High-Pressure Raman Spectra of *p*-Diiodobenzene

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We report a detailed experimental investigation of Raman phonon spectra of crystals of 1,4-diiodobenzene (*p*-DIB) in the pressure range 0−7.5 GPa. Strong modifications of spectral profiles as a function of pressure suggest the possibility of two pressure-induced phase transitions at 0.4 and 1.7 GPa. Quasi-harmonic lattice dynamics (QHLD) calculations, based on intermolecular atom−atom potentials, are applied to model the ambient *p*,*T* crystal structure and the pressure dependence of the Raman-active lattice phonons.

1. Introduction

The 1,4-dihalogenobenzenes, *p*-DXB (X = Cl, Br, I), are interesting crystal systems in that they exhibit several temperature- and pressure-induced solid−solid-phase transitions.[1] While Cl and Br derivatives have been widely studied since the early seventies on changing both temperature and pressure,[2,3] for 1,4-diiodobenzene (*p*-DIB) only a phase transition at high temperature is known,[4] whereas its spectroscopic investigation under pressure was prevented by experimental difficulties.[1] To further investigate on this field, we have revisited the high-pressure Raman spectra of *p*-DIB in the lattice phonon region, to reveal the possible occurrence of pressure-induced phase changes.[5]

In the present paper we present an experimental study of the lattice phonon Raman spectra of *p*-DIB up to 7.5 GPa. Strong modifications of spectral profiles at critical pressures indicate the possible presence of two pressure-induced phase transitions at 0.4 and 1.7 GPa. Further phase changes are likely to occur at higher pressures. Quasi-harmonic lattice dynamics (QHLD) calculations have been performed for a comparison with the experimental temperature[6] and pressure dependence of the lattice phonon frequencies. These calculations are based on a previous investigation[7] on the effects of the intramolecular degrees of freedom on the vibrational spectrum of crystalline *p*-DIB. Raman and IR spectra, phonon density of states, and specific heat were first computed neglecting all intramolecular degrees of freedom and then including them. In all cases it was found that the coupling between inter- and intramolecular vibrations is important and essential to reach agreement with the experimental data. This result was expected, since *p*-DIB has low-frequency intramolecular vibrations falling in the region of lattice phonons,[6−9] due to the large atomic weight of the iodines.

2. Experimental Section

Commercial *p*-DIB (Aldrich) was purified by sublimation under vacuum yielding single crystals as platelike samples. Hydrostatic pressures were obtained in a gasketed diamond anvil cell with a 4:1 methanol−ethanol pressure medium and measured by the ruby luminescence method.[10] Raman spectra were recorded in nearly backscattering geometry with a spectrometer coupled to a microoptical setup as in ref 11. Excitation was from the focused line of a Krypton ion laser (647.1 nm), and the pressure range investigated was ∼0−7.5 GPa.

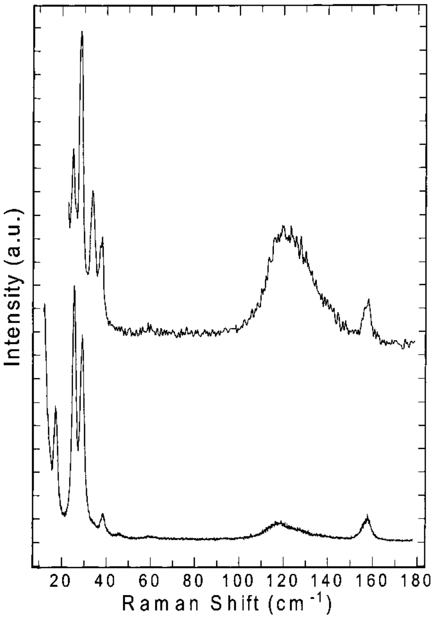

Figure 1. Raman phonon spectra of *p*-DIB at room temperature for two differently oriented single crystals.

3. Results

3.1. Raman Phonon Spectra. At ambient pressure, *p*-DIB shows two crystalline phases, both orthorhombic with space group *Pbca* (α phase) and *Pccn* (*β* phase), respectively, each with four molecules per unit cell in C_i symmetry sites.[5] The α phase is stable at ambient temperature, and the phase transition to the *β* phase occurs at ∼326 K. For the $k = 0$ lattice modes the factor group (D_{2h}) analysis predicts, for both phases, 12 rotational Raman-active ($3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g}$) phonons and 9 translational ($3A_u + 2B_{1u} + 2B_{2u} + 2B_{3u}$) ones, 6 of them IR-active. Previous work[6] on polarized Raman spectra of the α phase at 2 K has determined the symmetry assignment of all but one (with B_{2g} symmetry) intermolecular modes. In the same spectral range, by sampling differently oriented single crystals, we have observed a maximum of eight bands at room temperature. Two typical spectra are shown in Figure 1. The symmetry assignment of lattice modes at room temperature is

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TABLE 1: Experimental and Calculated Lattice Phonons at Different Temperatures (ambient pressure)[a]

	exptl		calcd	
symmetry	2 K	298 K	0 K	298 K
	160.1	*157.3*	*170.5*	*164.1*
A_g	135.3	117.0	164.1	150.3
	43.6	38.2	56.3	51.0
	31.4	29.1	36.7	32.2
B_{1g}	141.1	124.4	164.8	149.5
	38.0	34.4	59.8	52.7
	21.4	17.2	15.7	13.8
B_{2g}	158.2		163.6	150.6
	46.9		64.8	56.9
	(31.4)		47.4	42.0
B_{3g}	142.9	124.4	165.4	149.9
	35.7		49.2	43.4
	29.8	25.5	32.3	27.7

[a] Experimental values at 2 K are from ref 6. Values in italic refer to the lowest internal vibration. The lattice phonon at 124.4 cm^{-1}, corresponding to an unresolved (B_{1g} + B_{3g}) doublet at 298 K, has been listed in both symmetries.

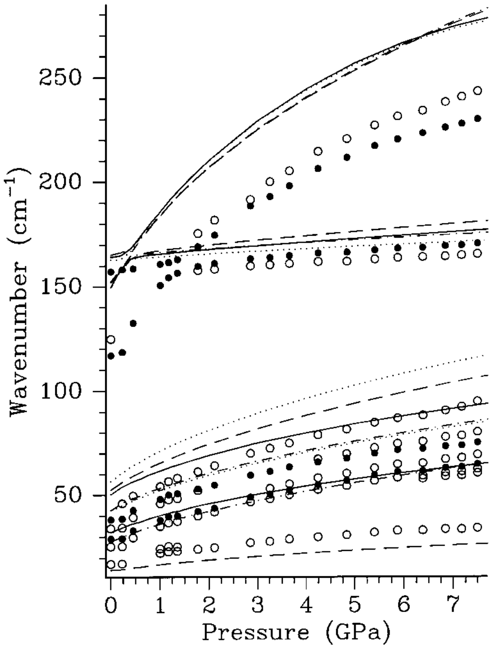

Figure 2. Pressure dependence of Raman-active lattice phonons. Experimental values: (●) A_g modes; (○) B_{1g}, B_{2g}, B_{3g}, and unassigned modes (see text). Calculated values: (—) A_g; (- - -) B_{1g}; (· · ·) B_{2g}; (- · -) B_{3g}.

readily done by comparison with the previous assignment[6] at 2 K and has been confirmed by polarized spectra on single crystals. The complete symmetry assignment of experimental data at 2 K and at 298 K, including the lowest intramolecular vibration at 157 cm^{-1}, is given in Table 1. The computed QHLD frequencies (section 3.3) are also reported in this table.

3.2. Pressure Dependence of Phonon Spectra. High-pressure Raman spectra have been recorded at 298 K up to ~7.5 GPa. Lattice phonons shift to higher wavenumbers on increasing pressure. The experimental peak wavenumbers vs pressure of the most intense Raman-active lattice phonons are shown in Figure 2, where the experimental trends are compared with the computed values of section 3.3. Experimental symmetry assignment at higher pressures is uncertain, due to the possible presence of phase transitions and new modes. Therefore only A_g modes are experimentally assigned and are indicated as full circles.

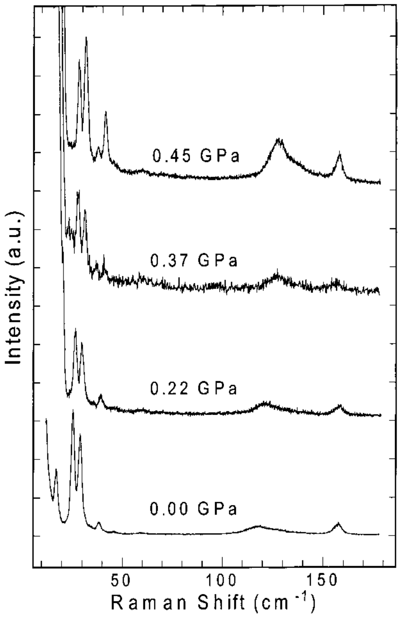

Figure 3. Raman phonon spectra of *p*-DIB in the pressure range 0−0.5 GPa (room temperature).

The behavior under pressure of *p*-DIB crystals is most interesting as it shows peculiar changes of the spectral profiles. This is attributed to possible different crystal phases forming at the transition pressures. For a better discussion of the experimental data we treat separately, in the following, the three pressure ranges where the most significant modifications of Raman phonon spectra occur. The described experiments refer to seven different crystals.

3.2.1. Pressure Range 0−1 GPa. This is the only pressure region previously studied for solid *p*-DIB.[1] The crystal was described to darken, starting at about 0.5 GPa, making impossible any measurement above 1 GPa. This behavior was indicated as reversible on releasing pressure, with no further detail. Although we do not observe anything similar on our samples, we notice instead that, in most cases, crystals undergo decomposition upon irradiation with the focused laser beam (647.1 nm) at ~0.4 GPa. No effect is observed at ambient pressure, nor above 0.4 GPa, despite prolonged irradiation time and increasing laser power onto the crystals. No further investigation has been made of this intriguing behavior, although one cannot rule out that a photochemical reaction might take place, occurring via the triplet state[12] whose energy could be tuned, at this pressure, in resonance with the laser line. For crystals surviving this photochemical change, new features appear in the spectra at the critical pressure of 0.4 GPa, as shown in Figure 3. The lowest phonon at 17 cm^{-1} is not detected at 0.37 and 0.45 GPa, and a band at 38 cm^{-1} appears in the spectrum, clearly indicating a reorientation of the crystal, as documented in Figure 1. At 0.45 GPa a distinct doublet is observed in the 40 cm^{-1} region and the intensities of high-frequency phonons increase sizably. The presence of a critical pressure at 0.4 GPa is also indicated by an intrinsic inhomogeneity of the sample, as reflected by the anomalous drop of the signal-to-noise ratio of the light scattering in the spectrum at 0.37 GPa of the figure. We therefore believe that the anomalous photochemical behavior of *p*-DIB crystal in this range of pressure is somewhat related to a physical change in the lattice, corresponding to the pressure-induced phase transition hypothesized by Adams near 0.5 GPa.[1]

3.2.2. Pressure Range 1−2 GPa. A pressure-induced phase transition is possibly detected at 1.7 GPa, as shown in Figure

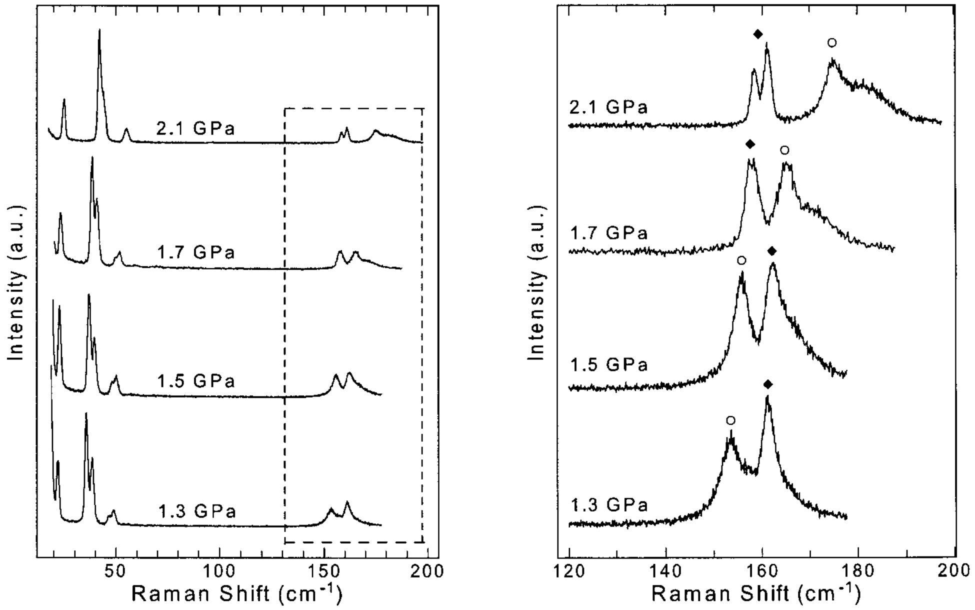

Figure 4. Raman phonon spectra of *p*-DIB in the pressure range 1−2 GPa (room temperature). The right panel shows an enlarged view of the crossing region of the highest lattice phonon (○) with the lowest internal mode (◆).

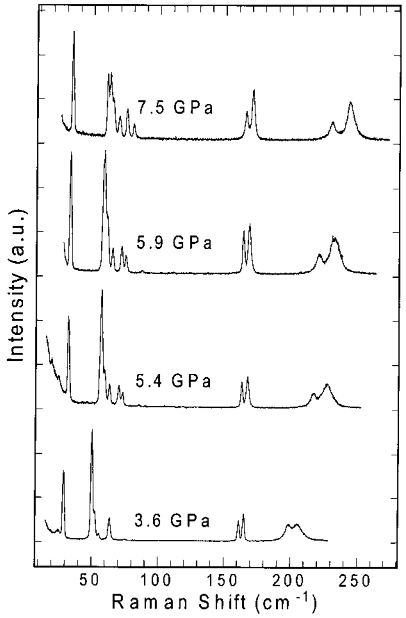

Figure 5. Raman phonon spectra of *p*-DIB in the pressure range 3−7.5 GPa (room temperature).

4. The major spectral changes observed at the transition pressure involve a merging in a single band of each of the two doublets of the low-frequency phonons. Striking changes also arise in the high-wavenumbers region of the spectrum: there is a crossing of the lattice phonon at $\sim$150 cm^{-1} with the intramolecular vibration at $\sim$160 cm^{-1}, whose coupling produces a decrease of the latter peak wavenumber at 1.7 GPa (see right panel of Figure 4) followed by a splitting into a doublet above 2 GPa.

3.2.3. Pressure Range Above 2 GPa. On increasing pressure above 2 GPa the spectrum becomes more resolved, as expected from the spreading of bands due to the pressure shift of the vibrational modes. This is clearly seen in Figure 5, where Raman phonon spectra up to 7.5 GPa are shown. An interesting feature at this pressure is the equivalence in the spectral profile resolution between the low-temperature[6] and high-pressure spectra, once taken into account the different band shifts. However, not all observed spectral features can be interpreted on the only basis of the increased pressure shift. In fact, at 3.6 GPa and above 5 GPa, some new modes appear which may suggest the occurrence of further modifications of the crystal phase. This is further evidenced by the difference of polarized spectra at ambient and high pressure. Indeed, whereas in the former case A_g symmetry phonons are completely separated by the B_{1g}, B_{2g}, and B_{3g} modes, as seen in Figure 6 (lower panel), at higher pressures (Figure 6, upper panel) all phonon bands, though weakly polarized, mix in both scattering polarizations, independently of their symmetry. This observation is beyond the effect of depolarization of strained diamonds, as checked by linear dichroism measurements of blanck diamonds up to 4 GPa. Therefore, this implies that molecules in the unit cell do not maintain any longer the mutual orientations they have in the ambient pressure structure.

3.3. Lattice Dynamics Calculations. Modeling a crystal like *p*-DIB, whose phase diagram displays several temperature- and pressure-induced solid−solid-phase transitions, is an extremely challenging task. In fact, the general problem of identifying a potential model which reproduces the structure and the dynamics of a crystal in its different crystalline phases is still unsolved and becomes even more difficult when, like for *p*-DIB, the experimental structure as a function of pressure is not known. A full account of our QHLD calculations on the two ambient pressure phases, α and *β*, is beyond the aim of this work and will be the subject of a future project. Here we report the results on the pressure dependence of the lattice modes at room temperature, to be compared to the experiments reported in the previous sections.

The crystal of *p*-DIB was modeled starting from the experimental[5] structure of the α phase at 298 K, which contains four molecules in the unit cell, with only one asymmetric unit. The potential model includes both intermolecular and intramolecular interactions and is fully described in ref 7. The intermolecular potential is expressed with an atom−atom model of the Buckingham type:[13,14] $V_{ij}(r_{ij}) = A_{ij} \exp(-B_{ij}r_{ij}) - C_{ij}/r_{ij}^6$, with C and H parameters taken from ref 15 and I parameters derived from 9,10-diiodoanthracene.[16] The C−I and H−I parameters are computed via “mixing rules”,[14] as: $A_{ij} = (A_{ii}A_{jj})^{1/2}$, $B_{ij} = (B_{ii} + B_{ij})/2$, and $C_{ij} = (C_{ii}C_{jj})^{1/2}$. The rigid molecule approxima-

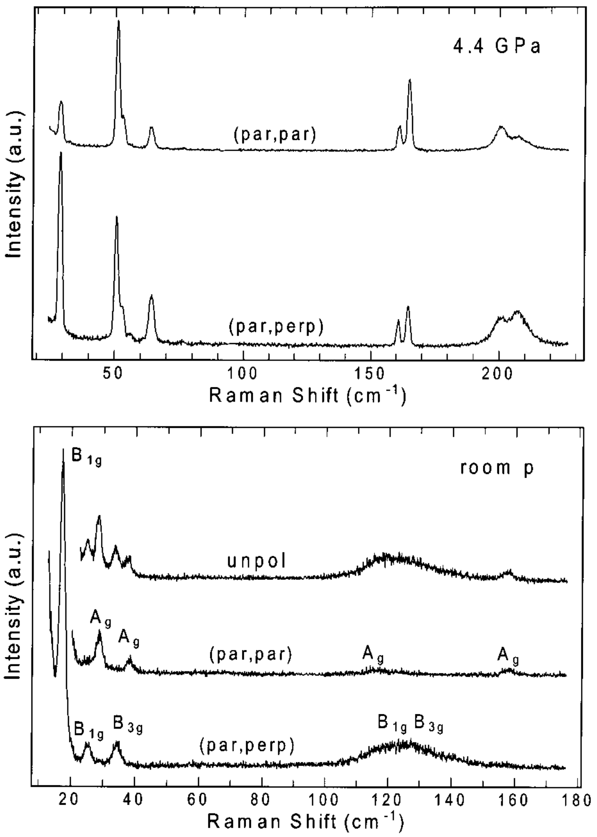

Figure 6. Polarized Raman phonon spectra of *p*-DIB at ambient pressure (lower panel) and at 4.35 GPa (upper panel). Due to the symmetry of the polarizability matrix elements, when laser and scattering are both polarized parallel to a principal crystal axis (par,par), only A_g modes can be active, whereas for the perpendicular scattering polarization noncoincident with a crystal axis (par,perp), two out of the three B_{1g}, B_{2g}, and B_{3g} symmetry phonons are detectable. Unlike at ambient pressure, above 3 GPa all phonons appear in both polarization configurations, for the same sample, though with a different polarization ratio.

TABLE 2: Experimental and Calculated Structural Parameters at Ambient Pressure: Cell Axes *a, b, c* and Cell Volume *V*

	exptl	calcd	
parameter	298 K	298 K	0 K
a (Å)	17.000	16.625	16.502
b (Å)	7.323	6.995	6.877
c (Å)	6.168	6.252	6.187
V (Å^3)	767.86	727.02	702.17

tion has been relaxed, as described in refs 7, 17, and 18, by including in the calculations the coupling between the lattice vibrations and the eight lowest intramolecular modes, with frequencies $\leq$ 600 cm^{-1}. The intramolecular frequencies and eigenvectors have been determined with ab initio calculations[7] performed with Gaussian98,[19] using a 3-21G basis set in combination with a B3LYP exchange-correlation functional. No frequency scaling has been necessary.

The thermodynamical equilibrium structure at each selected temperature T and pressure p is determined by minimizing the free energy $G(p,T)$ with respect to the structural parameters, following the method previously described.[20,21] We have then computed the phonon frequencies for each structure. The computed structures of the α phase at 0 and 298 K (ambient pressure) are reported in Table 2, where they are compared with the available experimental data. The corresponding phonon frequencies, listed in Table 1, show a satisfactory agreement with the experimental data for both the lattice vibrations and the lowest internal mode.

To model the pressure behavior of the Raman spectrum we have first calculated the structure at 298 K for each pressure p. Then we have computed, for every structure, the phonon frequencies. The computed frequencies as a function of pressure are overlapped in Figure 2 to the experimental values. The agreement with the experiments is good: the frequency range and the overall pressure dependence are well-reproduced. In particular, in the high-wavenumbers region, the avoided crossing between the highest lattice phonon and the lowest Raman-active internal mode is well-reproduced. Unlike other more favorable cases,[21−23] the possible occurrence of phase transitions is not predicted in our calculations. This can be due to a failure of our potential or, more likely, to the fact that it has been optimized only on the ambient p,T structure, since possible high-pressure crystal structures are unknown.

4. Conclusions

The present work has shown the presence of a variety of phenomena related to the response to pressure of crystalline *p*-DIB. Raman phonon spectra, in the lattice phonon region, and their dependence on pressure are sensitive probes for perturbations of the crystal environment dictated by changes of intermolecular interactions. Two pressure-induced phase transitions have possibly been identified at 0.4 and 1.7 GPa. The intriguing features appearing at the first transition pressure, as previously observed,[1] can probably also be related to some photochemical transformations in the solid state and require further investigation. Large variations of spectral profiles also occur at the highest pressures reached in this study and might well be suggestive of further pressure-induced phase changes. X-ray structural studies at high pressure would give a definitive answer to the interpretation of the present experimental data.

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