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Assignment of the Raman active lattice vibrations in various phases of 1,2,4,5-tetrabromobenzene and 1,2,4,5-tetrachlorobenzene crystals

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Results of polarized Raman spectroscopy are reported and used to obtain complete assignment of the optical lattice modes of 1,2,4,5-tetrabromobenzene crystals for both the beta and gamma phases. Similar information is provided for the beta phase of 1,2,4,5-tetrachlorobenzene crystal. The results are compared with lattice-dynamics calculations. Discrepancies with previously reported measurements and calculations are discussed and rationalized.

I. INTRODUCTION

Understanding of the control of reactivity by the lattice remains the central problem of solid state chemistry. Crucial to this is elucidation of the intermolecular interactions which determine the lattices of the reactant and product as well as the solid solution which may or may not exist during the course of the solid state reaction.

Halogenated hydrocarbons have had a particularly important role in the study of lattice effects in solid state chemistry.[1,2] The halogen effect, wherein substitution of a halogen on an aromatic ring changes the packing from the typical herringbone arrangement characteristic of hydrocarbons to a stacked geometry, where the molecules are within the 4 Å found necessary for reaction, is perhaps one of the most striking examples of the role of intermolecular interactions and resulting lattice control of solid state reactivity.[2] In spite of the long time over which the halogen effect has been known, it yet resists quantitative explanation. This arises, in large part, from the difficulties presented in understanding the role of the halogens in lattice dynamics. Such difficulties may be attributed to the large anharmonicity which appears to be characteristic of crystals of halogenated aromatic hydrocarbons. Insofar as a phase transition may be viewed as a reaction,[3] more quantitative understanding of the halogen effect may be obtained through the study of different phases of the same halogenated aromatic.

The study of the lattice dynamics of organic molecular crystals is useful for gaining a better understanding of the intermolecular forces that exist in condensed phases. Of particular interest are the responses to those forces that arise due to anharmonicity in the potential energy. Lattice vibrations, which are a principal manifestation of the intermolecular forces in crystals, have been examined by both experimental and theoretical means in numerous crystalline systems. Experimental approaches to the problem have primarily employed Raman and infrared spectroscopy to measure the frequencies of the vibrational lattice modes. However, convincing symmetry assignments of the observed lattice modes have been made for only a small fraction of the molecular crystals studied, leaving many systems with only minimal descriptions of their lattice dynamics and the intermolecular forces involved. Theoretical calculations have also been performed for a number of molecular crystals in order to determine the frequencies, symmetries, and, in some cases, eigenvectors of their respective lattice modes. Comparisons of these results with experimental data have shown good agreement for some systems, but difficulty in obtaining good intermolecular potentials for the calculations has often led to unsatisfactory results.

In an effort to better understand the intermolecular potentials in molecular crystals, we recently reported a piezomodulated Raman spectroscopic study of 1,2,4,5-tetrabromobenzene (TBB).[4] In that study, the 22 cm^{-1} lattice mode in the room-temperature beta phase and the 28 cm^{-1} mode in the high-temperature gamma phase of TBB were found to be particularly anharmonic as evidenced by their responses to the applied modulated stress. A proper interpretation of the data, however, necessitates a complete and accurate set of symmetry assignments for the Raman active lattice modes in TBB, especially when comparing the piezomodulated Raman responses observed from different lattice modes.

Symmetry assignments for the Raman active lattice modes of both the beta and gamma phases of the TBB crystal have been tentatively proposed.[5] Due to difficulty in obtaining suitable single crystals, however, only partially polarized Raman spectra could be obtained in the reported study. In addition, not all of the Raman active modes allowed by the symmetry of the lattice could be observed. Consequently, the assignments were not based solely on experimental data, but relied heavily on a proximity criterion using frequencies obtained from a lattice-dynamics calculation.[5,6] In another study,[7] assignments were made by analogy to those obtained for 1,2,4,5-tetrachlorobenzene (TCB)[8] which is isomorphous with TBB.[9]

Given the difficulties and uncertainties associated with the TBB studies, a reinvestigation of the symmetry assignments for the Raman active lattice modes in both TBB and TCB was initiated in our laboratory. The results cast doubt on published lattice-dynamics calculations for both TBB and TCB which claim agreement with experiment.[5,6,8,10]

In this report, we present polarized Raman spectra of TBB in the lattice mode frequency region for both the beta

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phase at room temperature and the gamma phase at 330 K. From the observed spectra, a completely new set of symmetry assignments for the Raman active lattice modes in each of the phases is obtained. Raman spectra and new mode assignments are also obtained for the beta phase of the isomorphic TCB crystal at room temperature. Finally, a lattice-dynamics calculation for TBB is performed in order to consider the accuracy of the lattice potential that has been developed for this molecular crystal.

II. EXPERIMENTAL PROCEDURE AND BACKGROUND

A. 1,2,4,5-tetrabromobenzene

TBB was obtained from Aldrich Chemical and was purified by vacuum sublimation. Slow recrystallization from saturated chloroform solutions produced colorless, columnar crystals, some of which were twinned. Care was taken to insure that single crystals were chosen for spectral measurements to avoid ambiguities in interpreting the spectra.

Since the crystals were grown below 313 K, their structure was that of the beta phase.[11] The monoclinic ($P2_1/a$) crystal structure of the beta phase of TBB has its two molecules in the primitive unit cell located at centers of inversion. The two molecules lie in neighboring stacks oriented along the crystallographic c axis. The structure of the high-temperature gamma phase of TBB[12] differs from that of the beta phase by only a small displacement of the molecules, which results in a slight alteration of the unit cell parameters. The space group and the number and symmetry of molecular sites in the primitive unit cell are retained in the high-temperature phase. A comparison of the structures of the beta and gamma phases is shown in Fig. 1 in which views down the c axis of the unit cells for each of the two phases are overlayed.

The typical habit of the TBB crystal is shown in Fig. 2. Face assignments were made using optical methods. Several crystals were measured to assure reliability of the assignments.

In order to assign the Raman active vibrational modes in TBB, a scattering geometry similar to that used in the assignment of the lattice modes in TCNQ° [13] was expected to give the clearest results. In this geometry, the incident face was (010), while the scattering face was (001). The latter occurred naturally in the TBB crystals, but the (010) face had to be cut using an ultramicrotome. Subsequent goniometry showed that the cut faces were normal to the b axis to within 1° of the theoretical angles.

Identification of the directions of polarization and propagation of the light traveling through the TBB crystal in the Raman experiment requires determination of the optical indicatrix. Since the crystal is monoclinic, symmetry dictates that one dielectric axis of the indicatrix coincide with the b axis and that the other two axes lie in the ac plane. The latter two, which were identified by viewing the (010) face of TBB under crossed polarizers, are illustrated in Fig. 3 along with the principal directions determined for the (110) and $(1\bar{1}0)$ faces.

The principal refractive indices of the TBB crystal at 5145 Å were determined from specular reflectivity measurements. The refractive index n_b was obtained directly from a measurement on (001) with light polarized along the b axis, while $n_{a'}$ and $n_{c'}$ were determined indirectly from reflectivities measured along the principal directions of the (001) and (110) faces. The measured values of the principal refractive

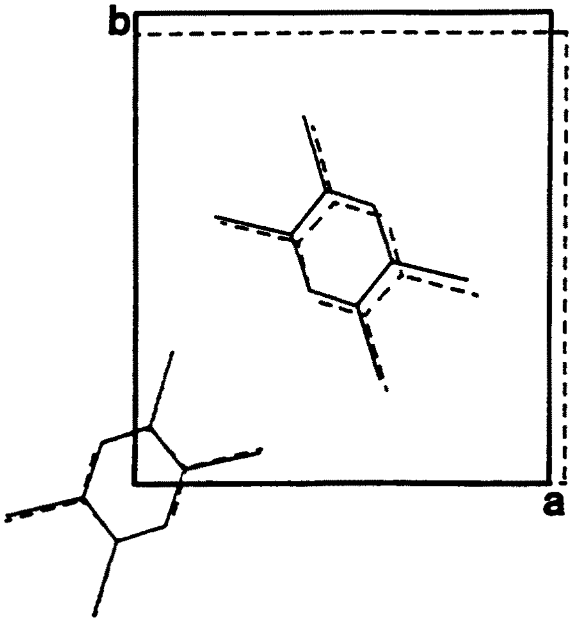

FIG. 1. Overlayed views of the unit cells of the beta (dashed line) and gamma (solid line) phases of TBB looking down the c axis (after Ref. 5).

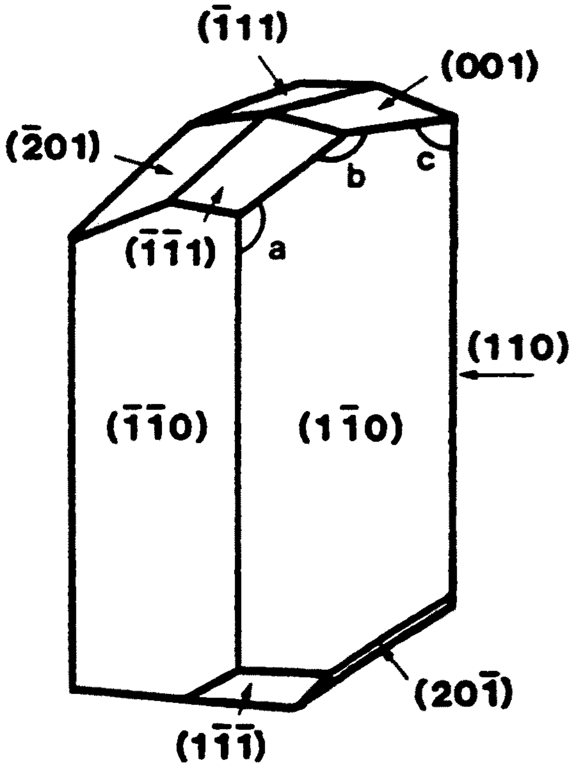

FIG. 2. The crystal habit of the beta phase of TBB.

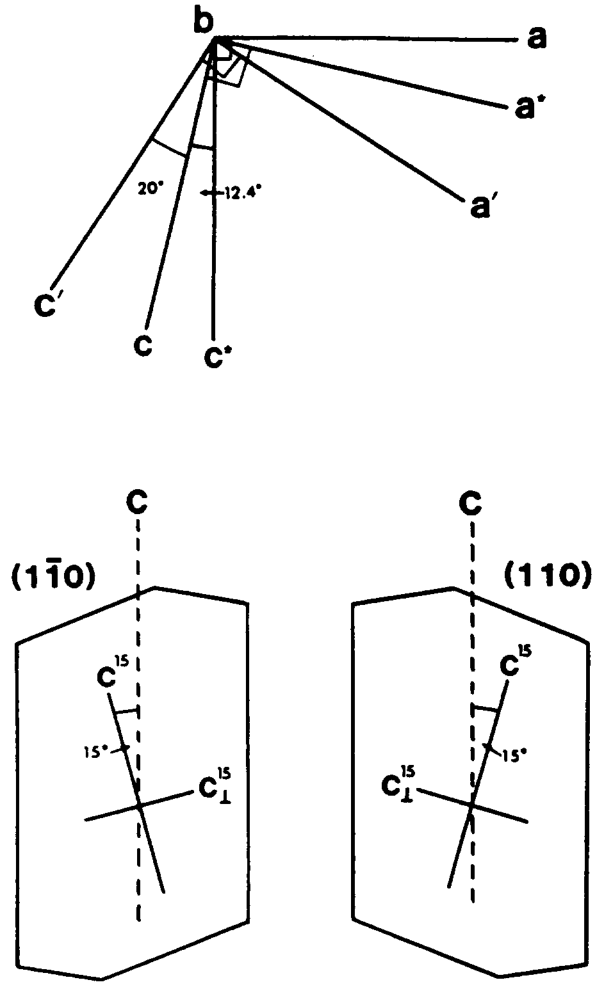

FIG. 3. Identification of the principal directions in the beta phase of TBB along which light was polarized and analyzed in the Raman spectra. In (a), the a', b, and c' principal axes are shown relative to the crystallographic axes of TBB. The principal directions on (1$\bar{1}$0) and (110) in TBB are indicated in (b) relative to the c axis.

indices are $n_{a'} = 2.00$, $n_b = 1.96$, and $n_{c'} = 1.63$ (all to ± 0.05).

The scattering geometries used in the Raman spectra, given in Porto notation,[14] were $b(c'b)c^*$, $b(a'b)c^*$, $b(c'a^+)c^+$, and $b(a'a^+)c^+$, where c^* is the appropriate reciprocal lattice vector. The polarization and propagation directions specified are those of the incident and scattered light as it traveled through the TBB crystal. Since the incident light entered the crystal parallel to the b axis, it did not refract and its polarization in the bulk was unaffected. This was also the case for scattered light collected along the c^* axis having its polarization along b. However, light collected parallel to the c^* axis and polarized along the a axis actually traveled inside the crystal along the c^+ axis with polarization along a^+. These directions, as illustrated in Fig. 4, were calculated for 5145 Å using the measured optical indicatrix. The 11° change in the polarization and propagation directions results from the crystal optics.

Using the C_{2h} point group, a symmetry analysis of the unit cell indicates that both the beta and gamma phases of the TBB crystal have nine optical lattice phonons with symmetries given by

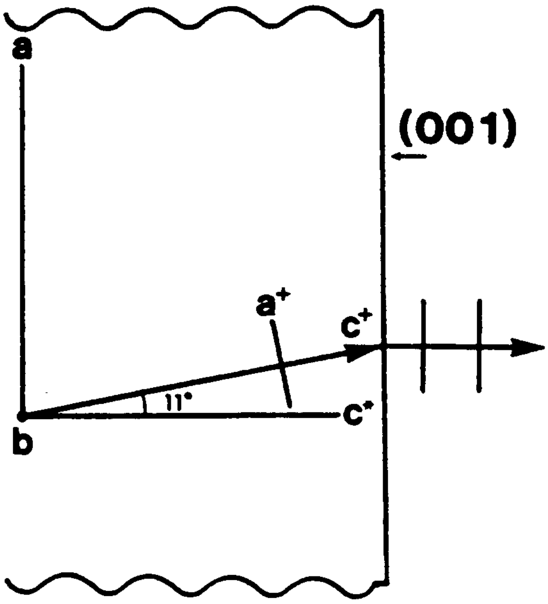

FIG. 4. The effect of crystal optics in the beta phase of TBB. Scattered light detected in the c^* direction that was polarized along a actually traveled in the crystal along c^+ with polarization along a^+.

$$\Gamma = 3A_g + 3B_g + 2A_u + B_u .$$

Only modes that are symmetric with respect to inversion are Raman active and correspond to librational motions of the molecules. The remaining modes are infrared active and involve molecular translations. By symmetry, the Raman spectra measured in the $b(c'b)c^*$ and $b(a'b)c^*$ scattering geometries should only display bands corresponding to B_g active phonons, while the $b(c'a^+)c^+$ and $b(a'a^+)c^+$ spectra should contain only A_g phonon peaks.

Polarized Raman spectra of single crystals of TBB were measured from 8 to 60 cm^{-1} in order to assign the symmetries and frequencies of the lattice modes in both the beta and gamma phases. The high-temperature phase was obtained by bathing the crystal sample in a stream of heated air. The 5145 Å line of an argon ion laser having a power of 55 mW at the sample was used as the source beam. The remaining instrumentation has been described previously.[13] Spectra were recorded at 0.5 cm^{-1} intervals with a bandpass of 1.4 cm^{-1}. The measured frequencies are accurate to ± 1 cm^{-1}.

B. 1,2,4,5-tetrachlorobenzene

TCB that was 98% pure was obtained from Aldrich Chemical and recrystallized by slow evaporation from chloroform at room temperature. The crystals were found to have the same crystal habit[15] as TBB and the principal directions on the {110} faces were determined to be identical to those observed in the TBB crystal. Since TCB is known to display twinning about the c axis,[9] care was taken to choose a single crystal.

The polarized Raman spectra of the beta phase of TCB were measured from 10 to 70 cm^{-1} at 300 K with the exciting light provided by the 6328 Å line of a helium–neon laser operating at about 10 mW at the sample. For the first spectrum, the incident and scattering faces were $(1\bar{1}0)$ and $(\bar{1}\bar{1}0)$, respectively, with the incident light polarized along the c^{15} principal direction of $(1\bar{1}0)$ and the scattered light analyzed along c^{15} of $(\bar{1}\bar{1}0)$ (see Fig. 3). The scattered light was analyzed along the $c_\perp^{15}$ axis in the second spectrum.

Because of the isomorphism of the TCB and TBB beta phase crystals, the optical lattice mode analysis and symmetry selection rules for the two compounds are identical. TCB has no gamma phase, but does pack in a triclinic alpha phase at low temperature.[15]

III. RESULTS

A. Beta phase of 1,2,4,5-tetrabromobenzene

The Raman spectra of the beta phase of TBB at 298 K are shown in Figs. 5 and 6. Evidence is seen for all six of the Raman active lattice phonons present in TBB. In the $b(c'b)c^*$ and $b(a'b)c^*$ (B_g) spectra, four distinct peaks are observed at 15.5, 21.5, 43, and 47.5 cm^{-1}. A shoulder is also seen on the low-energy side of the 43 cm^{-1} band. The $b(c'a^+)c^+$ and $b(a'a^+)c^+$ (A_g) spectra display peaks at 15.5, 21.5, and 41.5 cm^{-1} and a shoulder at the same frequency as seen in the B_g spectra.

The proximity of the peaks identified at 41.5 and 43 cm^{-1}, coupled with the reported accuracy of the measured frequencies, raises the possibility that these peaks may correspond to the same vibrational mode. However, this is a question of error in the resetability of the monochromator and not its calibration. Any doubts are dispelled by study of Fig. 7 in which A_g and B_g spectra are plotted together. It can be seen that, whereas the 15.5 and 21.5 cm^{-1} peaks appearing in both spectra do coincide, the bands at 41.5 and 43 cm^{-1} clearly arise from different transitions.

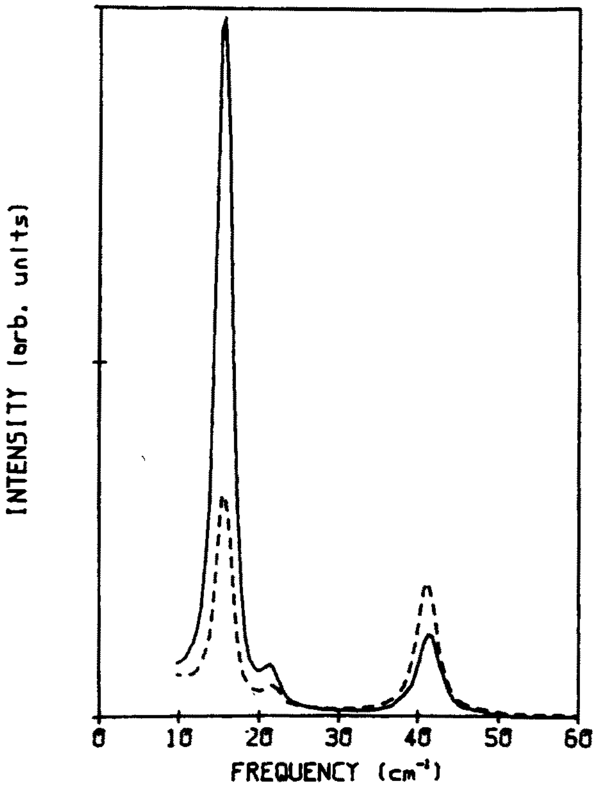

FIG. 6. Room-temperature Raman spectra of the beta phase of TBB measured from 8 to 60 cm^{-1} in the $b(c'a^+)c^+$ (solid line) and $b(a'a^+)c^+$ (dashed line) scattering geometries. The two curves are plotted on the same intensity scale.

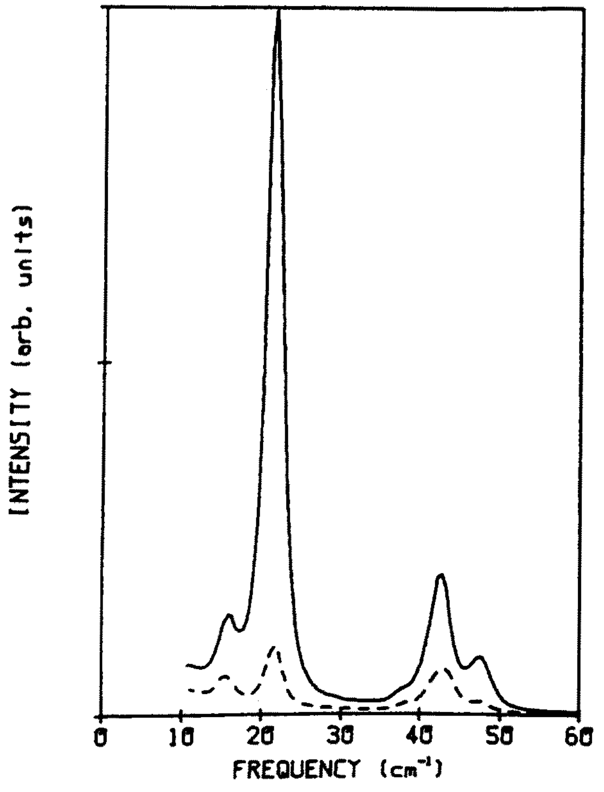

FIG. 5. Room-temperature Raman spectra of the beta phase of TBB measured from 8 to 60 cm^{-1} in the $b(c'b)c^*$ (solid line) and $b(a'b)c^*$ (dashed line) scattering geometries. The two curves are plotted on the same intensity scale.

In an effort to accurately determine the frequency and symmetry of the mode corresponding to the shoulder observed in both the A_g and B_g spectra, Raman measurements in other scattering geometries were made. The configuration exhibiting the best resolution of this structure employed (110) as the incident face and $(\bar{1}10)$ as the scattering face. The interfacial angle between these two naturally occurring faces is 93.4, so a near 90° scattering experiment is possible. The exciting light was polarized along the $c_\perp^{15}$ principal direction of (110) and the scattered light was analyzed along $c_\perp^{15}$ of $(\bar{1}10)$ (refer to Fig. 3), although these were not the actual polarizations inside the crystal. The most intense peak of the spectrum, shown in Fig. 8, is a band located at 39 cm^{-1} which corresponds to the shoulder in question. Rotating the polarizer and analyzer to align them along the c^{15} principal directions of the (110) and $(\bar{1}10)$ faces, respectively (see Fig. 3), produced the Raman spectrum plotted in Fig. 9. The 39 cm^{-1} band is just resolvable in this configuration.

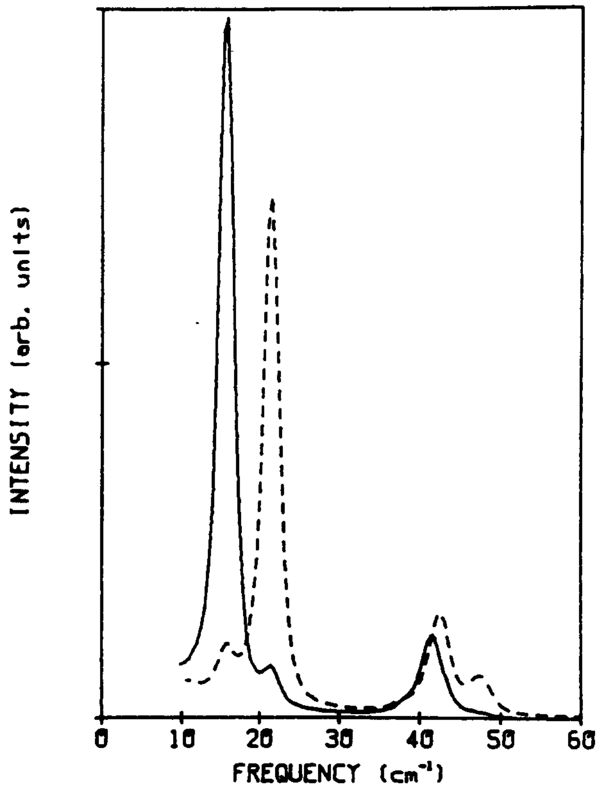

FIG. 7. Room-temperature Raman spectra of the beta phase of TBB measured from 8 to 60 cm^{-1} in the $b(c'a^+)c^+$ (solid line) and $b(c'b)c^*$ (dashed line) scattering geometries. The two curves are plotted on the same intensity scale.

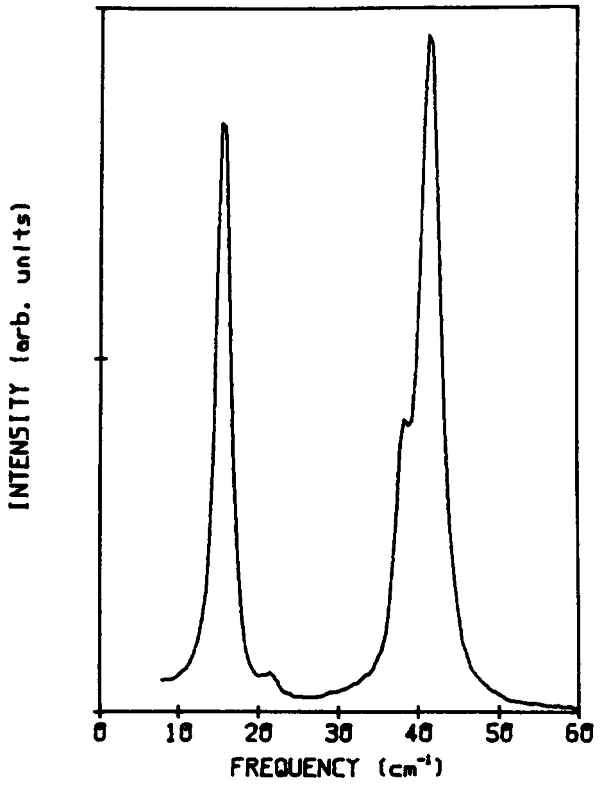

FIG. 9. Room-temperature Raman spectrum of the beta phase of TBB measured from 8 to 60 cm^{-1} with incident light directed normal to (110) and polarized along c^{15} and scattered light detected normal to ($\bar{1}$10) and analyzed along c^{15}.

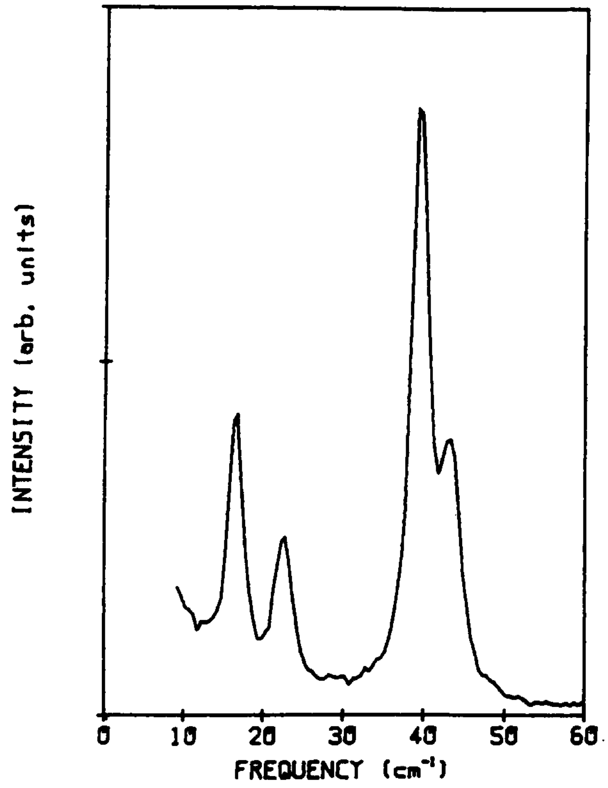

FIG. 8. Room-temperature Raman spectrum of the beta phase of TBB measured from 8 to 60 cm^{-1} with incident light directed normal to (110) and polarized along c_1^{15} and scattered light detected normal to ($\bar{1}$10) and analyzed along c_1^{15}.

B. Gamma phase of 1,2,4,5-tetrabromobenzene

The Raman spectra of the gamma phase of TBB at 330 ± 5 K are found in Fig. 10. The $b(c'a^+)c^+$ spectrum (dashed line) has four distinct peaks at 14.5, 28, 35.5, and 41 cm^{-1} and two shoulders located on either side of the 91 cm^{-1} band. The $b(c'b)c^*$ spectrum (solid line) also shows evidence for six vibrational transitions, with peaks at 14.5, 28, 35.5, and 39.5 cm^{-1} and two shoulders on the high-energy side of the 39.5 cm^{-1} band. The 39.5 and 41 cm^{-1} modes give rise to the two low-energy shoulders observed in the $b(c'a^+)c^+$ and $b(c'b)c^*$ spectra, respectively. On the other hand, the high-energy shoulder is seen in both spectra around 43.5 cm^{-1}.

As with the beta phase, Raman spectra were measured in other scattering geometries to help determine the frequencies and symmetry assignments of the Raman active lattice phonons in the gamma phase. The first of these configurations was described above for the beta phase spectrum shown in Fig. 9 and very nearly represents a (cc) spectrum. The other configuration used (001) and (110) for the incident and scattering surfaces, respectively. The exciting laser beam was directed along the c axis and polarized along b, while the scattered light was collected normal to (110) and analyzed along the c^{15} principal direction of (110). This scattering geometry closely approximates a (bc) spectrum and produces essentially the same beta phase spectrum as that represented by the solid line in Fig. 5. The gamma phase

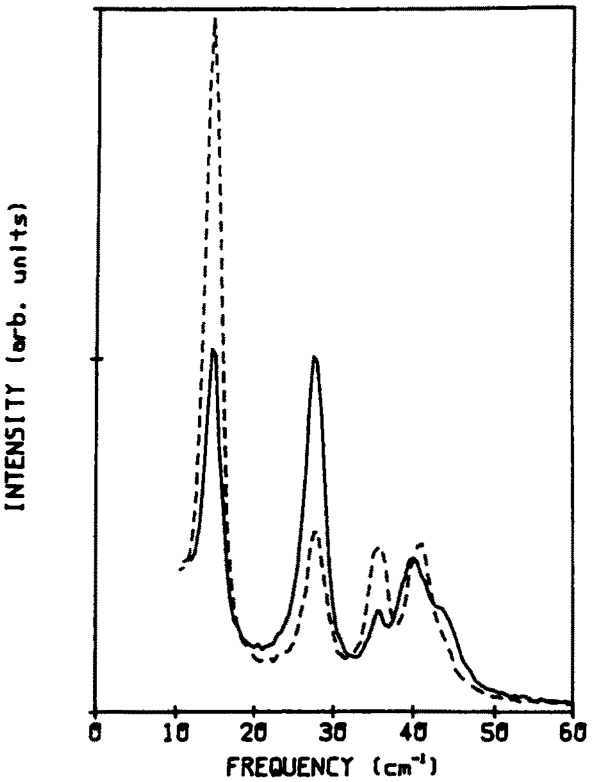

FIG. 10. Raman spectra of the gamma phase of TBB at 330 K measured from 8 to 60 cm^{-1} in the $b(c'b)c^*$ (solid line) and $b(c'a^+)c^+$ (dashed line) scattering geometries. The two curves are plotted on the same intensity scale.

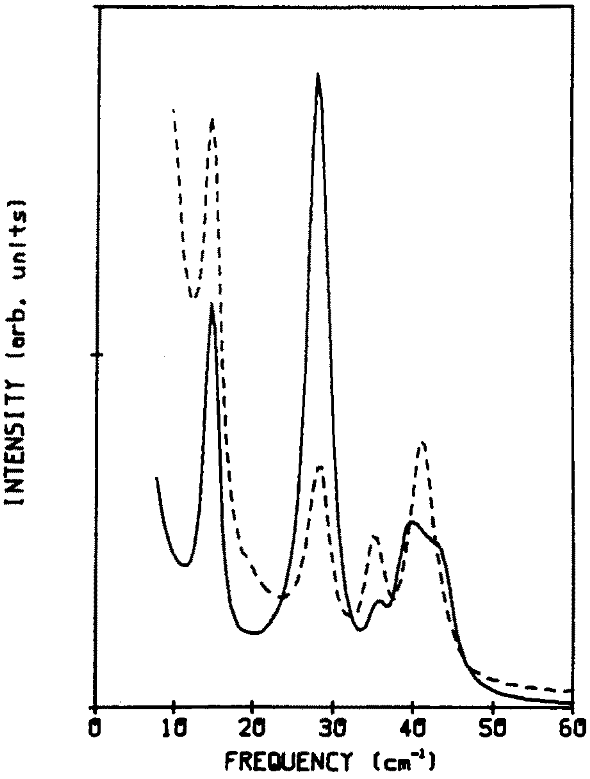

FIG. 11. Raman spectra of the gamma phase of TBB at 330 K measured from 8 to 60 cm^{-1}. The spectrum indicated by the dashed line nearly represents a (cc) spectrum, while the spectrum shown by the solid line is close to a (bc) spectrum. The intesity scales for the two spectra are different.

spectra are plotted together in Fig. 11. The figure allows an unambiguous identification of the six Raman active lattice modes and confirms the phonon frequencies obtained from the other spectra.

C. Beta phase of 1,2,4,5-tetrachlorobenzene

The Raman spectrum of TCB shown in Fig. 12 employed a scattering geometry symmetrically equivalent to that used for the spectrum of TBB found in Fig. 9. This produces essentially a (cc) spectrum of the TCB beta phase. Its resemblance to the corresponding (cc) beta phase spectrum of TBB is striking, although this is to be expected owing to the isomorphism of the TCB and TBB crystal structures. Three distinct peaks are seen in the TCB spectrum at 20, 45, and 49 cm^{-1} along with a weak band around 36 cm^{-1}. The other TCB spectrum, plotted in Fig. 13, was analyzed for scattered light polarized nearly perpendicular to c. It also displays the bands at 20, 45, and 49 cm^{-1}, as well as a very strong peak at 35.5 cm^{-1} and an additional band at 57.5 cm^{-1}.

IV. DISCUSSION

A. Beta phase of 1,2,4,5-tetrabromobenzene

The measured lattice mode frequencies for the beta phase of TBB are consistent with the values reported in a previous Raman study done at ambient temperature.[5] All six Raman active modes have been identified in the polarized

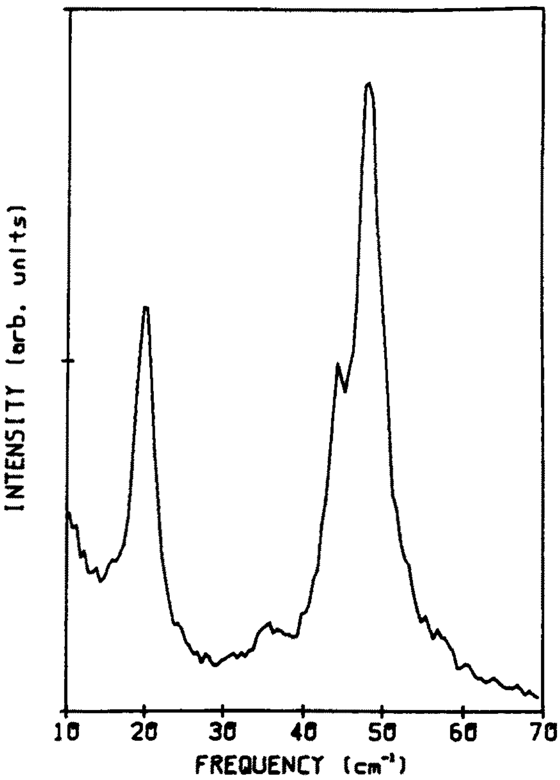

FIG. 12. Room-temperature Raman spectrum of the beta phase of TCB measured from 10 to 70 cm^{-1} with incident light directed normal to $(1\bar{1}0)$ and polarized along c^{15} and scattered light detected normal to $(\bar{1}\bar{1}0)$ and analyzed along c^{15}.

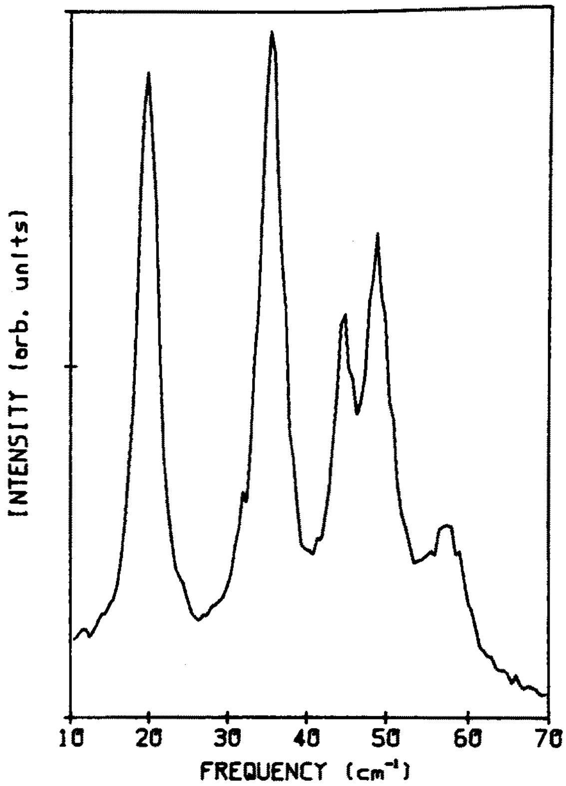

FIG. 13. Room-temperature Raman spectrum of the beta phase of TCB measured from 10 to 70 cm^{-1} with incident light directed normal to $(1\bar{1}0)$ and polarized along c[15] and scattered light detected normal to $(\bar{1}\bar{1}0)$ and analyzed along $c_{\perp}$[15].

spectra. The four modes around 40 cm^{-1} are resolved here for the first time.

In considering the symmetry assignments for the lattice modes observed in the beta phase spectra, one immediately notices that both the A_g and B_g spectra have more than the allowed number of bands predicted by symmetry. Moreover, several modes have structure appearing in both sets of spectra. This "breakthrough scattering" has long been a problem in the polarized Raman spectroscopy of single crystals. It arises from structural defects or converging light in the crystal and has been discussed previously in detail.[13,16]

Despite the breakthrough scattering, it is easily discerned from Fig. 7 that the bands observed at 21.5, 43, and 47.5 cm^{-1} in the $b(c'b)c^*$ spectrum correspond to the three lattice phonons having B_g symmetry. The bands at 15.5 and 41.5 cm^{-1} in the $b(c'a^+)c^+$ spectrum represent two of the three A_g modes. The remaining mode at 39 cm^{-1} must, by default, also have A_g symmetry. Additional experimental evidence, however, allows for a more positive assignment. Since the Raman spectrum in Fig. 9 is very nearly a (cc) spectrum, only A_g modes should be observable in it. The appearance of peaks at 15.5, 39, and 41.5 cm^{-1}, with a small breakthrough of the 21.5 cm^{-1} band, confirms the assignment of the three totally symmetric lattice phonons. Finally, an analysis of the crystal optical effects on the external polarizations employed in the spectrum shown in Fig. 8 indicates that this spectrum has a large (bb) component, which suggests again that the 39 cm^{-1} mode is A_g active.

The frequencies and symmetry assignments of the lattice phonons in the beta phase of TBB are tabulated in Table I along with a comparison to the results reported previously in the literature. The disparity in the three sets of assignments is due to a variety of reasons. For set A, problems in obtaining purely polarized spectra forced the assignments to rely heavily on frequency proximity criteria using a lattice-dynamics calculation.[5] That calculation, however, was performed without minimizing the lattice energy with respect to the unit cell constants for the TBB crystal.[6] As a result, the frequencies and symmetries obtained were for a strained (non-equilibrium) lattice.[17] That errors can result from a lattice-dynamics calculation on a strained lattice has been demonstrated in the literature.[18] The lack of a lattice energy minimization, as well as the possible inapplicability of the crystal potential employed in the TBB calculation, would explain the discrepancy between the lattice mode assignments in set A and those obtained in this work.

In another Raman study of TBB,[7] the lattice mode assignments in set B were proposed based on an analogy to those obtained from polarized Raman data of TCB.[8] Since the beta phase structure of TCB[9] is isomorphous with the beta phase of TBB, it is expected that the assignments of the TCB lattice modes would be the same except for a slight increase in the frequencies. Therefore, symmetry assignments made by analogy should be quite reliable. The desire to resolve the discrepancy between the assignments for TBB in set B and those given in this work prompted the polarized Raman study of TCB in the lattice mode frequency region presented herein.

B. Gamma phase of 1,2,4,5-tetrabromobenzene

The lattice mode frequencies measured at 330 K in the gamma phase of TBB show good agreement with previously reported values for the Raman bands at 14.5, 28, and 35.5 cm^{-1}.[5,7] Only one additional peak, around 90 cm^{-1}, could be observed in those studies, although frequencies for three transitions in this region have been estimated at 36, 38.5, and 40 cm^{-1}.[7] The Raman spectra in this work show that three of the Raman active lattice vibrations have frequencies in this energy range. However, the polarized data place their energies instead at 39.5, 41, and 43.5 cm^{-1}. The proximity of the bands would make it very difficult to identify each of them in an unpolarized spectrum.

TABLE I. Raman active lattice modes in the beta phase of TBB.

	Frequency (cm^{-1})		
	300 K		150 K
Factor group symmetry	This work	A (Ref. 5)	B (Ref. 7)
A_g	15.5	22.5	21
B_g	21.5	15.5	17
A_g	39	37.0	39
A_g	41.5		46/50.5
		41.0	
B_g	43		44.5
B_g	47.5	46.0	46/50.5

The symmetry assignments for the gamma phase lattice modes in TBB are somewhat hindered by significant amounts of breakthrough scattering in each of the spectra. This was largely due to the defects introduced into the crystal as it passed through the phase transition upon warming to 330 K. Nevertheless, the spectra still allow for an unambiguous assignment of the six Raman active lattice phonons for the gamma phase of TBB. Based on the relative peak intensities observed in Fig. 10, the modes at 14.5, 35.5, and 41 cm^{-1} have A_g symmetry, while those at 28, 39.5, and 43.5 cm^{-1} are B_g. The spectra plotted in Fig. 11 confirm these assignments, particularly for the bands observed around 40 cm^{-1}.

Other proposals of symmetry assignments for the Raman active lattice modes in the gamma phase of TBB have also been made.[5,7] They are shown in Table II along with the assignments made in this work. The assignment in set C was again based primarily on a lattice-dynamics calculation and was made especially difficult by the lack of identification of all six of the Raman active bands. The assignment made in set D apparently was based on analogy to the assignments of the lattice modes in the beta phase of TBB. As discussed above, the discrepancies between these two sets of assignments and those determined in this work are probably due to uncertainties in the lattice-dynamics calculations and to an accretion of errors in the analogies used that began with incorrect assignments for TCB. Of course, given the experimental and calculative limitations under which the earlier investigators were working, such difficulties with assignments are not surprising.

C. Beta phase of 1,2,4,5-tetrachlorobenzene

The frequencies observed for the lattice modes in the beta phase of TCB are in excellent agreement with those reported in previous studies.[7,8,19] Pasquier and Le Calve[7] estimate a sixth frequency around 52 cm^{-1}, apparently based on a very weak shoulder observed in their room-temperature Raman spectrum. Therefore, of the six Raman active lattice phonons present in TCB, five can be identified in the spectra in Figs. 12 and 13. The peaks at 20, 45, and 49 cm^{-1} in the (cc) spectrum should be assigned to lattice modes of A_g symmetry, with the weak structure near 36 cm^{-1} appearing due to breakthrough scattering. The two bands identified at 35.5 and 57.5 cm^{-1} in the other TCB spectrum must then correspond to modes of B_g symmetry, since both A_g and B_g bands are allowed in this scattering geometry. The mode at 52 cm^{-1} reported by Pasquier and Le Calve would then also be B_g active.

The assignments of the Raman active lattice phonons in the beta phase of TCB are tabulated in Table III along with those proposed in a previous experimental study.[8] A significant discrepancy exists between the two sets of assignments. Indeed, the (cc) polarized Raman spectrum of TCB reported in the earlier study is radically different from the one obtained in this work. On the other hand, the assignments for TBB resulting from this work, which are also listed in Table III, show a one-to-one correspondence with those of TCB. Such a comparison reinforces the new assignments proposed for TCB herein.

A possible reason for the difference between the polarized Raman spectra of TCB obtained here and those reported previously would be a misidentification of the crystal axes in establishing the scattering geometries. The identification of these axes in the present study is based on Herbstein's[15] report of the crystal morphology and is supported by the symmetry observed in the crystal habit and principal directions for the {110} faces. In addition, the conformity of the TCB habit with that of TBB, in which the crystal faces were accurately determined by optical goniometry, confirmed the axial identification.

V. LATTICE-DYNAMICS CALCULATION OF BETA PHASE OF 1,2,4,5-TETRABROMOBENZNE

Lattice-dynamics calculations using atom–atom intermolecular potentials have been applied to many systems and their usefulness in the determination of symmetries, frequencies, and molecular motions associated with lattice vibrations has been widely demonstrated.[17] A lattice-dynamics calculation for TBB is already in the literature[6] but, as mentioned previously, the results do not agree with the experimentally determined assignments made in this study for the Raman active lattice modes. Therefore, a calculation for the beta phase of TBB was performed to determine whether including a minimization of the crystal energy would offer a better result.

The method and program used in the calculation are described in detail elsewhere.[20-22] The crystal energy was calculated using the atom–atom intermolecular Buckingham potential, given by

TABLE II. Raman active lattice modes in the gamma phase of TBB at 330 K.

Factor group symmetry	Frequency (cm^{-1}) This work	C (Ref. 5)	D (Ref. 7)
A_g	14.5	14.5	27
B_g	28	···	13.5
A_g	35.5		32.5
		28.0	
B_g	39.5		36
A_g	41	40.0	38.5/40
B_g	43.5	34.0	38.5/40

TABLE III. Raman active lattice modes in the beta phases of TCB and TBB at 300 K.

Factor group symmetry	Frequency (cm^{-1}) TCB beta phase This work	TCB beta phase Ref. 8	TBB beta phase This work
A_g	20	35	15.5
B_g	35.5	21	21.5
A_g	45	46	39
A_g	49	58	41.5
B_g	···	49	43
B_g	57.5	···	47.5

TABLE IV. Unit cell constants for the TBB crystal determined from a minimization of the lattice potential energy.

Unit cell parameter	Calculated	Observed[a]
a (Å)	10.109	10.323
b	11.030	10.705
c	3.803	4.018
β (deg)	100.9	102.4
ϕ	18.5	17.9
ψ	335.0	328.0
θ	309.6	308.4
Lattice energy (kcal/mol)	-24.7	...

[a] Reference 11.

$$V_{ij} = A_{ij}\exp(-B_{ij}r_{ij}) - C_{ij}r_{ij}^{-6},$$

where r_{ij} is the distance between the ith and jth atoms belonging to different molecular uinits and A_{ij}, B_{ij}, and C_{ij} are empirical constants whose values depend on the types of atoms. Convergence of the crystal energy in TBB was obtained by summing the interactions over 97 molecules that were contained in a nearly spherical volume of the lattice having a radius of about 15 Å. The values for the A, B, and C parameters for carbon and hydrogen were taken from the work of Williams.[23] Several sets of parameters have been derived for bromine and its interactions with carbon and hydrogen.[6,24] While each resulted in approximately the same eigenvectors for the lattice phonons, set I from Ref. 6 was used in the final calculation because it produced the best fit to the experimentally measured unit cell constants of the TBB crystal.

The potential energy of the TBB crystal was minimized with respect to the monoclinic unit cell constants a, b, c, and β as well as to the Euler angles ϕ, ψ, and θ which define the orientation of the molecules in the cell. For the purpose of the calculation, the molecules were taken to be rigid bodies. The constants for the energy minimized crystal structure are listed in Table IV along with the measured values of the beta phase at room temperature.[11] The agreement between the two sets of data is quite good.

With the crystal potential-energy function in hand, the lattice-dynamics problem was solved at $T \approx 0$ K under the harmonic and rigid body approximations for a wave vector at the center of the Brillouin zone. The frequencies, symmetries, and eigenvectors obtained for the nine optical lattice modes in TBB are listed in Table V. The eigenvectors for the Raman active modes, which involve only librational motions of the molecules, are shown as rotation vectors described in terms of the molecular axes where z is normal to the plane of the molecule, x contains the C–H bonds, and y is perpendicular to x and z. The eigenvectors for the infrared active modes, which involve only translational movement of the molecules, are given in abc^* crystallographic coordinates for easier visualization of these motions. All the vectors have been normalized.

For comparison with the results of the calculation, the frequencies observed in the beta phase of TBB for the Raman active modes at 12 K and the infrared active modes at 90 K are also given in Table V. The frequencies have been placed in the table according to the symmetry assignments made in this study for the Raman active modes and by Pasquier and Le Calve[7] for the infrared active modes. While the agreement between experiment and calculation is reasonable with the greatest disparity between the observed and calculated frequencies for a given mode being 15 cm^{-1}, it is worrisome that both sets of data do not ascend in energy when they are paired according to the experimental symmetry assignments. This can be attributed to inadequacies in the potential energy function derived for the TBB crystal where parametrization of the bromine interactions is particularly problematic. Although it successfully reproduces the observed crystal structure, it is not capable of an accurate prediction of the lattice vibrational frequencies. Nevertheless, the symmetries of the modes are well established.

VI. CONCLUSION

This polarized Raman study of the single crystals of TBB and TCB has produced complete and consistent sets of symmetry assignments for the Raman active lattice modes for both the beta and gamma phases of TBB and for the beta

TABLE V. Lattice-dynamics calculation for TBB.

Symmetry	Frequency (cm^{-1}) Calculated	Observed	Eigenvectors[a] R_x	R_y	R_z	T_a	T_b	T_c
A_g	26.3	18[b]	0.665	0.742	-0.077	0	0	0
B_g	26.9	22[b]	-0.685	-0.008	0.729	0	0	0
B_g	33.4	49[b]	-0.670	0.589	-0.452	0	0	0
A_g	35.6	47[b]	-0.397	0.918	0.005	0	0	0
A_u	39.4	39[c]	0	0	0	0.009	0	0.999
A_g	40.6	40[b]	0.114	0.106	0.988	0	0	0
B_g	44.4	54[b]	0.202	0.970	0.139	0	0	0
B_u	49.6	58[c]	0	0	0	0	1.0	0
A_u	51.6	51.5[c]	0	0	0	-0.999	0	0.009

[a] Librational displacements are given by the R coordinates and translational displacements by the T coordinates. The coordinate axes used are described in the text.

[b] Measured at 12 K in Ref. 7.

[c] Measured at 90 K in Ref. 7.

phase of TCB. As one would predict from the isomorphism of their beta phase crystal structures, the assignments for the lattice modes in the TBB and TCB molecular crystals show a one-to-one correspondence, with the mode frequencies for TCB being somewhat higher than those for TBB. In addition, the assignments for the lattice modes in the gamma phase of TBB are quite similar to those obtained for the beta phase, which is consistent with the similarities observed in their crystal structures.

A comparison of the lattice-dynamics calculations performed previously for the beta phase of TBB[6] with those presented here reveals significant differences between the two calculations, even though identical Buckingham potential parameter sets were used. This was attributed to the inclusion of the lattice energy minimization in the calculation employed in this work. None of the studies is capable of calculating frequencies and symmetries for the lattice vibrations in the beta phase of TBB that agree with the assignments determined from the polarized Raman spectra presented herein. The calculation for the gamma phase of TBB[6] also fails in this respect. These conclusions emphasize the need for an improved potential-energy function for this crystal system. Potentials once thought to have successfully calculated lattice mode frequencies and symmetries for the beta and gamma phases of TBB[5] are now found inadequate.

A similar problem exists for TCB. Potential-energy parameters derived from a series of chlorinated benzenes[10] were thought to have correctly calculated the lattice mode frequencies and symmetries of both the beta and alpha phases of TCB.[8,25] However, the new assignments made in this work for the Raman active lattice modes in the beta phase, together with low-temperature Raman frequencies measured in the alpha phase,[7] reveal that this is not the case. This means that the potential-energy function is not entirely transferable over the range of chlorinated aromatics. Other potentials for the chlorinated hydrocarbons have been derived,[2,18,26,27] but the lattice dynamics of TCB were not calculated in these studies. Such calculations, in light of the new Raman assignments given for TCB, would be a good test of their adequacy.

These results point to the importance of complete experimental and calculational lattice dynamics studies of halogenated aromatic organic crystals for understanding of intermolecular interactions and the resulting lattice effects on the control of solid state reactivity. The apparent difficulty of transferability of the halogen atom–atom potentials is manifest in the present study. Further theoretical study of the polarizability changes induced when species are in the solid state is clearly warranted. Until such developments occur, the understanding of halogenated hydrocarbon crystals' lattice dynamics and insight into the role intermolecular forces will be difficult to obtain.

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