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On the Phase Transition in Sym-trioxane†

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Polarized Raman spectra of sym-trioxane single crystals have been recorded in the intra- and inter-molecular regions. Three phonons were observed at room temperature at 59.6, 64.3, and 84.8 cm^{-1}, belonging to E symmetry. Temperature dependent Raman spectra were also recorded which showed the following important features: (a) polarization data could not be obtained below *ca.* 65 K; (b) the phonon at 85 cm^{-1} (300 K) splits into two modes at 63 K and the splitting grows continuously to 1.6 K, the lowest temperature reached in this study; (c) the phonons at 60 and 65 cm^{-1} (300 K) show a constant-slope linear increase in energy from 300 to 65 K at which point the slope changes considerably; and (d) linewidths of these latter two modes evidence discontinuous changes at 63 K. Temperature dependence of the observed $E(T_x, T_y)$ phonon splitting follows approximately an equation of the form $\eta(T)/\eta(1.6\text{ K}) = |(T_c - T)/T_c|^{1/4}$. The phase transition is discussed in terms of various mechanisms and models which could be applicable in the absence of a distinct soft mode feature.

I. INTRODUCTION

Soft mode theory[1] is the prevailing basis for the understanding of phase transitions in solids and temperature dependent light scattering experiments have been preoccupied with finding the "soft mode" in each material investigated. Molecular crystals (non-charged, weakly bound solids) as a rule do not evidence soft mode behavior in light scattering spectra; in fact, we are aware of only one reported soft mode for a molecular solid—tetrachloro-p-benzoquinone.[2] Consequently, these systems present a problem for the accepted soft mode mechanisms of higher order phase transitions in solids. In the present study of sym-trioxane an attempt has been made to characterize the temperature dependence of all intra- and inter-molecular vibrational modes even in the absence of a distinct soft mode feature.

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The non-standard behavior of molecular solids, in general, is of course a major motivation for their study. Additionally, since molecular solids have relatively short range forces compared to ionic crystals it is expected that the critical region may be much more accessible in these systems than in ionic ones. This follows from the inverse relation between the correlation or coherence length and the reduced temperature[3] $\varepsilon = (T_c - T)/T_c$. In other words, departures from infinite range force theories (mean field or Landau theory) may be readily observable in molecular crystals.

Experimentally there are a number of attractive features about these solids: simple crystal structures, ease of crystal growth (large oriented single crystals are obtainable), and known chemical and structural composition. Sym-trioxane, the system of interest for this study, is an exemplary member of this class of solids. It is a cyclic trimer of formaldehyde ($OCH_2 \cdot OCH_2 \cdot OCH_2$) with high molecular ($C_{3v}$) symmetry, high crystal symmetry (R3c with 2 molecules/primitive unit cell at sites of C_3 symmetry), and uniaxial optical properties. Large (2 × 2 × 2 cm) single crystals of trioxane are readily grown and oriented.

A solid–solid phase transition under high pressure has been reported for trioxane by Brasch *et al.*[4] X-ray study of the structure at 103K and one atmosphere did not evidence a phase transition.[5] Thomas,[6] observing the Raman spectrum of sym-*trithiane* at 30K, predicted, based on structural and symmetry analogies, that there will be no change in the structure of sym-trioxane to 30K.

Trioxane has previously been used as a host material to study properties of sym-triazine in what was hoped to be a high symmetry environment.[7] It was found, however, that optical and Stark data were identical to those for isotopic mixed crystals of triazine itself. On the basis of these observations, it was predicted that, similar to triazine, trioxane would also undergo a low temperature phase transition ($100K \leqslant T_c \leqslant 4K$).

In this work polarized Raman spectra are reported for oriented single crystals of sym-trioxane. Careful room temperature data were collected in order to resolve the ambiguity in assignment of phonons. Temperature dependent polarized spectra were obtained from 300 to 1.6K in an attempt to locate the phase transitions ($T_c \sim 63K$, *vide infra*), search for soft mode behavior, and evaluate any cooperative or critical behavior in terms of existing theories. Evidence for the phase transition at $T_c \sim 63K$ is found in polarization data, temperature dependent frequency shifts and linewidth of phonons, and a splitting of a degenerate phonon that grows to a maximum value at 1.6K. In Section III these data are presented and discussed and in Section IV an attempt is made to understand the phase transition itself in terms of current theoretical expectations.

II. EXPERIMENTAL

Trioxane purchased from Aldrich Chemical Co. was heated with $LiAlH_4$ in an atmosphere of helium to remove H_2O and H_2CO.[7,8] Purified trioxane, free from higher polymers, was sublimed into crystal growing tubes and large single crystals were grown from the vapor. Trioxane forms a uniaxial room temperature crystal which is readily oriented along the optic axis (z) by optical conoscopic techniques. Throughout this process care was taken to shield samples from direct irradiation by fluorescent lights as they tend to cause photodecomposition of trioxane to H_2CO with subsequent polymerization to polyoxymethylene.

The Raman apparatus consisted of an argon ion laser, an $f/5.8$ $\frac{1}{2}$ meter double monochromator with two 1800 groove/mm holographic gratings. A cooled photomultiplier tube (RCA C31034A-02) operated in a photon counting mode was used for detection. Calibration was achieved by recording Fe–Ne hollow cathode emission lines over the entire spectral region studied.

The crystal was mounted on a sample header and suspended in a Janis variable temperature dewar. Temperature was controlled (to roughly ± 0.1K) by helium gas flow, a heater, and pumping rate over the sample chamber. Sample temperature was measured with a calibrated diode (DT-500K, Lake Shore Cryotronics, Inc.) mounted in the metal block holding the sample. The sample mounting header has both rotational and translational sample positioning adjustments while the system is cold.

During the experiments, it was observed that after long exposure to focused laser radiation (5145 Å) trioxane shows some signs of polymerization. Low frequency Raman lines were observed (11, 14, 17 cm^{-1}) which we attribute to polymer chain motion. Accordingly, a new sample was used each time an experiment was run.

III. RESULTS AND GENERAL DISCUSSION

The molecular symmetry of trioxane is C_{3v} and it crystallizes[5] in the trigonal system C_{3v}^6 (R3c) with two molecules per primitive unit cell. Each molecule lies on a three-fold rotation axis (z or c axis) and repeats itself after rotation of 48° 35′ and translation of $\pm\frac{1}{2}c$ along the rotation axis. This structure seems to hold to 103K according to available X-ray data.

Results of our Raman scattering studies can be classified into three basic categories: assignment of phonon region; exciton splitting as a function of temperature in the intramolecular (high frequency) region; and temperature dependent phonon spectra. Each area will be treated separately below and

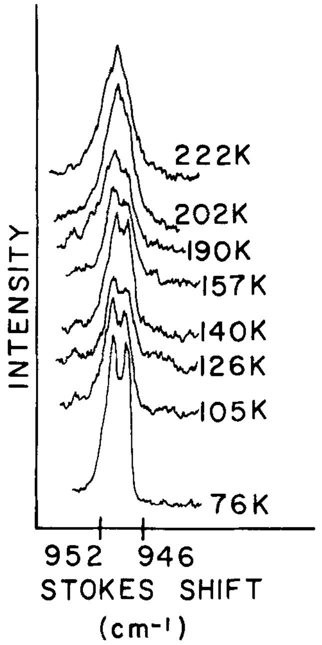

FIGURE 2 Temperature dependent Raman spectra for the mode at 952 cm^{-1} in sym-trioxane. The spectra show a discontinuous splitting of ~2 cm^{-1} at 190 K. This splitting does not evidence any phase transition, since the X-ray study of sym-trioxane at 103 K did not show any change in the crystal structure.

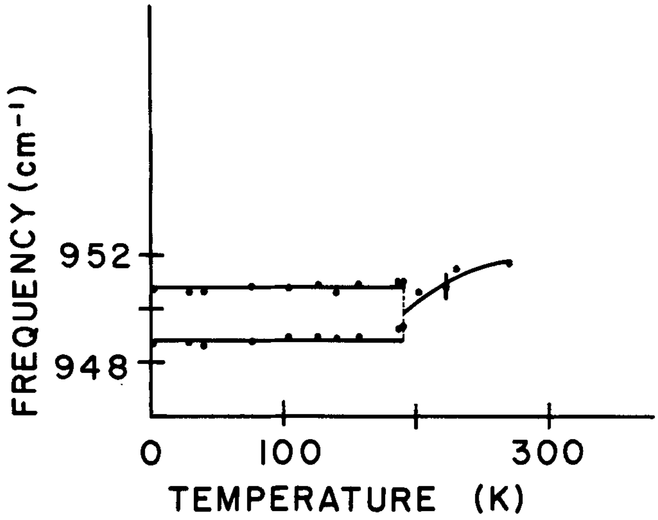

FIGURE 3 Frequency shift (cm^{-1}) vs. temperature (K) for the split mode at 952 cm^{-1} in sym-trioxane. The vertical line at the full circle shows the average error in the observed data.

to any phase dynamics in the crystal. The rather unexpected decrease in frequency with decreasing temperature is most likely associated with resonance interactions among neighboring intramolecular modes. The splitting is undoubtedly caused by exciton interactions and can be seen to be encompassed in the high temperature linewidth. It is worthwhile pointing out that all splittings and shifts observed as a function of temperature are not necessarily associated with phase dynamic behavior.

c. Phonons

The phonon region evidences four important temperature dependent effects in trioxane. First, at *ca.* 65K and below it is no longer possible to obtain polarized Raman spectra. Second, the mode at 85 cm^{-1} (E, T_x, T_y) splits into two peaks at 63K and the splitting grows continuously to 1.6K (the lowest temperature attainable in these studies). Third, all phonons increase in frequency in a linear fashion as temperature decreases but at *ca.* 65K there is a change in the slope of the frequency–temperature dependence, even for the $E(T_x, T_y)$ mode. Fourth, linewidths of the two phonons that do not split change abruptly at 63K. We believe these four factors are ample evidence for a phase transition occurring at roughly 63K in sym-trioxane, especially when taken with our previous prediction of a phase transition between 100 and 1.6K.[7]

Figure 4 presents Raman spectra of the phonon (E, T_x, T_y) in the 85 cm^{-1} region as a function of temperature. The splitting of this weak feature is relatively obvious beginning at roughly 63K. Temperature dependence of the splitting is plotted in Figure 5. In addition, the general, roughly linear, increase in the phonon frequency can also be clearly perceived. No such splittings are observed for the other two E symmetry (R_x, R_y) librational modes at 65 and 60 cm^{-1}.

While the modes at 60 and 65 cm^{-1} do not split they do show a rather pronounced and interesting temperature dependence. Both modes increase linearly with temperature up to *ca.* 65K and then show little or no temperature dependent behavior from 65 to 1.6K. Linear increase in phonon frequency with decreasing temperature is to be expected, in general, and can be attributed to normal lattice dynamics for systems without phase transitions.[11] However, the abrupt change in slope at 65K is clearly associated with the change in lattice dynamics for the new phase. These data are plotted in Figure 6.

As can be seen in Figure 1, the linewidth of these two librational phonons is also temperature dependent. Figure 7 plots the full width at half maximum (FWHM) intensity for the modes in question and again a discontinuity can be seen at the transition temperature of 63K.

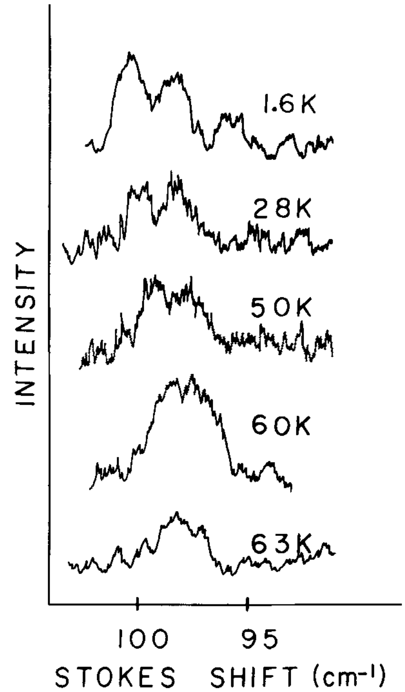

FIGURE 4 Raman spectra of the phonon at 84.8 cm^{-1} as a function of temperature in sym-trioxane. This phonon splits at about 63 K and the splitting magnitude grows continuously as the temperature is decreased. This behavior shows evidence for a second order phase transition.

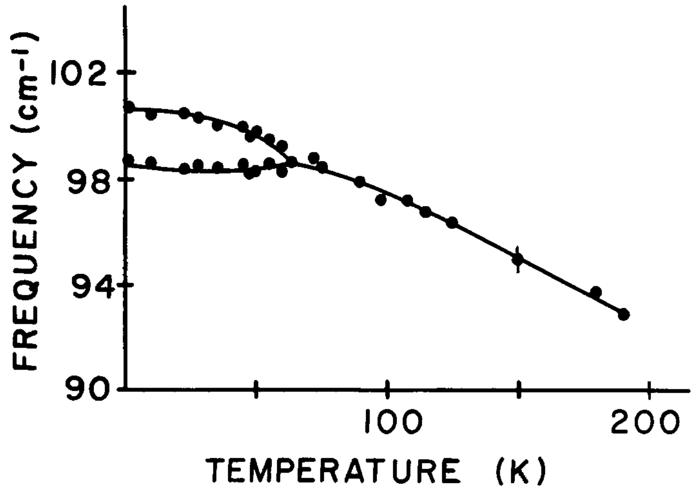

FIGURE 5 Temperature dependence of the $E(T_x, T_y)$ phonon (at 84.8 cm^{-1}) below and above transition temperature T_c = 63 K. The vertical line at the full circle shows the average error.

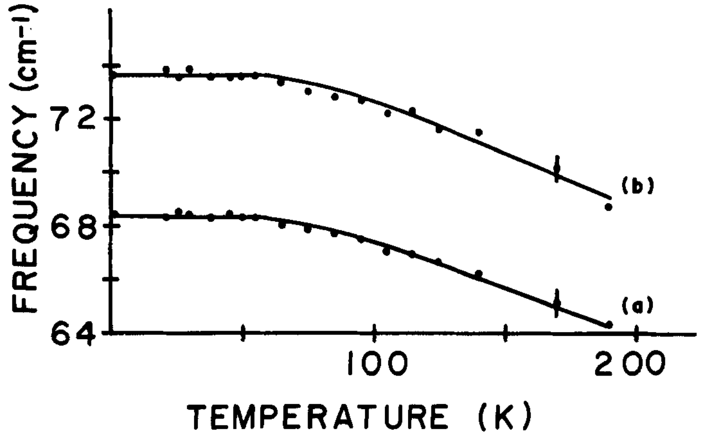

FIGURE 6 Frequency shift (cm^{-1}) vs. temperature (K) for the phonons at (a) 59.6 and (b) 64.3 cm^{-1} (room temperature) respectively below and above $T_c = 63$ K. Vertical line at the full circle shows the average error in the observed data.

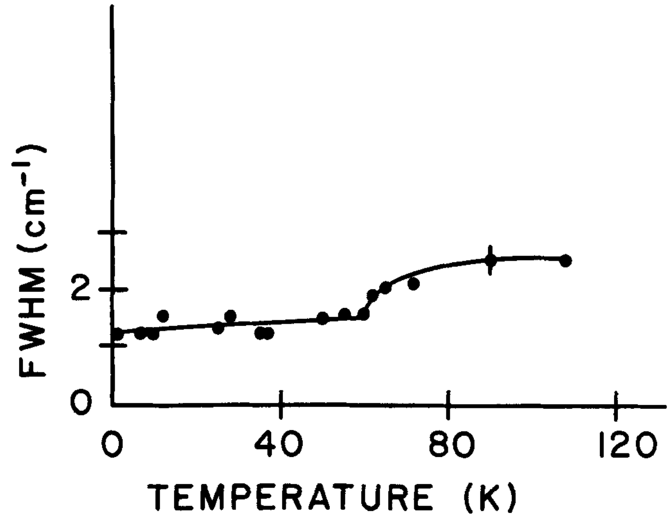

FIGURE 7 Behavior of FWHM (Full Width Half Maximum) in cm^{-1} as a function of temperature (K) for the phonon at 59.6 cm^{-1}. The other phonon at 64.3 cm^{-1} also shows the same behavior in terms of FWHM vs. temperature. The vertical line at the full circle illustrates the average error.

the next section will deal with the phase transition as evidenced by temperature dependent phonon spectra.

a. Assignment of phonons

According to a factor group analysis, there are eight lattice modes in sym-trioxane: $2A_1 + 2A_2 + 4E$. Six of these modes are optic phonons ($1A_1 + 2A_2 + 3E$) and two are acoustic ($A_1 + E$). Four of the optic modes are Raman active: A_1 (*aa* + *bb*, *cc*) + $3E$ (*aa* − *bb*, *ac*, *ab*, *bc*) in which the letters in parenthesis represent non-zero elements of the polarizability tensor for the particular Raman active irreducible representation.

Recently Kobayashi[9] and Thomas[6] independently tried to assign the phonons in trioxane employing polarized Raman spectroscopy. However,

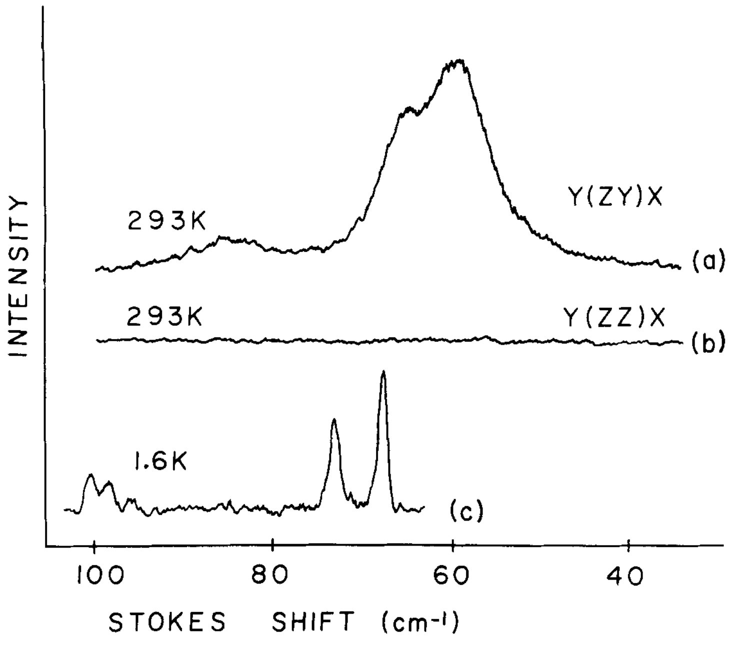

FIGURE 1 Raman spectra of sym-trioxane single crystals in the phonon region: (a) and (b) show polarized spectra at 293 K with *y*(*zy*)*x* and *y*(*zz*)*x* orientations respectively, and (c) shows unpolarized spectrum at 1.6 K. *y*(*zy*)*x*: the symbols inside the parentheses are, left to right, the polarization of the incident and of the scattered light, while the ones to the left and right of the parentheses are propagation directions of the incident and of the scattered light, respectively. These spectra were recorded under the following conditions: slit width 35 microns, full scale of 100 counts/sec., time constant 10 sec., scan rate 1 Å/min., excitation 5145 Å, and power of 150 mw.

Kobayashi could observe only two distinct Raman active modes of E symmetry at 62 and 85 cm^{-1}. Due to polarization leakage and/or crystal imperfection scattering he assigned another phonon of A_1 symmetry at 62 cm^{-1}. Thomas found three phonons of E symmetry at 59, 64, and 85 cm^{-1}. We have attempted to resolve this problem by taking careful polarization measurements at high resolution.

Based on the above discussion of Raman active phonons in trioxane an unambiguous assignment of these modes can be made by investigating two polarizability components, α_{zz} and α_{zy} (i.e., α_{cc} and α_{cb}). The α_{zz} component will excite A_1 modes and the α_{zy} component will excite E modes. By comparing polarized Raman spectra of oriented single crystals in $y(zy)x$ and $y(zz)x$ polarization geometries in Figures 1a and 1b respectively, it is evident that there are three frequencies which appear in the E mode $y(zy)x$ orientation at 59.6, 64.3, and 84.8 cm^{-1}. No A_1 mode intensity can be found in the spectrum from 10–150 cm^{-1}. The average background over this spectral range was about 10–15 counts/sec. in both polarizations (other specific experimental conditions are stated in the figure caption). These modes are more obvious in the 1.6K spectra of Figure 1c.

b. Internal modes

Temperature dependent Raman spectra of single crystals were recorded from 295 to 1.6K in the intramolecular region ($\sim$200–3000 cm^{-1}). Polarization measurements on oriented single crystals are possible over the range 295 to 65K. However, polarization measurements were not possible below 65K even though crystals remained of high optical quality to 1.6K. This lack of polarization is associated with the phase transition and is most likely caused by formation of microcrystalline domains and internal fractures in the samples.

In the intramolecular region of the Raman spectrum there is one feature, at 952 cm^{-1} (300K), that shows an apparently discontinuous splitting with decreasing temperature. Onset of this splitting is at 190K and its magnitude (2 cm^{-1}) is temperature independent below this temperature. This mode has been assigned[9,10] to a difference band [ν_s(COC) − δ(OCO)] but since the feature is observed at 1.6K it must be associated with either a fundamental or combination.

Figure 2 shows the temperature dependent Raman spectra in the 950 region and Figure 3 gives a graphical presentation of temperature dependent line positions and splittings of this feature. In addition to the splitting, these figures indicate that the 950 cm^{-1} feature decreases in energy roughly 2 cm^{-1} upon cooling from 295 to 190K. Clearly these observations are not related

IV. THE PHASE TRANSITION—DISCUSSION AND SPECULATION

In view of the discussion of the last section we can state with some confidence that sym-trioxane undergoes a phase transition at 63K. This transition is probably a higher order or continuous phase transition. The latter conclusion is based on the temperature dependence of the splitting of the 85 cm^{-1} phonon in the low temperature phase as will be discussed in some detail below.

The fundamental treatment of phase transitions must be based on thermodynamics, in particular the functional dependence of the free energy on its variables. Transition orders are classified by discontinuities in derivative orders of the free energy (i.e., G, the Gibbs free energy). The connection with spectroscopy is made through a model relating G, say, to the intermolecular potential energy. For a second order transition the free energy can be expanded, in the vicinity of the transition, in a power series in the parameter that determines how the two phases differ from one another. This parameter

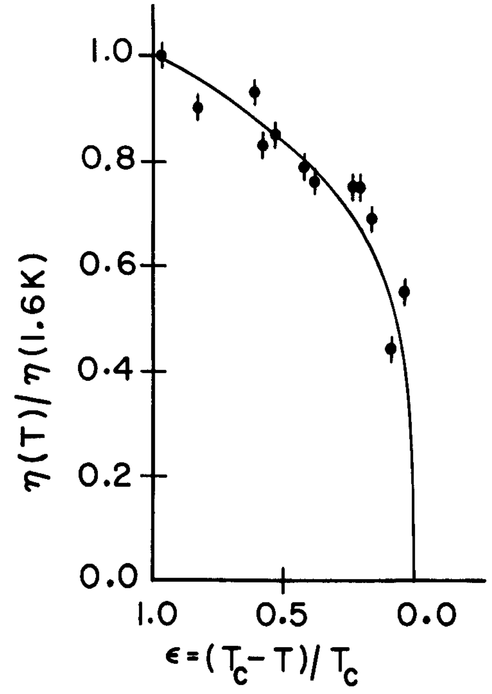

FIGURE 8 Normalized splitting for the phonon at 84.8 cm^{-1} in sym-trioxane is plotted as a function of reduced temperature. The full circles illustrate the observed data and the vertical line at the full circle indicates the average error. The continuous plot is the function $y = (x)^{1/4}$. This plot is discussed more fully in Section IV of the text. The lowest value of $\eta(T)/\eta(1.6\ \mathrm{K})$ that is experimentally accessible is roughly 0.3.

is called the order parameter and can be, for example, electric polarization, magnetization, or a molecular displacement coordinate such as a normal mode. By further assuming temperature dependences for the coefficients in this expansion of the form $[(T_c - T)/T_c]^{\zeta}$, this procedure generates temperature dependences for the order parameter ϕ, generalized suspectibilities χ, and the observed spectroscopic frequency associated with the normal coordinate order parameter. The procedure is well known and discussed in a number of different references.[3,12]

These ideas lead to the concept of a soft mode, whose normal coordinate is the order parameter and whose frequency goes to zero at the phase transition point. As emphasized in the introduction, soft modes, which seem abundant in ionic solids, are apparently the rare exception in molecular solids. Indeed, they are neither observed for trioxane nor sym-triazine.[13,14] Soft mode theory has so dominated the discussion of phase transitions in solids that it becomes difficult to discuss phase behavior in their absence. It thus remains the task of the experimentalist to discover other spectroscopic manifestations of phase transitions and critical phenomena.

In practical terms any physical observable which varies with temperature in the above prescribed fashion ($|T_c - T)/T_c|^{\zeta}$) having the property of being zero in the high symmetry phase and non-zero in the low symmetry phase, can be considered to be an *experimental or effective order parameter*. It is, of course, the hope that this effective order parameter is actually related in a fundamental way to the theoretical order parameter used in the expansion of the free energy in the vicinity of the transition point.

In mean field or Landau theory[12] both the frequency and the order parameter have the same temperature dependence through the relations

$$\chi \alpha \frac{1}{\omega^2}, \quad \chi \alpha \left|\frac{T_c - T}{T_c}\right|^{-1} \quad \text{and} \quad \phi \alpha \left|\frac{T_c - T}{T_c}\right|^{1/2}$$

For an effective order parameter to evidence mean field behavior some property (e.g., a splitting) should depend on reduced temperature, say, as

$$\eta(T) = \eta(0)\left|\frac{T_c - T}{T_c}\right|^{1/2}$$

If the effective spectroscopic parameter is indeed related to the true order parameter (or an unobserved soft mode frequency) and its temperature exponent is not equal to $\frac{1}{2}$ this would be considered to be a deviation from mean field (infinite interaction range) theory.

In the present study, splitting of the phonon at 85 cm^{-1} $E(T_x, T_y)$ at 63K reflects the extent of the phase transition and the normalized splitting ratio $\eta(T)/\eta(1.6\text{K})$ may be considered an effective order parameter. Figure 8 shows the plot of $\eta(T)/\eta(1.6\text{K})$ as a function of reduced temperature $\varepsilon = (T_c - T)/T_c$.

The continuous curve in the figure illustrates the behavior of $y = x^{1/4}$. No attempt has been made to make an exact graphical fit to these data because it is not altogether clear how this dependence relates to theory. It can be seen, however, that the observed data do indeed lie close to the line $y = x^{1/4}$. Within the limitations of the above remarks concerning effective order parameters, Figure 8 indicates that a mean field theory does not describe the phase transition in sym-trioxane. Similar behavior (in the intramolecular region) has been observed by us[14] and others[13] for sym-triazine, which has a similar crystal structure and molecular orientation.[14]

It may well be possible to construct a detailed microscopic model for a transition mechanism in this system. One such relatively obvious example, considering that a translational (T_x, T_y), degenerate E phonon is the only one that splits, would be that trioxane molecules move off the threefold (c) axis perhaps towards one another. Of course, this motion could take place in three possible equivalent directions about the *c*-axis, leading to domains and/or microcrystalline structure. While this picture seems consistent with our data, it is by no means unique or experimentally demonstrated.

Finally, it is probably worthwhile to speculate about the absence of soft modes in sym-trioxane and other (triazine, etc.) molecular solids. We have considered four possible alternatives to classical soft modes ($\omega \rightarrow 0$ and $T \rightarrow T_c$ in less symmetric phase) in molecular crystals and these are individually discussed below.

1) Relaxation modes—These are low frequency modes centered about zero energy, typically associated with an order–disorder or double well potential transition mechanism.[1,12] The zero frequency response is associated with a slow, large amplitude tunneling motion. Such motion is certainly possible in many molecular systems but it is unlikely that all molecular solids have these properties.

2) $k \neq 0$ Soft Mode—Since little neutron scattering has been done on molecular crystals undergoing phase transitions, it is possible that of those systems carefully studied by light scattering almost all have anomalies in their phonon spectra at $k \neq 0$. However, simple soft mode considerations predict that at least one component of this motion should be totally symmetric in the low symmetry phase and thus in principle observable by Raman techniques.

3) Anharmonic Mode Coupling—For this mechanism there may well be a soft mode initially that begins to condense but through anharmonic mixing with other modes of the crystal, anti-crossing interactions prevent this motion from becoming completely soft. There is actually some physical appeal to this mechanism because the complex local motions often suggested for a phase transformation can only be composed of linear combinations of many normal coordinates.

4) Acoustic Soft Modes—It is possible that the majority of molecular solids undergoing phase transitions evidence anomalies in their low frequency acoustic spectra. Almost no studies of this spectral region have been made, particularly as a function of temperature. The anomalies could arise through interaction with optical modes or by direct instability of one of the elastic parameters. It is difficult to evaluate this mechanism until further studies are made.

Of the four suggestions for phase transition dynamics, relaxation modes, mode coupling, and acoustic soft modes seem the most generally applicable. Each of course could apply to different situations and individual solids so that no particular generalization need be appropriate to all molecular solids. It is, however, clear that the low frequency portion of the molecular solids spectral response is important for all of these mechanisms. Brillouin scattering should therefore be an important tool in the study of these phase transitions and we are presently engaged in obtaining Brillouin spectra of a number of different molecular solids near their phase transition temperatures.

V. CONCLUSIONS

A phase transition is observed in sym-trioxane at $T_c = 63$K based on temperature dependent splittings, shifts, and linewidths in the phonon spectrum. Moreover, it is not possible to obtain polarization data for any region in the spectrum of sym-trioxane at temperatures below 65K. The temperature dependent splitting of a phonon at 85 cm^{-1} (300K) indicates that the transition is of a higher order or continuous nature. It is suggested that, in the absence of a genuine soft mode, the phonon splitting could serve as an "effective" or "experimental" order parameter. As such it is found that the normalized splitting depends on reduced temperature with an exponent of $\sim\frac{1}{4}$ and thus does not apparently obey mean field theory. Finally, it is pointed out that random temperature dependent splittings in the intramolecular exciton spectra need not be related to any phase dynamics.

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