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K.M. White
University of Nebraska - Lincoln

Craig J. Eckhardt
University of Nebraska - Lincoln, ceckhardt1@unl.edu

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Single crystal Raman spectra of 1,2,4,5-tetrabromobenzene: Calculational and experimental assignment of the internal modes

K. M. White[a] and C. J. Eckhardt[b]
Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0304

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A detailed study of the fundamental internal modes of the 1,2,4,5-tetrabromobenzene crystal has provided assignments of Raman-active modes consistent with polarized single-crystal measurements. A normal-mode calculation based on a valence force field derived from brominated and chlorinated benzenes is found to be in excellent agreement with the assignments. Additional bands arising from anharmonic interactions of the fundamentals are also assigned. © *1998 American Institute of Physics.* [S0021-9606(98)00225-6]

I. INTRODUCTION

In the study of supramolecular systems, the understanding of intermolecular interactions is critical. Perhaps the most common, although not necessarily simple, supramolecular assembly is the crystal. Molecular crystals afford a particularly facile way to study intermolecular forces. These systems are useful because there is usually a large energy separation between the so-called external modes that arise from intermolecular forces and the internal modes that are characteristic of bonding in the molecules comprising the crystal. With crystals comprised of molecules that are reasonably fluctional, the frequency gap is small or vanishes. Such systems, although of great interest, present difficult questions regarding anharmonicity and the mode couplings from which it arises. Nevertheless, an investigation of the complete set of vibrational modes in crystals should provide valuable insights into interactions in supramolecular assemblies. To this end we have engaged in a study of intermolecular forces in molecular crystals. In the system chosen to initiate this course of investigation, 1,2,4,5-tetrabromobenzene (TBB), there is an appreciable separation between the frequencies of the internal and external vibrational modes.

In previous papers we have reported a study of the Raman-active optical lattice modes for the β and γ phases of TBB,[1] an investigation of the anharmonicity of these modes using piezomodulated Raman spectroscopy,[2,3] and a determination of lattice mode motions using the same technique.[4] These studies have made some reference to characteristics of the intramolecular modes of TBB. Consequently, it was necessary to have access to the set of symmetry assignments for the Raman-active molecular modes of TBB in order to provide a complete picture of the Raman-active optical modes in this crystal.

Raman spectra of the intramolecular vibrations in crystalline TBB have been reported previously.[5,6] Each of these reports included a set of symmetry assignments. However, the two sets were not in full agreement. One assignment set was incomplete and no indication was given as to how the assignments were made.[5] No description of the Raman experiment itself was offered, making it difficult to ascertain the accuracy of the reported vibrational frequencies and the validity of the assignments. The other assignment set was based on unpolarized spectra measured from TBB powder samples.[6] Therefore, no intensity polarization ratios could be analyzed to confirm the assignments. Although the assignment was complete, it relied upon estimated frequencies for some fundamental modes that were not directly observed in the Raman spectrum.

To complete our investigation of the internal vibrations in crystalline TBB, we report polarized Raman spectra of the intramolecular modes measured from single crystals. We present the relevant experimental information and the data obtained from the measurements. The results are used to assign the fundamental modes, together with some transitions arising from anharmonic interactions. Some differences from previously reported frequencies and assignments are observed. Finally, a calculation based on a valence force field is performed and the frequencies and symmetries obtained are used to confirm the assignment of experimental data.

II. EXPERIMENT AND RESULTS

TBB is particularly well suited to crystal spectroscopy since its crystals exhibit a large separation between internal and external vibrational modes. The TBB obtained from Aldrich Chemical was purified by vacuum sublimation and subsequently crystallized from chloroform at an ambient temperature. The resulting crystals of the β phase possess $P2_1/a$ symmetry (monoclinic) with $Z=2$. Details of the crystal morphology and optical properties are described in Ref. 1.

The polarized Raman spectra of the intramolecular vibrational modes of TBB were measured at room temperature from 60 to 1600 cm^{-1} and also in the 3030–3070 cm^{-1} range. The scans were limited to these frequency regions, since the objective was to locate and assign the fundamental modes only. Measurements were made using a polarized argon ion laser beam tuned to 514.5 nm. Raman scattered light was collected through an analyzer and detected using meth-

[a]Current address: 3M Company, St. Paul, MN 55144-1000.
[b]Author to whom correspondence should be addressed.

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TABLE I. Frequencies and relative intensities of bands observed in Raman spectra of TBB.

Frequency (cm^{-1})	Relative peak height[a] (arbitrary units) $b(a'b)c^*$	$b(a'a^+)c^+$	$b(c'a^+)c^+$	$b(c'b)c^*$
3048	51	20	10	13
1549	sh	⋯	⋯	3.5
1537	8	22	5	6
1523	12	6	3.5	6
1340	1	5	3	1.5
1243	⋯	1	1.5	1
1145	2.5	13	4	4
1122	9	26	6.5	9
866	1	1	2	1
800	1.5	w	w	4.5
667	19	60	19	16
657	9.5	28	8	8
453	2	6	2	4.5
317	2	7	13	9
220	150	185	53	60
208	(7)	(sh)	(20)	(8)
203	(4)	78	(23)	65
125	660	83	70	140

[a]The values listed for all four scattering geometries are based on the same intensity scale. Values in parentheses indicate that the band significantly overlaps neighboring bands. Weak bands are denoted by w and shoulders by sh.

ods described elsewhere.[7] Signals were amplified by an electrometer and fed to a chart recorder. Spectra were obtained via a continuous scan of the monochromator, which was calibrated over the pertinent wavelength range using the spectral lines of a low-pressure mercury lamp.

The scattering geometry employed in the measurement had (010) as the incident crystal face and (001) as the scattering face. While the latter is a naturally occurring face for TBB, (010) had to be cut by means of an ultramicrotome. The spectra were obtained for the $b(c'b)c^*$, $b(a'b)c^*$, $b(c'a^+)c^+$, and $b(a'a^+)c^+$ polarizations, where a' and c' are the optical principal directions in the (010) face and a^+ and c^+ are the polarization and ray directions, respectively, for scattered light collected along c^* and polarized perpendicular to b.[1] The frequencies, which were determined to an accuracy of $\pm 2\ cm^{-1}$, are listed in Table I, along with the relative heights of their respective bands in each of the four scattering geometries. The tabulated intensities have not been corrected for crystal optical effects or detector response.

The measured Raman spectra were in general agreement with data reported previously. However, a discrepancy in the frequencies of the fundamental modes was observed. A study by Francis and Harris,[5] in which no mention of calibration of the Raman experiment was made, reported values that averaged $5\ cm^{-1}$ higher in energy than those observed in this work. Frequencies obtained in a study done by Yadav and Shanker[6] were higher still. In their work, calibration was provided by a spectrum of liquid chloroform. More importantly, they did not observe the four fundamental modes we identified at 800, 453, 208, and $125\ cm^{-1}$. The $125\ cm^{-1}$ band was the most intense one we observed in the Raman spectra.

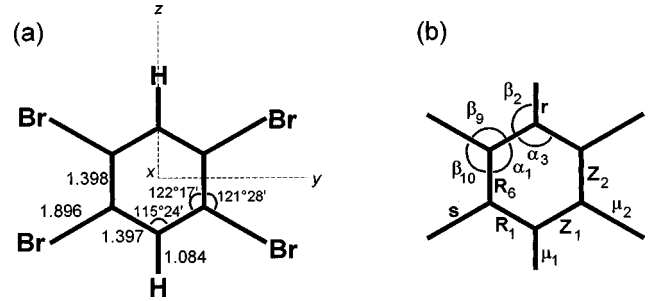

FIG. 1. (a) Molecular structure of TBB as determined from x-ray crystallography of the crystal (Ref. 18). (b) Coordinates used in the calculation of normal modes in TBB. In-plane stretches are represented by s, r, and R coordinates, in-plane bends by α and β coordinates, out-of-plane bends by μ coordinates, and torsional (three-bond) bending by Z coordinates. D_{2h} symmetry applies to the molecular representations in both (a) and (b).

III. DISCUSSION

There are 30 intramolecular vibrational modes in TBB. Symmetry analysis of the planar molecule under the D_{2h} point group indicates that the symmetry species for the normal modes are

$$\Gamma = 6a_g + 1b_{1g} + 3b_{2g} + 5b_{3g} + 2a_u + 5b_{1u} + 5b_{2u} + 3b_{3u}.$$

The a_g, b_{3g}, b_{1u}, and b_{2u} modes correspond to in-plane vibrations and the b_{1g}, b_{2g}, a_u, and b_{3u} modes to out-of-plane vibrations. For this analysis, the molecular x axis is defined perpendicular to the plane of the molecule, the z axis is parallel to the C–H bonds, and the y axis is orthogonal to these two axes [Fig. 1(a)]. Because of the inversion symmetry of the molecule, only molecular modes having an even parity are Raman active. The remaining modes are infrared active, except for the two a_u modes, which are inactive.

Since the TBB molecules lie at sites of inversion in the crystal, the symmetries of the intramolecular vibrations are correlated through the C_i site group into the C_{2h} factor group of the unit cell (Table II). Effects of the crystal field influ-

TABLE II. Correlation diagram for intramolecular modes in TBB.

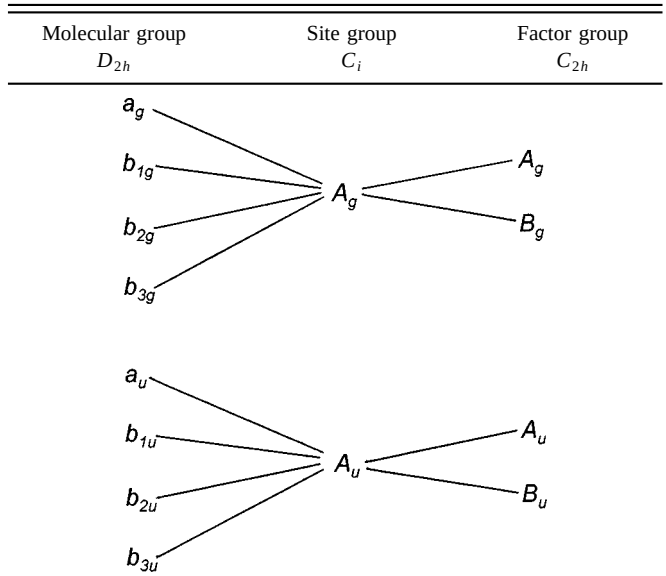

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TABLE III. Theoretical relative intensities corresponding to intramolecular modes observable in Raman spectra of the TBB crystal.[a]

Symmetry species	Scattering geometry $b(a'b)c^*$	$b(a'a^+)c^+$	$b(c'a^+)c^+$	$b(c'b)c^*$
b_{1g}	0.01	0.25	0.43	0.46
b_{2g}	0.03	0.27	0.08	0.38
b_{3g}	0.00	0.50	0.00	0.04
a_g (xx)	0.00	0.00	0.47	0.04
a_g (yy)	0.24	0.16	0.01	0.01
a_g (zz)	0.24	0.09	0.00	0.01

[a]Relative intensities are valid only to compare peak heights of Raman bands observed in the scattering geometries listed for a single mode having a given symmetry.

enced by the factor group and site symmetries can generally be ignored, however, because coupling of intramolecular vibrational modes in TBB has been shown to be small.[3] Thus, the oriented gas model can be employed to assign the molecular modes in TBB under the D_{2h} point group.

The fundamental intramolecular vibrations in TBB were assigned following previously described methods for molecules of D_{2h} symmetry.[8,9] The procedure relies on polarized Raman spectra of the molecule in the melt, powder, or solution phases to determine the a_g modes, after which the nontotally symmetric Raman active modes are assigned with the aid of an oriented gas calculation. The intensity I of a Raman band corresponding to the intramolecular mode j is given by

$$I_j = A_j[\mathbf{e}_e^{\dagger}\boldsymbol{\alpha}_j\mathbf{e}_s]^2, \tag{1}$$

where $\mathbf{e}_s$ and $\mathbf{e}_e$ are unit vectors along the polarizations of the scattered and exciting light, respectively, $\boldsymbol{\alpha}_j$ is the Raman tensor for the appropriate symmetry species of mode j, and A_j is a constant of proportionality.[10] By measuring the Raman spectra in various scattering geometries, a set of relative intensities for each vibrational mode can be obtained. The symmetries of the nontotally symmetric modes may then be assigned by comparison of the experimental relative intensities to the calculated relative intensities derived for each of the modes of b_{1g}, b_{2g}, and b_{3g} symmetry. These theoretical relative intensities were determined for the scattering configurations employed in the TBB Raman spectra and are listed in Table III.

A. Totally symmetric fundamentals

Assignment of the totally symmetric intramolecular vibrations in TBB from polarized Raman spectra of isotropic phases was unsuccessful. Very intense Rayleigh scattering masked the Raman bands of the melt and powder, and TBB could not be dissolved in sufficient concentration to observe the bands in solution. As a result, these modes were assigned based on the very high intensity of their Raman bands[8] and by analogy to the assignments given for 1,2,4,5-tetrachlorobenzene (TCB).[11] The latter approach was aided by a normal coordinate analysis of TBB (see Sec. III D).

Using the above criteria, the bands at 125, 220, 667, 1122, 1523, and 3048 cm^{-1} are readily assigned as the six a_g fundamentals in TBB. The band at 1523 cm^{-1} does not display the high intensity of the others, but corresponds well to the 1549 cm^{-1} a_g mode in TCB. Our assignments agree with those proposed by Francis and Harris,[5] except for the mode at 667 cm^{-1}, which they attributed to a b_{2g} fundamental. The assignment of this vibration will be considered later in greater detail. The 3048 cm^{-1} mode, which was not observed by Francis and Harris, was assigned by Yadav and Shanker,[6] although at a significantly higher frequency of 3065 cm^{-1}. Their other assignments are consistent with ours, except for the lowest-energy a_g mode that they assigned to a band they observed at 155 cm^{-1}.

The totally symmetric bands, in general, are relatively intense in the $(a'b)$ scattering geometry, and for those at 125, 1523, and 3048 cm^{-1}, this particular polarization produced the highest intensity. In contrast, the oriented gas model predicts negligible intensity for the nontotally symmetric modes in the $(a'b)$ polarization. Consequently, relative intensities for the a_g modes were also calculated using Eq. (1) for the four experimental scattering geometries (see Table III). Of the three totally symmetric elements in the D_{2h} Raman tensor, the yy and zz elements would be expected to make the greatest contribution to the Raman intensities of the in-plane a_g vibrations [see Fig. 1(a)]. The calculated relative intensities for both of these elements were, in fact, greatest for the $(a'b)$ scattering geometry, followed by the $(a'a^+)$ polarization. The intensities predicted for the $(c'b)$ and $(c'a^+)$ polarizations were much smaller. These results are qualitatively observed in the polarized Raman data for the a_g modes assigned here, thus confirming the assignments.

B. Nontotally symmetric fundamentals

The Raman bands corresponding to the nontotally symmetric vibrations in TBB are inherently much less intense than those of the a_g modes. As a result, reliable assignments based on calculated relative intensities can be made for only half the bands. The remaining bands were assigned using the vibrational assignments proposed for TCB[11] and the normal coordinate analysis of TBB.

Four peaks in the intramolecular Raman spectrum of TBB are sufficiently intense to assign using the calculated relative intensities in Table III. The sole b_{1g} fundamental vibration is easily identified at 317 cm^{-1}, as determined from its high relative intensity observed in the $(c'a^+)$ and $(c'b)$ scattering geometries. A b_{2g} fundamental at 203 cm^{-1} was assigned, based on its intense bands in the $(a'a^+)$ and $(c'b)$ spectra. Finally, the bands at 453 and 1537 cm^{-1}, both of which were strongest in the $(a'a^+)$ spectrum, were attributed to b_{3g} fundamentals.

The assignments of the remaining b_{2g} and b_{3g} fundamentals in TBB were not based on the polarized Raman data due to the weak intensities and strong overlap of their spectral bands. By analogy with the TCB assignments, the modes at 208, 800, and 1243 cm^{-1} were attributed to the remaining three b_{3g} modes. In a similar fashion, the band at 866 cm^{-1} was assigned as a b_{2g} fundamental. These assignments of nontotally symmetric fundamentals are in agreement with those of Francis and Harris.[5] In contrast, the corresponding assignments proposed by Yadav and Shanker differ significantly for three of the modes.[6] They did not observe the 208

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or 800 cm^{-1} modes and the frequencies they estimated for them from overtone or combination bands were about 50 cm^{-1} too low. In addition, they did not observe the 453 cm^{-1} band and instead assigned the mode at 234 cm^{-1}.

The assignment of one b_{2g} mode still needs to be considered. Based on the assignments in TCB, the remaining b_{2g} fundamental would be expected in the 600–700 cm^{-1} frequency region. A likely candidate for the assignment would be the band at 657 cm^{-1}. In fact, Yadav and Shanker assigned this band, which they observed at 662 cm^{-1}, to this mode.[6] In contrast, Francis and Harris attributed this band to an a_g mode and instead assigned the band at 667 cm^{-1}, which they reported at 672 cm^{-1}, to the b_{2g} fundamental.[5] While their polarized phosphorescence microwave double resonance data apparently support such an assignment, it is in doubt from the standpoint of the Raman data. Neither the 667 nor 657 cm^{-1} band displays polarized Raman ratios that correspond to the oriented gas predictions for a b_{2g} mode, and the large intensity of the band at 667 cm^{-1} suggests that it is unlikely that it arises from a nontotally symmetric vibration. Therefore, the assignment must be based on additional information.

Examination of the vibrational assignments in TCB indicates that its corresponding b_{2g} mode is not observable in the Raman spectrum. It was finally placed at 681 cm^{-1} after an analysis of the measured combination bands.[11] This suggests that the mode would display very low intensity in the TBB Raman spectrum also, thereby ruling out the 667 or 657 cm^{-1} bands for the assignment. In addition, the normal coordinate analysis of TBB, which indicates that the mode in question involves both an out-of-plane deformation of the benzene ring and wagging of the bromine atoms, places its frequency at 698 cm^{-1} (see Table IV). A search of the Raman spectrum in the region of this frequency indeed reveals a very weak, but reproducible, shoulder on the high-energy side of the 667 cm^{-1} band. Thus, the shoulder at 670 cm^{-1} is assigned to the final b_{2g} fundamental in TBB.

TABLE IV. Comparison of the experimentally assigned intramolecular modes of TBB with the normal mode calculation.

Mode	Symmetry	Frequency (cm^{-1}) Observed	Calculated	Potential energy distribution[e] (%)
Raman active modes				
ν_1	a_g	3048	3070	$r(99)$
ν_2	a_g	1523	1522	$R_6(54),R_1(28)$
ν_3	a_g	1122	1104	$R_1(46),s(31),R_6(22)$
ν_4	a_g	667	667	$\alpha_3(36),s(19),\alpha_1(16)$
ν_5	a_g	220	225	$s(64),R_1(13),\alpha_3(10)$
ν_6	a_g	125	118	$\beta_{10}(65),\beta_9(33)$
ν_9	b_{1g}	317	326	$\mu_2(83),Z_1(17)$
ν_{15}	b_{2g}	866	858	$\mu_1(74),Z_1(19)$
ν_{16}	b_{2g}	670	698	$\mu_2(77),Z_1(20)$
ν_{17}	b_{2g}	203	206	$Z_2(47),\mu_2(36)$
ν_{23}	b_{3g}	1537	1530	$R_1(65),\beta_2(20)$
ν_{24}	b_{3g}	1243	1234	$\beta_2(75),R_1(17)$
ν_{25}	b_{3g}	800	795	$s(49),\alpha_1(28),\beta_{10}(18)$
ν_{26}	b_{3g}	453	464	$\beta_{10}(49),\beta_9(43)$
ν_{27}	b_{3g}	208	210	$s(45),\alpha_1(33),\beta_9(12)$
Infrared active modes				
ν_7	a_u	570[a]	607	$\mu_2(99)$
ν_8	a_u	45[b]	49	$Z_2(72),Z_1(25)$
ν_{10}	b_{1u}	3070[c]	3070	$r(99)$
ν_{11}	b_{1u}	1297[c]	1309	$R_1(69),\beta_{10}(18)$
ν_{12}	b_{1u}	1019[c]	1046	$\alpha_1(33),s(25),\alpha_3(18)$
ν_{13}	b_{1u}	429[c]/388[d]	399	$s(71),\beta_{10}(19)$
ν_{14}	b_{1u}	135[b]	136	$\beta_9(42),\beta_{10}(41)$
ν_{18}	b_{2u}	1418[c]	1428	$\beta_2(56),R_6(17),R_1(16)$
ν_{19}	b_{2u}	1200[c]	1207	$R_1(51),R_6(44)$
ν_{20}	b_{2u}	1110[c]	1065	$R_1(34),\beta_2(32),R_6(14),s(14)$
ν_{21}	b_{2u}	521[c]	540	$s(87)$
ν_{22}	b_{2u}	120[b]	128	$\beta_{10}(61),\beta_9(30)$
ν_{28}	b_{3u}	880[c]	870	$\mu_1(75),Z_1(21)$
ν_{29}	b_{3u}	388[c]/429[d]	436	$\mu_2(64),Z_1(33)$
ν_{30}	b_{3u}	96[b]	105	$\mu_2(44),Z_1(34),\mu_1(21)$

[a]Assigned in this work.
[b]Observed in Ref. 12.
[c]Assigned in Ref. 13.
[d]Assigned in Ref. 14.
[e]Percent of total energy represented by the listed coordinate for the given mode is indicated in parentheses. See Fig. 1(b) for normal coordinate designations.

C. Overtone and combination bands

While the Raman spectra of TBB in the intramolecular vibrational energy region were measured with the intent of assigning the fundamental modes, bands arising from overtone and combination transitions in the molecule were also observed. It can be seen from Tables I and IV that the Raman bands at 657, 1145, 1340, and 1549 cm^{-1} remain to be assigned. The peaks at 1340 and 1549 cm^{-1} are weak, which is typical for anharmonic transitions. This makes it difficult to determine their symmetries based on relative intensity data from the polarized Raman spectra. The consideration of assignments made previously for the overtone and combination bands in the Raman spectrum of TCB[11] offers no comparable assignments for these bands in TBB. However, similarities between the two molecules suggest that the anharmonic transitions observed in their Raman spectra should arise from the same combinations of fundamental modes. With this constraint, analysis based on frequency values alone makes it possible to assign each of the bands.

The 1340 cm^{-1} band is attributed to the first overtone of the 667 cm^{-1} fundamental. The corresponding mode in TCB is found at 684 cm^{-1}. A band at 1350 cm^{-1} in the TCB Raman spectrum would then represent the first overtone. This frequency had been assigned as a combination of the 1165 and 190 cm^{-1} fundamentals,[11] but no combination band could be found comprising the corresponding TBB fundamentals at 1122 and 125 cm^{-1}. For the 1549 cm^{-1} peak, a combination of the 1243 cm^{-1} b_{3g} and 317 cm^{-1} b_{1g} vibrations is assigned. The corresponding fundamentals at 1240 and 348 cm^{-1} in TCB then account for the combination band observed in the Raman spectrum at 1590 cm^{-1}. This band had been assigned as a combination of the 1240 and 352 cm^{-1} fundamentals, but again no band could be found comprising the corresponding TBB fundamentals near 1243 + 220 cm^{-1}.

The remaining Raman peaks at 657 and 1145 cm^{-1} are much more intense than the other anharmonic bands. Moreover, they appear close to intense a_g modes at 667 and 1122 cm^{-1}, respectively, and, in the various scattering ge-

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ometries, have relative intensities similar to their neighboring bands. These observations suggest that these two bands are enhanced by Fermi resonance. The combination of the 453 and 208 cm^{-1} b_{3g} modes, giving rise to an a_g transition, is attributed to the 657 cm^{-1} band observed in Fermi resonance with the 667 cm^{-1} a_g peak. Both of the 453 and 208 cm^{-1} modes involve in-plane stretching and bending motions of the bromine atoms (see Table IV). Other possible combinations are less probable since they involve difference bands and higher-order overtones.

The band at 1145 cm^{-1} is attributed to the first overtone of a spectrally inactive a_u vibration of TBB (estimated near 570 cm^{-1}) in Fermi resonance with the 1122 cm^{-1} a_g band. Identification of the a_u mode follows from an analysis of a strong Fermi resonance between the 1418 cm^{-1} fundamental and the 1442 cm^{-1} combination band in the infrared spectrum of TBB.[12] In TCB, the corresponding combination band was assigned to the 860 cm^{-1} b_{2g} and 600 cm^{-1} a_u modes.[11] In TBB, the corresponding b_{2g} mode was assigned at 866 cm^{-1}, suggesting that the corresponding a_u mode in TBB has a frequency in the vicinity of 570 cm^{-1}. To complete the analogy, the first overtone of the corresponding a_u mode in TCB has also been observed in its Raman spectrum at 1205 cm^{-1}.[11]

Additional evidence exists for locating this TBB a_u mode near 570 cm^{-1}. While the crystal structure of TBB determined from x-ray crystallography allows for D_{2h} symmetry of the molecule within experimental error, the reported coordinates actually show the molecular symmetry to be reduced to that of the C_i site symmetry. Thus, the crystal field may be sufficiently large to perturb the molecular structure. From Table II it is seen that under these conditions the molecular a_u vibrations would then be described by the A_u representation of the C_i point group and would become weakly infrared active. Indeed, the infrared spectrum of TBB does show a weak, but reproducible, band near 570 cm^{-1}.[13] Yadav and Shanker reported it at 560 cm^{-1}.[6] A similar effect is reported for solid hexabromobenzene, in which the molecular symmetry is reduced to D_{3d}, allowing a corresponding mode to be observed at 567 cm^{-1} in the infrared spectrum.[15] The corresponding structure near 600 cm^{-1} in the infrared spectra of TCB[11,13] indicates that the same effect likely occurs in that crystal as well.

D. Normal coordinate analysis

A normal coordinate analysis of the intramolecular vibrations in TBB was performed following the method of Wilson, Decius, and Cross[16] using a computer program adapted by McIntosh and Peterson.[17] The TBB molecule was assumed to have D_{2h} symmetry with the average x-ray determined structure[18] shown in Fig. 1(a). The coordinates for the hydrogen atoms were estimated using a C–H bond length of 1.084 Å.[19] The mirror symmetry of the molecule allowed separation of the calculation into two parts, each with its own set of force constants. The in-plane vibrations were solved first, followed by the determination of the out-of-plane vibrations. A valence force field was used in both of the calculations.

The internal coordinates used to describe the vibrational modes in TBB were defined to maintain the molecular symmetry, and are shown in Fig. 1(b). The force constants corresponding to the in-plane coordinates were taken from the work of Le Calve and Labarbe,[20] in which they calculated vibrational frequencies for the dibromobenzenes. These force constants, except for those referring to the C–Br stretches and bends, were transferred directly from the valence force field derived by Scherer[19] for a series of chlorinated benzenes.

A set of force constants for the out-of-plane coordinates was not so easily obtained. Scherer[21] has determined a set for the chlorinated benzenes, but they could not be used in the TBB calculation because the program used in this work employed a different definition of the torsional internal coordinate[22] making Scherer's out-of-plane force constants nontransferable. One study that made use of the torsional coordinate definition in question was that by Gambi *et al.*,[23] in which a set of out-of-plane force constants for benzene were derived. However, reproduction of Gambi's calculated frequencies was accomplished only when his force constant H_z, representing the torsion about $C-C$ bonds in the ring, was reduced to 0.2315 and the torsional interaction force constant f_z^m was set to zero.

Starting with the altered force constants of Gambi *et al.* for benzene and using Scherer's set of constants for the chlorobenzenes[21] for an estimation of the relative magnitudes, a new set of out-of-plane force constants was obtained for TCB and its two possible deuterated derivatives by a simultaneous, nonlinear least squares fit to their observed vibrational frequencies using the Simplex algorithm of Nelder and Mead.[24] The resulting force field produced a slightly better fit between the calculated and observed frequencies than that obtained by Scherer. This is to be expected, however, since these force constants were refined for a much smaller set of molecules, making them less general. Nevertheless, the out-of-plane force constants obtained here for TCB are of sufficient quality to be used in the calculation of the out-of-plane fundamental vibrations in TBB. All force constants employed in the TBB calculations are tabulated in Table V.

The calculated frequencies and symmetries of the Raman and infrared active intramolecular fundamental modes in TBB are shown in Table IV, along with experimentally observed values. The modes have been designated following the convention of Herzberg.[25] No refinement of the force constants was attempted since they would be severely underdetermined in a fit to the observed frequencies of TBB alone, and no further meaningful information would be obtained. The potential energy distributions obtained from the calculation for each of the modes is also in Table IV.

The observed and calculated frequencies for the Raman active modes have been paired according to the symmetry assignments made in the above discussion. A very satisfactory fit is observed, especially when considering that a majority of the force constants used were transferred directly from the chlorinated benzenes. In essentially all cases, the calculation confirms the assignments made herein for the fundamental, Raman-active, vibrational modes in TBB.

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TABLE V. Force constants used in the normal coordinate calculation for TBB.[a]

In-plane force constants					
s	3.3000	r	5.1165	R_1	6.5000
R_6	6.5000	α_1	0.8651	α_3	0.9886
β_2	0.5083	β_9	0.7461	β_{10}	1.2613
sR_1	0.4101	sR_6	0.3202	$s\beta_{10}$	0.6544
$RR(o)$	0.8290	$RR(m)$	−0.4696	$RR(p)$	0.2789
$R_1\alpha_1$	0.2901	$R_1\beta_2$	0.1012	$R_1\beta_9$	0.1969
$R_6\beta_{10}$	0.1868	$\beta_{10}\beta_{10}$	0.3716		
Out-of-plane force constants					
μ_1	0.2878	μ_2	0.3666	Z_1	0.2400
Z_2	0.3200	$\mu_1\mu_1(p)$	−0.0080	$\mu_1\mu_2(o)$	0.0188
$\mu_1\mu_2(m)$	−0.0096	$\mu_2\mu_2(o)$	0.0478	$\mu_2\mu_2(m)$	−0.0205
$\mu_2\mu_2(p)$	−0.0059	$\mu_1Z(o)$	−0.0336	$\mu_1Z(m)$	−0.0067
$\mu_2Z(o)$	−0.0121	$\mu_2Z(m)$	−0.0061	$ZZ(o)$	−0.0067

[a]See Fig. 1(b) for normal coordinate designations.

The calculated frequencies for the infrared active modes are also listed with their observed values. Those based on the assignments proposed by Hamann[13] are given for the modes down to 388 cm^{-1}. An assignment proposed by Yadav and Shanker differs somewhat, exhibiting poorer agreement with the calculated frequencies.[6] In a partial assignment proposed by Garrigou–Lagrange *et al.*,[14] the band at 429 cm^{-1} in TBB is assigned to b_{3u} instead of b_{1u} symmetry, based on polarized infrared measurements on TCB single crystals. This change forces an exchange of the assigned symmetries of the 429 and 388 cm^{-1} bands, giving a better fit to the calculation. However, their other assignments derived from gas phase TCB spectra result in a poorer correspondence. Using a frequency proximity criterion, possible assignments for the low-frequency modes are proposed from infrared measurements of TBB by Rao *et al.*[12] The latter study, however, reported more bands than could be accounted for by the infrared active lattice and intramolecular fundamental modes expected in this frequency region for TBB. Finally, the a_u mode assigned in this work around 570 cm^{-1} and reported by Yadav and Shanker[6] at 560 cm^{-1} is also included in Table IV.

IV. CONCLUSIONS

The TBB crystal in its β phase is a system wherein the separation between the internal and external modes is large. This permits effective partitioning of the molecular and intermolecular potentials. Assignments of the Raman-active intramolecular modes in TBB based on polarized spectra of the single crystal show very good agreement with a normal coordinate analysis of the molecule using a valence force field derived from existing data on both brominated and cholorinated benzenes.

Although largely focused on the fundamental vibrations of the molecules, the Raman spectrum provides evidence for anharmonic molecular interactions in overtone and combination bands. Some structure is also attributed to Fermi resonance.

The role of the lattice in affecting the molecular vibrations is found to be quite small. Nevertheless, it is manifested in what is apparently a static distortion of the molecule to inversion symmetry. Most of the modal behavior may, however, be correlated with the D_{2h} pseudosymmetry of the molecule. The lattice modes, which are necessarily anharmonic, appear to exhibit no significant coupling with the internal modes.

The TBB crystal can safely be used as a model of a supramolecular system where the internal and external modes are uncoupled. With assignment of the infrared active modes and determination of the acoustic modes, the TBB crystal may serve as a relatively simple model system, where independence of the molecular and intermolecular potentials has been quantitatively demonstrated. With this study, TBB is, to the best of our knowledge, the only molecular crystal with detailed assignments and examination of anharmonic interactions of both the internal and external Raman-active modes.

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[1] K. M. White and C. J. Eckhardt, J. Chem. Phys. **90**, 4709 (1989).
[2] K. M. White and C. J. Eckhardt, Phys. Rev. Lett. **59**, 574 (1987).
[3] K. M. White and C. J. Eckhardt, J. Chem. Phys. **103**, 3279 (1995).
[4] K. M. White and C. J. Eckhardt, J. Chem. Phys. **92**, 2214 (1990).
[5] A. H. Francis and C. B. Harris, J. Chem. Phys. **57**, 1050 (1972).
[6] R. A. Yadav and R. Shanker, J. Raman Spectrosc. **18**, 555 (1987).
[7] K. M. White, K.-H. Brose, and C. J. Eckhardt, J. Chem. Phys. **85**, 5551 (1986).
[8] A. Girlando and C. Pecile, Spectrochim. Acta A **29**, 1859 (1973).
[9] M. Suzuki, T. Yokoyama, and M. Ito, Spectrochim. Acta A **24**, 1091 (1968).
[10] G. Turrell, *Infrared and Raman Spectra of Crystals* (Academic, London, 1972).
[11] J. R. Scherer and J. C. Evans, Spectrochim. Acta **19**, 1739 (1963).
[12] N. B. Rao, M. Rangacharyulu, P. Venkatacharyulu, and D. Presmaswarup, Org. Magn. Reson. **22**, 1 (1984).
[13] S. D. Hamann, High Temp.-High Press. **8**, 317 (1976).
[14] C. Garrigou-Lagrange, N. Le Calve, and C. Vigna-Lou, J. Chim. Phys. **63**, 1454 (1966).
[15] M. Suzuki, Spectrochim. Acta A **33**, 921 (1977).
[16] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations, The Theory of Infrared and Raman Vibrational Spectra* (Dover, New York, 1955).
[17] D. F. McIntosh and M. R. Peterson, ''General vibrational analysis programs utilizing the Wilson GF matrix method for a general unsymmetrized molecule,'' Quantum Chemistry Program Exchange, Program No. 342, Indiana University Chemistry Department, 1977.
[18] G. Gafner and F. H. Herbstein, Acta Crystallogr. **13**, 706 (1960).
[19] J. R. Scherer, Spectrochim. Acta **20**, 345 (1964).
[20] N. Le Calve and P. Labarbe, Spectrochim. Acta A **26**, 77 (1970).
[21] J. R. Scherer, Spectrochim. Acta A **23**, 1489 (1967).
[22] R. L. Hilderbrandt, J. Mol. Spectrosc. **44**, 599 (1972).
[23] A. Gambi, S. Giorgianni, A. Passerini, and S. Ghersetti, Spectrosc. Lett. **14**, 675 (1981).
[24] J. A. Nelder and R. Mead, Comput. J. **7**, 308 (1965).
[25] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945).

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