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Order–disorder transition in triethylenediamine: A Raman scattering study

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Abstract

Order–disorder transition in triethylenediamine has been investigated by Raman spectroscopy. Large increase in linewidth accompanied by discontinuous decrease in the mode frequencies are observed across the transition to the disordered cubic phase at 351 K. Except for a few modes, the magnitude of discontinuity in frequency is much less compared to that expected for the given volume change. Most of the doubly degenerate modes show abrupt increase in linewidth at the transition temperature, which is understood to be due to dynamic disorder in the cubic phase.

Keywords: Raman Spectroscopy; Order–disorder transformations; Molecular solids

1. Introduction

Molecular crystals consisting of highly symmetric globular molecules are ideal systems for understanding the packing in crystalline lattice, role of various non-bonded interactions, etc. At ambient conditions, many of these globular molecules are orientationally disordered and transform into an ordered low symmetry phase at lower temperatures. Physics of orientationally disordered crystals continues to be an interesting topic of basic research [1]. Attempts towards rigorous theoretical treatments of the phenomenon for a wide range of compounds have shown that there are a few important aspects, such as the role of translation–rotational coupling, existence of order parameter, symmetry considerations, etc., to be investigated in order to have complete understanding of the mechanism of transition to the ordered phase [1]. It is often observed that the underlying driving mechanism in the apparently similar systems, for example, in the case of C_{60} and C_{70}, is quite different [2]. Similar to these carbon cages, a number of highly symmetric hydrocarbon-based molecular systems like methane [3], adamantane [4], bicyclooctane [5], cyclohexane [6], etc. exhibit order–disorder transitions. Related nitrogen-based systems, like hexamethylenetetramine (HMT) and triethylenediamine (TED), which are isoelectronic to adamantane and bicyclooctane (BCO), respectively, show a different behaviour. The transition temperature T_c increases with increase in nitrogen atoms [7], i.e. of the systems BCO, quinuclidine and TED, BCO has the lowest T_c and TED has the highest, while HMT does not exhibit order–disorder transition up to melting [8]. There has been active research, both experimental as well as computational work, on the phase transition behaviour in molecular systems such as adamantane [9] and TED [7] as well as their derivatives [10,11]. Hydrogen-bonded monosalts of TED are known to exhibit transitions related to proton-disordering and are considered to be ferroelectrics of potential technological importance [12]. Besides basic research interest, charcoal filters impregnated with TED are expected to be useful in nuclear reactors in the event of an accident owing to its ability to efficiently absorb noxious gases from air streams and radioiodine [13].

Triethylenediamine $[N(CH_2CH_2)_3N]$ exists in an ordered hexagonal structure at ambient conditions (space group: $P6_3/m$) with two molecules per unit cell [14]. Above 351 K, it exists in an orientationally disordered cubic phase ($Fm3m$); this transition was found to be associated with a large entropy as well as volume change [15–17]. Reynolds used Ising model to describe the behaviour [17] and reported that the configurational entropy could account for only about 40% of the measured change in entropy. Quasielastic neutron scattering studies [7] revealed that in the disordered phase, the molecules perform reorientational jumps between six equilibrium positions around the C_3 axis together with a tumbling of the molecule from a [111] lattice direction to an equivalent position.

Spectroscopic studies of order–disorder transition provide useful information on the extent of rotational–vibrational coupling, effect of disorder on phonon frequencies, and soft

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mode behaviour (if any) which are useful in modelling the transition [17]. Earlier Raman spectroscopic study by Sauvajol [18] reported the behaviour of external modes in the ordered phase over a temperature range of 110–330 K. In another Raman study, the activation energy associated with the reorientation process was estimated from the line shape analysis of the C–C symmetric stretching mode [19]. In the present work, we report the changes in the Raman spectrum of TED across the order–disorder transition.

2. Experimental details

Raman spectra of unoriented crystal bits of TED are recorded in the temperature range 295–413 K from inside a capillary inserted in a high temperature cell. Temperature is controlled to an accuracy of better than ±1 K using a Eurotherm temperature controller. The 532 nm laser line is used to excite the Raman spectrum and the power on the sample was 15 mW. Scattered light was analysed by a 0.9 m single monochromator [20] coupled with a super-notch filter and detected using a cooled CCD (Andor Technology). Resolution limited linewidth at 550 nm is measured to be about 2 cm^{-1} for an entrance slit opening of 50 μm.

3. Results

At ambient conditions, the site symmetry of the TED molecule is C_{3h}. Assignment of the Raman spectrum of TED in the ordered phase has been carried out by Sauvajol [21]. Owing to the centro-symmetric nature of the crystal, the Raman and the IR bands are mutually exclusive [22]. Raman spectrum of TED at ambient conditions agrees well with that reported earlier [21]. Raman bands arising due to C–H stretching motion appear in the region 2850–3000 cm^{-1}. Most of the other internal modes of the molecule appear in the region 300–1700 cm^{-1}. Three Raman active lattice modes appear at frequencies less than 100 cm^{-1} [18]. In this work, we restrict to the study of internal modes at high temperatures.

All the internal modes of TED were followed as a function of temperature. Figs. 1 and 2 show the evolution of Raman spectra at high temperature. At 351 K, there is an abrupt decrease in the frequencies of many of the internal modes accompanied by significant line broadening. The C–N stretching mode at 972 cm^{-1}, which is of symmetry A_g, shows a discontinuous decrease in frequency (by 7 cm^{-1}) at 351 K. Fig. 3 shows the temperature dependence of the mode frequencies. The mode at 1345 cm^{-1}, identified as due to the CH_2 twist [21], shows largest discontinuity across the transition. The mode at 800 cm^{-1} is not observed in the high temperature phase. Fig. 4 shows the variation of linewidth of some of the Raman bands across the transition. Most of the internal modes exhibit an abrupt increase in linewidth across the transition. It may be mentioned that in the earlier Raman studies also, rapid broadening of A_g and E_{1g} lattice modes was observed prior to the transition [18]. This was attributed largely to the onset of disorder besides the cubic and quartic anharmonicity. In the present work also, large increase in the linewidth is noticed at the transition point. Further rise in temperature from 353 to 413 K (melting point: 433 K) does not produce significant increase in linewidth as compared to that across the transition.

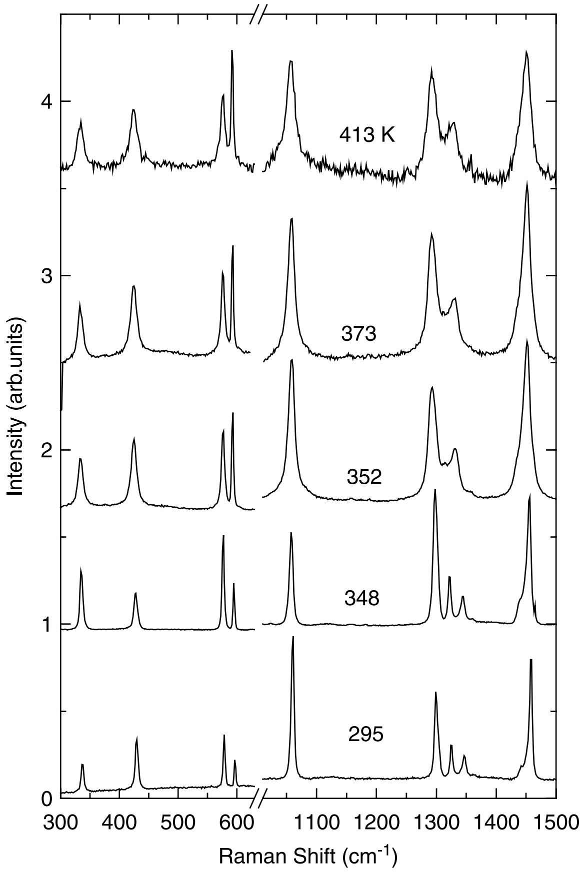

Fig. 1. Raman spectra of some of the internal modes (NC_3 deformation, C–N stretch and CH_2 bending) of TED at various temperatures. Note the discontinuous decrease in mode frequency and increase in linewidth across the order–disorder transition above 351 K.

4. Discussion

4.1. Temperature dependence of mode frequencies

In the absence of any transition, varying the temperature produces a monotonic change in the vibrational spectrum. Across a phase transition, discontinuous changes in mode frequencies are sometimes observed which reflect the nature of changes in intermolecular interaction in different phases. For example, in the case of adamantane, across the order–disorder transition, molecules are oriented in such a way as to reduce certain non-bonded H···H repulsion [23], which is reflected in the phonon spectrum in the ordered phase [24]. Systems wherein the volume change across order–disorder transition is small, such as adamantane, C_{60} [24,25], spectral changes across the order–disorder transitions are mainly due to changes in crystal symmetry.

In the present studies, not many new modes are observed in the ordered phase, except for the mode around 800 cm^{-1}.