High-pressure Variable Temperature Raman Studies on Hexamethyl Benzene Crystals

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The Raman spectra of hexamethyl benzene and HMB-d_{18} have been recorded as a function of temperature between 4 K and 400 K and as a function of pressure up to 8kbar. In the low-frequency region, librational and torsional modes have been distinguished. The spectra indicate a phase transition to a high-pressure phase IV. The polarized infrared spectra of single crystals have also been observed at different temperatures.

INTRODUCTION

Hexamethyl benzene has a triclinic unit cell at room temperature containing one molecule.[1] The core of the molecule which lies almost in the (ab) plane of the crystal has the benzene structure. The methyl groups CH_3 are attached to the C_6 frame at each of the six corners. There is a phase transition at 383 K to an orthorhombic structure and a λ-point transition near 115 K.[2-3] These changes then lead to three phases: phase I (438–383 K), phase II (383–115 K) and phase III (<115 K). The structure below 115 K is as yet unknown.

Various physical techniques have been used to study the phase transitions, including neutron scattering, nuclear magnetic resonance, infrared and Raman, ultraviolet and visible spectroscopy.[4-16]

The Raman spectrum of hexamethyl benzene has been given considerable attention recently.[12] The one-phonon spectrum is particularly sensitive to the symmetry of the unit cell, as variations in symmetry are invariably accompanied by changes in selection rules.

The vibrations can conveniently be divided into three types: (1) internal vibrations of the atoms within the molecules; (2) external modes of the whole molecules which may be libratory or translatory; (3) torsional modes of the methyl groups with respect to the benzene frame.

The low-frequency region of the Raman spectrum ($\nu < 200$ cm^{-1}) has been studied extensively in the last few years. Significant changes are observed in the spectrum during the transition from phase II to phase III.

The problem is mainly to differentiate between the bands due to the librational lattice modes and the low-frequency methyl torsional mode, always assuming that there is not too much mixing between these two mode types.

HIGH-PRESSURE TECHNIQUE

With a view to obtaining additional information on the low-frequency Raman spectrum, which may contribute to finding new phases and to our understanding of the nature of phase transitions, a high-pressure study was undertaken. By application of pressure, degeneracies in the spectrum may be removed, and pressure shifts of various bands can be observed.

A new high-pressure cell for Raman spectroscopy has been constructed. The cell, shown in Fig. 1, is designed for 90° scattering geometry. It has been operated at hydrostatic pressures up to 8 kbar. The pressure is obtained by compression of gaseous helium at 2000 p.s.i. by means of a two-stage hydraulic compressor. The advantage of using helium gas is that it enables low-temperature work to be carried out. The cell is cooled by contact with a liquid-nitrogen jacket in an evacuated cryostat to below 100 K.

The cell is constructed of stainless steel and the windows are 3 mm thick single crystal sapphires optically polished and selected for minimum strain pattern. The input window port has a narrow angle suitable for laser excitation, and the output port has a wide angle (F/1.5) to enable efficient collection of the Raman scattered light. The residual laser light is effectively trapped and absorbed in the 1.5 mm gas inlet bore. The total attenuation in light signal due to the cell was found to be about 30% which can be attributed to reflections at the sapphire–air surfaces. A reasonable spectrum of laboratory air was obtained from the cell at atmospheric pressure, with single pass 1 W excitation at 4880 Å. The pressure seals are of the unsupported area type using brass rings to support the windows. These can easily be assembled and disassembled in a few minutes to change samples.
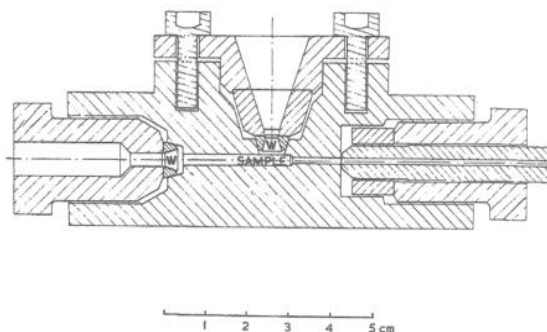

Figure 1. The high-pressure cell for Raman spectroscopy.

The Raman spectra of HMB and HMB-d_{18} have been studied under hydrostatic pressures up to 8 kbar, at temperatures from 300 K to less than 100 K. The sample region in the cell is a cylinder of 2.5 mm diameter and 6 mm length. Single crystals of suitable size and quality were grown from solution in benzene. A Spectra Physics argon ion laser operating at 4880 Å or 5145 Å was used, and to prevent the possibility of localized changes or other damage to the crystals the beam power was limited to about 200 mW. A Carey 81 Raman spectrometer completely modified to improve the stray light figure[17] was used to scan the spectrum to within 15 cm^{-1} of the exciting line, with a resolution of 2 cm^{-1}, and 1 sec integration time. Polarized infrared spectra at various temperatures were recorded with two Grubb Parsons spectrometers with indium antimonide and thermocouple detectors, respectively.

RESULTS

Figure 2 shows a plot of the low frequency Raman band frequencies from 4 K to 400 K and emphasizes the changes which occur at the transition temperatures.

In phase III the lattice frequencies exhibit a discontinuous frequency change at the λ-point. Two Raman bands are observed at 104 and 158 cm^{-1} just below the λ-point which are much higher than the frequencies observed in phase II. From the spectrum of HMB-d_{18} we find the higher frequency ratio $\nu_H/\nu_D = 1.33$ and hence the band is assigned to a methyl torsional vibration. The lower frequency band has $\nu_H/\nu_D = 1.12$ and thus is assigned to a libration about the x and y molecular axes.

In phase II the crystal structure is triclinic with space group C_i. There is one molecule per unit cell occupying a C_i site. The bands at 124 and 64 cm^{-1} at 120 K are associated with librations about the x and y axes (Fig. 3).

In phase I the crystal is orthorhombic with space group D_{2h} and there are four molecules in the unit cell.
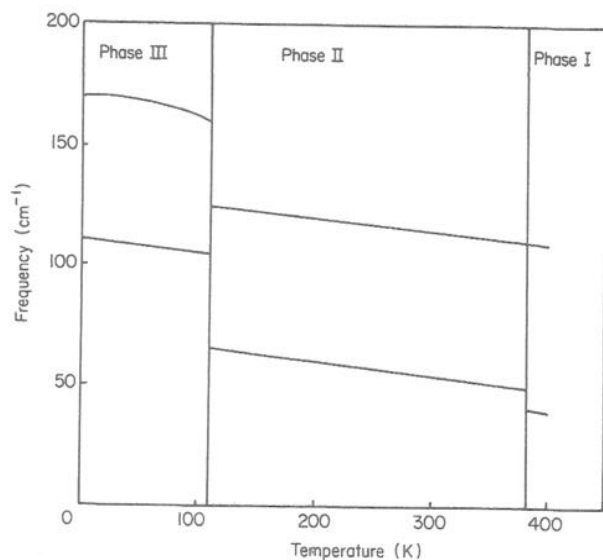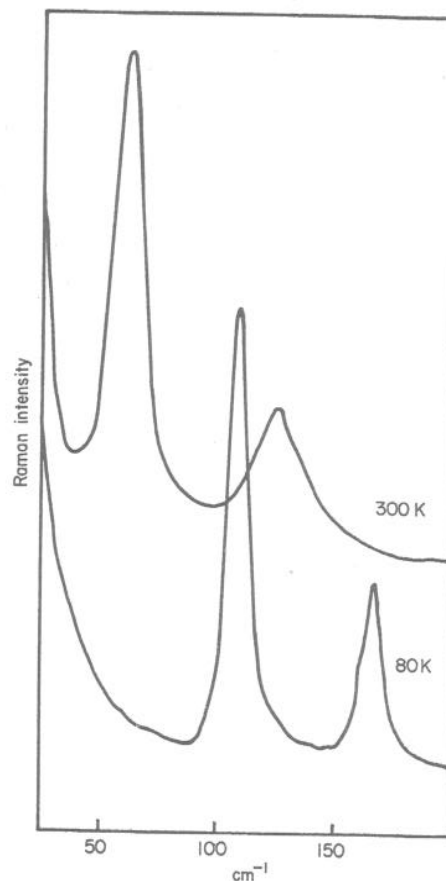

Figure 3. The low-frequency Raman spectra of HMB at 300 K (phase II) and 80 K (phase III).

Two bands are observed at 109 and 39 cm^{-1} at 400 K. One is due to a libration about the x axis and the lower frequency band is due to the libration about the y axis.

When pressure is applied at 300 K the spectra (Fig. 4) begin to show a marked change above 2.7 kbar. The strong band at 60 cm^{-1} decreases rapidly in intensity and an additional band emerges at 90 cm^{-1}. These two converge into a broad asymmetric band at higher pressures. The band at 120 cm^{-1} does not undergo any similar change. On reducing the applied pressure the spectrum reverts back to its original form at about 1.5 kbar. The changes in the spectrum proved to be reproducible through several pressure cycles, on various samples of HMB grown in different batches (Fig. 5). Spectra of deuterated HMB were also obtained. A similar behaviour was observed.

At 100 K when the applied pressure is raised from atmospheric pressure, a transformation is observed in the Raman spectrum of HMB at 2.5 kbar (Fig. 6). This transition is extremely sharp and the low-frequency spectrum is drastically changed. In the high-pressure region as the temperature is raised the three bands at 85, 110 and 125 cm^{-1} appear to broaden and converge into the room temperature high-pressure spectrum. In the 100 K spectrum of deuterated HMB no change was observed up to a pressure of 4 kbar, as is shown in Fig. 7.

It is expected that modes associated with molecular libration should exhibit different behaviour from the torsional modes of the methyl groups. It should be noted, however, that neither of the two bands observed
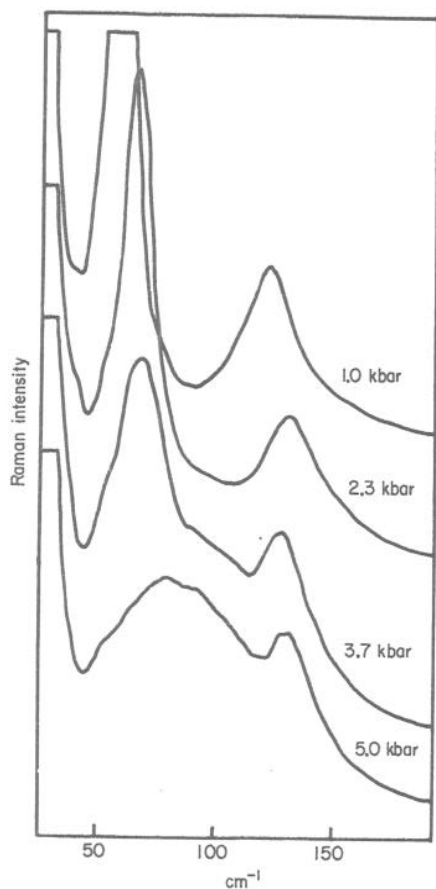

Figure 2. Plot of the low-frequency Raman bands in hexamethyl benzene as a function of temperature showing three different phases.

Figure 4. The low-frequency Raman spectra of HMB at 300 K as a function of pressure. Phases II and IV occur.

in phase II disappears or shifts anomalously during the transition to phase IV. Furthermore, both have similar positive frequency shifts as a function of applied pressure. This indicates that both of these bands should be assigned to librational modes of the molecule.
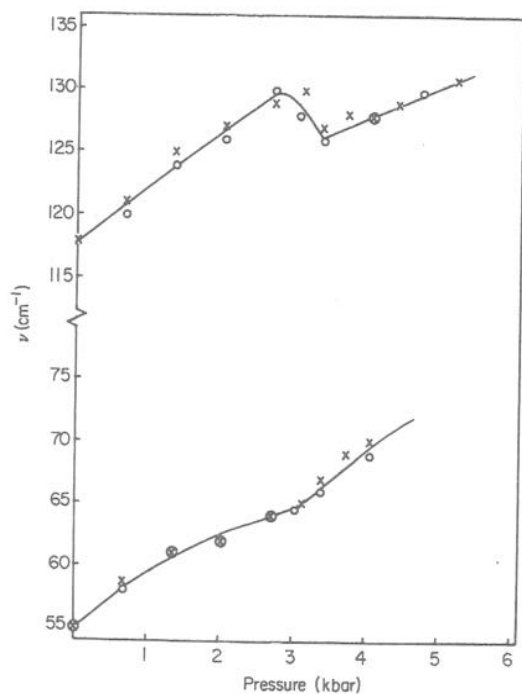

Figure 5. Pressure dependence of low-frequency modes of HMB at 300 K showing the phase II → IV transition. Experiments 1 and 2 are denoted by × and ○ respectively.
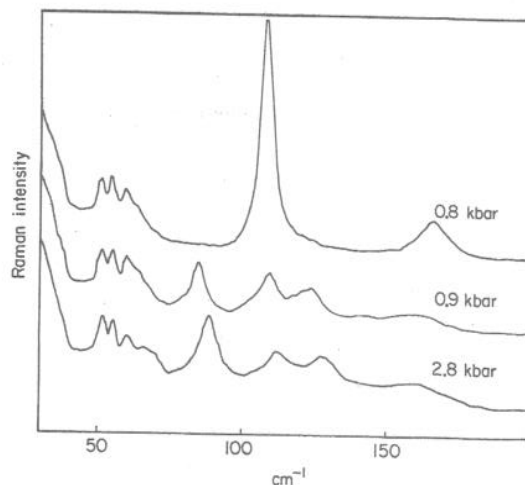

Figure 6. The low-frequency Raman spectra of HMB at 100 K showing phases III and IV.

The low-temperature results confirm some of the previous conclusions and enable completion of the assignment. The 108 cm^{-1} band observed in phase III in HMB splits into three bands in phase IV, all of which have a positive pressure shift. They are therefore
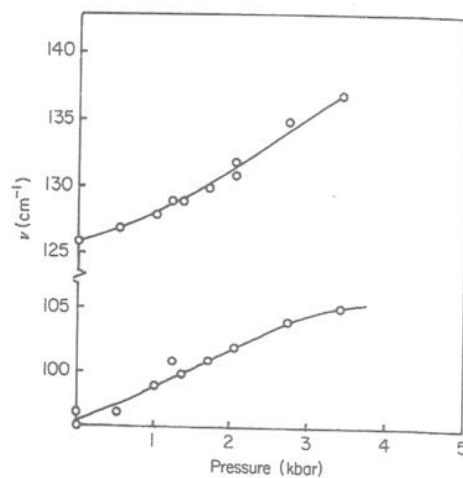

Figure 7. Pressure dependence of low-frequency modes in fully deuterated HMB at 100 K with pressure rising.
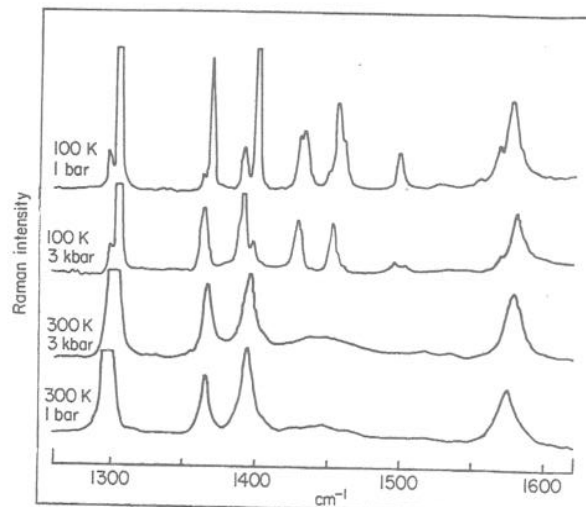

Figure 8. The pressure and temperature dependence of Raman spectra of HMB.
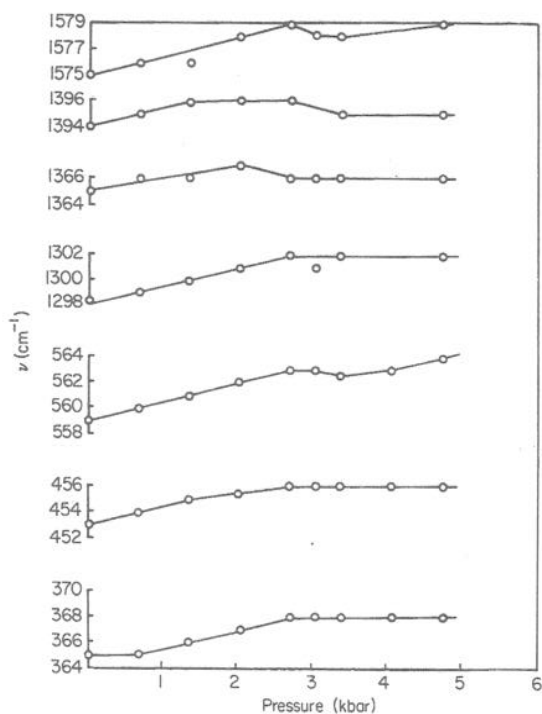
Figure 9. Pressure dependence of Raman active modes in HMB at 300 K. Phases II and IV.
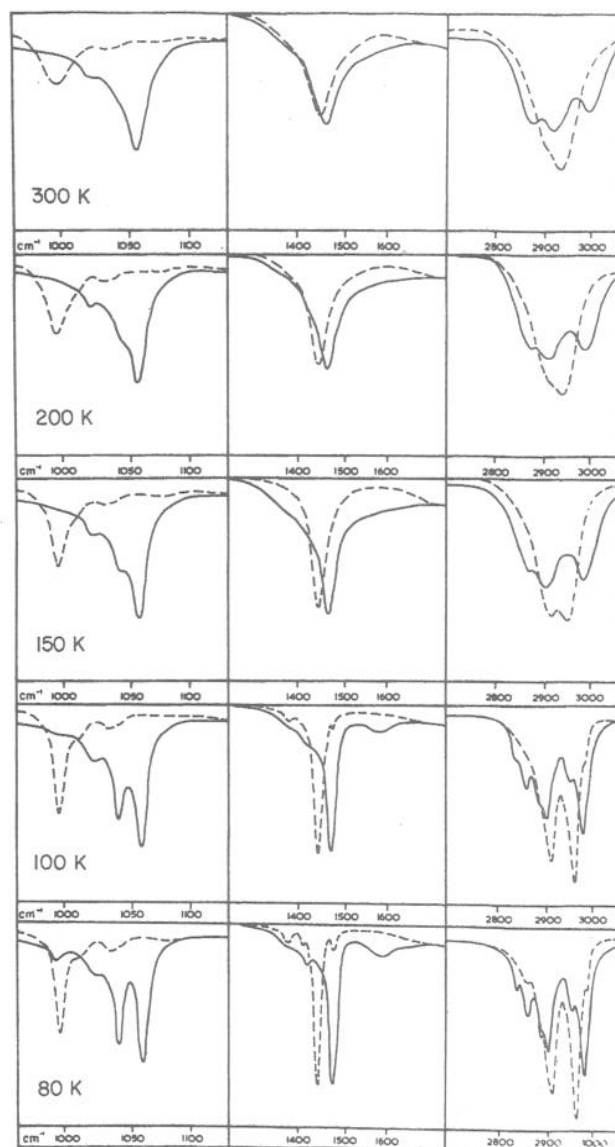

Figure 10. The temperature dependence of the polarized infrared absorption spectra of HMB, *bc* crystals face. ——— electric vector of radiation parallel to **b**. − − − − − electric vector perpendicular to **b**.

assigned to the three librations of the molecule which appears as one degenerate band in phase III. The intensity of the 165 cm^{-1} band observed in phase III in HMB is considerably reduced in the high-pressure phase, and has a negative pressure shift in the latter phase. The assignment of this band to the methyl torsional mode seems to be substantiated.

Figure 8 shows the Raman spectrum of hexamethyl benzene between 1250 and 1600 cm^{-1} at different pressures and temperatures. The most notable feature is the appearance of bands between 1400 and 1500 cm^{-1} at 100 K. In Fig. 9, discontinuities in the frequencies of internal modes of vibration as a function of pressure at 300 K show the transition from phase II to phase IV. However, the changes of frequency of the internal modes with pressure are small and do not provide as much information as the studies on the low-frequency bands.

The polarized infrared absorption spectrum of a thin *bc* crystal is shown in Fig. 10 as a function of temperature. The vibrations involved are mainly those associated with the methyl groups. Below the λ-point there is a marked splitting of the absorption lines, revealing an increase in the order of the methyl groups.

pressure is applied to HMB indicate the existence of a pressure-induced phase transition. The transition is observed both at 100 K (from phase III) and at 300 K (from phase II). The high pressure phase appears to be of a similar nature at both temperatures and is considered to be a new phase IV.

CONCLUSIONS

The changes in the low-frequency region of the Raman spectrum which occur when the hydrostatic

Acknowledgements

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