

A polarized single crystal Raman study of the librational phonons in *p*-diiodobenzene

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Single crystal polarized Raman spectra of *p*-diiodobenzene in the region from 0 to 300 cm^{-1} are presented for sample temperatures from 2 to 330 K. Eleven of the twelve predicted *gerade* librational phonons are unambiguously assigned in terms of their space group symmetries. The temperature dependence of the Raman spectra does not show a soft *gerade* phonon at the nearly second-order phase transition which occurs at 326 K. A significant anharmonicity for molecular motions above the *I-I* axis is indicated by the observation of overtones and combinations and broadening of these phonons as the temperature is raised from 2 K.

INTRODUCTION

The dynamic properties of molecular solids are currently being studied by a wide variety of theoretical and experimental methods. Theoretical efforts have involved the development of semiempirical potentials for the calculation of phonon frequencies,¹ as well as treatment of the unstable or "soft" phonons associated with second order structural phase transitions.² Experimentally, the lattice modes of wave vector $k \approx 0$ are most easily studied by far infrared and Raman spectroscopy, while inelastic neutron scattering experiments can map the phonon dispersion curves across entire Brillouin zones.

In the present investigation, the temperature dependence of the librational phonons of *p*-diiodobenzene has been studied by Raman spectroscopy. This material undergoes a remarkably sharp solid-solid phase transition at 326.3 K (53.1°C), marked by a very small enthalpy of transition (0.128 cal/g)³ and a significant decrease in the hole drift mobility in photoconductivity.⁴ The phase transition has also been observed by changes in the optical birefringence, Weissenberg x-ray diffraction pattern,⁵ and molar volume of the substance.⁶

The microscopic nature of this phase transition is of interest both because of its effect on photoconductivity and because of the low enthalpy of transition, indicative of a nearly second order phase change. Second order phase transitions and their associated "soft" phonon modes are an active research field in solid state physics and statistical mechanics, especially for ferroelectric materials.^{7,8} However, only a small number of molecular solid-solid phase transitions have been studied closely by vibrational spectroscopy, and most of these have been clearly first order.⁹ Exceptions are a recent Raman study of a phase transition of *sym*-triazine which has a very small latent heat¹⁰ and a study of a Raman active soft phonon in tetrachloro-*p*-benzoquinone.¹¹

The following Raman work was begun in order to better understand the *p*-diiodobenzene phase transition. It was our hope that this nearly second order transition would manifest itself in the Raman spectrum by the ap-

pearance of a soft phonon mode. In this respect the experiments reported here were unsuccessful—no soft mode was observed. However, we have been able to observe and assign all but one of the *gerade* lattice modes. We have also obtained some information about the motion of the *p*-diiodobenzene molecule near the phase transition.

The previous spectroscopy of *p*-diiodobenzene has involved assignment of the intramolecular vibrations,¹² single crystal singlet-triplet absorption spectroscopy,¹³ and inelastic neutron scattering.¹⁴ The low frequency Raman spectra of *p*-dichlorobenzene and *p*-dibromobenzene have also been reported,^{15,16} as well as a study of the phonon dispersion curves of *p*-dichlorobenzene obtained from neutron scattering experiments.¹⁷

EXPERIMENTAL

p-Diiodobenzene was purified by crystallization from ethanol and subsequent zone refining in the dark. The material is light stable as a solid, but tends to photodissociate in the liquid phase and in solution. Single crystals grown using a Bridgeman furnace were cleaved with a razor blade, cut again along the extinction directions observed between crossed polarizers, and finally polished with benzene. The cleavage plane is known to be perpendicular to the crystallographic *a* axis; this fact and conoscopic identification of the optic plane (*ab*) completed the absolute orientation of the single crystal.

The Raman spectra were recorded using a Jarrell-Ash Czerny-Turner double monochromator, with 100 to 500 mW 4880 Å excitation delivered to the sample by a Spectra-Physics 165 argon ion laser, after passing through a narrow band interference filter to remove plasma lines. The signal was detected with an RCA C31034 photomultiplier. The single crystals or powder filled capillaries were mounted on a copper block with Dupont silicone grease. The temperature of the block was controlled by a balance between small resistance heaters and a flow of cold helium or nitrogen gas. For experiments below 0°C, the temperature was measured with a platinum resistor, while a copper-constantan thermocouple was used for the experiments above that temperature. The entire assembly was contained with-

in a Janis Research Dewar. Temperature measurement for the crystal is estimated to be accurate to within at least $\pm 5\%$, while frequencies are no worse than $\pm 0.5 \text{ cm}^{-1}$.

RESULTS

The room temperature crystal structure of *p*-diiodobenzene has been reported.¹⁷ The space group is *Pbca* (D_{2h}^{15}) with four molecules per unit cell at special positions such that the site symmetry is C_i . In a rigid molecule approximation, group theory predicts that for a crystal of *Pbca* (D_{2h}^{15}) symmetry and four molecules per unit cell, there should be 24 lattice modes of $k=0$. Twelve of these modes are of *gerade* symmetry and thus observable by Raman spectroscopy, nine are *ungerade* and infrared active, while the three acoustic modes of A_u symmetry are observable by neither optical technique. The 12 *gerade* lattice modes are all librational modes with irreducible representations $3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g}$. The *ungerade* lattice modes are all translatory vibrations.

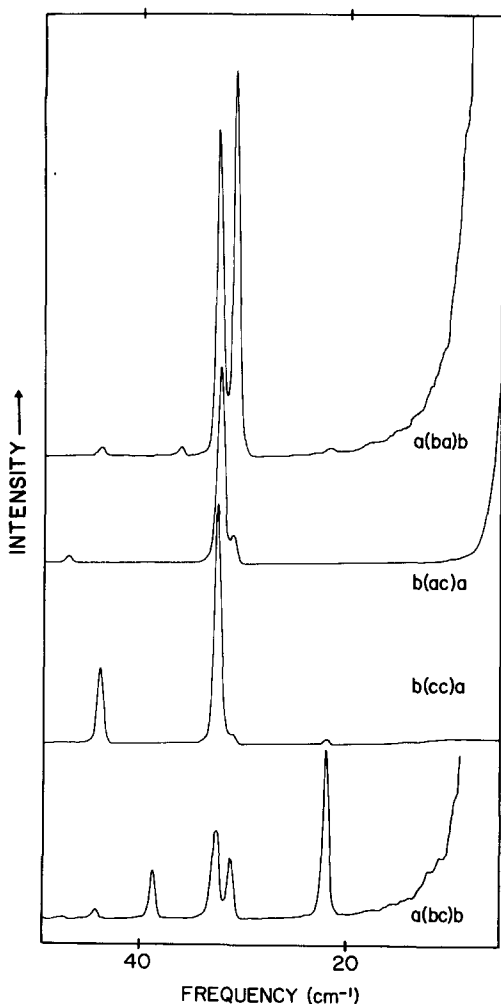


FIG. 1. The polarized Raman spectra at 2 K of *p*-diiodobenzene in the 0–50 cm^{-1} region. The scale in this and all other figures, although labeled in cm^{-1} , is linear in wavelength. The unit cell axis convention is the same as in Ref. 15. The labels $a(bc)d$ indicate that the beam was incident along the a direction polarized in the b direction and exited along the d direction polarized in the c direction.

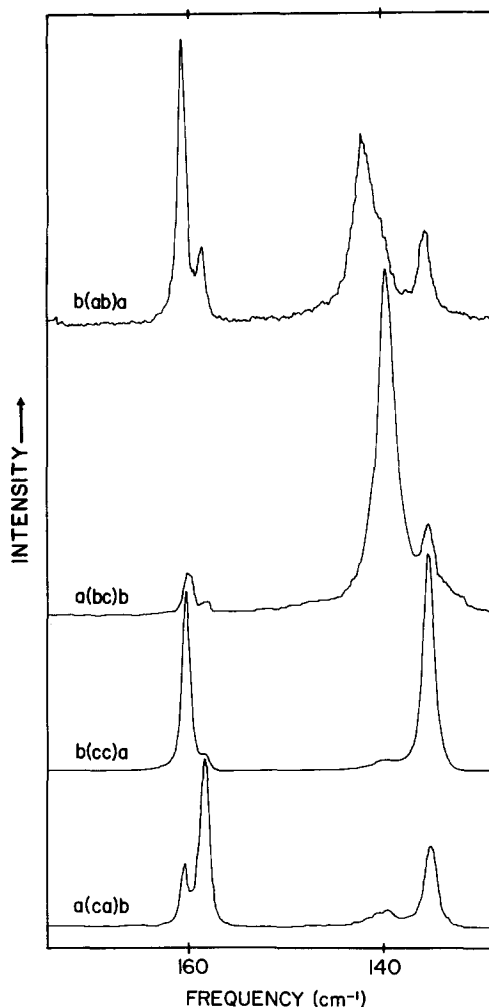


FIG. 2. The polarized Raman spectra at 2 K of *p*-diiodobenzene in the 130–170 cm^{-1} region.

Figures 1 and 2 illustrate the polarized single crystal spectra obtained at 2 K which were used for the assignment of the intramolecular modes. Eleven of the 12 predicted modes can be assigned as shown in Table I.

TABLE I. Summary of 2K low frequency Raman spectra.

Frequency (cm^{-1})	Polarization	Symmetry
21.4	<i>bc</i>	B_{3g}
29.8	<i>ab</i>	B_{1g}
31.4	a^2, b^2, c^2	A_g
(31.4)	<i>ac</i>	$(B_{2g})^a$
35.7	<i>ab</i>	B_{1g}
38.0	<i>bc</i>	B_{3g}
43.6	a^2, b^2, c^2	A_g
46.9	<i>ac</i>	B_{2g}
135.3	a^2, b^2, c^2	A_g
141.1	<i>bc</i>	B_{3g}
142.9	<i>ab</i>	B_{1g}
158.2	<i>ac</i>	B_{2g}
160.1	...	Intramolecular ^b $C-I$

^a Tentative assignment as discussed in text.

^b See Ref. 10.

The moments of inertia of the *p*-diiodobenzene molecule can be calculated from the approximate molecule structure¹⁷ and are found to be $3135 \text{ amu} \cdot \text{\AA}^2$, $3046 \text{ amu} \cdot \text{\AA}^2$, and $91 \text{ amu} \cdot \text{\AA}^2$. The ratio of the reciprocal of the square roots of these moments are 1:1.01:5.9 and we therefore expect the rotatory vibrations to group into eight low frequency modes and four higher frequencies as is observed. This analysis is, of course, only qualitative because of the variety of force constants which may be involved and because the molecular axes do not coincide with the crystal axes.

One interesting feature of the Raman spectrum of *p*-diiodobenzene is the presence of overtone and combination modes, as shown in Fig. 3. Although such modes are forbidden in the harmonic oscillator approximation, the polarizations and frequencies of two of these lines confirm their assignment as two-phonon transitions, as given in Table II.

TEMPERATURE DEPENDENCE

Both the linewidth and frequency of the phonon modes vary significantly as a function of temperature, as illustrated in Figs. 4 and 5. The substantial broadening of the high frequency phonons (which correspond to librations about the *I-I* axes) indicates a large anharmonic-

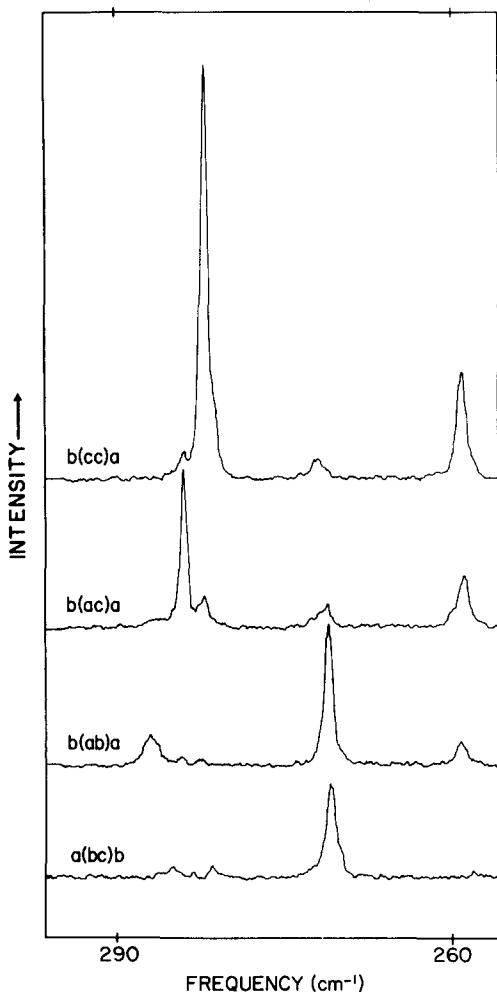


FIG. 3. The polarized Raman spectra at 2 K of *p*-diiodobenzene in the 260–290 cm^{-1} region.

TABLE II. Summary of 2K data for overtone and combination region.

Frequency (cm^{-1})	Polarization	Symmetry	Assignment
256.1	...		Intramolecular ^a <i>C-I</i>
269.3	...		Intramolecular ^a <i>C-I</i>
281.5	a^2, b^2, c^2	A_g	$2 \times 141.1 = 282.2$ $(B_{2g})^2 = A_g$
283.5	<i>ac</i>	B_{2g}	$141.1 + 142.9 = 284.0$ $B_{3g} \times B_{1g} = B_{2g}$
286.6	...		

^a See Ref. 10.

ity in these motions. The high frequency modes also tend to change frequency by the largest absolute amount, but the fractional decrease is fairly uniform for all the Raman modes.

As the temperature is increased through the phase

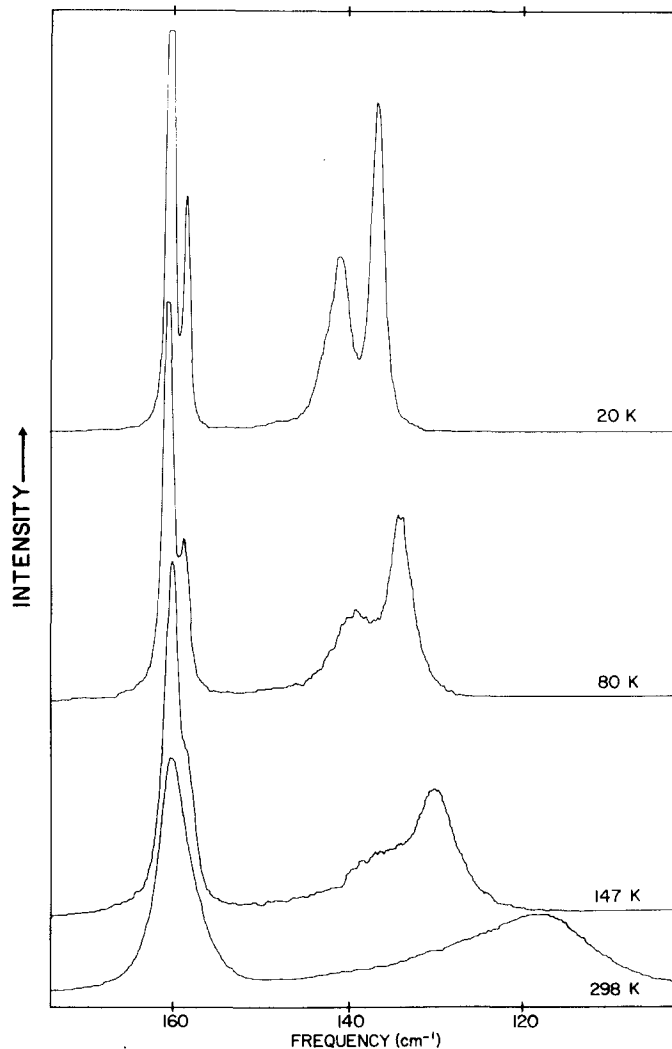


FIG. 4. The unpolarized Raman spectrum of a diiodobenzene crystal at various temperatures.

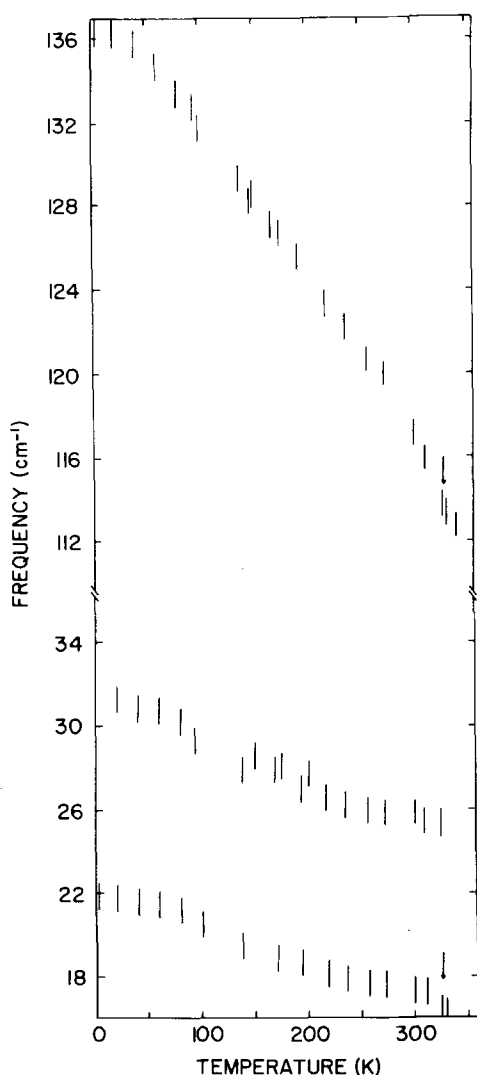


FIG. 5. The temperature dependence of the frequencies of three of the rotatory phonons of *p*-diiodobenzene. The vertical bar lengths represent an estimated uncertainty of 0.5 cm^{-1} . The arrows mark the position of the phase transition at 53°C . Note the scale change.

transition, two significant changes occur in the spectrum, as shown in Fig. 6. First, the strong low frequency doublet at about 30 cm^{-1} broadens and coalesces into a single broad line. Second, the relative intensities of the peaks in the $30\text{--}45 \text{ cm}^{-1}$ region appear to change. Unfortunately, the lines of the $100\text{--}200 \text{ cm}^{-1}$ region are too broad to analyze at this temperature.

DISCUSSION

The assignment of the single phonon transitions based on their polarization is straightforward; the only problem is the absence of the 12th phonon (with B_{2g} symmetry) predicted by group theory. At least three explanations are possible for such an absence: (1) the frequency of the mode puts it too close to the exciting laser line to be observable, (2) the intensity of the transition is too small to be detected, or (3) the missing mode is accidentally degenerate with another transition. The efficiency of the double monochromator was such that frequencies as low as 10 cm^{-1} could have been observed,

and it is unlikely that a phonon for *p*-diiodobenzene would have a frequency below that. (The lowest frequency in *p*-dibromobenzene is 22.5 cm^{-1} at 80 K).¹⁶ It is unlikely that the intensity of the missing mode is extraordinarily small, but this cannot be excluded.

There is some evidence that the missing mode is obscured by accidental overlap with a stronger line. The 31.4 cm^{-1} line, which is assigned as having A_g symmetry, is the strongest line in the spectrum and also the least polarized (see Fig. 1). The significant intensity observed in the *ac* polarization is consistent with the presence of a B_{2g} mode at this frequency. No significant frequency shift is observed between the *ac* and *cc* polarizations, however, and there is also significant intensity in the *ba* and *bc* polarizations which may indicate some crystal misorientation. The assignment of this B_{2g} mode as 31.4 cm^{-1} is therefore tentative.

The four high frequency librational phonons range from $135\text{--}160 \text{ cm}^{-1}$ with a mean frequency of 144 cm^{-1} . Each *gerade* representation occurs once in this group. The other eight phonons have a mean frequency of 35 cm^{-1} (assuming that the first B_{2g} mode is at 31 cm^{-1}) and range from $21\text{--}47 \text{ cm}^{-1}$. This separation of the rotatory phonons into two distinct groups is certainly due to the large difference in the moment of inertia of the *p*-diiodobenzene molecule about the *I-I* axis compared to the nearly identical and much larger moments about the two perpendicular axes. The projection of a unit vector along the *I-I* axis on the *a* axis direction of the crystal is 0.85 (an angle of 32°)¹⁷ which, in combination with the large ratio of the moments of inertia ($I_x/I_z = 34$), is probably sufficient to make the higher frequency torsions nearly pure rotations about the *I-I* axis. The subdivision of the low frequency *gerade* phonons into to molecular axis rotations is probably not possible because of the extensive mixing that almost certainly occurs among these modes.

The bands at 160 , 256 , and 260 cm^{-1} are assigned as internal modes on the basis of the observation of similar frequencies in solution spectra (at 157 , 241 , and 255 cm^{-1})¹⁰ and because of their lack of unique polarization. The lack of polarization of the internal modes is due to their unresolved correlation (factor group) splitting. The lines at 281 and 283 cm^{-1} are assigned, respectively, as the first overtone of the 141 cm^{-1} libration and as the combination of the former with the 143 cm^{-1} mode on the basis of their frequency coincidence (assuming an anharmonicity of 0.6 cm^{-1} or 0.4%) and their polarization. The weak line at 287 cm^{-1} remains unassigned.

Most of the structural information accessible by Raman spectroscopy is contained in the measurement of the temperature dependence of the lattice frequencies and their linewidths. Since the phase transition at 53°C appears to be only a slight structural modification, it was hoped that one of the coupled molecular rotations might be a soft mode with a strong frequency-temperature dependence. While the temperature dependence of the high frequency librational modes is much more pronounced than for the corresponding modes in *p*-dichloro- and *p*-dibromobenzene,¹³ there is absolutely no evidence

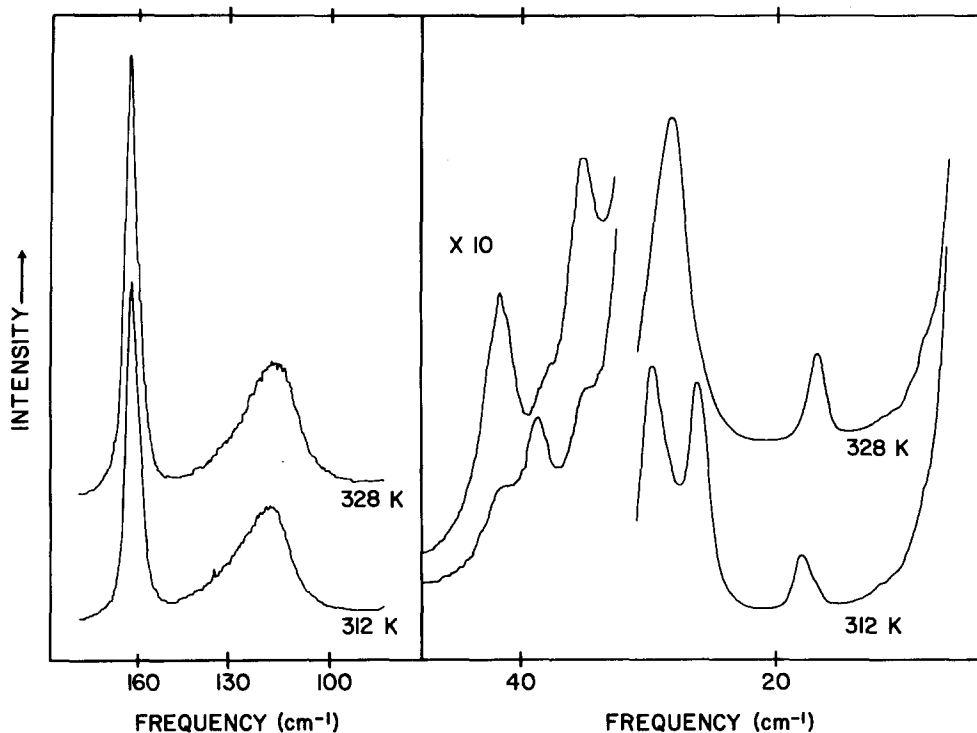


FIG. 6. The Raman spectrum of *p*-diiodobenzene in the 0–170 cm^{-1} region at temperatures just below and just above the phase transition temperature of 326 K.

that any of these modes are soft modes. We conclude on the basis of the spectral and preliminary x-ray data that the structural modification is likely to be predominantly a transitional motion causing elongation of the unit cell.

The high frequency phonons, corresponding to librations about the *I*–*I* axes, show a pronounced broadening with increasing temperature. This fact plus the observation of overtones involving these modes indicates that these phonons are more anharmonic than the lower frequency modes, which show less broadening and no overtones. It is possible that this rotational motion about the *I*–*I* axis couples to the transitional aspect of the phase transition. Unfortunately, the extreme line broadening that occurs near the phase transition temperature precludes a determination of the symmetry of the high temperature phase. Attempts at freezing in the high temperature form by rapid cooling to liquid nitrogen temperature were unsuccessful.

CONCLUSION

From 2 K polarized single crystal Raman spectra, 11 of the 12 predicted *gerade* phonons of *p*-diiodobenzene have been observed and assigned. The temperature dependence of the Raman spectrum has been recorded from 2 K through a phase transition at 326 K. No soft phonon mode is observed, indicating that this nearly second order transition does not occur exclusively via a $k=0$ librational mode. Although the exact nature of the phase transition remains uncertain, a significant anharmonicity in molecular motion about the *I*–*I* axes is observed. This anharmonicity may indicate a participation of these modes along with acoustic or transitional modes in the phase transition. Infrared measurements are currently under way, in order to observe the be-

havior of the translational phonons.

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