were placed on both sides of the DAC to increase the transmission through these small area samples. Spectral resolution was again 2 cm^{-1} and transmittance spectra were obtained by taking the ratio of sample and background transformed interferograms, derived from 2000 and 1000 co-added rapid scans respectively. Wavenumber accuracy and resolution performance were checked by recording the spectrum of polystyrene film.

Ruby fluorescence spectra were excited by the 514.5 nm line of an argon ion laser operating at powers up to 100 mW, and recorded with a double monochromator equipped with a cooled photomultiplier detector, coupled to photon counting electronics. Pressure gradients in the sample, estimated by monitoring the widths of the ruby peaks, were insignificant except at the highest applied pressures, near 10 GPa. To avoid hysteresis effects, spectra were always recorded after increasing the pressure by small increments of about 0.5 GPa and allowing equilibrium to be established. For some spectra, especially for samples at low pressures, interference fringes were present. These could usually be reduced by adjusting the DAC screws asymmetrically to slightly degrade the parallelism of the opposing diamond faces.

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RESULTS

Infrared spectra of solid bromoform at three selected pressures are shown in Figure 2. The wavenumbers of eleven peaks (five fundamentals and six combinations), which could be unambiguously tracked over the pressure range 0 to 10 GPa, are plotted as a function of pressure in Figure 3. These have been fitted to linear curves, the intercepts and slopes of which are listed in Table 1, which also contains correlation coefficients, percentage wavenumber changes over this pressure range, and suggested assignments. For the present work, wavenumber accuracy is estimated to be ±1 cm^{-1} and pressure errors should be less than ±0.1 GPa except at the highest values where they could approach ±0.3 GPa.

DISCUSSION

Bromoform is a symmetric top molecule, with point group C_{3v}. It has $3 \times 5 - 6 = 9$ degrees of internal freedom, which, by standard group theoretical analysis, result in six normal modes of species $3A_1 + 3E$, with all modes Raman and infrared active. Selected wavenumber values for these modes of isolated molecules have been documented by Shimanouchi (9). In the liquid and α-phase crystal, the dynamical disorder will give broader and slightly shifted peaks as a result of intermolecular perturbations. The spectra of the ordered β and γ-phases can be predicted by the correlation method (10) linking the symmetry species of the free molecule, site and unit cell, as shown in Figure 4. This indicates that in the γ-phase no splittings of any modes (apart from those resulting from isotopic effects which are known to be very small) should be observed in either Raman or infrared spectra. In the lower symmetry β-phase, splittings of the degenerate E modes are predicted and have been observed for samples at low temepratures (2,3). However, the separations between peaks are small, and at ambient temperature and elevated pressures, the peaks are significantly broader, and splittings are not likely to be resolved.

The correlation diagram also predicts two far-infrared librational modes for the γ-phase, with that for the L_{xy} mode (hindered rotation about axes perpendicular to the principal molecular axis) splitting into two components for the β-phase. Because of the large moments of inertia for the $CHBr_3$ molecule, these librational modes are at very low waveneumbers (2,3) (<60 cm^{-1}) and could not be observed in the present study. It was also found that the ν_3 mode near 220 cm^{-1} was too broad and weak to be consistently detected at higher pressures.

Our estimate of the freezing pressure of bromoform at ambient temperature, 295 K, obtained by careful measurements of the ruby fluorescence spectrum for a DAC sample in which solid and crystal co-existed, as viewed in a polarizing

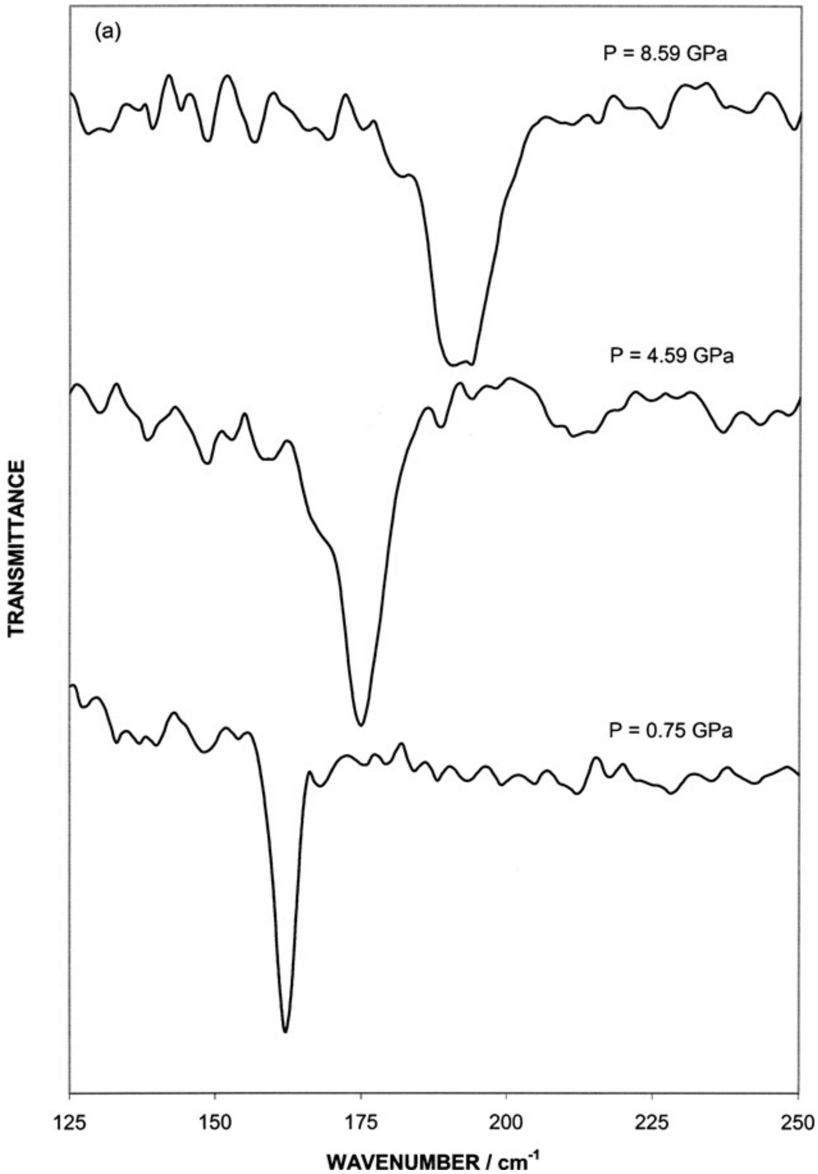

Figure 2. Infrared Spectra of Solid Bromoform at Three Selected Pressures. (a) 125–250; (b) 500–1500; (c) 2950–3150; (d) 4000–4400 cm^{-1}.

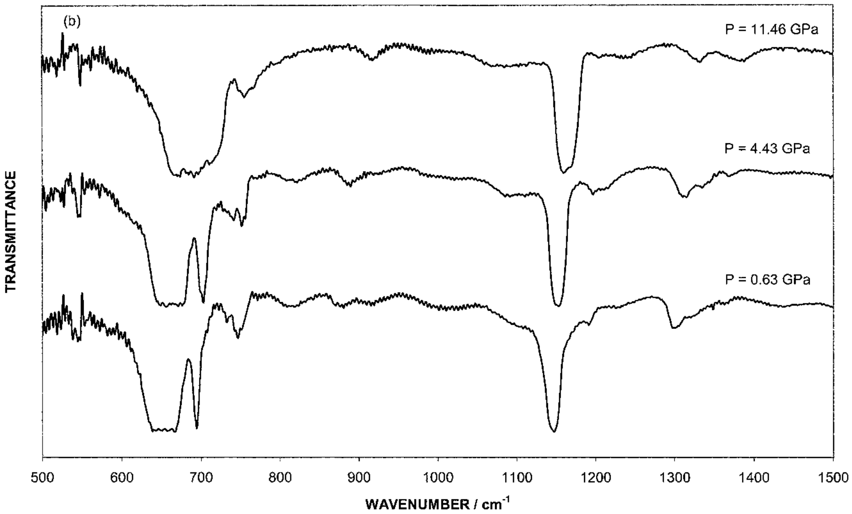

Figure 2. *Continued*

(*continued*)

microscope, is 0.13 ± 0.02 GPA, which is in excellent agreement with a previous estimate (6). The polycrystalline sample usually formed could be converted into a monocrystal by loosening the DAC screws until a small single crystallite remained, and then slowly tightening them again. Other than occasional cracking of the monocrystal at higher pressures, no further changes were observed in the microscope – in other words there is no visual evidence of any solid state phase transitions. The infrared spectra also appear to evolve smoothly and show no evidence of abrupt changes, and the wavenumber versus pressure curves show no obvious discontinuities.

It is possible that the extremely thin samples required for these transmission experiments behave differently than bulk samples, with the solid state phase transitions being inhibited by the increases significance of surface effects. Alternatively, the changes in the infrared spectra related to these three very similar structures may be relatively minor and escape detection. It is probably significant that the peaks which show the largest changes in the Raman studies (6,7) are related to lattice modes and ν_3, the symmetric deformation internal mode, none of which could be detected in this infrared study. We conclude that these infrared spectra are unfortunately inconclusive in confirming these phase transitions and establishing the pressures at which they occur. In view of the fact that other simple molecular crystals have been shown to have different structures at high pressures than at low temperatures (11,12), and because changes in the observed spectra

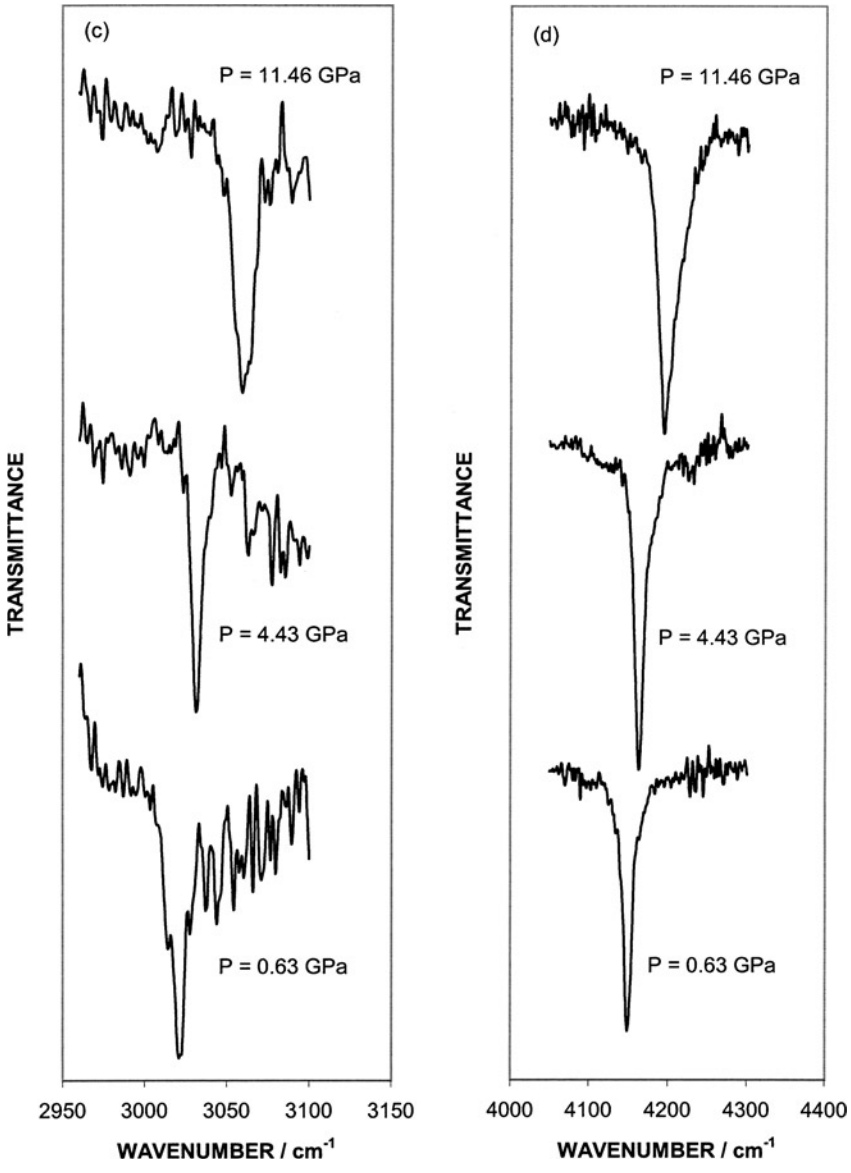

Figure 2. *Continued*

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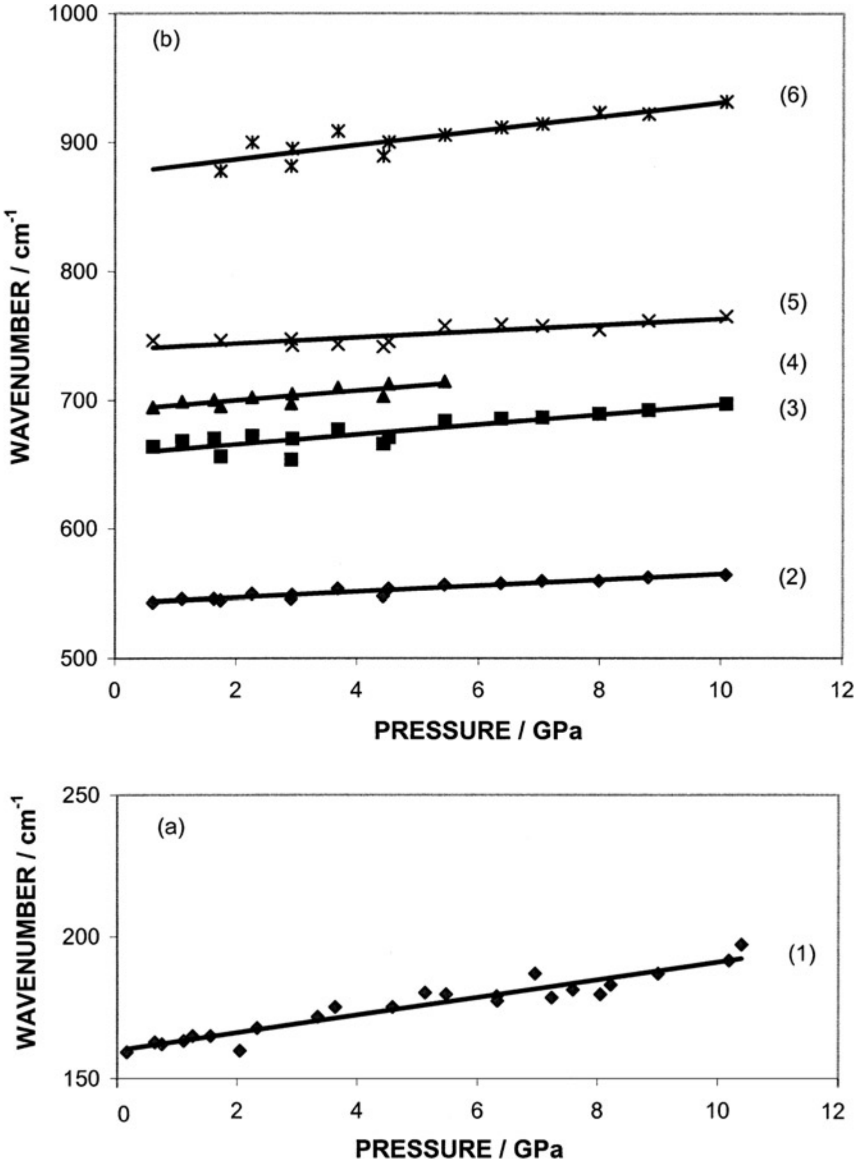

Figure 3. Plots of Peak Wavenumbers versus Pressure for Solid Bromoform. (a) 150–250; (b) 500–1000; (c) 1100–1400; (d) 3000–4500 cm^{-1}. Lines are labelled 1 to 11 with corresponding slopes and intercepts listed in Table 1.

(*continued*)

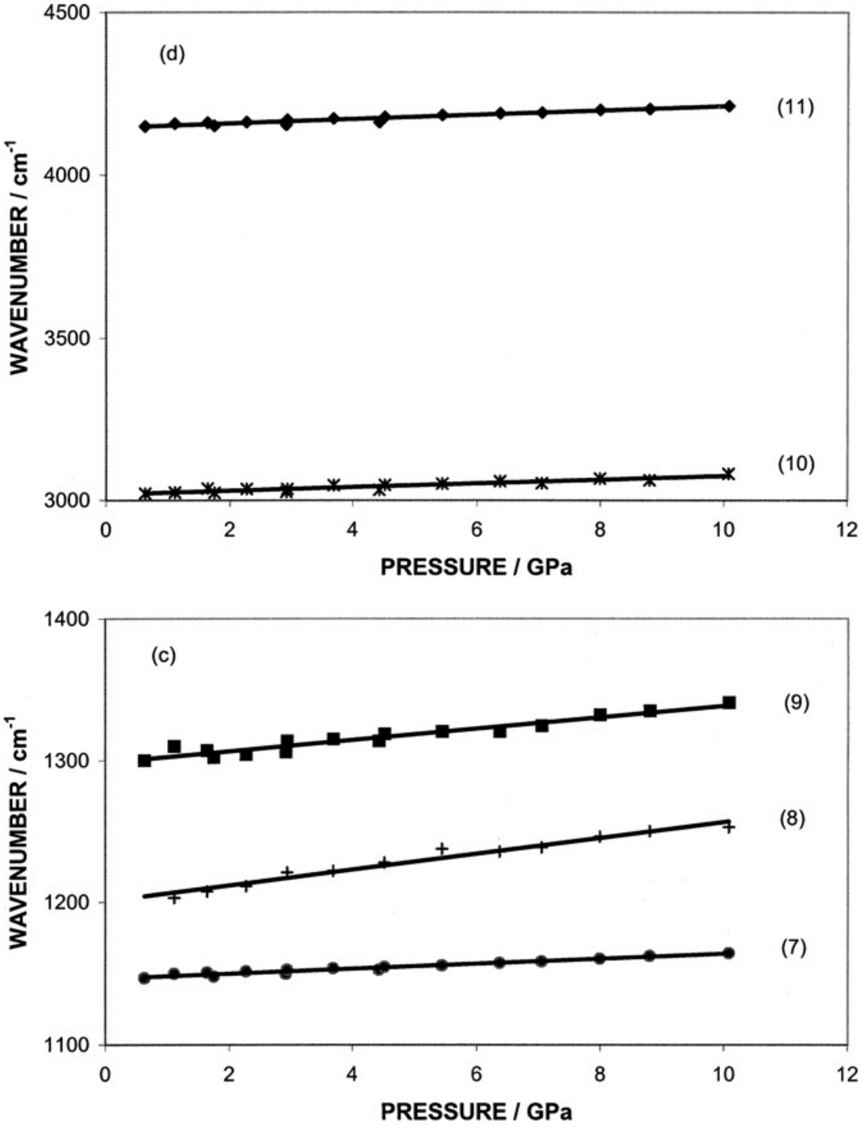

Figure 3. *Continued*

Table 1. Linear Fits to Wavenumber Versus Pressure Curves

Line No.*	Intercept (cm^{-1})	Slope (cm^{-1}/GPa)	R^2 Value†	Change (%)	Assignment
1	159.9	3.11	0.92	19.4	ν_6
2	542.3	2.26	0.92	4.2	ν_2
3	658.0	3.86	0.76	5.9	ν_5
4	692.2	3.81	0.73	5.5	$\nu_2 + \nu_6$
5	739.3	2.41	0.70	3.2	$\nu_2 + \nu_3$
6	875.6	5.54	0.80	6.3	$\nu_3 + \nu_5$
7	1146.5	1.73	0.96	1.5	ν_4
8	1200.7	5.58	0.96	4.6	$\nu_2 + \nu_5$
9	1298.5	4.00	0.93	3.1	$\nu_4 + \nu_6$
10	3017.6	5.77	0.88	1.9	ν_1
11	4145.4	6.65	0.93	1.6	$\nu_1 + \nu_4$

* See Fig. 3.
† R is correlation coefficient.

are relatively small, we believe that the phase transitions in bromoform require further study, particularly with X-ray or neutron diffraction techniques, before it is established that the sequence with increasing pressure is the one proposed on the basis of Raman studies (6,7), namely liquid $\rightarrow \alpha \rightarrow \beta \rightarrow \beta + \gamma \rightarrow \gamma$.

The infrared spectra are appreciably richer than their Raman counterparts, with many second order features being detected, some being surprisingly more

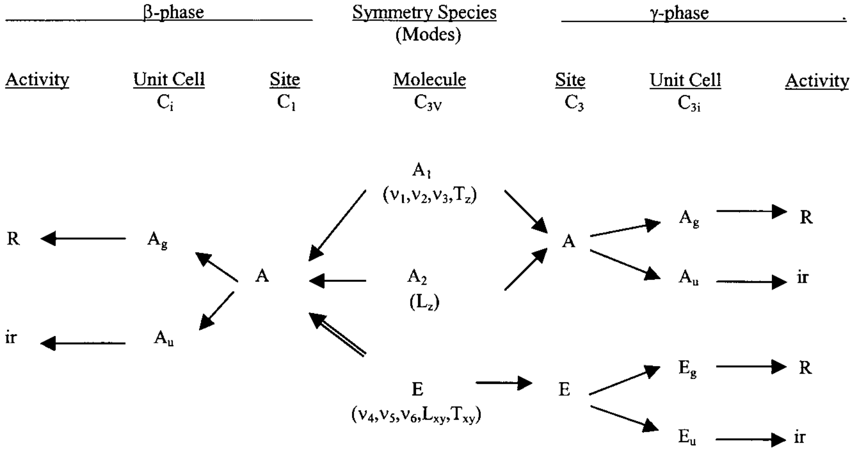

Figure 4. Correlation Diagram for Solid Bromoform: β and γ-phases. ν_n internal modes; L: librations; T: translations; R: Raman active; ir: infrared active.

intense than fundamentals. For example, at all pressures the combination $\nu_1 + \nu_4$ is about four times more intense than the fundamental ν_1. The percentage changes in the peak wavenumbers over the pressure range 0 to 10 GPa are generally quite small, as seen in Table 1, indicating that molecular distortion is relatively minor. The only exception is the low wavenumber fundamental ν_6, where the change is close to 20%. This suggests that the equilibrium Br-C-Br angles may change slightly, as pressure is increased and the bromine bilayers are forced into closer proximity.

Work is in progress on the infrared spectra of the related compounds iodoform and chloroform at high pressures and will be reported in later papers.

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