

Infrared spectroscopy of biphenyl under hydrostatic pressure

K. K. Zhuravlev

Department of Physics, Washington State University, Pullman, Washington 99164-2814

M. D. McCluskey

Department of Physics and Institute for Shock Physics, Washington State University, Pullman, Washington 99164-2814

(Received 22 April 2002; accepted 29 May 2002)

Changes in the conformations of conjugated molecules affect the optical and electronic properties significantly. Hydrostatic pressure has been used to probe the conformations of biphenyl ($C_{12}H_{10}$) and deuterated biphenyl ($C_{12}D_{10}$) at liquid-helium temperatures. Infrared (IR) spectra of these materials have been taken up to a pressure of 2 GPa. A disappearance of certain IR absorption peaks has been found to occur between 0.07 and 0.45 GPa, due to the phase transition from a twisted to a planar conformation. Numerical simulations together with group-theoretical analysis have been performed to identify the nature of the vibrational modes that lose IR activity upon planarization.

© 2002 American Institute of Physics. [DOI: 10.1063/1.1494776]

I. INTRODUCTION

With the recent advances in organic light-emitting diodes¹ and lasers,² organic materials have received attention for optoelectronic device applications. In conjugated polymers, the π -electrons are delocalized along the molecule, resulting in band gaps in the visible region of the spectrum. The conformations of conjugated molecules affect the optical properties significantly.³ As molecules transform from twisted to planar conformations, the overlap between π -electrons on neighboring rings increases, resulting in a redshift of the band gap. The application of hydrostatic pressure is an excellent means for probing the vibrational, structural, and optical properties of conjugated molecules.⁴ Raman spectroscopy has been used to investigate the planarization of para-hexaphenyl.^{5,6} Combined experimental and computational studies of biphenyl showed a redshift in the optical spectra due to conformational changes.⁷

Polyphenyl molecules, such as biphenyl, undergo a phase transition in which the molecules transform from a twisted to a planar conformation. In biphenyl, the phase transition has been studied by the methods of electronic absorption and emission;⁸ neutron,⁹ x-ray,¹⁰ Brillouin,¹¹ and Raman scattering;¹² nuclear magnetic¹³ and electron paramagnetic resonance.¹⁴ In these studies it was found that such a transition occurs when either temperature^{8-11,13} or pressure¹² rises above certain critical values. In Ref. 12, however, only torsional lattice modes were observed experimentally. In the present work we analyze the behavior of the *internal* hydrogen modes in biphenyl under pressure.

It is now known that the biphenyl has, in fact, two incommensurate phases, II and III. In both of these phases, the phenyl rings are twisted,¹⁵⁻¹⁷ but the angle of the twist is modulated through the crystal structure. The difference between the modulation vectors distinguishes the two phases. At atmospheric pressure the transition from high-temperature phase I to phase II occurs at $T=40$ K, and from phase II to phase III at $T=17$ K. The critical pressures at liquid helium temperatures are approximately 0.18 and 0.05 GPa, respec-

tively. Our experimental technique is sensitive to the transition from phase II to phase I, when the molecules transform from a twisted to a planar conformation. This pressure-induced "flattening" leads to the novel observation that certain peaks in the IR spectrum disappear.

Recently we reported the flattening of para-quaterphenyl under hydrostatic pressure, and the transition point was determined to be between 0.7 and 1 GPa at liquid-helium temperatures.¹⁸ The phase transition in para-quaterphenyl resulted in the disappearance of five infrared (IR) absorption peaks in the spectral range corresponding to hydrogen out-of-plane bending modes. A group-theory analysis supported the supposition that certain IR peaks disappear upon planarization. However, there was an uncertainty about the character of motion of atoms within the molecule for those modes that lose IR activity in the planar conformation.

In order to resolve these problems, a new series of experiments was performed on biphenyl and deuterated biphenyl. The substitution with deuterium provides additional spectroscopic information, in order to determine the exact identities of the vibrational modes. One may expect that a biphenyl molecule under pressure behaves similarly to that of para-quaterphenyl. The smaller number of atoms in biphenyl, as compared to para-quaterphenyl, is advantageous for *ab initio* calculations. In this paper, experimental and group-theoretical results for biphenyl and deuterated biphenyl are presented, as well as the results of numerical simulations of the IR spectra for these molecules.

II. EXPERIMENT

To generate pressures up to 2 GPa, we used a piston-cylinder diamond-anvil cell.¹⁹ Type-I diamonds with culet diameters of 700 μm were used. After a 250- μm thick stainless steel gasket was indented to a thickness of 100 μm , a 340- μm diam hole was drilled in the center of the indentation. Nitrogen was used as a pressure medium and was loaded into the gasket hole, along with the sample, by liquid immersion.²⁰ To determine the pressure at liquid helium tem-

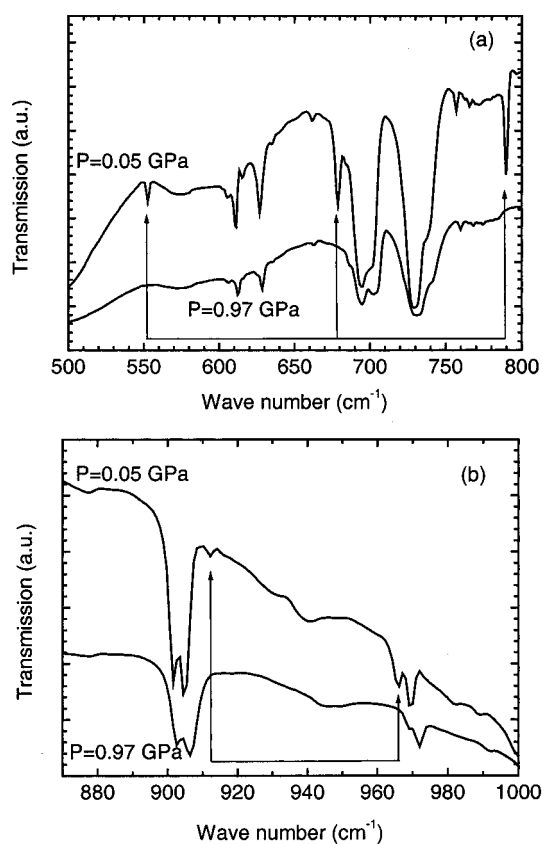


FIG. 1. (a)–(b) Absorption spectra of biphenyl below and above the phase-transition pressure, at a temperature of 8 K.

peratures, we measured the IR absorption peak of the ν_3 vibrational mode of isolated carbon dioxide impurities in the solid nitrogen matrix.²¹

Mid-IR absorption spectra were obtained with a Bomem DA8 vacuum Fourier transform IR spectrometer with a KBr beamsplitter. The samples were kept at a temperature of 8 K in a Janis continuous-flow liquid-helium cryostat with wedged zinc selenide windows. The spectral range was 500–5000 cm^{-1} and the instrumental resolution was 2 cm^{-1} . The type-I-diamond absorption band prevented measurements between 1100 and 1400 cm^{-1} . An off-axis parabolic mirror and light-concentrating cone focused the light through the first diamond and onto the sample. The light then passed through the second diamond and onto a Ge:Cu photoconductor detector. After a spectrum was measured, the diamond-anvil cell was warmed to room temperature and the pressure was adjusted.

Two samples were investigated. First, pretreated biphenyl ($\text{C}_{12}\text{H}_{10}$), hereafter referred to simply as biphenyl, was measured. Second, deuterated biphenyl ($\text{C}_{12}\text{D}_{10}$), or biphenyl- d_{10} , was measured. In the latter sample, every hydrogen was replaced by a deuterium, with an isotopic purity of 98%.²² The IR spectra for biphenyl are shown in Fig. 1 and spectra for deuterated biphenyl are shown in Fig. 2.

Peaks that disappear at high pressures are indicated by arrows. The spectral range from 500 to 1100 cm^{-1} corresponds to out-of-plane motion of hydrogen atoms in which the atomic displacement is perpendicular to the plane of the appropriate ring. There are three peaks in the biphenyl spec-

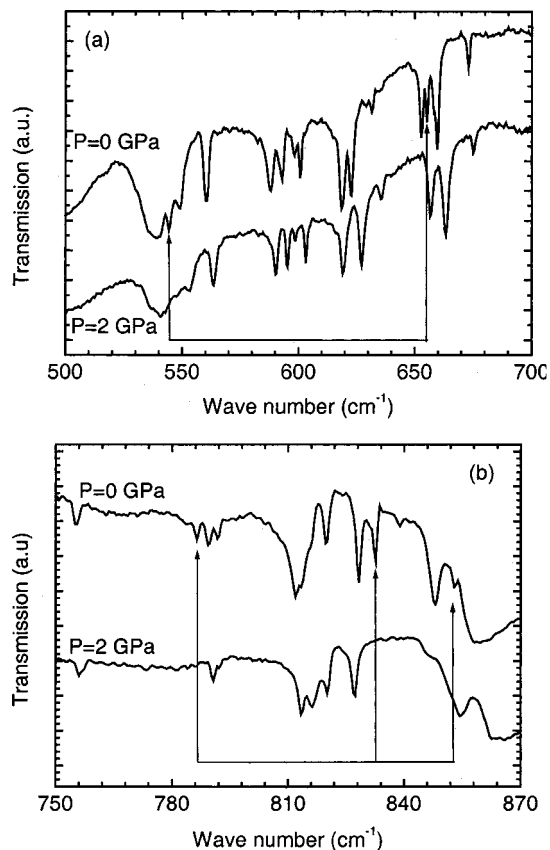


FIG. 2. (a)–(b) Absorption spectra of deuterated biphenyl below and above phase-transition pressure, at a temperature of 8 K.

trum in the range 500–800 cm^{-1} that disappear upon the phase transition [Fig. 1(a)]. The spectral range from 1100 to 1800 cm^{-1} includes in-plane hydrogen bending modes. Upon substitution with deuterium, hydrogen-related frequencies should decrease by some factor, which in an “ideal” case is $\sqrt{2}$. From Fig. 2(a) it is seen that there are two peaks, at 545 and 655 cm^{-1} , that disappear in deuterated biphenyl. Relative to the hydrogen peaks at 679 and 790 cm^{-1} [Fig. 1(a)], the deuterium peaks are shifted downward by a factor less than $\sqrt{2}$. The deviation from the ideal case is due to anharmonic effects as well as significant motion of the carbon atoms. In the observed spectra the strongest peaks were found to be due to out-of-plane hydrogen motion.

The pressure-dependent shifts of several out-of-plane hydrogen bending modes are plotted for biphenyl in Fig. 3. In Fig. 4 we plotted the normalized intensities for two peaks that disappear after the phase transition, as a function of pressure. The intensity of the peak at approximately 836 cm^{-1} was chosen as a reference for the normalization. At a pressure between 0.07 and 0.4 GPa, the integrated absorbance of the peaks at 790 and 841 cm^{-1} drops to zero, to within experimental uncertainty. Our results are in agreement with those of Ref. 12, which reported a phase transition at 0.18 GPa.

III. GROUP THEORY

To explain the disappearance of IR activity for certain vibrational modes, we applied group theory to analyze the

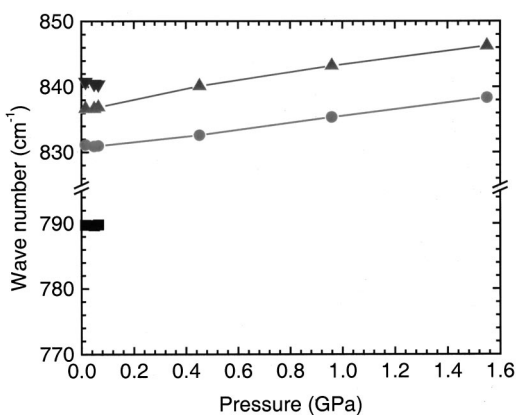


FIG. 3. Frequency shifts of four biphenyl peaks, corresponding to hydrogen out-of-plane bending modes, as a function of pressure.

normal vibrational modes of the molecules. The z -axis in our analysis is directed along the main axis of the molecule, the x -axis is in the molecular plane for the planar conformation, and the y -axis is perpendicular to the plane. A schematic diagram of biphenyl in its twisted conformation is shown in Fig. 5(a). The twisted conformation of biphenyl belongs to the D_2 point group. The vibrational modes can be classified as follows:

$$\Gamma = 15A \oplus 13B_1 \oplus 16B_2 \oplus 16B_3.$$

Modes belonging to the B_1 , B_2 , or B_3 irreducible representations are IR-active, for a total of 45 IR-active modes. For the planar configuration, biphenyl belongs to the D_{2h} point group. The vibrational modes are given by

$$\Gamma = 11A_g \oplus 4A_u \oplus 3B_{1g} \oplus 10B_{2g} \oplus 6B_{3g} \\ \oplus 10B_{1u} \oplus 6B_{2u} \oplus 10B_{3u}.$$

Modes belonging to the B_{1u} , B_{2u} , or B_{3u} irreducible representations are IR-active, for a total of 26 IR-active modes. Upon planarization, some of the B_1 , B_2 , and B_3 modes transform into B_{1g} , B_{2g} , and B_{3g} modes, which are IR-inactive. This disappearance of certain IR absorption peaks is in qualitative agreement with our experimental observations.

In our previous work, we proposed two models.¹⁸ The first model assumed that there are only nearest-neighbor or

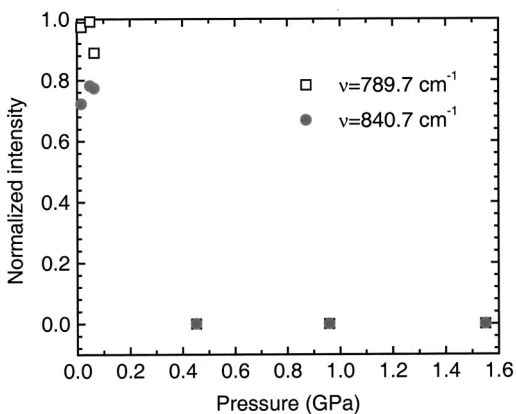


FIG. 4. Normalized intensities of two modes that lose IR activity upon planarization.

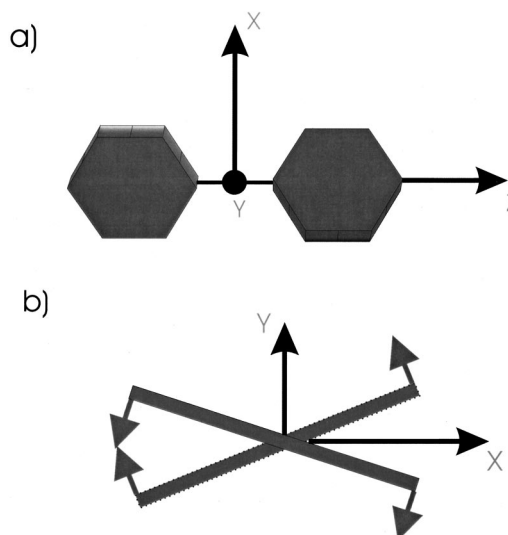


FIG. 5. (a) Schematic diagram of the biphenyl molecule in the twisted conformation. The solid hexagons represent phenyl rings. (b) Schematic diagram of one out-of-plane hydrogen bending mode, that becomes IR-inactive upon planarization.

next-nearest-neighbor interactions between hydrogen atoms. From this assumption, it follows that certain IR modes would be degenerate. In the case of biphenyl, there would be three peaks that disappear in the IR spectrum, two B_1 modes and one B_3 mode. In the twisted conformation, B_1 modes induce a dipole moment along z -axis. In the second model, the disappearing modes are assumed to belong to either B_2 or B_3 representations, which have induced dipole moments along the y - and x -axis, respectively. Such modes would have greater intensities than the B_1 modes, due to the larger induced dipole moments. As shown in the next section, our calculations tend to support the second model.

In Fig. 5(b), one of the B_3 modes is shown schematically. The cross sections of the phenyl rings are represented as rectangles and the dipole moments, induced by the motion of hydrogen atoms, are shown by the arrows. In the twisted conformation, the mode has a net induced dipole moment in the x -direction. In the planar conformation, the dipoles exactly cancel, so that the mode is IR-inactive.

IV. NUMERICAL ANALYSIS

Ab initio calculations are used extensively to model molecular and atomic systems. Some recent calculations of the biphenyl structure can be found in Refs. 23 and 24. We also performed *ab initio* calculations in order to simulate the IR spectra of biphenyl and deuterated biphenyl, using GAUSSIAN 98W.²⁵ We used the density functional theory (DFT) Becke 3-parameter method²⁶ with the Lee–Yang–Parr correlation functional and the basis set 6-31G(*d*), which adds *d*-orbitals to heavy atoms. The results of our calculations are consistent with those of Rubi *et al.*²³ and Furuya *et al.*²⁴

For the twisted structure, the calculated dihedral angle between two phenyl rings is 38° for biphenyl and 35° for deuterated biphenyl. Electron diffraction experiments on biphenyl in the gas phase yielded a dihedral angle of 40° , in good agreement with our calculations.²⁷ Numerical optimi-

TABLE I. Vibrational modes in biphenyl ($C_{12}H_{10}$) that are IR active in the twisted conformation but IR inactive in the planar conformation.

Calculated				Experiment	
Frequency (cm^{-1})	Normalized intensity	Symmetry	Mode character	Frequency (cm^{-1})	Normalized intensity
559.9	0.2622	B_3	H out-of-plane	552.9	0.272
628.6	0.0006	B_2	C-H in-plane	ND ^a	ND ^a
714.7	1	B_3	H out-of-plane	679.3	0.745
796.9	0.88	B_3	H out-of-plane	789.7	1
860.9	0.086	B_1	H out-of-plane	840.7	0.720
938.5	0.15	B_3	H out-of-plane	912.1	0.041
968.7	0.1248	B_2	H out-of-plane	965.8	0.377
995.6	0.0096	B_2	H out-of-plane	ND ^a	ND ^a
1116.1	0.061	B_1	H in-plane	ND ^{a,b}	ND ^{a,b}
1192.9	0.0002	B_3	H in-plane	ND ^{a,b}	ND ^{a,b}

^aND=not discovered.^bCalculated frequency lies within the diamond absorption band.

zation of the geometric structure of the molecules yields a configuration that belongs to the C_2 point group. This low symmetry is due to a distortion of the phenyl rings. However, the deviation from planarity in each phenyl ring is very small. To a good approximation, we can consider this molecule as belonging to the D_2 point group, and our previous group-theory analysis remains valid. The vibrational spectra calculations were made with the symmetry restricted to the D_2 point group. The planar conformation of the molecule, belonging to the D_{2h} point group, turns out to be stable during the calculations. One of the calculated frequencies is imaginary, however, indicating that the planar configuration is not a minimum on the potential energy surface.

A correspondence was made between vibrational modes in the planar and twisted conformations by examining similarities in the character of motion, reduced mass, frequency, and IR intensity for any given pair of modes. Frequencies that are IR-active in the twisted conformation but IR-inactive in the planar conformation, as predicted by this computation for the twisted conformation of biphenyl, are listed in Table I

together with the experimental results. The frequencies for vibrational modes in deuterated biphenyl are given in Table II. In biphenyl, we did not observe hydrogen in-plane modes because the frequencies of those modes lie within the diamond absorption band. In deuterated biphenyl, however, these modes are shifted downward in frequency and therefore become observable. In both tables the intensity normalization was carried out with respect to the highest-intensity peak. In order to illustrate the disappearance of IR-active peaks, the calculated intensity of two peaks at 715 and 797 cm^{-1} is plotted as a function of dihedral angle between the phenyl rings (Fig. 6). The outlying data point at 38° is probably due to the fact that all other angles correspond to non-optimal structures. The experimental intensities and frequencies approximately match the theoretical ones, with the exception of the experimental peak at $840.7 cm^{-1}$ for biphenyl. According to Fig. 3, there is a possibility that this peak simply merges with the peak at $836 cm^{-1}$, and is not in fact a "disappearing peak." The average ratio of experimental to calculated frequencies for biphenyl and deuterated biphenyl

TABLE II. Vibrational modes in deuterated biphenyl ($C_{12}D_{10}$) that are IR active in the twisted conformation but IR inactive in the planar conformation.

Calculated				Experiment	
Frequency (cm^{-1})	Normalized intensity	Symmetry	Mode character	Frequency (cm^{-1})	Normalized intensity
567.07	1	B_3	D out-of-plane	544.5	0.340
602.82	0.0018	B_2	D in-plane+ring distortion	ND ^a	ND ^a
668.63	0.14	B_3	D out-of-plane	655.3	0.752
670.04	0.1456	B_1	D out-of-plane	ND ^a	ND ^a
784.29	0.264	B_1	D out-of-plane+ring distortion	786.3	0.337
789.11	0.161	B_3	D out-of-plane+ring distortion	789.5	0.444
838.72	0.4535	B_3	D in-plane+ring distortion	832.5	1
844.02	0.0789	B_2	D in-plane	838.8	0.187
862.8	0.0301	B_2	D in-plane	853.0	0.188
1071.88	0.0005	B_2	D in-plane	ND ^a	ND ^a

^aND= not discovered.

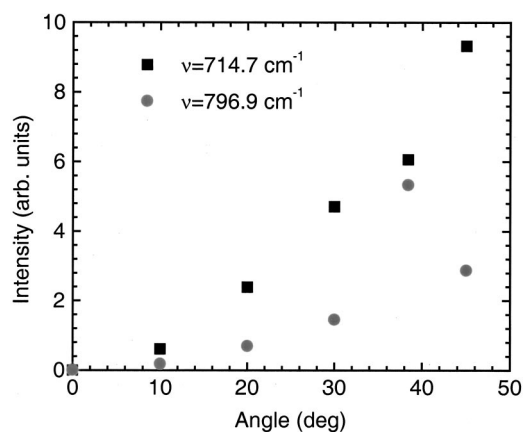


FIG. 6. Calculated intensity of two IR peaks as a function of the dihedral angle between phenyl rings.

are 0.987 ± 0.013 and 0.988 ± 0.005 , respectively. These values are consistent with the known overestimation of frequencies by this calculation method.²⁵

In Tables I and II the characters of the vibrational modes are described briefly. “H out-of-plane” corresponds to the hydrogen atoms moving perpendicular to the plane of a phenyl ring. “H in-plane” corresponds to the hydrogen atoms moving in the plane of a phenyl ring. “C–H in-plane” means that carbon atoms are moving significantly as well. The same descriptions apply for the deuterium atoms. “Ring distortion” indicates that carbon atoms are moving in or out of the phenyl-ring plane together, but asynchronously with the deuterium atoms. Calculations of the normal modes indicate the induced dipole moments are directed predominantly perpendicular to the z -axis. Exceptions to this rule include the calculated B_1 modes for biphenyl and deuterated biphenyl, at 1116.1 cm^{-1} (Table I) and 784.3 cm^{-1} (Table II), respectively.

Thus the calculations are consistent with the experimental results and support the second model proposed in Ref. 18, which stated that the disappearing peaks are B_2 and B_3 modes. The first model, in which only nearest- and second-nearest neighbor interactions were taken into account, can be eliminated.

V. CONCLUSIONS

In conclusion, experiments on the vibrational properties of biphenyl showed that these molecules flatten under pressure, resulting in the disappearance of specific IR peaks. Using numerical calculations we were able to evaluate the frequencies of molecular vibrations and identify the nature of those modes that disappear upon planarization. The close correspondence between the calculated and experimental

spectra indicates that the majority of these vibrational modes have induced dipole moments that are perpendicular to the main axis of the twisted molecule.

ACKNOWLEDGMENTS

The authors wish to acknowledge E. Haller and J. Beeman for providing the Ge:Cu detector, and S. Watson for construction of the diamond-anvil cells. This work was primarily supported by the U.S. National Science Foundation through Grants Nos. DMR-9901625 and DMR-0203832. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. Partial support was also provided by WSU’s Institute for Shock Physics through the DOE, Grant No. DE-FG03-97SF21388.

- ¹M. Gross, D. C. Müller, H.-G. Nothofer, U. Scherf, D. Neher, G. Bräuchle, and K. Meerholz, *Nature (London)* **405**, 661 (2000).
- ²J. H. Schön, Ch. Kloc, A. Dodabalapur, and B. Batlogg, *Science* **289**, 599 (2000).
- ³H. W. Furumoto and H. L. Ceccon, *IEEE J. Quantum Electron.* **6**, 262 (1970).
- ⁴M. Chandrasekhar, S. Guha, and W. Graupner, *Adv. Mater.* **13**, 613 (2001).
- ⁵S. Guha, W. Graupner, R. Resel, M. Chandrasekhar, H. R. Chandrasekhar, R. Glaser, and G. Leising, *Phys. Rev. Lett.* **82**, 3625 (1999).
- ⁶W. Graupner, R. Resel, G. Leising, R. Glaser, S. Guha, M. Chandrasekhar, and H. R. Chandrasekhar, *Synth. Met.* **101**, 180 (1999).
- ⁷P. Pusching, C. Ambrosch-Draxl, G. Heimel, E. Zojer, R. Resel, G. Leising, M. Kriechbaum, and W. Graupner, *Synth. Met.* **116**, 327 (2001).
- ⁸R. M. Hochstrasser, R. D. McAlpine, and J. D. Whiteman, *J. Chem. Phys.* **58**, 5078 (1973).
- ⁹P. Launois, F. Moussa, M. H. Lemeë-Cailleau, and H. Cailleau, *Phys. Rev. B* **40**, 5042 (1989).
- ¹⁰G. P. Charbonneau and Y. Delugeard, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **33**, 1586 (1977).
- ¹¹C. Ecolivet, M. Sanquer, J. Pellegrin, and J. De Witte, *J. Chem. Phys.* **78**, 6317 (1983).
- ¹²M. H. Lemeë-Cailleau, A. Girard, H. Cailleau, and Y. Delugeard, *Phys. Rev. B* **45**, 12682 (1992).
- ¹³D. H. Barich, R. J. Pugmire, D. M. Grant, and R. J. Iulucci, *J. Phys. Chem. A* **105**, 6780 (2001).
- ¹⁴A. Veron, J. Emery, and F. Lari-Guillet, *J. Phys. Chem. Solids* **56**, 51 (1995).
- ¹⁵C. Benkert, V. Heine, and E. H. Simmons, *J. Phys. C* **20**, 3337 (1987).
- ¹⁶C. Benkert and V. Heine, *J. Phys. C* **20**, 3355 (1987).
- ¹⁷C. Benkert, *J. Phys. C* **20**, 3369 (1987).
- ¹⁸K. K. Zhuravlev and M. D. McCluskey, *J. Chem. Phys.* **114**, 5465 (2001).
- ¹⁹G. Yu. Machavariani, M. P. Pasternak, G. R. Hearne, and A. Kh. Rozenberg, *Rev. Sci. Instrum.* **69**, 1423 (1998).
- ²⁰D. Schiferl, D. T. Cromer, and R. L. Mills, *High Temp.-High Press.* **10**, 493 (1978).
- ²¹M. D. McCluskey, L. Hsu, L. Wang, and E. E. Haller, *Phys. Rev. B* **54**, 8962 (1996).
- ²²Aldrich Chemical Co., Milwaukee, WI 53201.
- ²³M. Rubi and G. Zerbi, *J. Chem. Phys.* **242**, 123 (1999).
- ²⁴K. Furuya, H. Torii, Y. Furukawa, and M. Tasumi, *J. Mol. Struct.* **424**, 225 (1998).
- ²⁵M. J. Frisch *et al.*, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, Pennsylvania, 1998.
- ²⁶A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ²⁷O. Bastiansen, *Acta Chem. Scand.* (1947–1973) **3**, 408 (1949).