

## Laser Raman spectroscopy and its applications – especially in structural phase transitions

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**Abstract.** The usefulness of Raman spectroscopy as a powerful non-contact, nondestructive analytical tool has been well-demonstrated. A bird's eye-view of various techniques used for the study of various types of structural phase transitions is given. A few modern applications of laser Raman spectroscopic studies have been mentioned. Thermal variations near critical transition region in the position, halfwidths, intensities and shapes of few thermo-sensitive bands in a few organic and inorganic salts and complexes have been used to deduce the critical exponents  $\beta$  and the activation energy  $U$  for orientational disorder of  $\text{NCS}^-$  ions and  $\text{CH}_3\text{NH}_3$  type groups.

**Keywords.** Raman applications; phase transitions; critical exponents.

### 1. Introduction

Several experimental techniques are being used to detect and characterize the structural phase transitions (SPT) (Rao and Rao 1978; Muller and Thomas 1981; Iqbal and Owens 1984). SPT can be induced by varying the temperature and pressure of the sample or by changing the intensity or frequency of incident light falling on it. Mechanical methods are used to determine the elastic constants, Young's modulus etc. The measurements dealing with the thermal expansion, the specific heat, the heat capacity, the differential thermal analysis, scanning calorimetry, thermo electric power etc. are used for thermal characterization of SPT. The structural determination in different phases is conducted by X-ray, neutron and electron-diffraction. Electrical properties (like resistivity, Hall-coefficient, dielectric constant, permittivity), magnetic-susceptibility-anisotropy and resonance (EPR, NMR and NQR) techniques have also been used for the comprehension of the materials near SPT. The optical absorption and emission in ultraviolet, visible and infrared regions and the scattering techniques (neutron, Brillouin and Raman) have extensively been applied to characterize the nature and type of the reconstructive or distortive (displacive or order-disorder type) SPT (Rao and Rao 1978; Muller and Thomas 1981). The cases having positional, orientational or electronic spin disorders have been identified (Muller and Thomas 1981). Raman signatures of incommensurate phases have been also reported (Pal *et al* 1984). In this paper after discussing a few recent applications, some examples of the characterization of SPT through laser Raman spectroscopy will be presented. It will also be seen that the system near the transition temperature,  $T_c$ , becomes highly nonlinear. In an anisotropic and anharmonic single crystal, like that of  $\text{CsNCS}$ , one may observe, under specific experimental conditions manifestation of a "deterministic

chaos". Thus it is observed that Raman is a powerful micro-probe to study static and dynamic processes occurring at the atomic and molecular levels during an SPT.

## 2. Experimental

### 2.1 Typical experimental layout

For laser Raman work using spex 1403 Ramalog machine under Indian experimental conditions (which should be applicable to most southern tropical developing countries) a block diagram is given in figure 1. The voltage stabilizer is essential to eliminate the voltage fluctuations if the input voltage varies within 150–250 V. The three phase stabilizers give phase to phase constant voltage of  $400 \pm 5$  V for 5 Watt Spectra Physics Ar<sup>+</sup> laser and  $475 \pm 5$  V for the 20 W Spectra Physics Ar<sup>+</sup> laser. The water cooled Neslab HX-500 recirculating heat exchanger (chiller plant) run on 3 phase, 115 volts is used to cool the 5 W laser head and Spectra Physics 265 exciter. Likewise two air-cooled Neslab HX-750 units, with conductivity water in their tanks, are used to cool the 20 W Spectra Physics laser head, the dye laser and their power supplies. These chillers are essential as the tapwater, which is pumped directly from underground wells at the Indian Institute of Technology (IIT), Kanpur, maintains a temperature of 31°C throughout the year.

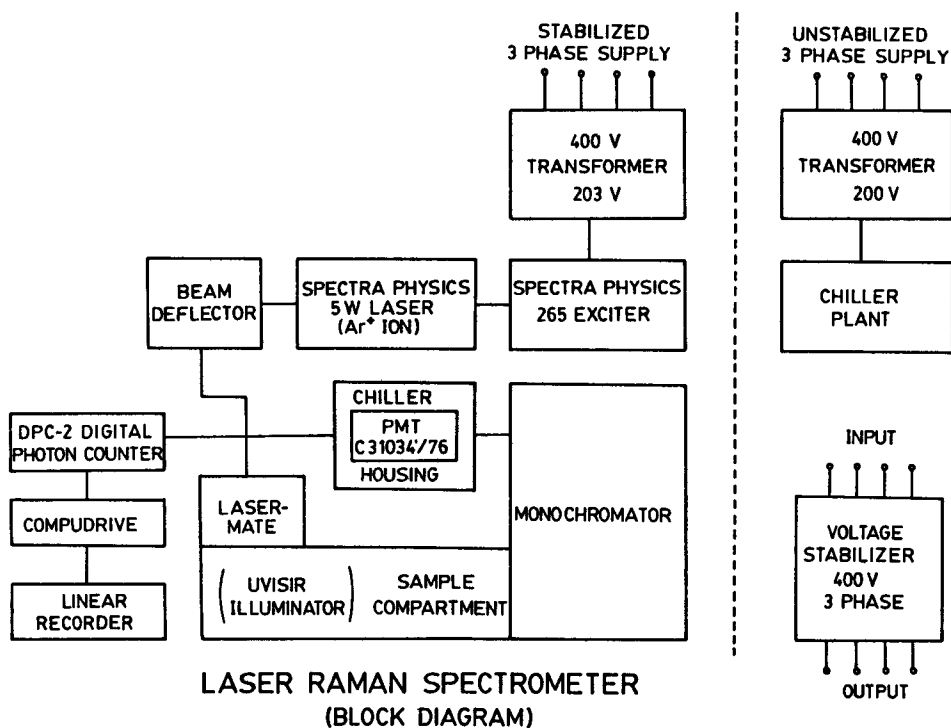


Figure 1. Block diagram for normal laser Raman (Ramalog) set-up at the Indian Institute of Technology, Kanpur.

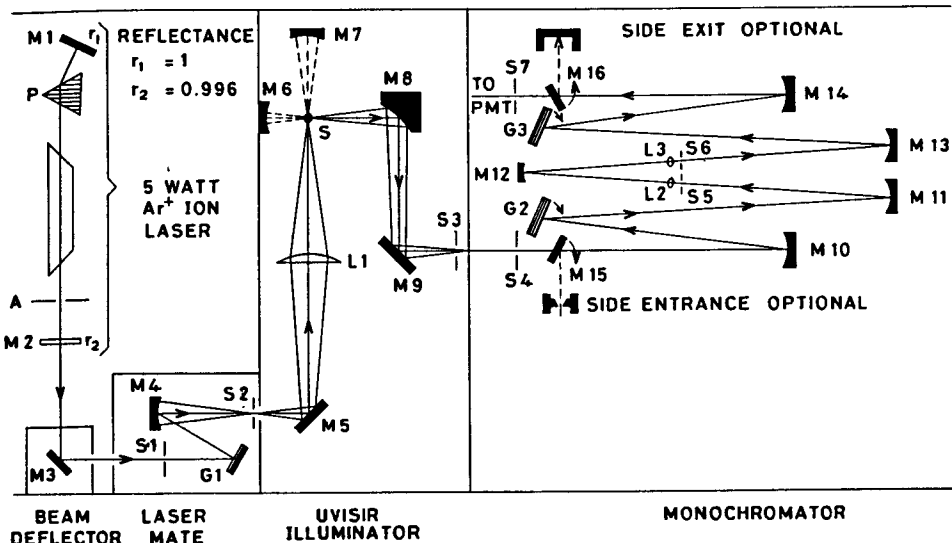


Figure 2. Ray-diagram of Spectra Physics Laser and Ramalog 1403 spectrometer.

## 2.2 The optical system

An optical line diagram is shown in figure 2 for the Ramalog machine. The output beam from the laser is directed through a beam deflector to the 'laser-mate', (a small grating spectrometer, used to get rid of the background plasma lines from the laser). The 'UVISIR illuminator' is the sample compartment. The laser line free from plasma background falls on the sample. The scattered light from the sample is collected through a combination of an elliptical mirror  $M_8$  and plane mirror  $M_9$  onto the first entrance slit  $S_3$  of a double monochromator. The scattered radiations are seen at  $90^\circ$  geometry after dispersion through the 1403 Ramalog machine by a C-31034/76 Ga-As photomultiplier (PMT) housed in a chamber thermoelectrically chilled to  $-30^\circ\text{C}$  through Peltier cooling to reduce the dark counts ( $< 30$  per second).

## 2.3 Spectral records

The output from the PMT is guided through the SPAD (single photon attenuator discriminator), digital counting system (DPC-2), compudrive and a linear chart recorder. Compudrive runs the chart paper synchronously with the monochromator gratings. The typical parameters given for Ramalog system are as follows:

The stray light reduction (Spectral purity) =  $10^{-14}$  at  $\Delta\nu = 20\text{ cm}^{-1}$  (from  $514.5\text{ nm}$ ); resolution =  $0.15\text{ cm}^{-1}$  (FWHM) at  $\text{Hg}^+$   $579.1\text{ nm}$ ; wave number accuracy =  $\pm 0.2\text{ cm}^{-1}$ , respectively.

## 2.4 General precautions

To maintain optimal laser performance it is essential to clean all optical, mechanical and water filter systems periodically. Likewise, replacement of the distilled (conductivity)

water used in the heat exchangers, after the resistance drops below 100 kilohms across the tube, is essential. The narrow passage of special filters in the power supplies, and narrow passage around the plasma tube and some of the interlocking flow switches can be blocked by small particulate matter (due to dust, corrosion, scale deposition etc). Periodic cleaning greatly helps to enhance the life of the complete Ramalog system.

### 2.5 Sample handling

It is worth mentioning that sample handling techniques vary with the nature and type of the materials to be investigated. The hygroscopic, dehydrating or air-sensitive (especially to oxygen or water in air) or corrosive (toxic) materials can be studied by sealing them under proper environmental conditions in a pyrex (non-fluorescent) glass or quartz container. Low pressure gases need sealed (epoxied by non-fluorescent cement) cells with Brewster angle quartz windows (to use multiple reflection technique) and high power lasers for excitation. Raman bands of non-totally symmetric vibrations are usually very broad and of weak intensity.

Microcrystalline or powder materials could be enclosed in capillary tubes or any other suitably shaped vessels. Pellet techniques are used for small amounts (50 mg) of sample to press after sprinkling it on the KBr pellet while still on a die. Local heating of sample could be reduced by diluting the (absorbing) materials in a matrix.

Rotating techniques for liquid and solid samples are available commercially to

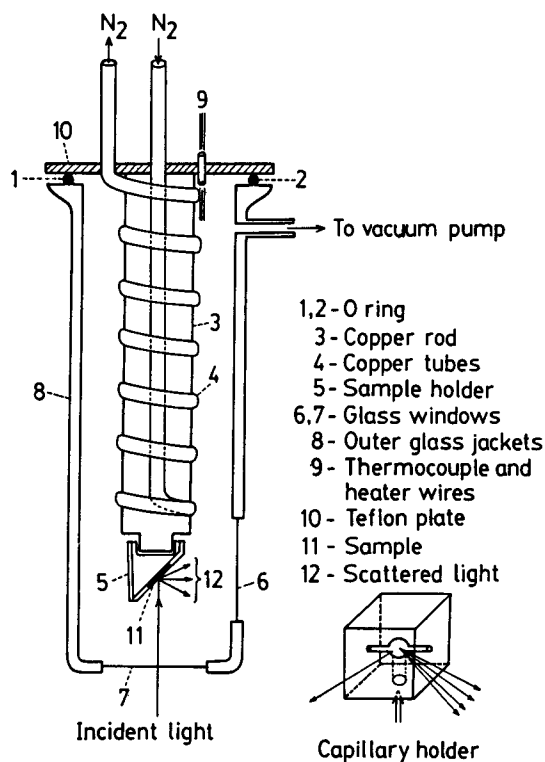


Figure 3. Design of low temperature cell for Raman studies in the range 63 to 300 K.

avoid heating (and hence decomposition) of samples which have absorption at the excitation wavelength.

Various types of special devices are made to keep the samples at specified controlled temperatures. The low temperature cell, fabricated and used in our laboratory is shown in figure 3. A double walled pyrex glass structure has an inner jacket at the bottom of which is attached through a kovar seal a rectangular copper attachment (cold finger) for holding the sample. The outer jacket has two quartz windows, one each for the incident laser beam and for collection of the scattered radiation, respectively. Liquid nitrogen is used as the coolant for the copper block (and the sample in it). To obtain temperature upto 63 K, an arrangement was made to evaporate the liquid nitrogen under reduced pressure using two rotary pumps. A 25-watt heater attached to the sample holder was used to control the temperature (within  $\pm 2$  K; and a Cu-Co thermocouple to measure the sample temperature within  $\pm 1$  K. Special sealing material, resistant to low temperatures, is to be used for work below liquid nitrogen temperature.

The spectra above 300 K were recorded with a locally fabricated cell (figure 4). It consists of three parts (1) the sample holder(s), (2) the heating block, and (3) the temperature controller.

The brass heating block  $18 \times 18 \times 38$  mm<sup>3</sup> has an 8 mm diameter hole drilled to a depth of 28 mm to insert the sample holder. The block is heated from three sides by 25-watt heaters fitted into grooves. On the bottom and on the fourth side two conical

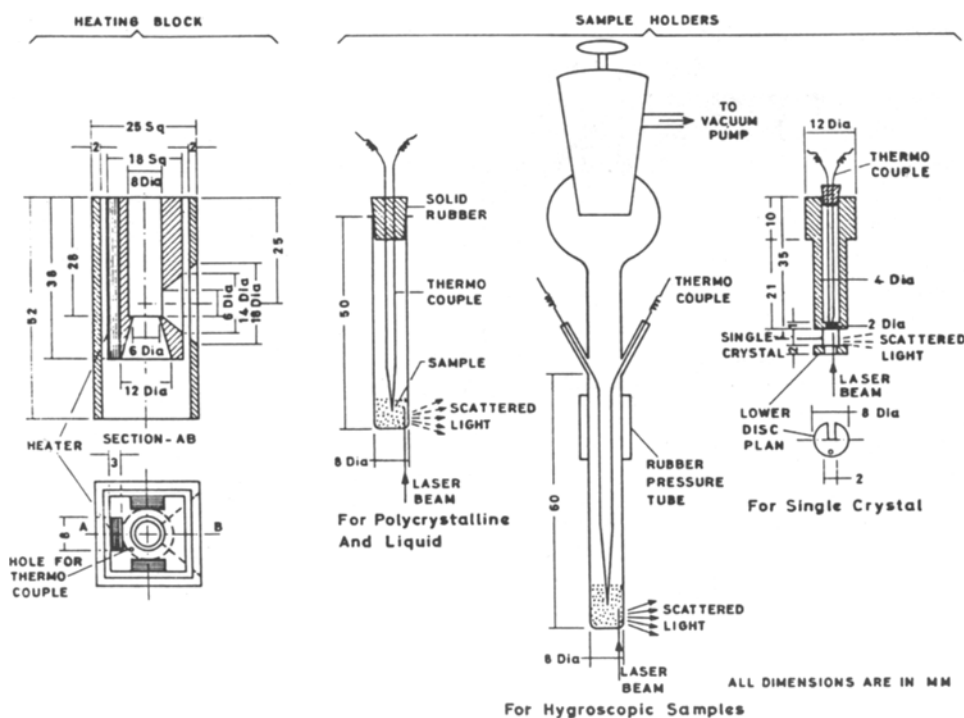


Figure 4. Design of a high temperature cell with different types of sample holders for Raman studies.

holes are drilled for the incident laser beam and the collection of scattered radiations, respectively. The system is mounted on a Spex three-way motion platform for alignment of the sample. Sample holders to study temperature dependence of liquids, polycrystalline and single crystal samples have been improvised in the lab (figure 4). One Cu–Co thermocouple is used to measure the temperature and another thermocouple for its control through a relay up to  $600 \pm 1$  K.

### 3. Raman spectroscopy applications

The micro-Raman technique is being used for tackling problems in geochemistry and geophysics (for study of rocks, ores and minerals) especially for solid and fluid inclusions (Bridoux *et al* 1984). Likewise identification, localization and characterization of gems, art materials, ancient sculptures, manuscripts and paintings, dust particles and pollutants (sulphates, silicates, oxides, particles); impurities in normal, bio-organic and inorganic materials (papers, textiles, plastics, ceramics, semiconductors, food, drugs, product of metabolism etc); evolution of molecular or crystalline composition and distribution of species in microscopic samples during chemical reactions (corrosion, thermal degradation, photochemical processes, electrochemistry, catalysis etc.) has been achieved by this novel technique (Bridoux *et al* 1984). We have established this facility at IIT, Kanpur, in 1990.

The optical levitation technique (in which 10 to 30  $\mu\text{m}$ , microsized solid particles are trapped in stable optical potential wells of the focussed beam of radiation from a cw laser) has been used to study Mie's natural mode resonances in Raman spectra of small glass spheres (Thurn and Kiefer 1984).

With dye lasers, the wavelength of excitation,  $\lambda_{\text{ex}}$ , could be matched with electronic absorption bands of any sample to get the condition of resonance Raman scattering. One could get 3 to 4 orders of magnitude resonance enhancement with lower input excitation intensities on biological, biomedical and other delicate samples to study their ground and electronically excited states. The low lying electronic states of the same parity as the ground state (e.g. in  $\text{Eu}^{3+}$ , GaP, Zn, Mg which have very low scattering cross-section  $\sigma_{\text{Ram}}$ ) have been investigated by this technique (Hudson and Sension 1989; Jain and Soni 1989).

The surface enhanced Raman spectroscopy (SERS) enhances  $\sigma_{\text{Ram}}$  by  $10^2$  to  $10^6$  for molecules inside adsorbates and microscopic structures of surfaces and interfaces due to 'long-range electromagnetic' or a short range 'chemical communication' between the adsorbate and the substrate. SERS produces vibrational signatures without external perturbations (like in IR) with good resolution (unlike LEEDS) (Chang and Funtak 1982).

The laser fields at two different frequencies  $\nu_L$  and  $\nu_S$  can force a Raman mode  $\nu_R$  of a medium to produce an oscillating dielectric constant, which interacts with the laser fields to produce directed coherent output beam frequencies  $n\nu_L \pm m\nu_S$  with intensity comparable with the parent laser(s) (Bist *et al* 1985).

Phonons in semiconductors (super lattices) and superconductors, semimetals etc have been studied (Bist *et al* 1989). Time-(pico-femto second) resolved Raman spectroscopy has been applied to study ultrafast processes as in photoisomerization and photo redox reactions in solution (Bist *et al* 1989). Biological samples have been studied for identification of conformational changes and characterization of nucleic acid components, gallstones, cancer studies and anti-cancer drugs, etc. (Bist *et al* 1989).

#### 4. Theoretical background on structural phase transitions:

In the soft-mode theory (Anderson 1960; Cochran 1960) a structural phase transition arises from a dynamical instability of the crystal against a particular vibration (soft mode  $\omega_{sm}$ ) which close to the transition temperature  $T_c$  can be represented as:

$$\omega_{sm} = c_{\pm} [T - T_c]^{1/2}$$

where  $c_+$  and  $c_-$  are the constants at temperature  $T > T_c$  and  $T < T_c$ , respectively. Usually  $\omega_{sm}$  is active only in the low temperature phase (Cowley 1989). The simplest form which is exhibited by Raman intensity of the soft mode  $I_{sm}$  is

$$I_{sm}(\omega) = \frac{B[n(\omega_{sm}) + 1]Q_{sm}^2}{\mathcal{J}m[\omega_{sm}^2 - \omega^2 - i\omega\gamma]}$$

where  $B$  is a constant,  $n(\omega_{sm})$  is the Bose occupation number and  $\gamma$  is the classical damping constant (independent of temperature) and  $Q_{sm}^2$  is the normal mode amplitude which is proportional to  $(T_c - T) \mathcal{J}m$  (Cowley 1989). Thus the frequency integrated intensity is proportional to  $T$  below  $T_c$  and should drop ideally abruptly to zero at  $T = T_c$ . All these predictions do not hold true always, yet one can get the critical exponents from temperature dependence of  $\omega_{sm}$  and  $I_{sm}$  near  $T_c$  in a few ideal cases.

##### 4.1 The critical region

It is known that below  $T_c$  two types of phonon density fluctuation dominate and couple with  $\omega_{sm}$  (Coombs and Cowbey 1973; Bruce and Cowley 1980), those leading to a change in: (1) the local temperature,  $T_c$  and (2) the rearrangement of energy between different modes, without change in  $T_c$ . The former types of fluctuations have a thermal diffusion constant  $D_T$  and relaxation time  $\tau(\mathbf{q})$ , related by

$$\tau(\mathbf{q}) = 1/D_T q^2.$$

The latter type of fluctuations have a range of different relaxation times but no strong wavevector ( $\mathbf{q}$ ) dependence. However, these processes make a definite contribution to the quasi-elastic scattering, especially close to  $T_c$  (Lyons and Fleury 1976, 1978).

Higher order perturbation theory explains the phenomena close to  $T_c$  where fluctuation of length scales are predominant during SPT (Bruce 1980) and become much greater than the interatomic spacing, giving rise to many universal properties for all systems having the same symmetry and identical interactions. An example being the universal static behaviour of the order parameter exponent  $\beta$  which has to be for the second order transition of the form:

$$Q_{sm} \sim (T_c - T)^\beta.$$

$\beta$  is expected to be a constant within a given universality class. This mean field (soft mode) theory gives  $\beta = 1/2$ . Experimentally it is observed that  $\beta = 1/3$  for  $\text{BaTiO}_3$  (Muller and Berlinger 1971). Likewise, the susceptibility,  $\chi$ , and the specific heat,  $C$ , are supposed to exhibit behaviour like

$$\chi(T) \sim (T - T_c)^{-\gamma},$$

$$C(T) \sim (T - T_c)^{-\alpha},$$

with the value of  $\gamma \rightarrow 1$  and  $\alpha \rightarrow 0$  for all systems under mean field theory. [Experimentally it is known that  $\gamma$  varies between 1 to 1.4 and  $\alpha$  is known to have small (+) or (-) values depending on the universality class of the system.]

The dependence of integrated Raman intensity with reduced temperature  $t = (T - T_c)/T_c$  and of the width of the band near  $T_c$  have been used to compute the critical exponent  $\beta$  and the activation energy  $U$  (for different orientations) of the system (Sathaiah 1990).

It is to be emphasized that the order parameters  $\langle \eta \rangle$ , which are zero in the disordered (high temperature) phase, acquires a maximum value in the completely ordered state. In general, it is an observable quantitative property representing the macroscopic behaviour.

The order parameter,  $\eta$ , could be simply the difference in densities between two phases (for fluids near critical point). Likewise, the magnetization, the sublattice polarization or the lattice polarization could be the  $\eta$  for ferromagnets, antiferroelectrics, and ferroelectrics, in that order. A complex gap parameter,  $2\Delta/kT_c$  is the  $\eta$  for superconductor and a normal coordinate of soft mode,  $Q_{sm}$ , could be recognized as the  $\eta$  for a crystal near an SPT, and so on and so forth. As has already been mentioned before, critical exponent  $\beta$  for the order parameter,  $\eta$ , in mean field theory, turns out to be 0.5, but on other models it varies between 0.325 and 0.365 (Iqbal and Owens 1984). In the following section we present our results obtained recently on two systems from our laboratory.

#### 4.2 Structural phase transitions in thiocyanates, MNCS ( $M = NH_4, Rb, Cs$ and $Tl$ )

These ionic crystals have univalent cations and rod-shaped anions which are ordered below  $T_c$  and become uncorrelated above  $T_c$ . The Raman line shapes are very sensitive to orientational disorder. The results of investigation in these systems have been published elsewhere partially (Tewari *et al* 1985; Sathaiah *et al* 1989a, b). The CsNCS is shown to undergo a structural phase transition at 470 K from an orthorhombic to cubic phase and has been characterized spectroscopically as an order-disorder transition exhibiting primarily first-order nature (Sathaiah *et al* 1989a). A detailed study of the CN stretching frequency ( $2042 \text{ cm}^{-1}$ ) and the NCS in-plane librational mode around  $125 \text{ cm}^{-1}$  have given a consistent value of the order parameter exponent  $\beta = 0.35 \pm 0.02$ . The exponential enhancement of the halfwidth of the CN stretching mode,  $\gamma_{CN}$ , in the vicinity ( $425 < T < 455 \text{ K}$ ) of  $T_c$  is attributed to the reorientational fluctuations of  $\text{NCS}^-$  ions.

This variation of  $\gamma_{CN}$  can be represented as

$$\gamma_{CN} \propto e^{-U/kT}$$

where  $U$  is the activation energy for the reorientational motion and  $k$  is the boltzmann constant. An activation energy  $U = 0.46 \pm 0.01 \text{ eV}$  has been extracted in this case. Similar studies have been conducted in  $\text{TI-NCS}$  and  $\text{Rb-NCS}$  system (Sathaiah 1990), which also exhibit highly anharmonic, anisotropic and nonlinear character in the vicinity of the structural phase transitions. The constants  $\beta$  and  $U$  for these three thiocyanates are summarized in table 1.

The appearance of side bands in  $\nu_{CN}$  and  $\nu_{CS}$  regions in  $\text{Rb-NCS}$  and  $\text{TI-NCS}$  have been attributed to an internal electric field in their ordered orthorhombic phases (Sathaiah 1990).



**Table 1.** Critical exponent,  $\beta$  and activation energy,  $U$ , deduced from Raman studies in a few systems near structural transition temperature  $T_c$  (Sathaiah 1990).

| System | $T_c(K)$ | $\beta$ | $U(eV)$ |
|--------|----------|---------|---------|
| CsNCS  | 470      | 0.35    | 0.46    |
| RbNCS  | 440      | 0.45    | 0.29    |
| TlNCS  | 367      | 0.45    | 0.32    |

$\beta$  and  $U$  values are accurate within  $\pm 0.04$  and  $\pm 0.02$  eV, respectively

**Table 2.** The critical transition temperatures,  $T_c$ , and relevant computed parameters,  $\beta$  and  $U$ , in a few  $[C_nH_{2n+1}NH_3]_2MCl_4$  systems ( $M = Cd, Zn, Hg$ ) studied recently (Prasad 1990).

| System                 | Transition temp. $T_c(^{\circ}K)$ | $\beta$ | $U(eV)$ |
|------------------------|-----------------------------------|---------|---------|
| $[CH_3NH_3]_2CdCl_4$   | 163                               | 0.26    | 0.37    |
| $[CH_3NH_3]_2ZnCl_4$   | 426                               | 0.28    | 0.09    |
| $[CH_3NH_3]_2HgCl_4$   | 335                               | 0.31    | 0.13    |
| $[C_2H_5NH_3]_2CdCl_4$ | 216                               | 0.26    | 0.06    |
| $[C_3H_7NH_3]_2CdCl_4$ | 158                               | —       | 0.03    |

On keeping a CsNCS crystal near 431 K ( $T_c = 470$  K) and irradiating it with focussed laser light, temporal oscillations have been observed in the collected scattered light. The period doubling effects have been attributed to the successive thermal or photo-induced instabilities as some internal parameter changes with time in a self-controlled manner (Sathaiah *et al* 1989b).

#### 4.3 Structural phase transition in layered compounds

Raman studies have been conducted in  $(C_nH_{2n+1}NH_3)_2MCl_4$  (where  $n = 1$  to 3 and  $M = Hg, Cd$  and  $Zn$ ) recently in our laboratory (Prasad and Bist 1989, 1990; Prasad 1990). Most of these systems are known to undergo several SPT in the 500–577 K range. A synopsis of transitions observed and parameters computed on the basis of vibrational studies is given in table 2. The transitions are primarily due to the reorientational motion of the organic ion. The coupling between the  $MCl_4$  and the organic part is provided by N–H–Cl hydrogen bonding. In table 2, we have summarized the parameters deduced on the basis of vibrational studies for a few of the SPT. The activation energies calculated in different transitions for the reorientational motion of the organic complex ranges between 0.03 and 0.37 eV. Likewise the critical exponents vary in the range 0.26 to 0.31. The details regarding these computations have already been published (Prasad and Bist 1989, 1990).

## Conclusions

Vibrational studies have become very important tools to investigate both static and dynamic characteristics during equilibrium structural phase transitions. These studies also provide interesting information under non-equilibrium conditions, very close to  $T_c$ . Additionally, deep quantitative insight can be obtained regarding the nature and type of such transitions in both organic and inorganic systems.

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