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Raman Phonon Spectroscopic Study of Phase Transition in *trans*-Stilbene Crystal

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Raman phonon spectroscopy in the 10—170 cm^{-1} range has been used to study phase transition in *trans*-stilbene crystal. At 77 K, eight distinct phonon modes and an internal mode are observed whereas at 300 K the spectrum shows only four phonon bands and an internal mode. The temperature dependence of spectral pattern and some phonon band width suggest that the phase transition in this crystal is quasi-continuous over a small temperature range 215—225 K. The absence of a soft mode and a strong increase of the phonon band width, when approaching the T_c from below, suggest that the phase transition is of order-disorder type. The well established disordered structure of *trans*-stilbene crystal at room temperature attains an ordered structure at low temperature at least through one, possibly two order–disorder transitions.

Raman phonon spectroscopy has been used extensively to investigate phase transition in crystals.[1–4] Phonon spectroscopy is suited for such studies particularly in organic molecular crystals due to the fact that in such crystals the intermolecular forces are 10—100 times weaker than the intramolecular forces and the internal and external motions of molecules in most cases fall in different domain of frequencies. The lattice vibrational frequencies in organic crystals generally lie below 200 cm^{-1}. In *trans*-stilbene crystal, however, some internal modes representing torsion of the phenyl ring also lie in this low frequency range and the Raman active internal modes in this spectral range has been identified by Bree and Edelson.[5] We have used this Raman phonon spectroscopic technique to study phase transition in *trans*-stilbene crystal.

trans-Stilbene is a very flexible molecule in the ground state. The crystal belongs to the monoclinic space group $P2_1/c$ with four molecules in the unit cell.[6,7] At room temperature however the structure is highly disordered, one of the two independent sites shows orientational disorder.[6] In contrast to that at 300 K, at 113 K, the second orientation of the molecule at one of the sites almost disappears and the lattice becomes more ordered.[8] No studies of phase transition in *trans*-stilbene crystal based on standard X-ray or neutron diffraction technique seem to have been reported. Extensive Raman spectroscopic study of this crystal both in external lattice modes and in internal molecular modes by Bree and Edelson[5] did not observe any phase transition in 113—4.2 K range as no significant change in relative intensities of internal modes could be detected by them. However contrary to that observed in first-order structural phase transition, no sharp change in frequency or intensity may occur in second-order phase transition. Also often it is difficult to identify slow and gradual change in Raman band intensity. The study of Bree and Edelson[5] was, however, less extensive at high temperature domain.

Temperature dependence of phonon band width has been shown to be very useful to indicate phase transition in organic crystals.[3] The band width broadening is often related to the progressive setting of disorder when temperature increases.[9,10] When the translational symmetry of the crystal breaks due to disorder, some modes of the whole Brillouin zone can become Raman active. This broadens the phonon bands of the dispersive modes. Phase transition in this crystal at high-temperature domain has recently been reported by Ghoshal et al.[11] by "Photokinematical Approach" which utilized a luminescence intensity change of a dopant as the host crystal goes through a phase transition temperature. They identified two phase transitions in this crystal.

We have undertaken a careful study of Raman phonon spectral pattern and their band widths as a function of temperature. Our studies add further credence to the luminescence technique developed by Ghoshal et al.[11] for phase transition studies and in addition provide information about the nature of phase transition.

Experimental

The compound *trans*-stilbene was obtained from M/S Aldrich Chemical Company Ltd., U.S.A. and purified by repeated crystallization from benzene followed by zone refining with 75 passes. Crystals were grown in a bridgman furnace. Both polycrystalline samples and single crystals were used to obtain the Raman spectra. Unfortunately polarized spectra could not be studied due to lack of facilities.

Raman spectra were obtained using a Spex double monochromator Model 1403 and the 5145 Å line of Spectra Physics Model 2020-5 Argon Ion Laser. Spex Datamate 1B was used for data acquisition and analysis and the band position should be accurate within 1 cm^{-1}. A Superveritemp model 10DT of Janis Research U.S.A. was used to cool the crystal from room temperature down to 77 K. Temperatures were measured and controlled by Lake Shore Model 805 temperature controller. Liquid nitrogen temperature spectrum was run with the crystal immersed in the cryogen.

Results and Discussion

Temperature Dependence of Phonon Spectra. In *trans*-stilbene crystal, the four molecules in the unit cell occupy the inversion centers. Twelve librational phonons are expected to be Raman active. The Raman phonon spectra of *trans*-stilbene crystal at a series of

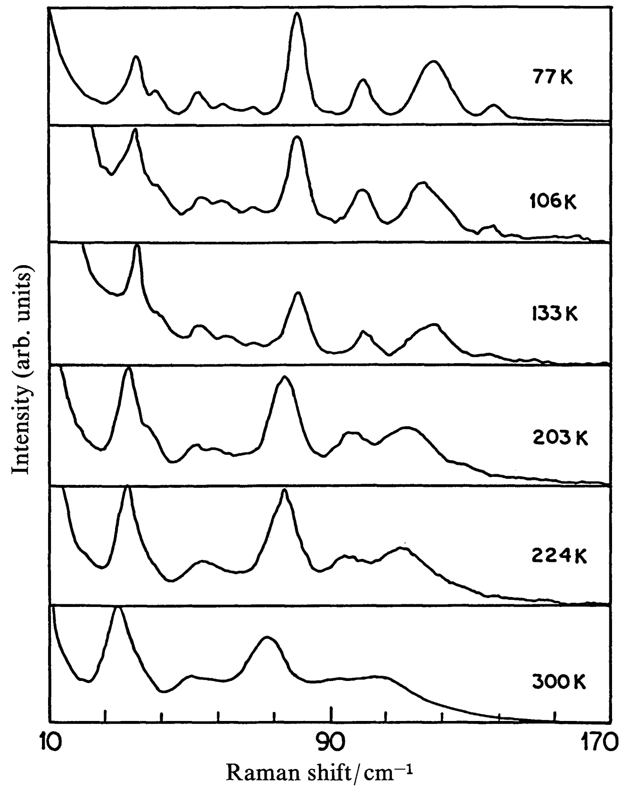

Fig. 1. Raman phonon spectra of *trans*-stilbene crystal at several temperatures. The spectral resolution is 1 cm^{-1}.

temperature are shown in Fig. 1. At 77 K, nine distinct low frequency modes at 34.4, 39.4, 52.2, 60.6, 68.2, 81.0, 99.4, 118.8, and 135.2 cm^{-1} are observed whereas at 300 K, only five broad bands at 29.4, 51.8, 71.8, 92.5, and 101.2 cm^{-1} persist. The 92.5 and 101.2 cm^{-1} bands at 300 K are very broad and are hardly resolved. Our low frequency Raman spectra at 77 K and that reported by Bree and Edelson[5] at 4.2 K can be compared and the bands can be easily correlated. Such correlation is shown in Table 1. Bree and Edelson assigned the quartet at 120.7, 123.4, 127.0, and 131.7 cm^{-1} as factor-group split components of an internal mode. We accordingly assign our 118.8 cm^{-1} band as an internal mode and the remaining eight as lattice modes.

Table 1. Correlation of Low Frequency Raman Bands (in cm^{-1}) at Two Temperatures

Bree and Edelson[5] (4.2 K)	Present work (77 K)
34.9	
40.5	34.4
46.1	39.4
58.0	52.2
64.7	60.6
68.1	
74.0	68.2
86.5	81.0
93.3	
105.3	99.4
120.7 123.4 127.0 131.9	118.8
143.9	135.2

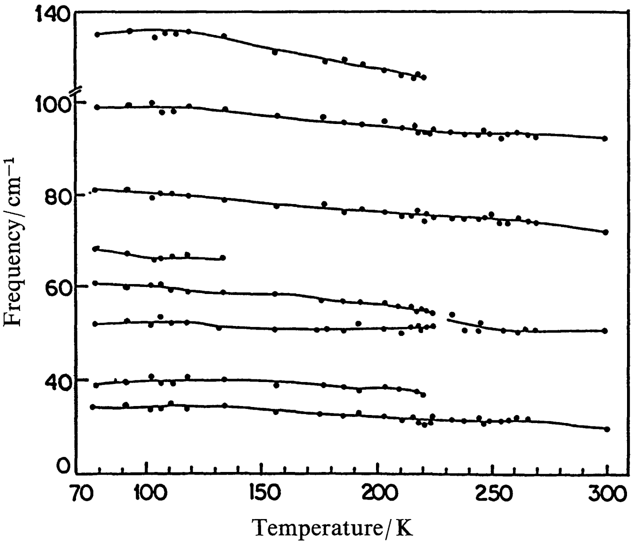

Fig. 2. Temperature dependence of Raman active lattice phonon frequencies in *trans*-stilbene crystal.

A close inspection of the spectra in Fig. 1. reveals that some distinct changes occur in a small temperature range 215—225 K. The medium intense broad phonon band of frequency 51.8 cm^{-1} observed at 300 K flattens out and splits into two bands of frequencies 51.2 and 57.2 cm^{-1} in the 215—225 K temperature range. A third component appears and becomes distinctly observable at 133 K as a phonon band of frequency 66 cm^{-1}. All these three bands intensify and shift to higher frequencies with cooling. At 220 K a third band at 124.8 cm^{-1} appears. These bands intensify and shift to higher frequencies as the temperature is lowered.

The temperature dependence of the Raman active phonon frequencies is shown in Fig. 2. As the temperature is raised, the phonon frequencies shift to lower values. The phonon band around 40 cm^{-1} shows a gradual decrease in intensity with increasing temperature and disappears after 215—225 K. Similar behavior is observed in the 135.2 cm^{-1} phonon band. The triplet structure in the 52—68 cm^{-1} region observed at low temperature fuses into a single broad band in this temperature domain. Further the intensity ratio of 29.4 and 71.8 cm^{-1} bands at 300 K and the corresponding bands at 34.4 and 81.2 cm^{-1} at 77 K are significantly different and this change occurs in the temperature domain 215—225 K.

All these results suggest that there is a continuous phase transition in *trans*-stilbene crystal spread over a small temperature range 215—225 K.

Temperature Dependence of Phonon Band Width. Temperature dependence of phonon band width indicates phase transition in organic crystals.[3] In Fig. 3 we

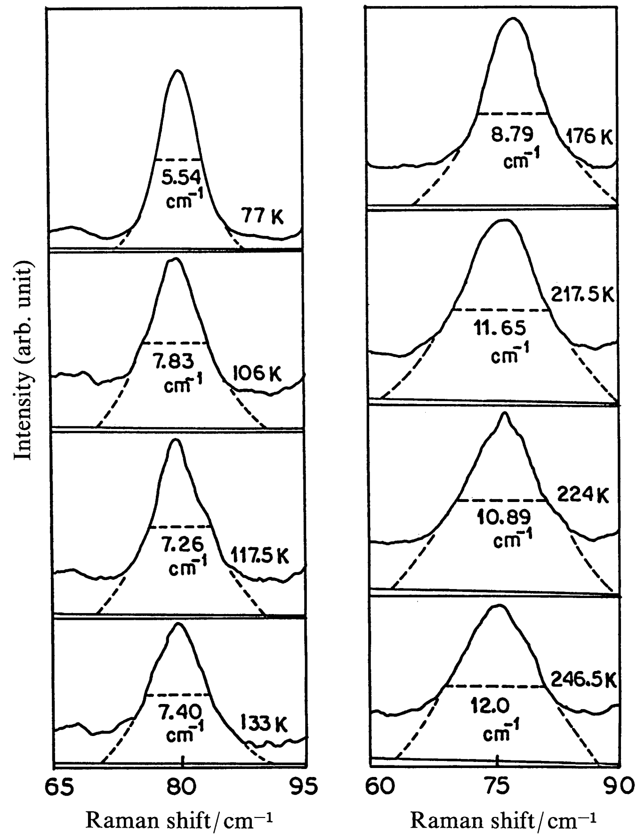

Fig. 3. Band widths (FWHM) of 81 cm^{-1} (at 77 K) band at several temperatures in extended scale. Extrapolation of the bands to the base line is shown by broken lines.

show 81 cm^{-1} (at 77 K) phonon band in extended scale at several temperatures near the transition regions and in Fig. 4. temperature dependence of band widths of 81 and 34.4 cm^{-1} (at 77 K) phonon bands are shown. The variation of width seems to be continuous or very close to be so except at two temperature domains where the continuity pattern is broken and the width shows some small but definite decrement with temperature rise. One of the break points of the curves coincides with the transition temperature region 215—225 K suggested by the temperature dependence of phonon spectral patterns. The other break point in the 105—115 K temperature region is not indicated in the spectral pattern. The change in the band width for this temperature region, however, seems to be within the error bar of the experimental Raman resolution and no definite conclusion about a phase transition at this temperature range can be drawn. The break points in the continuity pattern of the band width-temperature plot is more pronounced in 81 cm^{-1} phonon than in 34.4 cm^{-1} band. This is possibly due to the fact that the 34.4 cm^{-1} phonon band overlaps with other band at 39.4 cm^{-1} and the overlapping becomes significant at higher temperature. For the other modes, the quantitative analysis of their band widths has not been possible owing to their multiple overlapping.

Temperature Dependence of Internal Modes. We have also studied the Raman spectra of the crystal representing internal modes of *trans*-stilbene molecule at various temperatures. There is no significant change in the internal modes except that with lowering of temperature the frequencies change slightly to the higher values. However, the B_g mode at 558 cm^{-1} and the A_g mode at 869 cm^{-1} show distinct intensity reversal in a small temperature range around 110 K. This is shown in Fig. 5. This temperature domain agrees with the low temperature peak in the temperature dependence of band width plot as shown in Fig. 4. Ghoshal et al.[11] suggested a phase transition in the *trans*-stilbene crystal at this temperature from their luminescence studies. The agreements of our two approaches coupled with the photokinematical report of Ghoshal et al.[11] about a second phase transition at 110±5 K is interesting.

Nature of Phase Transitions. In first-order phase

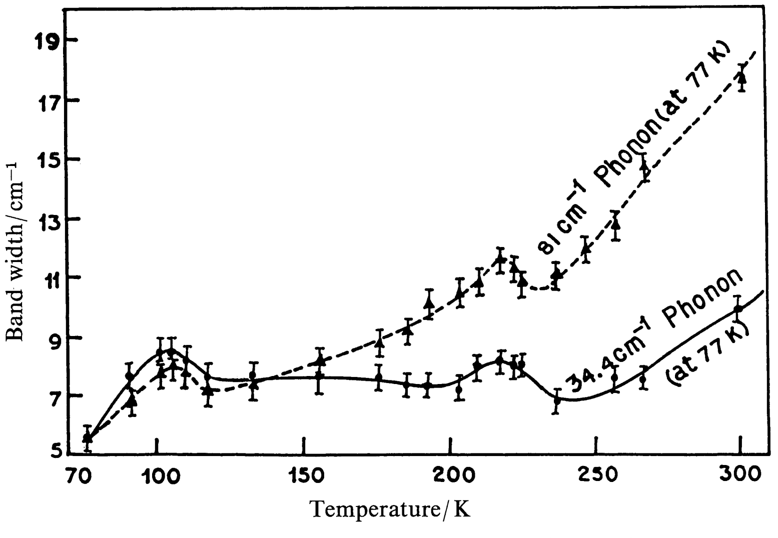

Fig. 4. Temperature dependence of band widths of Raman phonon bands of *trans*-stilbene crystal.

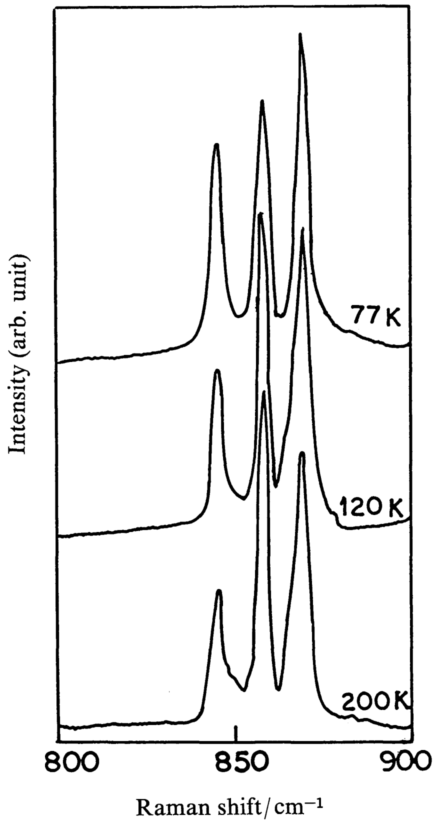

Fig. 5. Raman spectra of *trans*-stilbene crystal in 800—900 cm^{-1} region at several temperatures.

transition, the structural deformation occurs abruptly at one temperature. The second-order phase transition, on the other hand, is continuous and occurs over a temperature range. In *trans*-stilbene we find progressive evolution of phonon spectra as the critical temperature T_c (spread over a range) is approached with no sudden change. The phase transition of this crystal is quasi-continuous (pseudo-second order).

Order–disorder transition is described by a double well potential near T_c. In the phase above T_c there is large amplitude motions from one potential well to another. Below T_c, the molecules lie on the same side of the double well and oscillation occurs in an essentially quadratic well. The system then can be characterized by two characteristic frequencies, one is quasi-harmonic frequency within either side of the double well and a second frequency which describes the relaxational behavior from one well to the other.

In some cases where order–disorder phase transition is established,[12] a large enhancement of Rayleigh intensity is observed as T_c is approached from above. This has been attributed to the relaxational mode describing the jump from one side of the double well to the other. In our experimental result though such enhancement of Rayleigh intensity is not unequivocally established as the first phase transition temperature domain 215—225 K is reached. Such intensity enhancement is, however, observed as 105—115 K is approached. This is evident from Fig. 1. The second order–disorder phase transition at 105—115 K as proposed from "Photokinematical Approach" therefore, seems plausible.

X-Ray analysis shows that at room temperature, the structure of *trans*-stilbene is not highly ordered. One of the two independent sites show orientational disorder.[6] It is, therefore, expected that an ordered structure will be attained at some lower temperature. Indeed at about 113 K, the second orientation of the molecules in the lattice is hardly present.[8] It thus seems that the disordered structure of *trans*-stilbene crystal at 300 K attains the ordered structure at low temperature through at least one order–disorder transition.

Conclusion

We have used Raman phonon spectroscopy to study phase transition in *trans*-stilbene crystal. The temperature dependence of spectral pattern and phonon band width suggest that there is a quasi-continuous phase transition over a small temperature range 215—225 K. The absence of a soft mode and a strong increase of the phonon band width when approaching the T_c from below suggest that the phase transition is of order–disorder type. The disordered structure at room temperatute attains an ordered structure at low temperature through at least one, possibly two order–disorder transitions.

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