Lattice-Dynamical Study of the Abnormally Short Bond-Length in *trans*-Stilbene Molecules in a Crystal

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Lattice-dynamics calculations have been made on crystalline *trans*-stilbene under an atom–atom potential approximation, using both flexible and rigid molecular models in order to clarify the existence of the molecular motion suggested for explaining the abnormal bond-length of the central C=C bond. The intramolecular twisting of the benzene rings strongly couples with the overall rotation of the molecule in some manner, including the suggested manner. The coupled modes form phonon branches and show little dispersion.

The molecular flexibility or internal (intramolecular) rotation in small, simple molecules has attracted much attention for a long times. Such motions, however, hardly affect the bulk properties of compounds, except for the Schottky anomaly in the heat capacity of a solid at low temperatures. Indeed, in the cases of a rotation of the methyl group, the motion is usually well described by a one-particle scheme in which the effects of other molecules (methyl groups) are averaged out, thus giving a mean field,[1] though some cases have recently been discovered in which strong coupling between the methyl groups requires an extended scheme for a good description, and results in a quantum sine-Gordon breather mode, a normal mode in a nonlinear wave.[2,3]

The discovery of structural phase transitions in a series of compounds, the so-called *p*-polyphenyls,[4] extended the area of study concerning molecular flexibility to the macroscopic region, which includes the bulk properties of simple molecular solids. In crystalline biphenyl, for example, the twisting degree of freedom strongly couples with the translational degrees of freedom, and forms a phonon branch, which softens upon approaching the transition temperature, and drives the incommensurate phase transition associated with the molecular twisting.[5,6] After this discovery, some structural phase transitions have been identified as being closely related to the intramolecular motional degrees of freedom in the crystals of butterfly-like molecules, such as bis(4-chlorophenyl) sulfone[7,8] and of fluorine substituted *p*-polyphenyls.[9—11]

The molecule of *trans*-stilbene (C_6H_5–CH=CH–C_6H_5) has two "soft" intramolecular twisting degrees of freedom of the benzene rings. Spectroscopic studies of the molecular vibration in the gas,[12] liquid,[13] and crystalline[13,14] states have been extensively made, and have revealed that the characteristic energy of the intramolecular twisting degrees of freedom is low and within the range of the external lattice vibration of molecular crystals.[12,13]

The crystal of *trans*-stilbene has two molecules that are crystallographically independent, both of which lie on inversion centers.[15—19] One (molecule B) of the molecules shows an orientational disorder. The disordered structure can be analyzed as a superposition with an appropriate ratio (depending on the temperature) of molecules having primary and secondary orientations, both of which are consistent with the inversion symmetry of the site. The two orientations are, roughly speaking, related by the rotation of the molecule around the long molecular axis. The disorder is dynamical in nature, as shown from the results of a structural analysis at low temperature,[19] and the crankshaft motion (not an overall rotation) of the molecule is expected to be responsible for this disorder based on the results of NMR and NQR experiments[20] on a very similar compound, *trans*-azobenzene (C_6H_5–N=N–C_6H_5). The dynamical nature has recently been demonstrated in a different manner, as the discovery of a glass transition due to a freezing of this motion at about 170 K, by the present authors from a precise calorimetric measurement.[21]

Besides the orientational disorder, there is something anomalous in its crystal structure, i.e., the length of the central C=C bond of the other molecule (molecule A), determined from X-ray diffractometry, is abnormally short compared with that supposed by chemical intuition. The abnormally short bond-lengths of the central C=C bonds have also long been recognized in many derivatives of *trans*-stilbenes and in *trans*-azobenzene (the central N=N bond in this case).[22] Recently, this apparent shortening of the bond-lengths has been suggested to be due to some molecular motion.[22] The motion suggested is a combination of the overall rotation of a molecule and the intramolecular twisting of the benzene rings to keep the orientation of the rings, as shown in Fig. 1. Namely, two benzene rings are twisted by some angle which keeps the inversion symmetry of the molecule; simultaneously, the molecule itself (as described by the plane on

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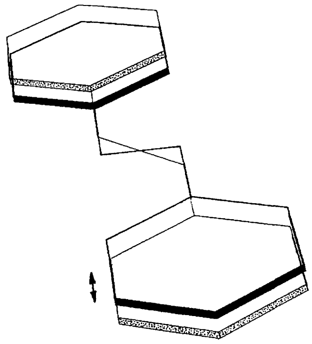

Fig. 1. Two *trans*-stilbene molecules related by composite motion suggested for the explaining of the abnormally short length of the central C=C bond in *trans*-stilbene molecule in crystal.[22] The motion retains the inversion (site) symmetry and keeps the orientation of the two benzene rings.

which the central CH=CH moiety lies) is also twisted by the same angle, but in the opposite sense. There is, however, no direct evidence of such a motion, though its experimental verification will be indirect in any case. It will therefore be valuable to carry out a computational study, because such a calculation can give a detailed sketch of any molecular motion from the molecular level. The purpose of the present paper is to clarify the following points: Is there the suggested motion in a crystal? Which is adequate for describing the motion, if any, of an extended or localized scheme? For these purposes, lattice-dynamics calculations in a harmonic approximation are made on crystalline *trans*-stilbene while incorporating the intramolecular twisting degrees of freedom of the benzene rings. Although the approximation has, of course, a limitation concerning its applicability, it is expected to deserve adoption as long as discussions concerning its results are restricted to within the qualitative level. In the present paper, the results of calculations are described, and the points mentioned above are discussed qualitatively.

Calculation

Molecular Model and Intermolecular Interaction. An idealized molecular model was assumed in the calculation, since the purpose of the present study was not to precisely reproduce the experimental crystal structure and properties. The benzene ring is a regular hexagon with a bond-length of 1.397 Å. The lengths of the single and double bonds between the carbon atoms are 1.474 and 1.353 Å, respectively. The C–H bond is assumed to be 0.995 Å. All of the bond-angles are of the sp^2 hybridized carbon atom, i.e., 120°. Only two intramolecular rotational (twisting) motions are incorporated as possible molecular deformation, because they are expected to be extremely soft compared with other molecular vibrations.[12] The combination of the motions of two benzene rings forms *gerade* and *ungerade* intramolecular motional modes, which are adopted as only elementary motions besides the translational and librational degrees of freedom in the lattice-dynamics calculation, resulting in a total of eight degrees of freedom per molecule. The intramolecular rotations in an isolated state are assumed to be free, due to the reason described later. The intermolecular interaction is approximated by the sum of the atom–atom potential of the Buckingham type, the parameters of which were taken from the literature.[23]

Lattice Energy, Crystal Structure, and Intramolecular Potential for Twisting. Prior to the lattice-dynamics calculation, an idealized crystal structure that should be realized in the present model at absolute zero was determined by minimizing the lattice energy while keeping the experimental space group $P2_1/c$ (C_{2h}^5) for consistency. The starting structure was that best-fit to the experimental crystal structure at 110 K.[19] All of the molecules at site B, molecules B, were assumed to occupy the primary orientation. The calculation was thus made for an idealized perfect crystal. Four lattice constants, six angles that describe the molecular orientation for two molecules, and two angles that describe the intramolecular twisting, i.e., a total of 12 variables, were taken into the minimization. Assuming free rotation for the intramolecular motions of the benzene rings, the minimization converged to a lattice energy of 94.8 kJ mol^{-1} with the following lattice constants: $a = 15.462$ (experimental,[19] 15.709 Å), $b = 5.878$ (5.723 Å), $c = 11.763$ Å (12.374 Å) and $\beta = 110.97°$ (111.90°). The resulting lattice energy is rather small compared with the experimental enthalpy of sublimation[24] (99.2 kJ mol^{-1}). The optimized lattice constants compared favorably with the experimental ones. The molecular orientations were within about 10° of the initial structure and the molecular conformation (in terms of the twist angles of 11° and 2° for molecules A and B, respectively) also showed a reasonable agreement with the observation (7° and 3°). On the other hand, a very low hump in the potential-energy curve at the planar molecular conformation drastically affected the optimized structure, especially in the molecular conformation. It therefore seems reasonable to assume in the calculation that the intramolecular twisting is free.

Some assignment[14,25] of the molecular vibrational bands in the infrared and Raman spectra has treated the *ungerade* mode lying at about 50 cm^{-1} and the *gerade* mode at about 100 or 150 cm^{-1}. The factor of two or three between two frequencies is rationalized if one remembers the fact that the principal motion in the *gerade* mode is brought about by the central CH=CH moiety, in contrast to the true rotation of the benzene rings in the *ungerade* mode; consequently there is a large difference not in the force constant, but in the effective moment of inertia. In addition, the spectroscopic results in the gas state[12] showed that the intramolecular potential for the twisting motion of *ungerade* symmetry is very anharmonic and flat. Indeed, the lowest level is only about 8 cm^{-1} from the bottom of the potential. The assumption of free rotation for both the *ungerade* and *gerade* modes in the isolated molecule is therefore consistent with the spectroscopic results.[12] It is also noted that the tossing vibrations of the benzene rings are expected to lie at around 50 cm^{-1},[25] much higher than the twisting motions.

Lattice-Dynamics. A lattice-dynamics calculation was performed on the basis of the formulation by Venkataraman and Sahni.[26] Flexible (eight degrees of freedom per molecule) and the rigid (six degrees of freedom per molecule) molecular models were adopted in the calculation. Calculations were also made on an idealized perfect crystal. The self-force constants were derived from the sum-rules for the translational–translational, translational–rotational, rotational–rotational, translational–twisting, and rotational–twisting degrees of freedom. The self-force constants for the twisting–twisting degrees of freedom were obtained by a direct summation of the individual contributions, molecule by molecule, because no sum-rule exists. The intramolecular contribution to the intramolecular twisting was neglected because of the reason described earlier. A calculation incorporating only the intramolecular twisting degrees of freedom was also made for the sake of a comparison.

The phonon density of states was obtained by summing the number of modes within 1 cm^{-1} over $100\times50\times50$ points distributed uniformly in one-fourth of the first Brillouin zone.

Results and Discussion

Figure 2 shows the one-particle potentials for the overall rotation along the long molecular axis, and for the composite motion that maintains the orientation of the benzene rings. In this figure, the angle denotes the rotation angle by which the central CH=CH moiety is twisted around the axis, parallel to the single bond between the central CH=CH moiety and a benzene ring, and passing through the inversion center of the molecule. Since two molecules are inequivalent to each other, the depth and shape of the potential curve are different. Indeed, only molecule B shows an apparent disorder of orientation, while molecule A does not. A general feature of the potential curves is, however, common: The coupling between the overall rotation and the *gerade* mode of the intramolecular twisting of the benzene rings significantly flattens the potential. This strongly suggests the existence of such a motion in the lattice-vibration modes for both molecules.

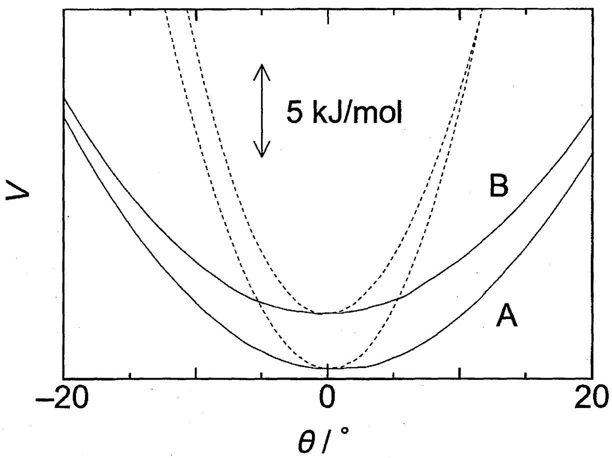

Fig. 2. One-particle potential energy (V) for the molecules A and B in crystalline *trans*-stilbene for the overall rotation (dotted line) and the composite motion (solid line) suggested for explaining the abnormally short length of the central C=C bond. The angle (θ) denotes the rotation angle by which the central CH=CH moiety is twisted around the axis, parallel to the single bond between the central CH=CH moiety and a benzene ring and passing through the inversion center of the molecule.

The results of a lattice-dynamics calculation at the center of the Brillouin zone (Γ point) are tabulated in Table 1, where the result of a calculation incorporating only the intramolecular twisting degrees of freedom is also included for a comparison. Since the calculation was made on an idealized perfect crystal to qualitatively see what occurs when the intramolecular twisting degrees of freedom are allowed, the coincidence between the calculated and experimental[14] frequencies are rather poor, partly because of the existence of a frozen-in disorder of the orientation of the molecule B.[21] Thus, in the following only qualitative features are discussed.

At the center of the Brillouin zone, no mixing occurs between the translational and rotational degrees of freedom, owing to the symmetry property. Similarly, the *gerade* mode of the intramolecular twisting interacts only with the rotational degrees of freedom and the *ungerade* mode with the translational degrees of freedom. Namely, the a_u and b_u modes consist of the translational degrees of freedom and the *ungerade* mode, whereas the a_g and b_g modes comprise the rotational degrees of freedom and the *gerade* mode. A small effect is, however, observed in the frequency of the b_u modes below 100 cm^{-1}. The modes with 137.6 and 144.4 cm^{-1} are of almost pure twisting degrees of freedom, as is clearly seen from the frequencies of the bare twisting modes. A small effect is also observed for the a_u modes. On the other hand, significant coupling is evident for both the a_g and b_g modes. Not only the modes with frequency in the region of the bare modes of the intramolecular twisting (between 110 and 120 cm^{-1}), but even the lowest-frequency mode also show a significant shift in frequency from 32.3 to 27.6 cm^{-1}. Consequently, all of the modes with a_g or b_g symmetry have a significant component of the eigenvector in the *gerade* mode of the intramolecular twisting degree of freedom. A detailed inspection over the components of the eigenvectors reveals that the a_g mode of 53.4 cm^{-1} and the b_g mode of 64.3 cm^{-1} have a component ratio according well to the motion suggested for molecule A. No corresponding mode has been observed for molecule B. The results at the Γ point imply that the motion suggested as a possible cause for an abnormal shortening of the central C=C bond possibly exists for molecule A, in accordance with an observation.[22] The anharmonicity of the potential that governs the motion probably makes the motion responsible for the apparent shortening.

The dispersion relations for the flexible and rigid molecular models are shown in Figs. 3 and 4, respectively. A calculation incorporating only the intramolecular twisting degrees of freedom gives similar dispersion curves to the most-upper four branches in the rigid molecular model for both the frequency and the dependence on the wavevector, resulting in strong mixing. From the comparison, it can be roughly said that eight intramolecular twisting modes are divided into two groups upon mixing with the translational and rotational degrees of freedom. One group has a frequency of around 50

Table 1. Calculated Lattice Vibrational Frequencies (in cm^{-1}) of Crystalline *trans*-Stilbene at Γ Point

Librational and twisting modes						Translational and twisting modes					
a_g			b_g			a_u			b_u		
Rigid[a)]	Flexible[b)]	Twist[c)]	Rigid[a)]	Flexible[b)]	Twist[c)]	Rigid[a)]	Flexible[b)]	Twist[c)]	Rigid[a)]	Flexible[b)]	Twist[c)]
35.5	31.6		32.3	27.6		38.7	37.8		46.3	46.1	
51.0	49.0		62.4	45.0		42.5	41.0		47.9	47.5	
72.4	53.4		76.4	49.6		50.5	48.5		53.4	53.0	
92.3	56.3		82.2	64.3		107.1	100.0		70.5	70.0	
125.3	74.0		126.1	77.8		109.0	106.3			137.6	137.5
134.1	95.0		136.2	83.2			132.9	126.4		144.4	144.0
	163.2	111.3		160.3	111.5		140.7	138.0			
	166.4	120.7		173.5	120.3						

a) Frequency using the rigid molecular model (six degrees of freedom per molecule). b) Frequency using the flexible molecular model (eight degrees of freedom per molecule). c) Frequency obtained incorporating only the twisting degrees of freedom (two degrees of freedom per molecule).

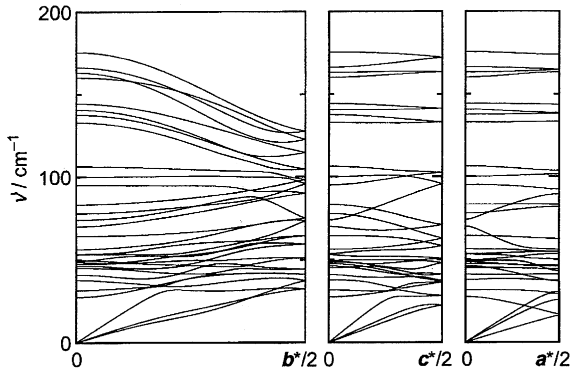

Fig. 3. Phonon dispersion relation of crystalline *trans*-stilbene calculated within the flexible molecular model.

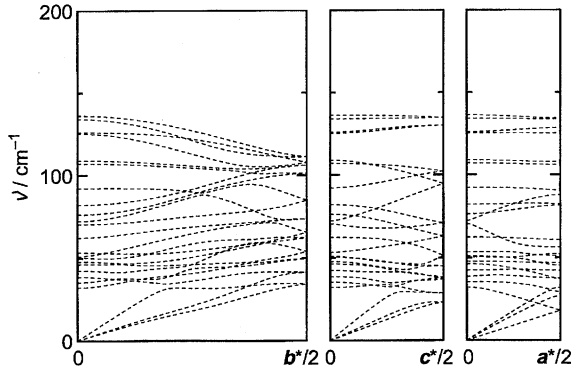

Fig. 4. Phonon dispersion relation of crystalline *trans*-stilbene calculated within the rigid molecular model.

cm^{-1} with little dispersion. The other group lies above 100 cm^{-1} and shows a rather large dispersion. This situation can be seen in Table 1, and even more clearly in the phonon density of states, as shown in Fig. 5. The lowest-frequency tails, i.e., the Debye parts of the densities of the states, are essentially the same for the flexible and rigid molecular models. A large difference can be recognized above 40 cm^{-1}. Especially, the difference is remarkable in the regions between 40 and 60 cm^{-1}, and above 130 cm^{-1}. Indeed, the integration of the difference between the phonon densities of states in the flexible and rigid models gives Fig. 6. In the former region, the integrated difference grows significantly from a small value to about one degree of freedom per molecule. This behavior implies that the modes closely related to the twisting degrees of freedom lie in this region, and that there is no significant dispersion for the modes. Between 70 and 130 cm^{-1} the integrated difference is roughly constant, and then rapidly increases to two degrees of freedom per molecule above 130 cm^{-1}. These features support the qualitative division of the modes closely related to the twisting degrees of freedom into two groups. It is noteworthy that the symmetries of the lowest two acoustic branches along the b^* axis are interchanged upon mixing with the twisting degree of freedom, resulting in a slight increase in the density of states of the lowest frequency region.

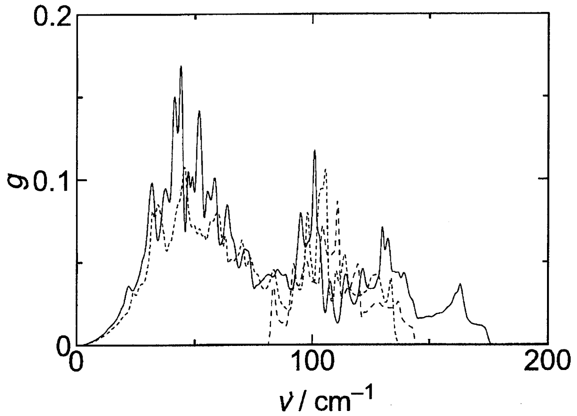

Fig. 5. Phonon density of states (g) for crystalline *trans*-stilbene calculated within the flexible molecular model (solid line) and the rigid molecular model (dotted line). The phonon density of states calculated incorporating only the twisting degrees of freedom are also shown by broken line for comparison.

The motion suggested in order to explain the abnormally short length of the central C=C bond belongs to the region between 40 and 60 cm^{-1}, as noted above. In respect to the fact that the correlation between motions (or vibration) of neighboring molecules plays no significant role, like molec-

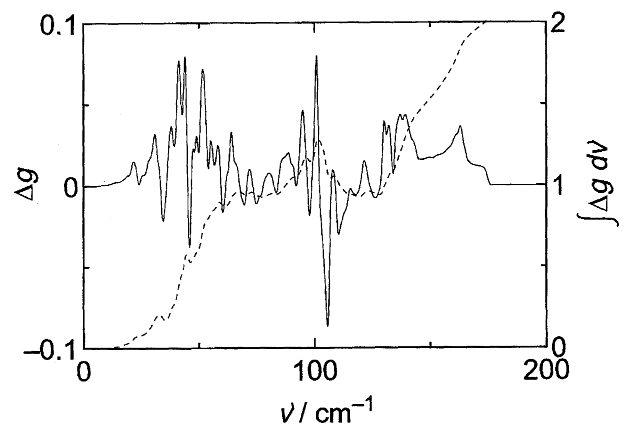

Fig. 6. Difference between the phonon density of states calculated within the flexible and rigid molecular models (solid line and left axis), and its integral from 0 cm^{-1} to the frequency (dotted line and right axis).

ular vibrations with much higher frequency than the lattice vibration, the suggested motion can be described as a one-particle motion.

There remains a point to be considered, i.e., why only molecules A show an abnormally short length of the central C=C bond. It is impossible to give a concrete answer regarding this point. One fact which must be taken into account is that molecule B shows an orientational disorder. Such a disorder unavoidably reduces the possibility of a precise determination of the bond-lengths. In other words, the disorder makes it difficult to detect the motion through the structural parameters. In addition, the results of the present calculation suggest that two modes (a_g and b_g symmetry) that correspond to the suggested motion are expected for molecule A, while no mode is expected for molecule B. Though the reason for these results is hard to describe both clearly and qualitatively, the result seems to have some relation with the point.

A comparison of the magnitudes of the heat capacity between *trans*-stilbene and *cis*-stilbene at low temperatures is interesting with respect to qualitatively validating the results of the present calculation, though no data have been reported concerning the latter, probably because of the difficulty to prepare a pure crystalline sample.[27] Since the two compounds are the same in mass, and the intermolecular interaction (van der Waals interaction) is also similar to each other, nearly the same magnitude of the heat capacity is expected, unless some extra contribution exists. No extremely "soft" intramolecular motion, like the motion under consideration, is expected for the molecule of *cis*-stilbene. Thus, *trans*-stilbene will show a larger heat capacity at low temperatures than does *cis*-stilbene, according to the large density of states between 40 and 60 cm^{-1}. The difference between the heat capacities of two compounds would be roughly approximated by the Einstein heat capacity for about one degree of freedom with a characteristic frequency of about 50 cm^{-1}.

In conclusion, a lattice-dynamics calculation on the crystalline *trans*-stilbene in the flexible and rigid molecular models shows that the motion suggested for explaining the abnormally short length of the central C=C bond[22] exists in a crystal and can be treated as a one-particle motion in the sense that there is no significant dispersion. There is a possibility to explain the reason why only molecule A shows a shortening from a possible type of coupling between the twisting and rotational degrees of freedom.

References

1) W. Press, "Single Particle Rotation in Molecular Crystals," Springer-Verlag, Berlin (1981).

2) F. Fillaux and C. J. Carlile, *Phys. Rev. B*, **42**, 5990 (1990).

3) F. Fillaux, C. J. Carlile, and G. J. Kearley, *Phys. Rev. B*, **44**, 12280 (1991).

4) H. Cailleau, J. L. Baudour, J. Meinnel, A. Dworkin, F. Moussa, and C. M. E. Zeyen, *Faraday Discuss. Chem. Soc.*, **69**, 7 (1980).

5) H. Cailleau, "Incommensurate Phases in Dielectrics 2, Materials," ed by R. Blinc and A. P. Levanyuk, North-Holland, Amsterdam (1985), Chap. 12.

6) N. M. Plakida, A. V. Belushkin, I. Natkaniec, and T. Wasiutynski, *Phys. Status Solidi B*, **118**, 129 (1983).

7) J. M. Corbero, D. J. Pusiol, D. E. Wolfenson, and A. H. Brunetti, *Phys. Status Solidi A*, **91**, K97 (1985).

8) K. Saito, K. Kikuchi, and I. Ikemoto, *Solid State Commun.*, **81**, 241 (1992).

9) K. Saito, Y. Yamamura, H. Saitoh, H. Matsuyama, K. Kikuchi, and I. Ikemoto, *Solid State Commun.*, **87**, 903 (1993).

10) H. Saitoh, K. Saito, Y. Yamamura, H. Matsuyama, K. Kikuchi, and I. Ikemoto, *Solid State Commun.*, **91**, 89 (1993).

11) K. Saito, Y. Yamamura, H. Saitoh, H. Matsuyama, K. Kikuchi, and I. Ikemoto, *Solid State Commun.*, **92**, 495 (1994).

12) T. Suzuki, N. Mikami, and M. Ito, *J. Phys. Chem.*, **90**, 6431 (1986).

13) Z. Meíc and H. Güsten, *Spectrochim. Acta A*, **34**, 101 (1978).

14) A. Bree and M. Edelson, *Chem. Phys.*, **51**, 77 (1980).

15) C. J. Finder, M. G. Newton, and N. L. Allinger, *Acta Crystallogr., Sect. B*, **30**, 41 (1974).

16) J. Bernstein, *Acta Crystallogr., Sect. B*, **31**, 1268 (1975).

17) A. Hoekstra, P. Meertens, and A. Vos, *Acta Crystallogr., Sect. B*, **31**, 2813 (1975).

18) J. Bernstein and K. Mirsky, *Acta Crystallogr., Sect. A*, **34**, 161 (1978).

19) J. A. Bouwstra, A. Schouten, and J. Kroon, *Acta Crystallogr., Sect. C*, **40**, 428 (1984).

20) Y. Ueda, N. Nakamura, and H. Chihara, *J. Phys. Soc. Jpn.*, **57**, 4063 (1988).

21) K. Saito, Y. Yamamura, and I. Ikemoto, *J. Phys. Chem. Solids*, **56**, 849 (1995).

22) K. Ogawa, T. Sano, S. Yoshimura, Y. Takeuchi, and K. Toriumi, *J. Am. Chem. Soc.*, **114**, 1041 (1992), and references therein.

23) D. E. Williams, *J. Chem. Phys.*, **47**, 4680 (1967).

24) J. A. Bouwstra, H. A. J. Oonk, J. G. Block, and C. G. de Kruif, *J. Chem. Thermodyn.*, **16**, 403 (1984).

25) K. Palmö, *Spectrochim. Acta A*, **44**, 341 (1988).

26) G. Venkataraman and V. C. Sahni, *Rev. Modern Phys.*, **42**, 409 (1970).

27) G. Fischer, E. Fischer, and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **77**, 685 (1973).