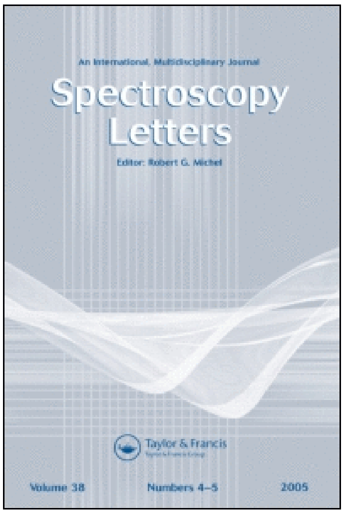

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INFRARED SPECTRA OF BENZENE AT HIGH PRESSURES

Key Words: Infrared Spectra, High Pressures, Benzene, Molecular Crystals, Phase Transitions

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ABSTRACT

Mid-infrared spectra in the ranges 400-1800 and 2700-4000 cm^{-1} are reported for benzene samples in diamond anvil cells at ambient temperature and pressures up to 10 GPa. The freezing pressure is confirmed to be 0.10±0.05 GPa. Changes in the spectra and in the sample appearance indicate that sluggish solid state phase transitions occur near 2.0 and 4.0 GPa. The wavenumber shifts with pressure for 27 selected peaks are plotted. Their small increases show that only minor distortions of the molecules occur, and there is no evidence of any weakening of intramolecular bonds in this pressure range.

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INTRODUCTION

Liquid benzene forms a molecular crystal when cooled to 278.5 K at ambient pressure or when compressed to 0.07 GPa at ambient temperature[1]. The structure of this phase I is orthorhombic, space group *Pbca* $\left(D_{2h}^{15}\right)$, and the unit cell contains four molecules.[2,3] No further phase transitions have been observed when the crystal is cooled to low temperatures at normal pressures. However, a sluggish first order transition to phase II, which is monoclinic with two molecules per unit cell, has been observed at a pressure of 1.4 GPa[4]. There is also evidence of a further first order transition to phase III near 4.0 GPa and a second order transition near 11 GPa[1]. The structure of phase III has not been determined, but its vibrational spectra suggest it is similar to phase II[5]. In addition to the reversible phase transitions mentioned above, it has been reported that benzene undergoes an irreversible transformation to a white solid at a pressure of 30 GPa at room temperature, which is stable on release to ambient pressure. It is postulated that under these extreme conditions, the benzene rings are opened and a highly cross-linked polymer is formed.[6]

Numerous spectroscopic investigations of the vibrations of solid benzene, mostly at low temperatures, have been published. These have been referenced and summarized in a recent paper by Thiery et al.[7], who compared the results of their normal coordinate analysis calculations with the available experimental data. Only three papers on the vibrational spectra of benzene at high pressures have been reported, and it appears that the infrared spectra of the internal modes and the dependence of their wavenumbers on pressure have not been fully documented. Adams and Appleby were limited to pressures below 4 GPa[5]; Pruzan et al. limited the analysis of their infrared spectra to the C-H stretching bands[6]; and Ellenson and Nicol studied only the Raman spectra[8]. In the present communication, we present mid-infrared spectra in the regions 400-1800 and 2700-4000 cm^{-1} of liquid and solid benzene in a diamond anvils cell at pressures up to 10 GPa. The objectives are to study the evolution of these spectra as a function of pressure, to confirm the existence of various phase transitions from the spectra and from plots of peak wavenumbers versus pressure, and to look for evidence of molecular distortion as a precursor to the irreversible breakdown at ultra-high pressures.[6]

EXPERIMENTAL TECHNIQUES

Liquid benzene was supplied by Baker Chemical Co. and had a minimum assay of 99.9%. Samples were loaded into a diamond anvil cell (DAC) of the piston-cylinder type, supplied by Diacell Ltd. The cell was equipped with type 2A diamonds and an inconel gasket, which was pre-indented by the diamonds to an initial thickness of about 0.1 mm and then drilled to produce a 0.25 mm diameter cavity for the sample. A few grains of ruby powder were included for in situ measurements of the sample pressure using the standard fluorescent technique.[9]

Mid-infrared spectra were recorded on a rapid-scan FTIR spectrophotometer (Nicolet, model IR42), equipped with a KBr beam divider, water-cooled globar source, air-bearing mirror movement and pyroelectric (DTGS) detector. The instrument was purged continuously with dry CO_2-free air. Polished brass coned light-pipes were used on both sides of the DAC to increase the level of the signals transmitted through these small area samples. Transmittance spectra were obtained by taking ratios of transformed interferograms from sample and background, derived from 4000 and 1000 co-added scans, respectively. The spectral resolution was typically 2 cm^{-1}, and this and the wavenumber accuracy were checked periodically by recording the spectrum of polystyrene film.

Ruby fluorescent 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. By monitoring the widths of the ruby peaks, it was deduced that pressure gradients in the sample were insignificant except at the highest applied pressures, near 10 GPa. Spectra were always recorded after increasing the pressure by a small increment (usually about 0.5 GPa) and waiting for about an hour to allow equilibrium to be established, (especially in the pressure ranges where sluggish phase transitions were expected), and to avoid the hysteresis effects often observed on releasing pressure. For spectra, particularly those of samples at low pressures, interference fringes were prominent. These could usually be reduced significantly by adjusting the DAC screws asymmetrically to slightly degrade the parallelism of the two diamond faces.

RESULTS

Mid-infrared spectra of liquid and solid benzene at four selected pressures are shown in Fig. 1 for the region 400-1800 cm^{-1} and in Fig. 2 for the region 2700-4000 cm^{-1}. The intermediate range 1800-2700 cm^{-1} is obscured by strong absorption from the diamonds. From the rich spectra, peaks which could be unambiguously tracked with increase of pressure were selected. Their wavenumbers are plotted as a function of pressure in Fig. 3. Table 1 contains assignments of peaks with symmetry species and their wavenumbers at selected pressures.

DISCUSSION

The benzene molecule is described by point group D_{6h}. There are $3\times12-6=30$ internal degrees of freedom, and the vibrational modes are distributed among the following symmetry species:

$$\Gamma_{INT}=2a_{1g}+1a_{2g}+1a_{2u}+2b_{1u}+2b_{2g}+2b_{2u}+e_{1g}+3e_{1u}+4e_{2g}+2e_{2u}$$

The a_{1g}, e_{1g} ande_{2g} modes are Raman active, and the a_{2u} and e_{1u} modes are infrared active. Hence for isolated molecules, 7 Raman, 4 infrared and 10 “silent” fundamental modes are expected. In the liquid state, many of these inactive

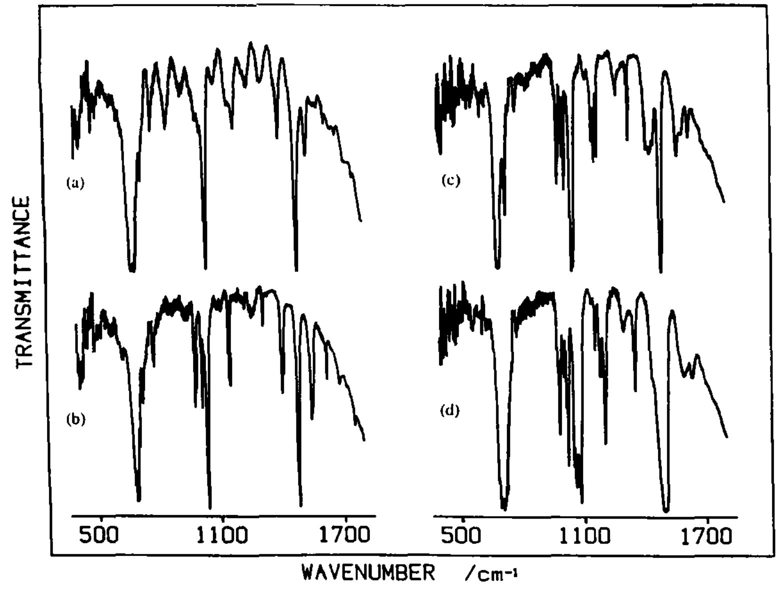

FIG. 1 Mid-infrared Spectra of Benzene at Selected Pressures
Range: 400-1800 cm^{-1}. Resolution: 2.0 cm^{-1}
(a) Liquid at 0.09 GPa (c) Crystal at 3.0 GPa
(b) Crystal at 0.30 GPa (d) Crystal at 9.3 GPa

modes become weakly active as a result of intermolecular perturbations. Most fundamentals have been observed, either directly or in combination, and assignments have been proposed by Shimanouchi[10].

The crystal structure of benzene I has been determined by X-ray and neutron diffraction[2,3]. The unit cell is orthorhombic, with space group $Pbca(D_{2h}^{15})$, and contains 4 molecules on sites which are centres of inversion ($\bar{1}$ or C_i). As a result of this low site symmetry, all ten ungerade modes are, in principle, infrared

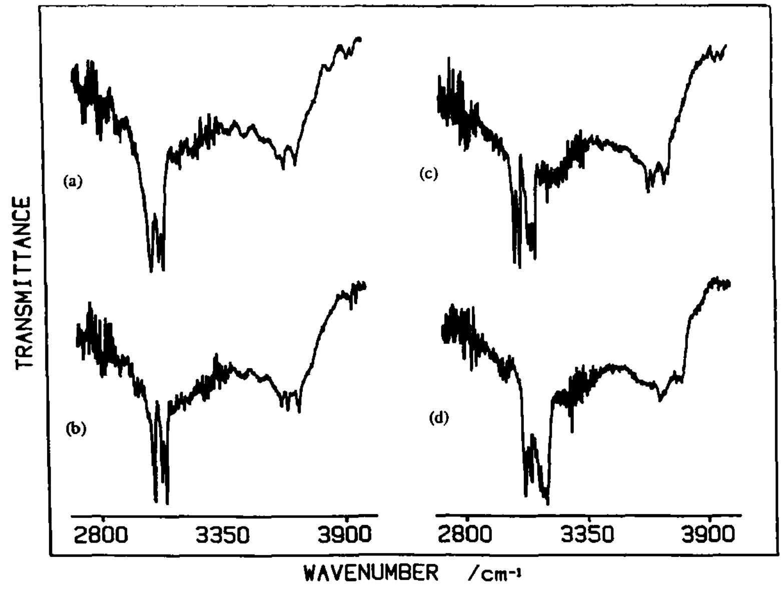

FIG. 2 Mid-infrared Spectra of Benzene at Selected Pressures
Range: 2700-4000 cm^{-1}. Resolution: 2.0 cm^{-1}
Pressures as for Fig. 1.

active, with the five degenerate modes $(3e_{1u}+2e_{2u})$ splitting into two components. Moreover, as a result of coupling of molecules in the unit cell, further splittings occur, with the non-degenerate modes having four components, of which three are infrared active, and the degenerate modes having eight components, of which six are infrared active. In crystalline benzene, phase II, the structure, determined by X-ray diffraction[4], is monoclinic, with space group $P2_1/c\ (C_{2h}^5)$. There are only two molecules per unit cell, and, as in phase I, they are on sites with inversion symmetry. Hence, all ungerade modes of the free molecule will be infrared

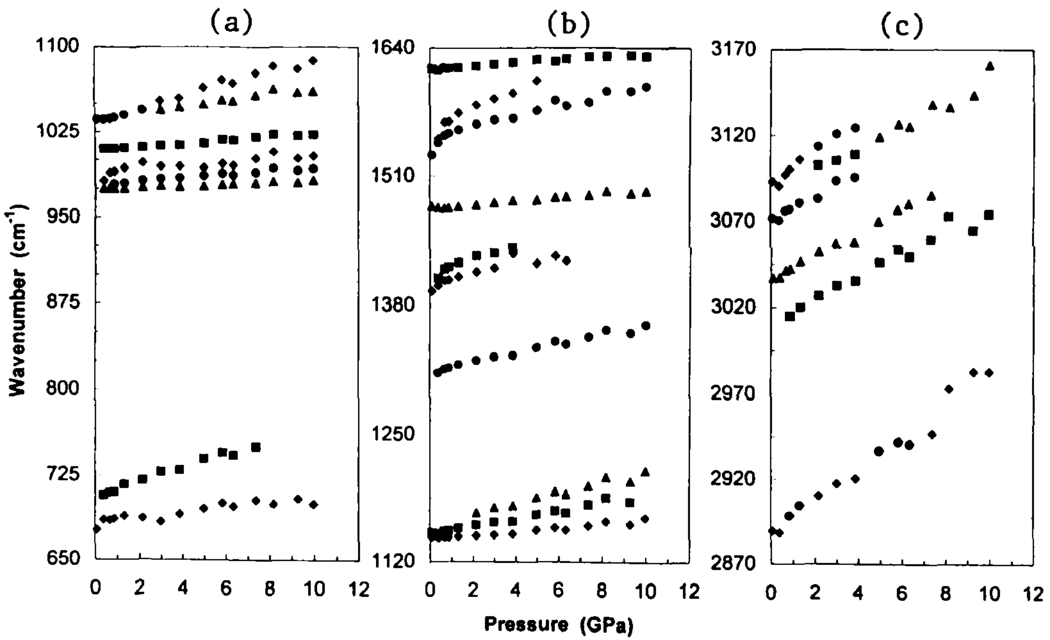

FIG. 3 Plots of Peak Wavenumbers versus Pressure for Crystalline Benzene. (a): Peaks 1-9; (b): Peaks 10-19; (c): Peaks 20-27. See Table 1.

TABLE 1

Infrared Spectra of Crystalline Benzene: Dependence of Peak Wavenumbers on Pressure

	Pressure / GPa ↣	0.39	0.67	0.87	1.32	2.16	3.00	3.87	4.98	5.84	6.34	7.37	8.18	9.29	9.98
# *	Mode (Species)^{x}	Wavenumber / cm^{-1}													
1	$\nu_4(a_{2u})$	685.2	684.9	686.0	688.7	686.8	683.4	690.2	695.2	700.3	697.2	702.6	699.4	704.3	699.5
2	$\nu_4(a_{2u})+\nu_L(g)$	706.9	709.4	709.9	716.5	720.5	727.6	729.3	739.5	745.0	742.5	749.8			
3	$\nu_{19}(e_{2u})$	975.0	975.1	974.9	975.0	976.1	977.5	976.7	977.1	978.7	979.2	979.9	981.5	980.8	982.7
4				978.9	979.8	982.0	983.4	984.2	986.3	988.2	986.7	988.9	993.0	991.0	992.7
5		981.8	988.4	989.5	993.1	997.7	994.2	994.5	993.4	997.2	995.4	1001.3	1007.5	1002.0	1004.0
6	$\nu_8(b_{1u})$	1009.7	1009.9	1009.9	1010.7	1011.2	1012.6	1013.0	1015.1	1018.6	1017.4	1020.6	1023.1	1022.1	1023.1
7	$\nu_{14}(e_{1u})$						1044.5	1046.8	1049.3	1053.1	1052.2	1057.2	1063.2	1060.1	1061.1
8		1035.9	1036.4	1037.7	1040.0	1044.2									
9							1052.3	1054.7	1064.1	1071.0	1067.9	1076.9	1083.1	1081.2	1088.1
10	$\nu_{10}(b_{2u})$	1143.8	1144.7	1144.7	1145.7	1146.6	1147.5	1148.2	1152.5	1154.6	1152.5	1156.8	1161.1	1158.6	1165.2
11		1148.7	1151.1	1151.7	1154.4	1157.5	1160.4	1161.1	1168.2	1172.2	1169.7	1178.6	1185.9	1181.5	
12						1170.1	1175.8	1177.5	1185.9	1192.0	1189.5	1197.9	1206.9	1202.6	1213.4
13	$\nu_9(b_{2u})$	1312.1	1316.0	1317.2	1320.6	1324.6	1328.4	1329.8	1337.6	1343.5	1340.8	1348.2	1355.1	1352.3	1360.6
14	$\nu_2(a_{2g})+\nu_{20}(e_{2u})$	1399.6	1404.9	1405.3	1408.5	1413.5	1417.5	1431.8	1422.2	1429.5	1424.8				
15	$\nu_7(b_{2g})+\nu_{20}(e_{2u})$	1406.7	1416.1	1418.2	1422.5	1429.3	1432.5	1437.6							
16	$\nu_{13}(e_{1u})$	1478.0	1477.4	1478.0	1479.0	1480.8	1483.6	1485.3	1485.8	1488.7	1489.3	1490.9	1495.0	1493.9	1495.0
17	$\nu_{13}(e_{1u})+\nu_L(g)$	1543.1	1551.2	1553.4	1556.9	1562.9	1567.4	1568.9	1576.4	1586.9	1581.5	1584.8	1596.6	1596.6	1601.4
18		1547.8	1564.5	1565.3	1574.2	1582.3	1588.7	1594.2	1606.7						
19	$\nu_8(b_{1u})+\nu_{18}(e_{2g})$	1617.3	1619.6	1619.4	1619.9	1621.5	1623.7	1625.2	1628.0	1626.4	1628.8	1631.4	1631.7	1632.8	1631.7
20	$\nu_9(b_{2u})+\nu_{18}(e_{2g})$	2888.1		2898.5	2904.4	2910.2	2917.3	2920.3	2937.1	2942.4	2941.0	2946.8	2973.1	2982.9	2982.8
21	$\nu_{12}(e_{1u})$			3014.9	3020.0	3026.7	3032.6	3035.3	3046.0	3053.4	3049.4	3059.3	3072.9	3064.8	3074.1
22		3037.1	3041.3	3042.2	3046.6	3052.1	3056.8	3057.7	3070.0	3076.9	3080.0	3085.3			
23		3070.4	3075.9	3076.9	3080.5	3083.0	3093.3	3095.4							
24	$\nu_6(b_{1u})$					3102.4	3105.1	3108.6							
25		3090.3	3096.9	3100.0	3105.7										
26	$\nu_{12}(e_{1u})+\nu_{18}(e_{2g})$					3113.5	3120.9	3124.5							
27									3119.1	3126.7	3125.4	3138.1	3136.3	3143.4	3161.0

* Peaks 1 - 9 are plotted in Fig 3a, 10 - 19 in Fig 3b and 20 - 27 in Fig 3c

^{x} Mode assignments are based on Ref 10; $\nu_L(g)$ refers to a gerade lattice mode.

active, with two components for the five non-degenerate modes and four for the five degenerate modes. Because the centre of symmetry is retained in both phases, no gerade modes will become infrared active. In the present room temperature study, many of these predicted components will not be resolved, but the widths of the composite peaks are an indicator of the number of components present. Because the unit cell is smaller for phase II, fewer components or somewhat sharper peaks might be expected.

Solid benzene I, formed by the application of a low external pressure (~0.10 GPa), usually consisted of a small number (~5) of randomly oriented crystallites, showing beautiful colours when viewed between crossed polarizers in a microscope. No attempt was made to grow a single crystal, so that orientation effects could be averaged and all allowed modes observed. On increasing the pressure to ~2.0 GPa, obvious changes to the appearance of the crystal were observed. Initially, striations across the crystallites appeared, followed by a sluggish breakdown into a powder-like sample with a multitude of grain boundaries visible. The spectra of the resultant benzene II show several distinct changes compared to those of benzene I, as will be discussed below. No further major changes in the sample's appearance were observed at higher pressures (up to 10 GPa). However, at pressures near 4.0 GPa, it was found that tightening the DAC screws failed to produce the usual increase in pressure. In fact, after leaving the sample for several hours and then remeasuring the pressure, a small decrease was found. Subsequent tests showed that this was not due to any sample leakage.

Hence a sluggish transition to benzene III is postulated, in which there is a volume contraction as a result of closer packing of the molecules. These results are similar to those observed previously near the upper limit of the pressure range covered in the work of Adams and Appleby.[5] Minor changes in the internal mode spectra were also detected at pressures near 4.0 GPa, as will be discussed later.

Extensive changes in the mid-infrared spectra of benzene are observed when crystallization occurs, as can be seen by comparing Figs 1(a) and 2(a) to 1(b) and 2(b) respectively. Many more peaks are observed for the solid, as might be expected from the above discussion based on a group theoretical analysis of benzene I. In addition, peaks are generally much sharper for the crystal, as a result of the more orderly arrangement of molecules. The changes observed in the transition from benzene I to II are less pronounced, as revealed by a comparison of Figs. 1(b) and 2(b) with 1(c) and 2(c), respectively. However, the several discontinuities listed below confirm that a phase change has indeed occurred:

(a) Peak #1, near 685 cm^{-1}, exhibits a change in slope in the wavenumber versus pressure plot (Fig. 3)

(b) Peak #8, near 1035 cm^{-1}, splits into two components above 2.0 GPa.

(c) A new peak (#12) appears near 1170 cm^{-1}.

(d) Peak #15 near 1405 cm^{-1} and peak #17 near 1545 cm^{-1} both exhibit changes in slope near 2.0 GPa (Fig. 3).

(e) Peak #25, near 3090 cm^{-1} splits into two components.

Similarly, a comparison of Figs 1(c) and 2(c) with 1(d) and 2(d) respectively, shows that at pressures near 4.0 GPa, further minor changes in the mid-infrared spectra are observed , providing supporting evidence of a possible phase transition near this pressure:

(a) Peak #5, near 1435 cm^{-1}, and peak #18, near 1605 cm^{-1} both disappear at pressures above about 4.0 GPa.

(b) Peak #20, near 2920 cm^{-1} and peak #22 near 3040 cm^{-1}, both exhibit changes in slope (Fig. 3)

(c) Three peaks (#23, 24 and 26) in the 3100 cm^{-1} region merge into a single peak (#27) near this pressure.

Many of the predicted components of the infrared active internal modes are only resolvable at low temperatures. In addition, peaks generally broaden with increase in pressure. Hence many of the inherent small splittings in the present room temperature study are effectively obscured. Under these circumstances, one can only claim that the changes observed in the mid-infrared spectra at the I → II phase transition are not inconsistent with the known structures of these phases. The relatively small changes observed for the postulated II → III transition suggest that the structure of phase III is similar to that of phase II. Finally, it is apparent from the spectra at the highest pressure recorded in this study (~10 GPa) that the molecular identity has been retained with only minor distortions. Moreover, it is seen in Fig. 3 that the wavenumbers of all internal modes, fundamentals and combinations, either monotonically increase with pressure or reach asymptotic values. There is no evidence of weakening of any intra-molecular bonds, which indicates that any precursor of the eventual break-up of the molecular ring structure of benzene[6] must occur at pressures greater than 10 GPa.

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