Raman Phonon Spectroscopic Study of Phase Transition in 4-Cyanopyridine Crystal

Subhasis CHAKRABARTI, Tridibendra Marayan MISRA,* Mahesh Kumar SARMA,† and Kanak Chandra MEDHI†
Department of Spectroscopy, Indian Association for the Cultivation of Science, Calcutta 700032, India
†Department of Physics, Gauhati University, Gawahati 781014, India
(Received July 3, 1990)

Raman phonon spectroscopy in the 10—170 cm^{-1} range has been used to study phase transition in 4-cyanopyridine crystal. At 77 K, ten distinct phonon modes and an internal mode are observed whereas at 300 K the spectrum shows only six phonon bands and an internal mode. The temperature dependence of spectral pattern and phonon band width suggest that the crystal goes through a phase transition around 120 K. Experimental result suggests that the phase transition is discontinuous with a small structural change.

Raman phonon spectroscopy is a useful technique to investigate phase transition in organic crystals.[1-4] Phonon spectroscopy is particularly suited for the purpose due to the fact that in such crystals the intermolecular forces are 10—100 times weaker than the intramolecular forces and internal and external motions of molecules fall in different domain of frequencies. The lattice vibrational frequencies in organic crystals generally lie below 200 cm^{-1}, however, some out of plane deformation and torsional mode may be active in this region. Infrared and Raman spectroscopic study and vibrational analysis of 4-cyanopyridine has been reported by Green and Harrison[5] and they have assigned the internal vibrations below 200 cm^{-1}. Medhi and Sarma[6] have reassigned some of the internal modes.

At room temperature 4-cyanopyridine crystallizes in the orthorhombic form and belongs to the space group *Pccn* with four molecules in the unit cell.[7] No studies of phase transition in 4-cyanopyridine crystal based on standard X-ray or neutron diffraction technique seem to have been reported. Recently Wong[8] has reported pressure induced phase transition in this crystal by Raman phonon spectroscopic technique. We have investigated temperature dependent phase transition in 4-cyanopyridine crystal using the same technique. In addition we have shown that temperature dependence of phonon band width study is very useful to indicate phase transition in organic crystals. Temperature dependence of some molecular internal vibrational frequencies also often indicates phase transition in organic crystals. In this paper we report the result of our studies which show that indeed there is a temperature dependent phase transition in this crystal and this transition may be structural as in the pressure induced transition.

Experimental

The compound 4-cyanopyridine was obtained from M/S Aldrich Chemical Company Ltd., U.S.A. and purified by zone refining with 200 passes. Crystals were grown in a Bridgeman furnace. Both polycrystalline samples and single crystals were used to obtain Raman spectra.

The Raman spectra were recorded using a Spex double monochromator Model 1403 equipped with a cooled photomultiplier tube and photon counting unit and the 5145 Å line of Spectra Physics Model 2020-5 Ar^+ laser was used as the excitation source. Datamate 1B was used for data acquisition and analysis. The band position measurement should be accurate within 1 cm^{-1}. A Janis research cryostat Superveritemp Model 10DT was used to cool the crystal from room temperature down to 77 K. Temperature was measured and controlled by Lake Shore Model 805 temperature controller. Some uncertainty is given to the temperature measurement. Local laser heating is expected to create a temperature gradient between the crystal and the sensor.

Results and Discussion

Temperature Dependence of Phonon Spectra. With four molecules in the unit cell of the crystal there are total 24 lattice phonon modes. Twelve zone-center phonons are Raman active. The Raman phonon spectra of 4-cyanopyridine crystal in 10—170 cm^{-1} range at a series of temperature are shown in Fig. 1. At 77 K, ten distinct low frequency modes at 20.6, 33.2, 45.0, 58.6, 71.8, 79.0, 86.2, 94.4, 114.2 and 120.6 cm^{-1} represent lattice modes and the mode at 148.0 cm^{-1} has been assigned as internal mode γ (CN) by Green and Harrison.[5] At 300 K only six phonon bands at 16.8, 29.2, 40.8, 62.0, 70.8, and 95.2 cm^{-1} persist. A close examination of these spectra reveal that some distinct changes occur at 120±1 K which can not be attributed simply to temperature change. As temperature is raised from 118 to 122 K, the 78.6 cm^{-1} (79.0 cm^{-1} at 77 K) phonon band disappears and the intensity of the band at 57.4 cm^{-1} (58.6 cm^{-1} at 77 K) increases. Intensity of this band decreases above and below 120 K. The 85.0 cm^{-1} (86.2 cm^{-1} at 77 K) phonon shows appreciable frequency shift. The 71.0 cm^{-1} (71.8 cm^{-1} at 77 K) phonon band also shows a frequency lowering by 4.4 cm^{-1} at this temperature. The 20.6 cm^{-1} frequency increases by 2.4 cm^{-1} at this temperature and then decreases gradually as temperature is raised. Much less sharp but definite shift is also observed with 120.6, 114.2, 94.2, 45.0, and 32.2 cm^{-1} phonon at this temperature. In Fig. 2 we show temperature dependence of some selected phonon frequencies. Many of the lattice

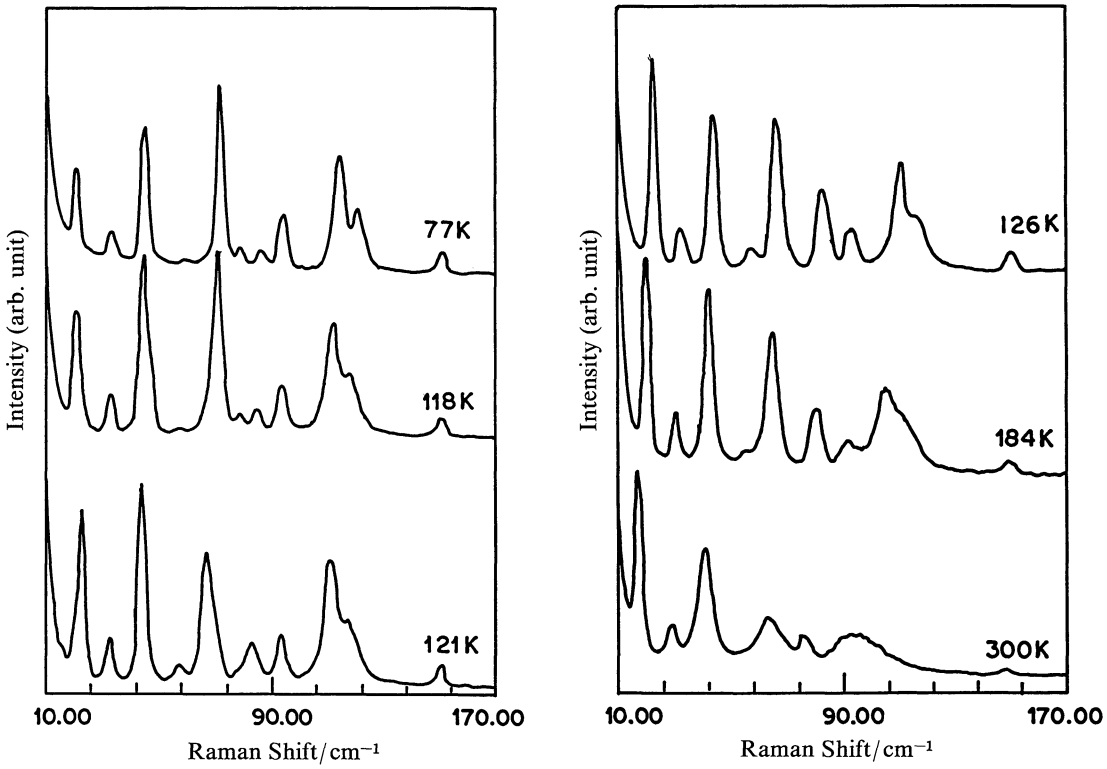

Fig. 1. Raman spectra of 4-cyanopyridine crystal in 10—170 cm^{-1} range at different temperatures.

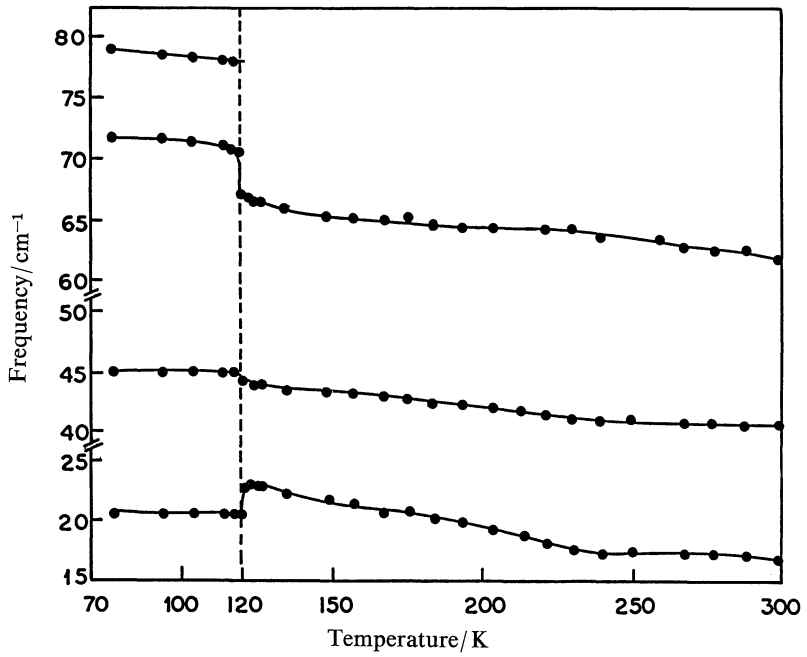

Fig. 2. Temperature dependence of some selected Raman active lattice phonon frequencies in 4-cyanopyridine crystal.

modes show discontinuous change in wavenumber as the crystal temperature is changed from 118 K to 122 K. Raman intensity decreases as the crystal is heated. This is a general observation. Around phase transition temperature there is decrease in frequency in most of the phonon modes but 20.6 cm^{-1} phonon shows reverse behavior. The frequency increases significantly during transition and then shows usual decrement with temperature.

All these results suggest that there is a definite discontinuous phase transition in 4-cyanopyridine crystal at 120±1 K.

Temperature Dependence of Internal Vibrations. We have studied the temperature dependence of internal

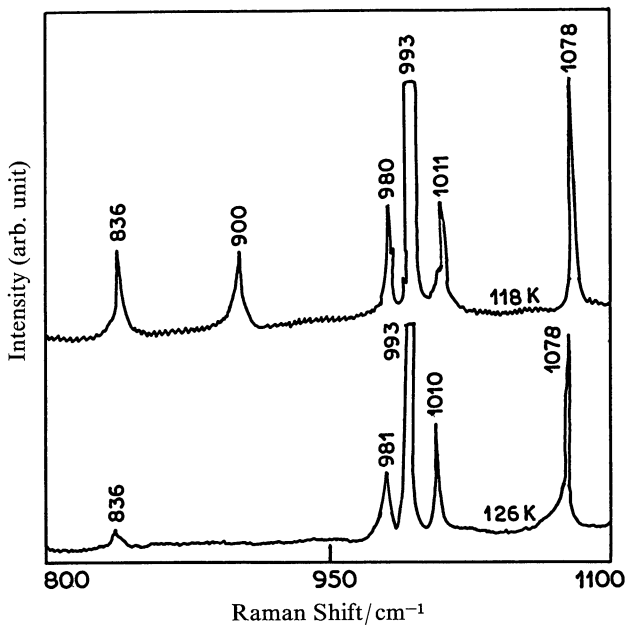

Fig. 3. Raman spectra of 4-cyanopyridine crystal in the 800—1100 cm^{-1} range below and above phase transition temperature.

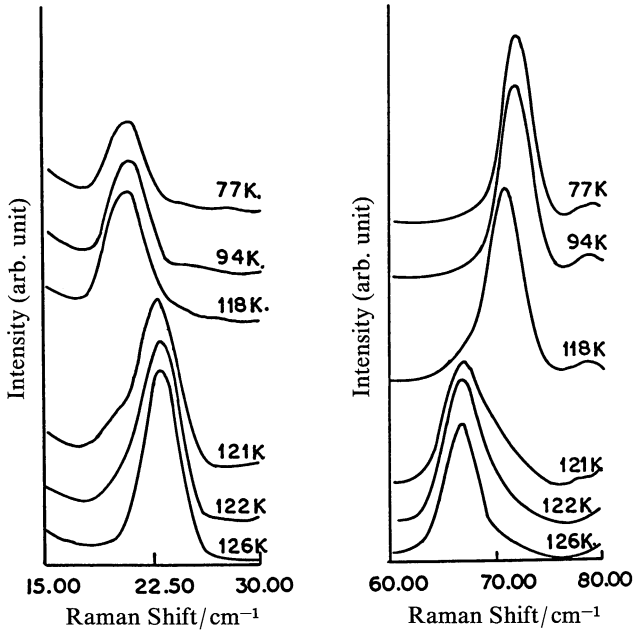

Fig. 4. 71.8 and 20.6 cm^{-1} (at 77 K) phonon bands in extended scale at several temperatures near transition region.

modes also. Though most of the spectral patterns remain unchanged below and above 120±1 K, some definite change is observed. Raman spectra in the 800 to 1100 cm^{-1} range in two phases are shown in Fig. 3. In the low temperature phase a band at 900 cm^{-1} appears. This vibration is of b_1 species and is only infrared active at room temperature.[6] Due to the structural change this vibration becomes Raman active in low temperature phase. Other changes observed are the changes in the intensity ratio of 993 and 1011 cm^{-1} bands and decreament of intensity of a band at 836 cm^{-1} in the high temperature phase.

Temperature Dependence of Phonon Bandwidth. Temperature dependence of phonon band width indicates phase transition in organic crystals.[3] In Fig. 4 we show 71.8 cm^{-1} (at 77 K) and 20.6 cm^{-1} (at 77 K) phonon bands in extended scale at several temperatures near the transition region. Indeed there is indication that new bands appear near the bands observed in one phase when the sample changes into another phase and this is shown as shoulders. Inspite of this, we have been able to measure the FWHM of these two bands. The spec-

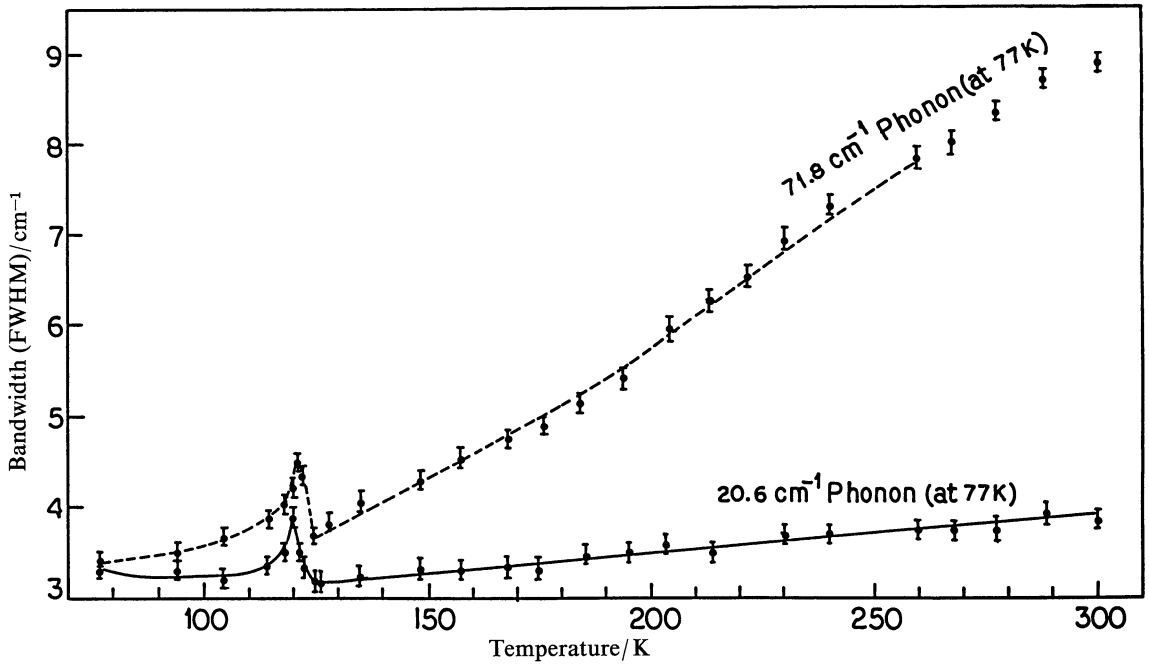

Fig. 5. Temperature dependence of band widths of Raman phonon bands of 4-cyanopyridine cryctal.

tra of Fig. 4 are considered to have been obtained because the phase transition is discontinuous and there is some temperature gradient in the sample. In Fig. 5 temperature dependence of band widths of these two bands are shown. The increase in the band widths of these two bands is large enough to be beyond the error of measurement. At 120±1 K the continuity pattern is broken and the width show some small but definite decrement with temperature rise. The temperature indeed is same as that observed in the temperature versus phonon frequency plot.

Nature of Phase Transition. Temperature dependence of phonon frequencies and band widths suggests that phase transition occurs in a small temperature interval 120±1 K. Raman study indicates that 79.0 cm^{-1} phonon disappears at these temperatures and for some other bands discontinuity as large as 4.4 cm^{-1} is also observed. Internal vibrational spectra in both the phases reveal that there is some small structural change which leads to the appearance of 900 cm^{-1} band at low temperature phase. Phase transition of 4-cyanopyridine is, therefore, a first order transition with small strutural change. The greatest change is observed in 71.8 cm^{-1} phonon band (at 77 K). The crystal lattice at low temperature phase seems to be distorted along the eigen vector of this phonon mode. This observation is similar to that reported by Wong[8] in pressure induced phase transition. However the 71.8 cm^{-1} phonon behaves differently in temperature and pressure induced phase transition. Whereas we have observed large discontinuous jumping in frequency on phase transition, Wong[8] reported only sharp discontinuity in frequency pressure plot at 10 kbar without any appreciable change in phonon frequency at higher pressure. Inspite of this, it seems probable that the phase transition we have observed at 120±1 K is the same as observed by Wong[8] at room temperature at a pressure 10 kbar.

Conclusion

We have used Raman phonon spectroscopy to study phase transition in 4-cyanopyridine crystal. The temperature dependence of spectral pattern and phonon band width suggest that there is a discontinuous phase transiton around 120 K. The lattice mode at 71.8 cm^{-1} (at 77 K) shows the greatest change (62 cm^{-1} at 300 K) while most of the other vibrations remains continuous in both the phases. The structural change is, therefore, considered small.

References

1) R. Zallen, C. H. Griffiths , M. L. Stade, H. Hayek, and O. Brafman, *Chem. Phys. Lett.*, **39**, 85 (1976).
2) B. A. Bolton and P. N. Prasad, *Chem. Phys.*, **35**, 334 (1978).
3) A. Girard, M. Sanguer, and Y. Delugeard, *Chem. Phys.*, **96**, 427 (1985).
4) Y. Ebisuzaki, L. H. Askari, and A. M. Bryan, *J. Chem. Phys.*, **87**, 6659 (1987).
5) J. H. S. Green and D. J. Harrison, *Spectrochim. Acta, Part A*, **33**, 75 (1977).
6) K. C. Medhi and M. K. Sarma, *Indian J. Phys.*, **64B**, 307 (1990).
7) M. Long, N. Sparrow, and P. Sommerville, *Acta Crystallogr., Sect. B*, **27**, 1986 (1971).
8) P. T. T. Wong, *J. Chem. Phys.*, **78**, 4840 (1983).