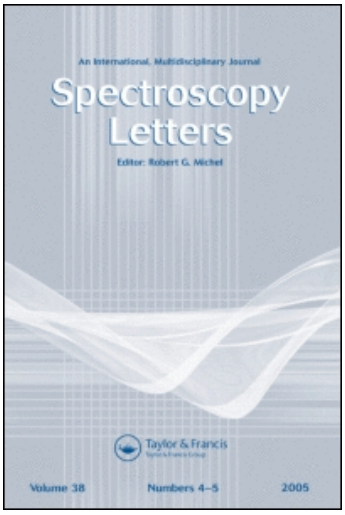

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RAMAN AND INFRARED SPECTRA OF IODOFORM AT HIGH PRESSURES

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ABSTRACT

Raman and infrared spectra are reported for iodoform samples in diamond anvil cells at ambient temperature and at pressures up to 5 GPa (Raman) and 10 GPa (infrared). The spectra appear to evolve smoothly and no evidence of any structural phase transitions is found. The dependence on pressure of 7 Raman and 13 infrared peak wavenumbers is presented. A large increase in intermolecular bonding strengths is confirmed, together with a moderate increase in intramolecular I-C-I bending forces. Color changes in the samples at high pressures are found to be mostly reversible, but long exposure to high fluxes of visible photons causes some molecular dissociation, with the release of iodine.

Key Words: Raman spectra; Infrared spectra; High pressures; Iodoform; Molecular crystals

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INTRODUCTION

In a recent paper from this laboratory, infrared spectra of the molecular crystal, bromoform $CHBr_3$, at high pressures were reported.[1] Results were compared to previous studies using Raman spectroscopy.[2,3] In this communication, we report on the Raman and infrared spectra of a related compound, iodoform CHI_3, at pressures up to 10 GPa.

Like the other haloforms, CHI_3 is a pyramidal symmetric top molecule, described by point group C_{3v}. The nine degrees of internal freedom lead to three non-degenerate symmetric modes (a_1 species) and three doubly degenerate asymmetric modes (e species), all of which are both infrared and Raman active. Wavenumber values for these normal modes have been given by Krasnov et al.[4] and by Medina et al.[5] and are listed in Table 1.

Unlike bromoform, which is known to have three crystalline phases in the temperature range 10–300 K at ambient pressure, only one phase of iodoform has been observed under these conditions. At elevated pressures and ambient temperature, an early suggestion by Bridgman[6] of several "small but definite transitions" between 0 and 5 GPa has never been confirmed.[7] The crystal structure of iodoform under ambient conditions has been determined by X-ray diffraction.[8,9] The unit cell is hexagonal with space group $P6_3(C_6^6)$, and contains two molecules on C_3 sites, as shown in Fig. 1. There is no dynamic disorder of the type found in the high temperature phase of bromoform.[1] All molecular C-H bonds are parallel to the c-axis of the unit cell, with triangles of iodine atoms perpendicular to this axis and with adjacent layers oriented at 60° to their neighbors.

Again in contrast to $CHBr_3$, in which all three crystalline phases are centrosymmetric, the CHI_3 structure has no inversion center and the unit cell has a net dipole. The spectroscopic consequence of this is that many modes are both Raman and infrared active.

There have been several previous spectroscopic studies of the vibrations of iodoform. These include Raman and infrared work on crystals

Table 1. Normal Mode Wavenumbers (cm^{-1}) of Iodoform

Mode	Mode Description	Krasnov et al.[4]	Medina et al.[5]
ν_6	Asymmetric C-I_3 bend	105	109
ν_3	Symmetric C-I_3 bend	153	152
ν_2	Symmetric C-I stretch	437	428
ν_5	Asymmetric C-I stretch	578	575
ν_4	C-H bend	1067	1060
ν_1	C-H stretch	3038	2977

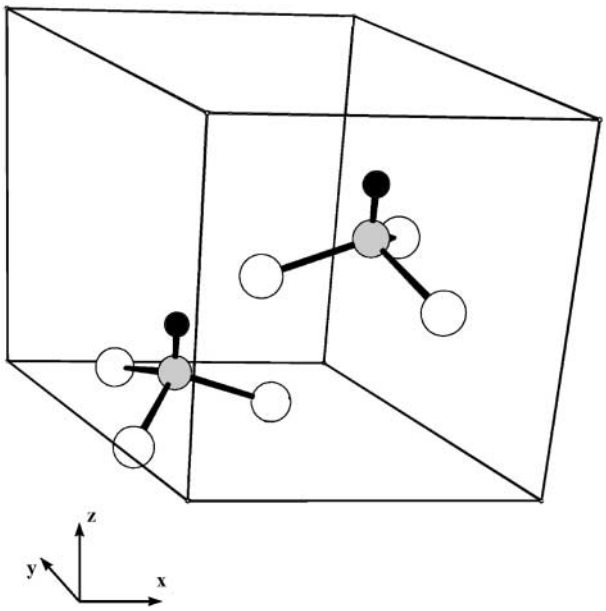

Figure 1. Crystal structure of iodoform. One third of the hexagonal unit cell is shown with the C-H axes of the two molecules aligned along the crystallographic c-axis. (data from Refs. 8,9).

between 10 and 300K by Neto et al.[10] and by Medina et al.,[5] as well as Raman papers by Dawson[11] and Dawson and Berenblut.[12] Some preliminary studies of iodoform at elevated pressures have been reported by Medina et al.[5] and by Cundill and Sherman,[13] but these were limited to pressures below 1.4 and 2.5 GPa respectively.

The aims of the present study are to extend Raman and infrared measurements to higher pressures, to check for evidence of any crystallographic phase transitions, to investigate any color changes and determine whether they result from shifts in the electronic band edge or from molecular dissociation, and to obtain estimates of changes in intermolecular and intramolecular force constants at these high pressures.

EXPERIMENTAL DETAILS

Crystalline CHI_3, a bright yellow powder, was purchased from Aldrich Chemicals and had a stated purity of >99%. Small single crystals were

grown from an acetone solution in an inert atmosphere and transferred to a diamond anvil cell (DAC) of the piston-cylinder type, fitted with an Inconel gasket. Typical sample sizes were 0.25 mm diameter and 0.12 mm thickness for Raman experiments and 0.38 mm diameter and 0.025 mm thickness for infrared measurements. For some mid-infrared samples, to avoid saturation of two strong fundamentals, CHI_3 powder was diluted in an approximate 1:5 ratio in potassium bromide before loading. A few grains of ruby powder were added to all samples for in situ pressure measurements.

Raman spectra were excited by an argon ion laser operating at a wavelength of 514.5 nm. Laser powers were kept as low as possible ($<$100 mW) to minimize sample damage. A back-scattering geometry was used, with radiation captured by a large aperture camera lens and focussed on the entrance slit of a double-monochromator. The detector was a photomultiplier, with cooled photocathode, coupled to photon counting electronics. Signals were processed by a personal computer which was also programmed to control spectrometer scans. A third monochromator could be introduced into the optical system for scans close to the exciting line. Wavelength calibration and resolution performance were periodically checked by recording plasma lines from the laser. These could be suppressed if necessary by means of a spike interference filter.

Infrared spectra were recorded on two Fourier transform instruments, one covering the far-infrared region (100–400 cm^{-1}) and the other the mid-infrared region (400–4800 cm^{-1}). Details of these spectrometers and the experimental techniques employed have been described in an earlier paper[1] and will not be repeated here.

The Raman spectrometer was also used for sample pressure measurements by means of the well-known ruby fluorescence method.[14] The widths of the two ruby spectral lines served as a convenient indicator of pressure gradients in the samples and these were minimal except at the highest pressures for the infrared samples. To minimize hysteresis effects, spectra were always recorded after increasing the pressure by small increments ($\sim$0.5 GPa) and allowing time for equilibrium to be established.

For all experiments, a spectral resolution of 2 cm^{-1} was used. Peak wavenumbers are estimated to be accurate to ± 1 cm^{-1} and errors in pressure measurements should be less than 0.1 GPa, except at the highest values ($>$9 GPa) where they could approach ± 0.3 GPa because of inhomogeneities in the samples.

RESULTS

Raman spectra of iodoform at ambient temperature and at three selected pressures are shown in Fig. 2. These measurements are limited to

pressures below 5 GPa because of severe darkening of the samples from yellow to orange to red to black and the resulting strong absorption leading to very weak Raman signals. These color changes are mostly reversible on release of pressure and are therefore attributed to shifts of the band edge in the visible spectrum. However, there is also evidence of some irreversible damage to the sample resulting from molecular dissociation with release of iodine, especially for higher laser powers and longer time exposures. Nevertheless, this smaller pressure range still represents a considerable extension over previous Raman work[5] which was limited to pressures below 1.4 GPa. Plots of wavenumbers vs. pressure for seven peaks which could be tracked over this pressure range are presented in Fig. 3. These have been fitted to linear functions, the slopes and intercepts of which are listed in Table 2, together with assignments and percentage changes of wavenumber over the range 0–5 GPa.

Far-infrared spectra of CHI_3 at three selected pressures are shown in Fig. 4, and corresponding mid-infrared spectra are displayed in Fig. 5. Since for these measurements, high fluxes of visible photons were avoided (ruby fluorescence experiments require only low levels) sample damage was avoided, and the color changes had no effect on the quality of the infrared absorption spectra. Hence spectra could be recorded for samples over a wider pressure range, 0–10 GPa, a considerable extension over previous work.[13] The rich spectra included all six intramolecular fundamentals and several combination bands. Lattice modes, which are at very low wavenumbers ($<60\,cm^{-1}$) could not be observed in this infrared study.

As can be seen in Fig. 5, two of the fundamentals, ν_4 and ν_5, are so strongly absorbing that saturation effects were observed for even the thinnest possible samples. To avoid this, dispersion of CHI_3 powder in a KBr matrix was used and the resulting spectra are shown in Fig. 6. Plots of wavenumber against pressure for 13 peaks which could be tracked over the whole pressure range are shown in Fig. 7. These have been fitted to linear curves, and their slopes and intercepts are listed in Table 3, together with suggested assignments and percentage changes in wavenumber over the pressure range 0–10 GPa. One mode, near $400\,cm^{-1}$, was observed with both far- and mid-infrared instruments, and its pressure dependence is displayed twice, with lines #3a and #3b respectively, which are in satisfactory agreement. In general, consistency between Raman and infrared data of corresponding modes is good, especially for the intercepts. Small discrepancies for values of the slopes are attributed to the limited range of pressures available for the Raman data.

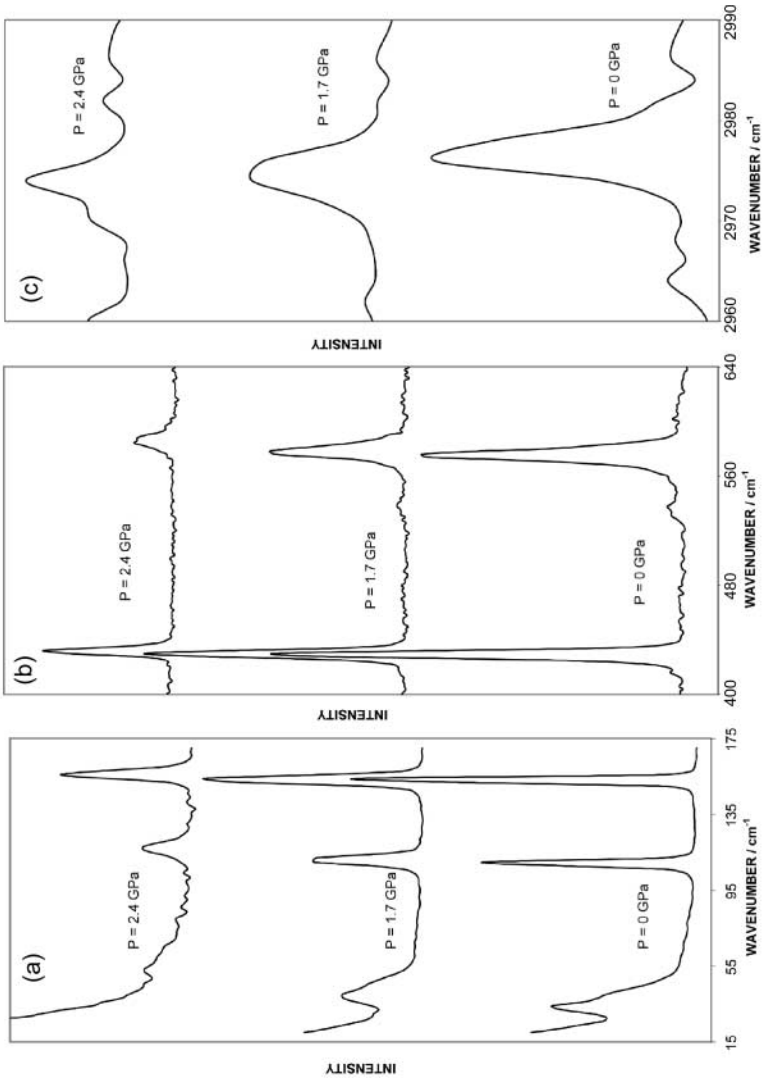

Figure 2. Raman spectra of solid iodoform at three selected pressures. (a) 15–175 cm^{-1}; (b) 400–640 cm^{-1}; (c) 2960–2990 cm^{-1}.

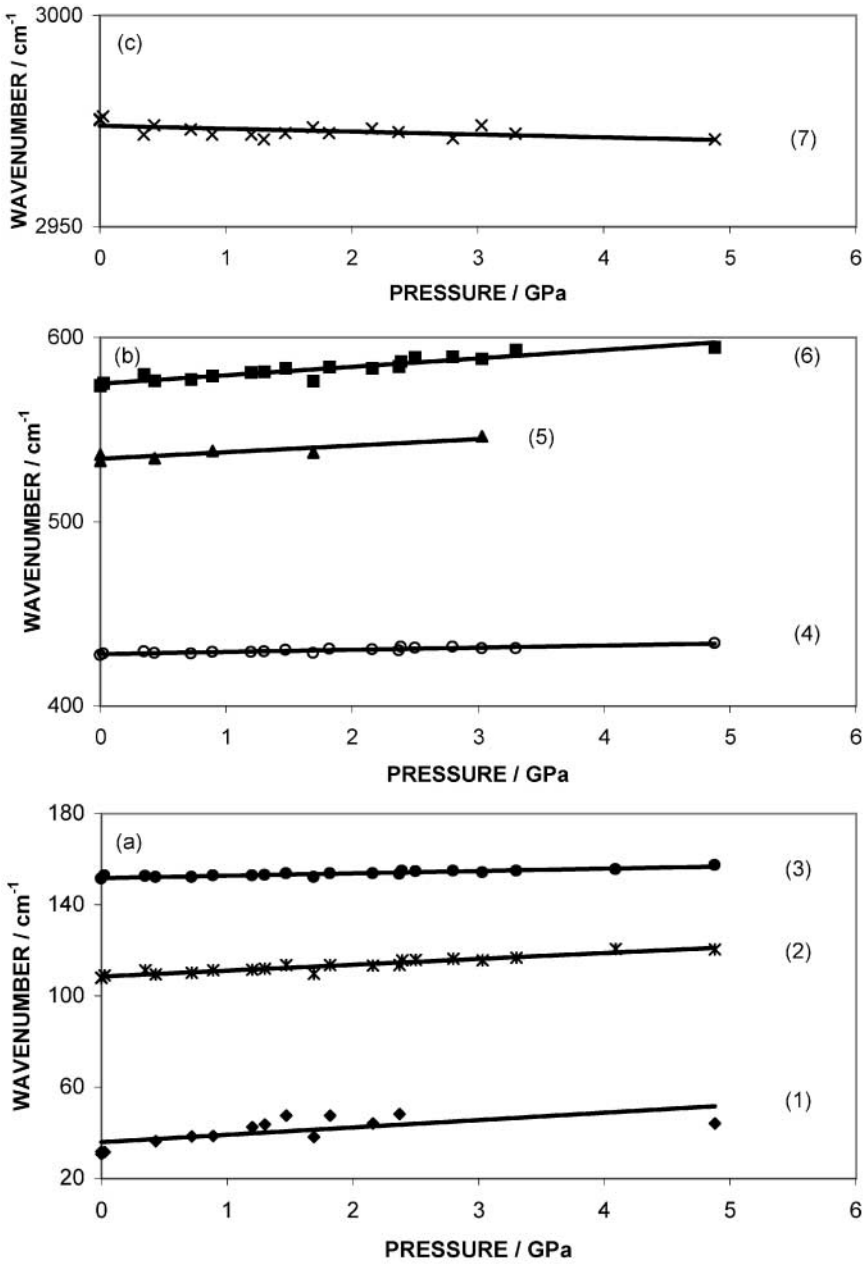

Figure 3. Plots of Raman peak wavenumbers vs. pressure for solid iodoform. (a) 20–180 cm^{-1}; (b) 400–600 cm^{-1}; (c) 2950–3000 cm^{-1}.

Table 2. Linear Fits to Wavenumber vs. Pressure Curves for CHI_3 (for Raman Data)

Line #	Intercept (cm^{-1})	Slope (cm^{-1}/GPa)	R^2-Value	% Change	Assignment
1	35.7	3.25	0.46	45.5	ν_L
2	108.4	2.58	0.91	11.9	ν_6
3	151.7	1.01	0.86	3.3	ν_3
4	427.9	1.20	0.84	1.4	ν_2
5	534.0	3.60	0.84	3.4	$\nu_2 + \nu_6$
6	574.9	4.54	0.87	3.9	ν_5
7	2973.9	−0.68	0.31	0.1	ν_1

DISCUSSION

There is no evidence from either the Raman or infrared spectra in this study of any solid state phase transitions for pressures up to 10 GPa. The spectra evolve smoothly with no observable discontinuities. Hence a discussion of the observed spectra will be presented in terms of the crystal structure determined at ambient pressure.[8,9] The correlation diagram for crystalline CHI_3, linking the symmetry species of the free molecule, site and unit cell, has been published previously[12] and gives the following results:

$$\text{Internal modes. } \nu_1, \nu_2, \nu_3\text{: } A(\text{Rir}) + B(-); \nu_4, \nu_5, \nu_6\text{: } E_1(\text{Rir}) + E_2(\text{R});$$

$$\text{Lattice modes. Librations: } A(\text{Rir}) + B(-) + E_1(\text{Rir}) + E_2(\text{R});$$

$$\text{Translations: } (A + E_1)(\text{acoustic}) + B(-) + E_2(\text{R}).$$

In the Raman spectra, a lattice peak with a high frequency shoulder, both assigned as librations, ($A + E_1$ species)[5] are observed under ambient conditions. These merge as the pressure is increased and show a sharp increase in wavenumber, the percentage change being 45.5%, corresponding to a 91% increase in intermolecular force constants over the pressure range 0–5 GPa, if harmonic interactions are assumed. One of the internal modes, ν_6 the degenerate bend, shows an increase of nearly 12% over the pressure range 0–10 GPa, which indicates a strengthening of the principal I-C-I intramolecular bending forces, possibly with a small change in the equilibrium I-C-I angles, as the molecules are forced into closer proximity. A similar effect was observed for bromoform.[1] The other internal modes

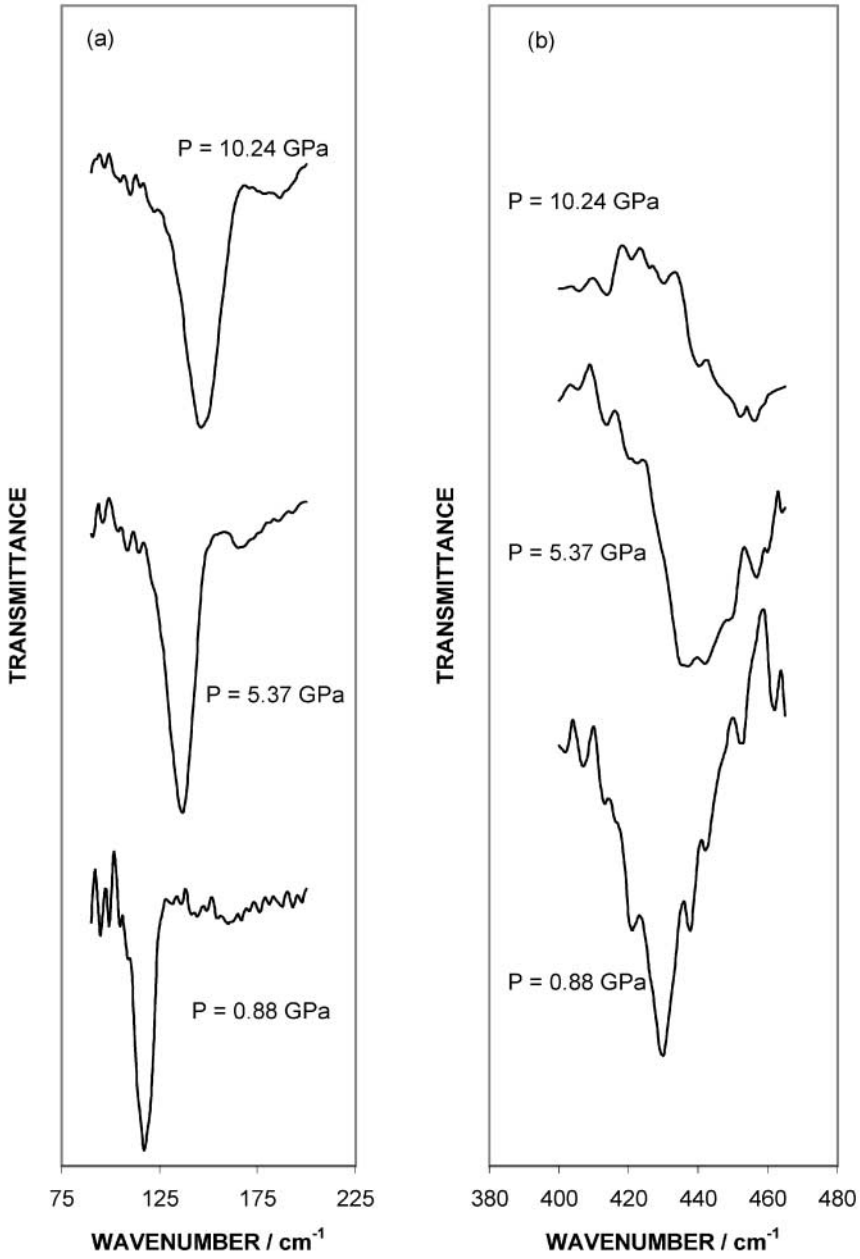

Figure 4. Far-infrared spectra of solid iodoform at three selected pressures. (a) 75–225 cm^{-1}; (b) 380–480 cm^{-1}.

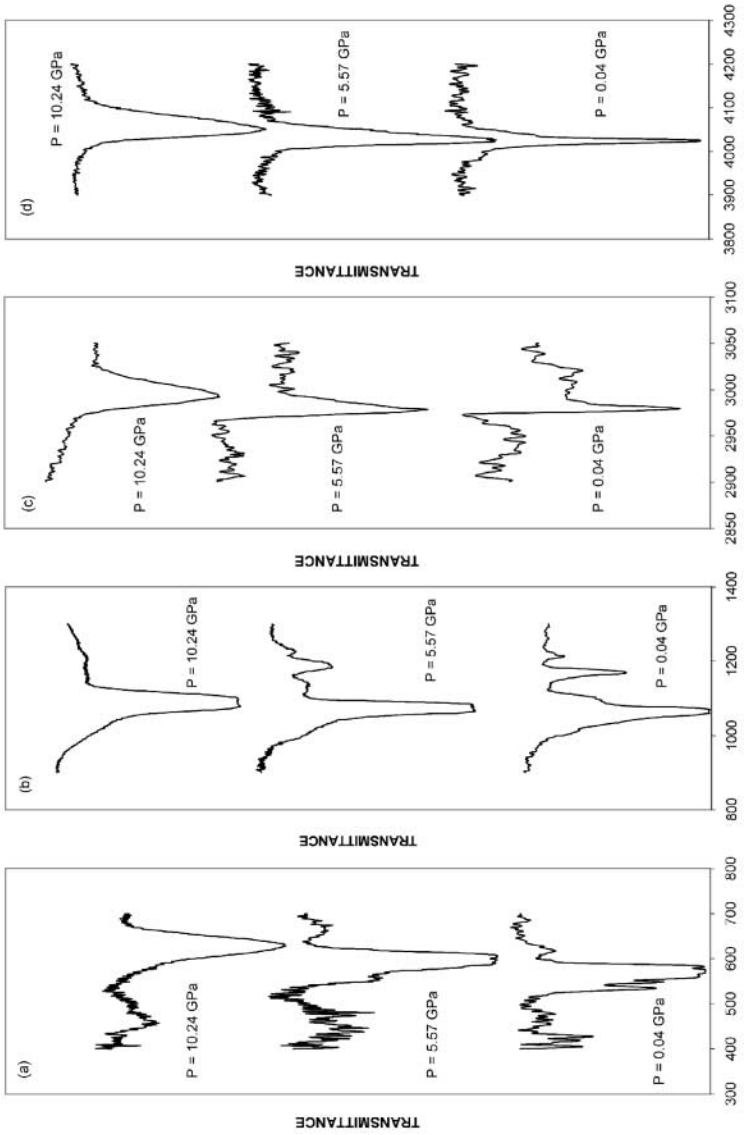

Figure 5. Mid-infrared spectra of solid iodoform at three selected pressures. (a) 300–800 cm^{-1}; (b) 800–1400 cm^{-1}; (c) 2850–3100 cm^{-1}; (d) 3800–4400 cm^{-1}.

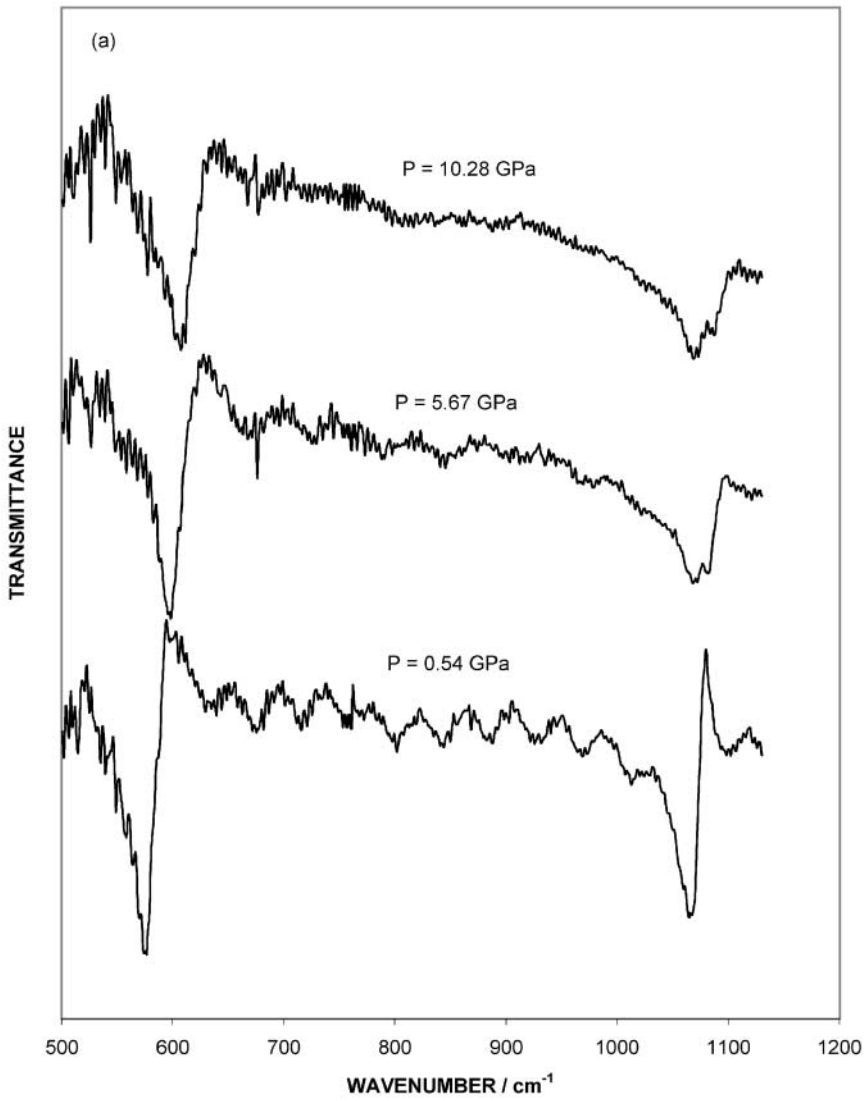

Figure 6. Mid-infrared spectra of solid iodoform (dispersed in KBr) at three selected pressures. 500–1200 cm^{-1}.

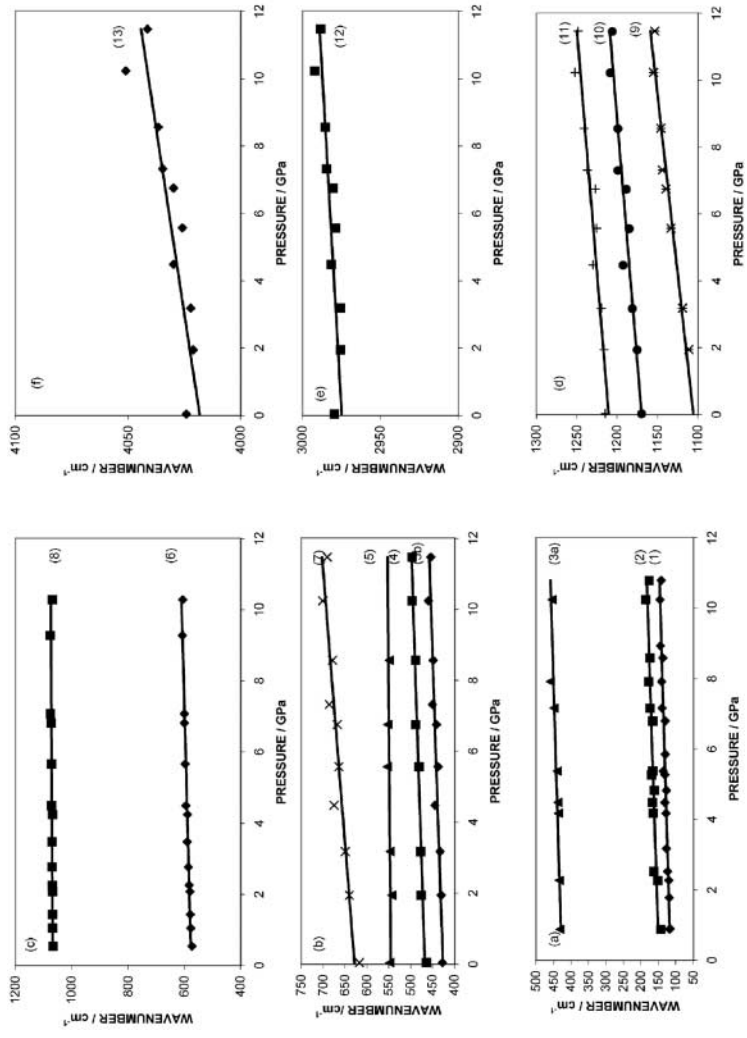

Figure 7. Plots of infrared peak wavenumbers vs. pressure for solid iodoform. (a) 50–500 cm^{-1}; (b) 400–750 cm^{-1}; (c) 400–1200 cm^{-1} (for samples dispersed in KBr); (d) 1100–1300 cm^{-1}; (e) 2900–3000 cm^{-1}; (f) 4000–4100 cm^{-1}.

Table 3. Linear Fits to Wavenumber vs. Pressure Curves for CHI_3 (from Infrared Data)

Line #	Intercept (cm^{-1})	Slope (cm^{-1}/GPa)	R^2 Value	% Change	Assignment
1	115.4	2.87	0.90	24.9	ν_6
2	147.8	3.31	0.82	22.4	ν_3
3a	425.9	3.08	0.85	7.2	ν_2
3b	426.3	2.73	0.88	6.4	ν_2
4	467.8	2.62	0.94	5.6	$\nu_2 + \nu_L$
5	545.7	0.65	0.34	1.2	$\nu_2 + \nu_6$
6	574.3	3.49	0.95	6.1	ν_5
7	628.3	6.45	0.86	10.3	$\nu_5 + \nu_L$
8	1067.0	0.71	0.53	0.6	ν_4
9	1105.3	4.67	0.95	4.2	$\nu_4 + \nu_L$
10	1169.7	3.40	0.91	2.9	$\nu_4 + \nu_6$
11	1210.4	3.45	0.90	2.8	$\nu_4 + \nu_3$
12	2974.7	1.24	0.71	0.4	ν_1
13	4018.1	2.27	0.77	0.6	$\nu_1 + \nu_4$

show much smaller increases, indicating that molecular distortion is not a major effect for this crystal at high pressures.

The infrared spectra are in general agreement with these interpretations. Both bending modes, ν_3 and ν_6, show substantial increases in wavenumber over the range 0–10 GPa, confirming the pressure effects on the principal I-C-I bending force constant. The other fundamental modes show smaller increases, as do most of the combination modes. There is a minor exception – the peak near 628 cm^{-1}, which is believed to involve a lattice mode, shows a larger increase because of the marked strengthening of intermolecular forces with increase of pressure. Although the C-H stretch, ν_1, has been fitted to a linear function like other modes, closer inspection shows that its wavenumber initially decreases slightly with pressure, confirming the small negative slope obtained from the Raman data, and then increases at higher pressures. This can be interpreted as a small charge transfer effect from the C-H bond to neighboring intermolecular bonds, followed by the more typical overall strengthening as compression is increased.

The other main conclusion from this work is that there is a major shift in the band edge of crystalline iodoform with pressure, resulting in drastic colour changes. In the presence of high fluxes of visible photons, as typically encountered in laser Raman spectroscopy, this leads to irreversible molecular dissociation with the release of iodine. Raman measurements were consequently limited to pressures less than about 5 GPa, but infrared

spectra, which are far less dependent on visible absorption effects, could be obtained up to about 10 GPa. In both cases these represent considerable extensions over previous work. Although good quality infrared data from samples at high pressures are generally more difficult to obtain than corresponding Raman data, this work shows that the infrared technique offers some advantages for color sensitive samples. Moreover, infrared spectra are typically richer, with many more combination modes being observable, as a comparison of Tables 2 and 3 confirms.

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