

MOLECULAR MOTIONS AND λ PHASE TRANSITION: RAMAN AND FAR-IR STUDIES OF NEAT AND ISOTOPIC MIXED HEXAMETHYLBENZENE CRYSTAL*

Paras N. PRASAD, Steven D. WOODRUFF and Raoul KOPELMAN

*Department of Chemistry, The University of Michigan,
Ann Arbor, Michigan 48104, USA*

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Raman and far-IR studies of hexamethylbenzene (HMB) low temperature crystalline phases (neat and isotopic mixed) are presented. The Raman phonon spectrum changes drastically during the λ -phase transition. Site splittings on two intramolecular modes of HMB- h_{18} (but on only one corresponding HMB- d_{18} mode) are observed in the room temperature phase (phase II) spectrum. These splittings disappear in the lower temperature phase (phase III). The methyl torsional bands are identified and a significant shift is observed for them during the phase transition. Also, while the λ -phase transition takes place at 113°K ($\pm 2^\circ\text{K}$) for HMB- h_{18} crystal, the transition temperature is 133°K ($\pm 2^\circ\text{K}$) for HMB- d_{18} . Our results suggest that (for phonon interactions) the symmetry in phase III is close to D_{3d} and reduces to C_i in phase II. Furthermore, the results support the mechanism of phase transition which involves a tilting of the methyl groups out of the benzene ring.

1. Introduction

The hexamethylbenzene (HMB) crystalline state has been a subject of extensive investigation for a long time [1–19]. The interest has been manifold:

(i) it undergoes two phase transitions, one around 383°K involving a change from triclinic (room temperature phase, we call it phase II) to orthorhombic structure (phase I) [2] and another, “higher order” (λ), phase transition takes place around 115°K [3, 4] and both phases (II and III) are assumed to have triclinic structure [5];

(ii) it is one of the simplest molecular crystals as in both phase II and III there is only one molecule per unit cell [5], being thus ideal for investigating solid state interactions among translationally equivalent molecules and their dynamical manifestations;

(iii) it is a prototype system for studying the role of internal methyl group rotations and possible collective rotations in phase transitions.

The lower temperature (115°K) phase transition has received considerable attention from spectroscop-

ists. As the crystal structure change during the phase transition is probably small, so that X-ray studies would not shed much light on the nature of the phase transition, various spectroscopic techniques such as NMR [6–9], neutron diffraction [10], neutron incoherent scattering [11, 12] and optical spectroscopy [13, 15, 19, 20] have been used to investigate the nature of the phase transition at the microscopic (molecular) level.

A sensitive criterion for studying the phase transition at the microscopic level is the unit cell symmetry, or the site symmetry (these are the same in the case of the hexamethylbenzene crystal – one molecule per unit cell). Thus any investigation which makes use of the selection rules based on the symmetry of the unit cell can provide valuable information regarding the phase transition. Unfortunately, NMR or neutron scattering transitions are not restricted by such selection rules. Optical spectroscopic investigations of the various excitations (electronic, vibronic, intermolecular vibrational and phonons) on the other hand do invoke crystal symmetry selection rules. Thus Schnepf [15], from his studies of electronic spectra of the two phases of hexamethylbenzene suggested that the site

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symmetry in the phase above 115°K (phase II) is C_i , whereas below 115°K (phase III) it may be as high as S_6 . However, electronic states in a molecular crystal are usually affected by the crystalline environment only to a small extent (the crystalline environment can be considered as a minor perturbation). Furthermore, the lowest electronic states which have been studied are non degenerate ($^1B_{2u}$, $^3B_{1u}$ in a D_{6h} framework) and by themselves are unable to reveal splittings due to the crystal symmetry. Vibronic bands, in principle, can yield such information but suffer from complication such as vibronic selection rules, appearance of overtones, combination bands and phonon structures. Intermolecular motions (phonon states) on the other hand are entirely due to solid state interactions and the crystal interaction is not a minor perturbation. In view of this, optical spectroscopy studies of phonon states should provide us with direct information about the unit cell symmetry and also about the degeneracies contained in the crystal symmetry. Also, the study of intramolecular vibrations of HMB which correspond to benzene degenerate vibrations can yield information about the degeneracies possible in the two phases. Furthermore, the study of methyl torsions, which are intermediate in nature with respect to intramolecular vibration on one hand and lattice vibration on the other [21, 22], can be of significant importance in this concern. The present investigation was undertaken with these considerations in mind.

We present experimental results on the Raman and far-IR spectra of hexamethylbenzene neat and isotopic mixed crystals in both phases II and III. The isotopic mixed crystal study helps us in identifying the nature of the transitions (intramolecular vibration, torsion or lattice vibration [22]) and also gives information about the role which dynamical interactions play in these motions.

The results show that though the barrier height for the methyl torsions does change the phase transition, the phase transition does *not* occur due to the onset of *free* rotation of methyl groups. The phonon structure changes drastically from one phase to the other. We also observe some changes in the Raman spectra of the intramolecular modes. These observations lead us to suggest that the site symmetry in phase III is close to D_{3d} and reduces to C_i in phase II. The nature of the phase transition is discussed with respect to such a change in site symmetry.

2. Experimental

Hexamethylbenzene- h_{18} and hexamethylbenzene- d_{18} (Merck, Sharp and Dohme, 98% atom deuterium) were purified by recrystallization from ethanol solution. For Raman experiments neat crystals and isotopic mixed crystals were grown from the melt in a capillary under vacuum. The capillary containing the crystal (which remained under vacuum) was used for the experiment. Regulated flow of cold nitrogen vapor provided a variable temperature bath: room temperature to 100°K. The temperature was measured with the help of a copper constantan thermocouple. The accuracy of the temperature measurement was about $\pm 2^\circ\text{K}$. To get temperatures lower than 100°K, helium vapor was used. The spectra were recorded photoelectrically using direct current on a Ramalog-Spex double spectrometer model 1401. An argon ion laser from Coherent Radiation Laboratory was used as the excitation source. The excitation line was the 4880Å laser emission which was selected by a suitable interference filter. The spectral resolution was about 1 cm^{-1} .

For far-IR experiments hexamethylbenzene neat and isotopic mixed crystals were grown from a benzene solution over water. This yielded thin crystal plates of large area. Crystals of thicknesses from 0.2 to 0.5 mm were used for the experiment. The experiments were done at room temperature and at liquid nitrogen temperature. For the latter, a low temperature cryostat was used which was evacuated between the inner and the outer dewar. The sample was mounted on the cold finger attached to the inner dewar which contained liquid nitrogen. The windows of the cryostat were made of polyethylene. The spectra were recorded in double beam operation on a Digilab Fourier transform spectrometer model FTS-16. 1000 scans were taken both for sample and reference. They were averaged, ratioed and the plot was smoothed. The resolution used was 2 cm^{-1} .

3. Results

Fig. 1 shows the Raman spectra of hexamethylbenzene- h_{18} (HMB- h_{18}) in the region 25 to 210 cm^{-1} at a series of temperatures. At room temperature (phase II) a moderately sharp band (halfwidth $\approx 10\text{ cm}^{-1}$) is observed at 55 cm^{-1} and a broad peak

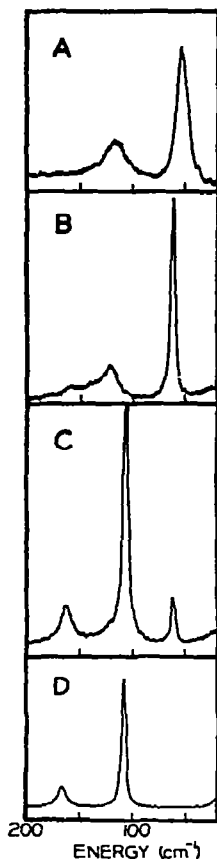


Fig. 1. The Raman spectra of neat HMB- h_{18} crystal in the region 25–200 cm^{-1} . A and B are, respectively, phase II spectra at room temperature and 116°K. Spectrum C corresponds to a mixture of phase II and III at 113°K and D is that of phase III at 93°K. The spectral resolution is $\approx 1 \text{ cm}^{-1}$.

(halfwidth $\approx 25 \text{ cm}^{-1}$) is seen at 120 cm^{-1} . With decrease in temperature, the 55 cm^{-1} band gradually shifts to 61 cm^{-1} at 116°K (right above the phase transition). At this temperature the band at 61 cm^{-1} has a halfwidth of 5 cm^{-1} . The band at 120 cm^{-1} is still broad ($\approx 15 \text{ cm}^{-1}$) and asymmetric, and it is hard to estimate the temperature shift. Also, with the lowering of temperature a broad shoulder starts appearing on the higher energy side of the 120 cm^{-1} band. Though it is hard to locate the peak position for this shoulder an approximate value is 160 cm^{-1} at 116°K. It took over 2 h to have a complete phase transition at a constant 113°K temperature. The spectrum changes markedly

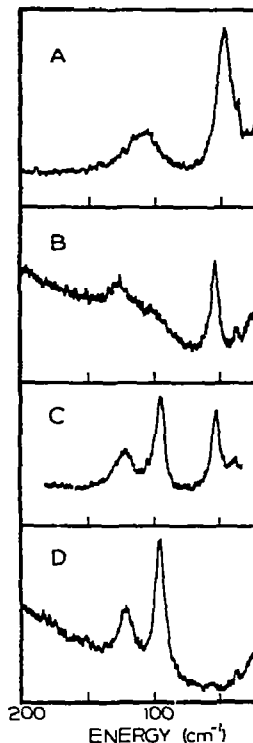


Fig. 2. The Raman spectra of neat HMB- d_{18} in the region 25–200 cm^{-1} at a resolution of 1 cm^{-1} . A and B are, respectively, phase II spectra at room temperature and 135°K. C is that of a mixture of phases II and III at 133°K. D is the spectrum of phase III at 126°K. The peak at 37 cm^{-1} in the spectra is due to an Ar ion non lasing emission.

during the phase transition. Spectrum C corresponds to a mixture of both phases, and it can be seen that the band at 61 cm^{-1} is disappearing while a strong and sharp band (halfwidth $\approx 5 \text{ cm}^{-1}$) at 108 cm^{-1} and a moderately sharp band (halfwidth $\approx 8 \text{ cm}^{-1}$) at 165 cm^{-1} appear. In spectrum D, phase II has disappeared completely and it is thus the spectrum of phase III, where we see bands at 108 and 165 cm^{-1} . Our results thus agree with those obtained by other workers [19, 20].

Fig. 2 shows the Raman spectra of HMB- d_{18} in the region 25 to 200 cm^{-1} taken at a series of temperatures. The features exhibited are similar to that of HMB- h_{18} . Again, at room temperature, we see a band at 50 cm^{-1} (halfwidth $\approx 10 \text{ cm}^{-1}$) and a broad peak

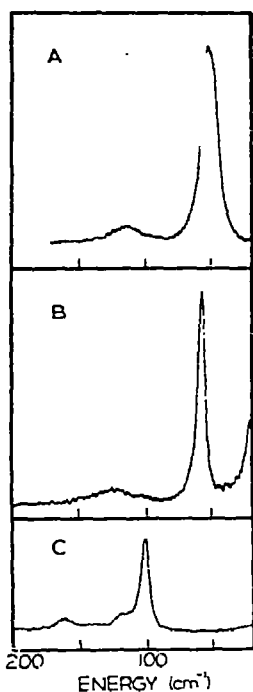


Fig. 3. The Raman spectra of 50% HMB- h_{18} and HMB- d_{18} isotopic mixed crystal in the region 25–200 cm^{-1} at a resolution of 1 cm^{-1} . A and B are, respectively, phase II spectra at room temperature and 120°K. C is the spectrum of phase III at 100°K.

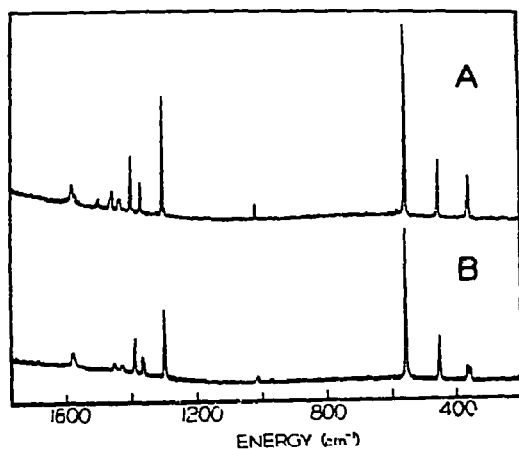


Fig. 4. The Raman spectra of HMB- h_{18} in the region 200 to 1800 cm^{-1} at a resolution of 1 cm^{-1} . A and B are, respectively, the spectra of phase III at 100°K and of phase II at 115°K.

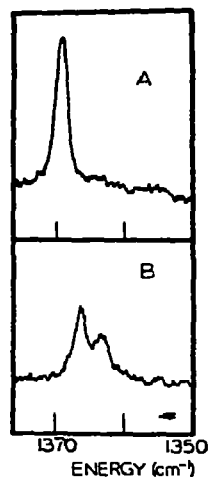


Fig. 5. The Raman spectra of HMB- h_{18} crystal in the region 1350–1380 cm^{-1} . A and B are, respectively, the spectra of phase III at 100°K and of phase II at 115°K.

at 110 cm^{-1} (halfwidth $\approx 25 \text{ cm}^{-1}$). As we lower the temperature, the peak at 50 cm^{-1} shifts to 55 cm^{-1} in going from room temperature to 133°K and the broad feature at 110 cm^{-1} is now replaced by two broad peaks at about 107 cm^{-1} and 125 cm^{-1} . The phase transition takes place at 133°K and the spectrum consists of bands at 95 and 125 cm^{-1} .

Fig. 3 shows a similar study on 50% HMB- h_{18} and HMB- d_{18} isotopic mixed crystals. At room temperature (A), the phase II spectrum consists of a band at 52 cm^{-1} and a very broad one (halfwidth 25–30 cm^{-1}) around 113 cm^{-1} . The phase transition takes place at 120°K. The phase III spectrum (C) at 115°K consists of peaks at 102 cm^{-1} , 160 cm^{-1} and a shoulder at 120 cm^{-1} . The spectra of HMB- h_{18} , HMB- d_{18} and a 50% mixture were also taken at several temperatures below 100°K (down to 25°K). Except for small frequency shifts and some sharpening no significant change was observed in their spectra.

We looked carefully for far-IR transitions in the region 27–200 cm^{-1} with samples of different thickness. There is no indication of any absorption band either in phase II or phase III in the neat crystals. From this we conclude that hexamethylbenzene does not have any IR active phonons in phases II and III.

We also made a comparative study of the Raman active intramolecular modes for phases II and III. Fig. 4 shows such a comparison for HMB- h_{18} in the region



Fig. 6. The Raman spectra of HMB- d_{18} crystal in the region $315\text{--}340\text{ cm}^{-1}$. A and B are, respectively, the spectra of phase III at 100°K and phase II at 135°K .

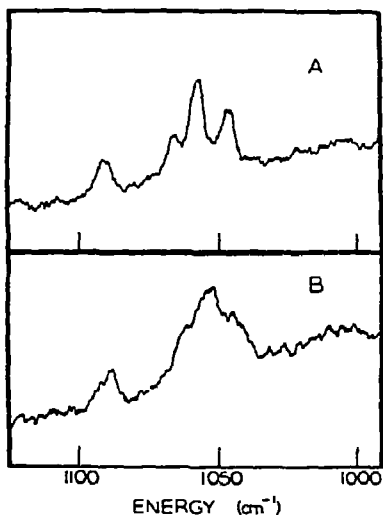


Fig. 7. The Raman spectra of HMB- d_{18} crystal in the region $1000\text{--}1100\text{ cm}^{-1}$. A and B are, respectively, the spectra of phase III at 120°K and phase II at 135°K .

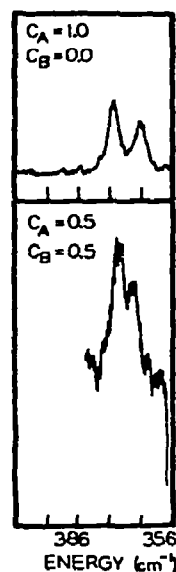


Fig. 8. The Raman spectra of neat and isotopic mixed crystals in the region $356\text{--}386\text{ cm}^{-1}$. C_A is the concentration of HMB- h_{18} and C_B that of HMB- d_{18} . The upper spectrum was taken at 120°K and the lower at 132°K .

200 to 1800 cm^{-1} . The most prominent change is observed on the 364 cm^{-1} fundamental of phase III which splits into a doublet at 360 and 369 cm^{-1} in phase II. A similar change takes place for the 1370 cm^{-1} band of phase III, which is replaced by peaks at 1365 and 1368 cm^{-1} in phase II. Fig. 5 shows this splitting at greater dispersion. The peak at 1402 cm^{-1} shifts to 1392 cm^{-1} in going from phase III to phase II.

A similar study was also made for HMB- d_{18} . The bands are in general broader compared to HMB- h_{18} ones. One possible source of broadening might be various isotopic impurities in the HMB- d_{18} samples, as it had only 98% deuterium atom purity. Again, the 329 cm^{-1} band which corresponds to the 364 cm^{-1} one of HMB- h_{18} splits into a doublet at 327 and 333 cm^{-1} in going from phase III to phase II. This feature is shown in fig. 6. Also in phase II of HMB- d_{18} there is a broad partially resolved band with peaks at 1045 , 1053 and 1062 cm^{-1} (fig. 7). The peaks sharpen considerably in phase III with the 1053 cm^{-1} peak shifting to 1056 cm^{-1} (fig. 7).

We also did an isotopic mixed crystal study on the intramolecular modes. The spectrum obtained in both

phases can be explained as a superposition of HMB- h_{18} and HMB- d_{18} spectra. In phase II, the doublets seen at 360 and 369 cm^{-1} in the HMB- h_{18} spectrum, and at 327 and 333 cm^{-1} in the HMB- d_{18} spectrum, seem to show some change in structure. This change for HMB- h_{18} is shown in fig. 8. We see that in the 50% isotopic mixture the splitting reduces from 9 to 5 cm^{-1} and the peaks broaden a little bit. The HMB- d_{18} band shows a similar behavior. As these bands are weak we were not able to get the guest spectra of dilute (10%) isotopic mixed crystals.

4. Discussion

The absence of any absorption in the far IR and the mutual exclusion of IR transitions and Raman transitions indicate that the site symmetry contains a center of inversion (at least effective) in both phase II and phase III (this is especially clear because the hexamethylbenzene crystal has only one molecule per unit cell). There are six phonon branches. At $k = 0$ (center of Brillouin zone) three are pure librational motions and are Raman active. The other three $k = 0$ motions are pure translational ones and belong to acoustical branches which are optically inactive.

Using our previously developed criterion [22] we find from the isotopic mixed crystal studies that in phase III the 108 cm^{-1} band in HMB- h_{18} (and the corresponding 95 cm^{-1} one in HMB- d_{18}) is due to a librational phonon (librational exciton [21]). The evidence is that this mode is in the amalgamation limit [22] and the energy shifts from one component value to another in going through the isotopic mixed crystals. Also, in phase III, the 165 cm^{-1} band of HMB- h_{18} and the 125 cm^{-1} one of HMB- d_{18} are due to methyl torsions. This again is derived from the isotopic mixed crystal study and the isotope shift. In 50% isotopic mixed crystals, we see two bands corresponding to both HMB- h_{18} and HMB- d_{18} , showing that this mode is in the separated band limit of the mixed crystal. Furthermore, the observed isotope ratio $\nu\text{HMB-}h_{18}/\nu\text{HMB-}d_{18} = 1.32$ is close to the theoretical value [19] 1.40 for the methyl torsion.

In phase II, at room temperature, the 55 cm^{-1} band of HMB- h_{18} and the 50 cm^{-1} one of HMB- d_{18} are again in the amalgamation limit as can be seen from the 50% isotopic mixed crystal spectrum (fig. 3).

The bands at 120 cm^{-1} in the HMB- h_{18} spectrum (fig. 1A) and at 110 cm^{-1} in the HMB- d_{18} spectrum (fig. 2A) are broad but seem to be in the amalgamation limit. These are, thus, due to librational phonon transitions. In the case of HMB- h_{18} the shoulder at 160 cm^{-1} (fig. 1B), which appears right above the phase transition (116°K), is due to methyl torsion and it shifts to 165 cm^{-1} in phase III (figs. 1C, D). In the case of HMB- d_{18} the peak corresponding to the 160 cm^{-1} shoulder of HMB- h_{18} in phase II is probably the broad feature at 125 cm^{-1} (fig. 2B). From the isotopic mixed crystal studies we thus conclude that in phase II there are two bands due to librational phonons while in the low temperature phase there is only one. The band due to methyl torsion shows a shift of about 0 to 5 cm^{-1} in going through the phase transition.

The intramolecular fundamental (364 cm^{-1} of HMB- h_{18} , 329 cm^{-1} of HMB- d_{18} in phase III), which splits into a doublet in phase II, is the 282 cm^{-1} excited state mode observed by Schnepf and McClure [14] in the absorption spectra of HMB- h_{18} . In a simple model this mode seems to correspond to the 846 cm^{-1} ground state mode of benzene [14, 23]. From fig. 8, we see that this splitting in phase II exists even in the isotopic mixed crystal, though the splitting decreases (from 9 to 5 cm^{-1} for HMB- h_{18}) and the transitions are somewhat broader. The broadening and the decrease of the splitting indicate the importance of dynamical interactions, but as the crystal in phase II has only one molecule per unit cell, the splitting cannot be a Davydov splitting. This is also supported by the observation that the splitting does not completely broaden in the 50% mixture. From all these considerations we conclude that the splitting is a "site" splitting of the mode which corresponds to an E_{2g} mode of benzene. We note here that, except for an "ideal mixed crystal" (dilute!) the site splitting contains dynamic (exciton) contributions [24].

The fact that the site splitting disappears in phase III, suggests that the site in phase III contains at least an approximate three-fold symmetry and that this symmetry is removed in phase II. The result is not surprising. If we look into the room temperature crystal structure of hexamethylbenzene [5], we find that the molecules are stacked in layers and lie almost exactly in the (001) crystallographic plane. The symmetry of this (001) layer is nearly hexagonal. This molecular ar-

Table 1
Correlation diagram for possible groups of hexamethylbenzene

C_{6h}	D_{6h}	D_{3d}	S_6	C_i
$A_g(R_z; x^2 + y^2, z^2)$	$A_{1g}(x^2 + y^2; z^2)$ $A_{2g}(R_z)$	$A_{1g}(x^2 + y^2; z^2)$ $A_{2g}(R_z)$	$A_g(R_z; x^2 + y^2)$	$g(R_x, R_y,$ $R_z; x^2 + y^2,$ $z^2, x^2 - y^2;$ $xy, xz, yz)$
B_g	B_{1g} B_{2g}			
$E_{1g}(R_x, R_y; yz, xz)$	$E_{1g}(R_x, R_y; yz, xz)$	$E_g(R_x, R_y; x^2 - y^2,$ $xy; yz; xz)$	$E_g(R_x, R_y; x^2 - y^2,$ $xy; yz, xz)$	$u(x, y, z)$
$E_{2g}(x^2 - y^2, xy)$	$E_{2g}(x^2 - y^2, xy)$			
$A_u(z)$	A_{1u} $A_{2u}(z)$	A_{1u} $A_{2u}(z)$	$A_u(z)$	
B_u	B_{1u} B_{2u}			
$E_{1u}(x, y)$	$E_{1u}(x, y)$	$E_u(x, y)$	$E_u(x, y)$	
E_{2u}	E_{2u}			

rangement is shown in fig. 9. The C_3 axis of the site is the "6-fold" molecular (carbon frame) axis which is perpendicular to the molecular plane. This is the z axis of libration. The X and Y axes are the two axes in the molecular plane. The point groups of the lowest order which contain C_3 and C_i as symmetry elements are S_6 , C_{6h} and D_{3d} . Table 1 shows the correlation among groups C_{6h} , D_{6h} , D_{3d} , S_6 and C_i . It can be seen that in both S_6 and C_{6h} symmetry all three librations R_x , R_y and R_z are Raman active, while in the D_{3d} point group R_x and R_y are Raman active but R_z is forbidden. As R_x and R_y are degenerate in all three symmetries, we should expect two librational phonon bands in the Raman spectra if the site has S_6 or C_{6h} symmetry. On the other hand, if the site symmetry is D_{3d} only one band due to libration is expected. The experimental observation of a single band due to librational phonons thus supports D_{3d} site symmetry in phase III. In phase II, as we have discussed earlier, the C_3 symmetry is reduced to C_i . In this symmetry the R_x and R_y degeneracy is removed and R_z becomes allowed. The broad

band at 120 cm^{-1} in the HMB- h_{18} spectrum, and at 110 cm^{-1} in the HMB- d_{18} spectrum, we attribute to the unresolved R_x and R_y librations, while the new band which appears at 55 cm^{-1} in HMB- h_{18} and at 50 cm^{-1} in the HMB- d_{18} spectra (room temperature) we attribute to the R_z libration. This assignment is also consistent with the fact that the libration R_z (the

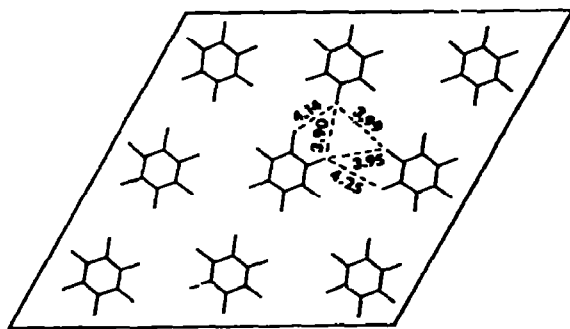


Fig. 9. The nearly hexagonal molecular arrangement [5] in the (001) layer of HMB- h_{18} crystal at room temperature.

Table 2

HMB- h_{18} frequencies (cm^{-1})		HMB- d_{18} frequencies (cm^{-1})		Nature of excitation	Symmetry in D_{3d} group
phase II (116°K)	phase III (115°K)	phase II (133°K)	phase III (125°K)		
61		55		R_z libration R_x and R_y libration	A_{2g}
120	108	≈ 107	95		E_g
≈ 160	165	≈ 125	125	methyl torsion	A_{2g}
360		327		intramo- lecular	E_g
369	364	333	329		E_g
1365	1370			intramo- lecular	E_g
1368				methyl torsion (?)	E_g (?)
1392	1401	1053 (broad)	1056		

libration about the six-fold molecular axis) has the largest moment of inertia and should be the lowest frequency libration if one assumes comparable force constants. Hamilton et al. [10], quote a value of 30 cm^{-1} for the R_z libration frequency which they calculate from the rms libration amplitude. This frequency, thus, represents some mean value. It should be remembered that our value corresponds to the $k = 0$ mode and if the $k = 0$ mode of this libration is at the top of the band, our result will be consistent with their predictions.

The 1370 cm^{-1} mode of HMB- h_{18} , which shifts and splits in phase II has been related to the 3056 cm^{-1} E_{2g} mode of benzene [23]. The 1392 cm^{-1} HMB- h_{18} band of phase II shifts to 1402 cm^{-1} in phase III. In the case of HMB- d_{18} , three partially resolved peaks are seen at 1045, 1053 and 1062 cm^{-1} in phase II (fig. 7) and are seen fully resolved in phase III with the 1053 cm^{-1} peak shifting to 1056 cm^{-1} . In view of similar frequency shifts during the phase transitions the 1056 cm^{-1} band of HMB- d_{18} appears to be analogous to the 1402 cm^{-1} HMB- h_{18} band. The isotope ratio $\nu\text{HMB-}h_{18}/\nu\text{HMB-}d_{18} \approx 1.32$ suggests that this mode may be another methyl torsion. As there are six methyl groups we expect three gerade modes (and three ungerade modes). In the D_{3d} point group one of them, which involves a geared methyl motion, belongs to the A_{2g} representation while the other two belong to the E_g representation. We thus attribute the 165 cm^{-1} band to the A_{2g} methyl torsion, and the 1402 cm^{-1} one may be the E_g methyl torsion. Ron and Hyams [20]* have assigned the 1402 cm^{-1} band of HMB- h_{18} to the degenerate CH_3 deformation mode.

The results of the present investigation are summarized in table 2.

Schnepf [15] from his electronic spectroscopic investigations, suggested that the molecular symmetry in the low temperature phase is probably C_i but possible as high as S_6 . The molecular symmetry should strictly speaking, be the site symmetry. As we adopted a D_{3d} symmetry, our results seem to be in conflict with those of Schnepf (however, see below). The electronic spectra of HMB- h_{18} has also been investigated by Gott [22]. He sees a vibronic band at 700 cm^{-1} from the origin in the HMB- h_{18} absorption spectrum of phase II at 77°K (super-cooled phase II). This band does not appear in the phase III spectrum. This vibration corresponds to the 1326 cm^{-1} (A_{2g}) vibration of benzene (in D_{6h} symmetry). It is allowed in the S_6 and C_{6h} symmetries but forbidden in D_{3d} (see table 1). This observation favors the D_{3d} symmetry for the molecule. The problem, however, arises in explaining the observation of the band due to geared methyl torsion which has A_{2g} symmetry and is forbidden in the D_{3d} point group but is allowed in the S_6 and C_{6h} groups. We think that the molecular symmetry is, perhaps, not far from D_{6h} . It is then possible that some interactions feel D_{3d} (or even D_{6h}) symmetry while for others (like the methyl torsion) the effective symmetry may be S_6 or C_{6h} .

Finally we would like to consider the nature of the

* Ron and Hyams [20] report that in their 2°K Raman spectra a new band appears at 737 cm^{-1} which they do not see in the spectra at higher temperatures ($\geq 100^\circ\text{K}$). Using a recently purchased Helitran TM cryotip from Air Products and Chemicals Inc., we were able to take the Raman spectrum of HMB- h_{18} at about 5°K . We have not seen any bands in the region 600 to 1000 cm^{-1} .

phase transition in light of the above discussed change in site symmetry. It has been suggested [15] that above the phase transition the methyl groups tilt out of the benzene planar ring. Such tilting can easily reduce the symmetry from D_{3d} to C_1 . Our results seem to support this mechanism of phase transition. We see that most bands due to methyl torsions change in frequency. Furthermore, the degenerate modes which show site splitting involve methyl motion. The largest site splitting is seen on the 364 cm^{-1} mode of HMB- h_{18} . This mode is the $C-CH_3$ \perp bending mode and corresponds to the 846 cm^{-1} $C-H$ \perp bending mode of benzene. The $C-CH_3$ \perp bending motion is expected to be greatly affected by the tilting of the methyl groups. The 1370 cm^{-1} mode of HMB- h_{18} which shows a 3 cm^{-1} site splitting in phase II also involves methyl group motion (derived from the benzene $C-H$ stretching). The degenerate ring vibrations do not show any splitting. From these considerations it seems that there is no distortion in the benzene ring*. Furthermore, the phase transition for HMB- h_{18} and HMB- d_{18} crystals does not take place at the same temperature and there is a difference of 20°K in the two transition temperatures. Such a large isotopic effect can easily be accounted for by the methyl tilting but not by the ring distortion or lattice distortion.

As the phonon frequencies shift significantly during the phase transition, it appears that the lattice interaction is very sensitive to the methyl group positions. This is what one would expect noticing that the methyl groups "stick out" and the crystal potential might be derived mostly from $C-H$ and $H-H$ atom-atom interactions among methyl groups of the neighboring HMB molecules. In such a situation, the methyl torsions interact significantly with the lattice motions. We think that the large deviation from the expected

ratio (1.3 compared with 1.4) is caused by mixing between the torsions and the phonons.

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* A possibility also exists that along with molecular distortion (methyl tilting) the neighboring planes get off-set in phase II, so as to readjust and minimize the free energy, and the phase transition involves both molecular distortions and lattice distortion.