STRUCTURAL TRANSITION AND ELASTIC ANOMALIES IN s-TRIAZINE, $C_3N_3H_3$

J.C. RAICH, E.R. BERNSTEIN and A. YOSHIHARA
Departments of Physics and Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

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Dynamical behavior of the coupled system of molecular orientations and acoustic phonons is investigated in order to provide a description of the structural phase transition in s-triazine, s-triazine molecular reorientations are in the fast relaxation limit. A softening of the acoustic phonon frequencies is found as $T \to T_c$.

s-triazine ($C_3N_3H_3$) is a molecular crystal which has been studied extensively over the past few years using various experimental and theoretical techniques [1–8]. The crystal exhibits a temperature- and pressure-induced structural phase transformation. The high-temperature (low-pressure) averaged structure is D^6_{3d} ($R\bar{3}c$), the low-temperature (high-pressure) one C^6_{2h} (C2/c). A Landau mean-field description of the phase transition has appeared [8]. This latter paper summarizes recent theoretical and experimental results on s-triazine.

The mean-field treatment indicates some "order–disorder" aspects in addition to the mainly "displacive" character of the transition [9–11]. For s-triazine the disorder in the alignment of the three-fold axis of the molecule relative to the crystal c axis is limited to a few degrees of solid angle in the high-temperature phase [8]. Thus, there is justification in assuming that molecular orientations and center-of-mass positions can be described in terms of small displacements of the molecules from their high-temperature equilibrium values. A description of elastic and orientational excitations in terms of acoustic and librational phonons should be both useful and informative. This is to be contrasted with the plastic phases of $NaNO_2$, NH_4Cl or KCN. In these latter crystals, reorientations of the NO_2^-, NH_4^+ or CN^- molecular ions involve large angular displacements. Typically, molecular reorientations are not well described in terms of small displacements about equilibrium orientations. Structural transformations for such "order–disorder" type materials have been most successfully described in terms of pseudospin–phonon coupled systems [9,12–15].

The interaction hamiltonian for a coupled phonon–libron system is written in the form:

$$H = \frac{1}{2}\sum_{k}\sum_{j=1}^{5}\left[P(kj)P^*(kj) + \omega_j^2(k)Q(kj)Q^*(kj)\right] + \sum_{k}\sum_{j=1}^{7}\sum_{j'=1}^{7} g(kjj')Q(kj)Q^*(kj') \,. \tag{1}$$

Here k indicates the wave vector and j the polarization index. Our notation is $j = 1, 2$ for the transverse acoustic (TA) phonons and $j = 3$ for the longitudinal acoustic (LA) phonons. The high-frequency optical phonons are neglected except for the librational excitations represented by angular displacements of the molecules about x and y rotation axes, R_x and R_y. The librations are labeled with $j = 4, 5$. The indices $j = 6, 7$ label the Fourier transforms of the higher-order terms R_xR_y and $\frac{1}{2}(R_x^2 - R_y^2)$, respectively. Following the mean-field treatment [8], all higher-order coupling terms are neglected. Calculation of TA and LA phonon frequencies $\omega_j(k)$, $j = 1, 2, 3$, is outlined in ref. [8]. There the librational frequencies $\omega_j(k)$, $j = 4, 5$ are also given under the assumption that they can be treated as Einstein modes at zero temperature and are therefore independent of k. Some of the coupling parameters $g(kjj')$ have also been treated as independent of k. In terms of the Landau theory phenomenological parameters [8]:

$$\omega_4^2 = \omega_5^2 = 2\mathcal{B}a/\hbar^2, \quad g(46) = g(57) = -\tfrac{2}{3}b, \quad g(66) = g(77) = c\,. \tag{2}$$

Here $\mathcal{B} = \hbar^2/2I = 0.215\ \mathrm{cm}^{-1}$, with $I = I_x = I_y$, the molecular moment of inertia, and the coefficients a, b, and c are defined in ref. [8].

Following the treatment of the dynamics of the Jahn–Teller transition [15], one can relate the remainder of the non-vanishing coefficients $g(kjj')$ to those of the Landau free energy expansion [8]. These coupling coefficients are most conveniently expressed in matrix form [13]

$$g(kjj') = \sum_{\alpha=1}^{3} e_\alpha(kj) g_{\alpha j'}(k)\,, \tag{3}$$

where the $e_\alpha(kj)$ are the phonon polarization vectors components for $j = 1, 2, 3$. In eq. (3) $j' = 4, 5, 6, 7$ and

$$g_{\alpha j'}(k) = \mathrm{i}\begin{bmatrix} Bk_y/(mI)^{1/2} & (Bk_x - Ak_z)/(mI)^{1/2} & Dk_y/m^{1/2} & (Dk_x - Ck_z)/m^{1/2} \\ (Bk_x + Ak_z)/(mI)^{1/2} & -Bk_y/(mI)^{1/2} & (Dk_x + Ck_z)/m^{1/2} & -Dk_y/m^{1/2} \\ Ak_y/(mI)^{1/2} & -Ak_x/(mI)^{1/2} & Ck_y/m^{1/2} & -Ck_x/m^{1/2} \end{bmatrix}, \tag{4}$$

with the coefficients A, B, C, D defined in ref. [8].

For $k = [k_x 00]$, eigenvectors for the phonon modes are found by diagonalizing the 3×3 acoustic dynamical matrix [8]. Polarization vectors have the form $\hat{e}(k_{x^+}) = ((1-\xi^2)^{1/2}, 0, -\xi)$ and $\hat{e}(k_{x^-}) = (\xi, 0, (1-\xi^2)^{1/2})$ the value of the parameter ξ depends on the elastic constants $\frac{1}{2}(c_{11} - c_{12})$, c_{14} and c_{44}, as well as the LA and TA phonon frequencies $\omega_+(k_x)$ and $\omega_-(k_x)$. If coupling between molecular orientations and strains e_6 and $e_1 - e_2$ can be neglected [8], $B = D = 0$ in the mean-field expansion. Assuming that the TA (–) mode is approximately polarized along the C_h direction [7], one can set $\xi = 0$. The above description thereby reduces to one involving coupled modes, the TA (–) acoustic phonon and the orientational coordinates R_y and $\frac{1}{2}(R_x^2 - R_y^2)$. Which of the corresponding coupling coefficients is actually dominant is not apparent. The quadratic orientational coordinates have the same role as the pseudospin or "spin" coordinates in other systems [13–15].

The above description of s-triazine is different from previous treatments of the dynamical coupling between translational and rotational modes [12–14]. These have generally assumed a disordered high-temperature phase and have neglected the rotational kinetic energy contribution to the hamiltonian (1). Because of the well-defined librations [16] in the high-temperature phase of s-triazine, the formulation (1) is thought to be preferable to that of the usual pseudospin coupled systems.

The hamiltonian (1) has been written with the high-temperature phase as reference configuration. Molecular orientations in the low-temperature phase are described by the non-vanishing of some of the thermal expectation values of the operators R_x, R_y, R_xR_y, and $\frac{1}{2}(R_x^2 - R_y^2)$. The discussion here is limited to the high-temperature phase for which all these expectation values vanish. The dynamic behavior of the coupled system can be determined from the linearized equations of motion in the standard fashion [13,15,17].

To compare the predictions of the present theory with recent inelastic neutron scattering measurements for the phonon branch $[k_x 00]_{TA}$ polarized along [001], a calculation of correlation functions for phonon and orientational coordinates is required. The method of Green's functions is chosen as the most convenient; in particular, we follow the approach and notation of ref. [17]. The equation of motion for the Green's functions has the form

$$\omega\langle\langle Q^*(kj)|P(k'j')\rangle\rangle = \hbar^{-1}\langle[Q^*(kj), P(k'j')]\rangle - \mathrm{i}\langle\langle Q^*(kj)|\mathrm{d}P(k'j')/\mathrm{d}t\rangle\rangle\,. \tag{5}$$

Eq. (5) may be employed to develop a chain of equations for the various Green's functions:

$$G_{j2} = \langle\langle Q^*(k1)|P(kj')\rangle\rangle, \quad (j, j') = (1, 1), (3, 5)\,,$$

$$G_{j2} = \langle\langle Q^*(k1)|Q(kj')\rangle\rangle, \quad (j, j') = (2, 1), (4, 5), (5, 7)\,,$$

which are linearized in the usual fashion. The chain of equations is terminated with the one for G_{52}, into which a damping term is introduced:

$$\omega G_{52} = i\gamma[2g(k77)G_{52} + g(k17)G_{22} + 3g(k57)G_{42}] \ , \tag{6}$$

where γ describes a temperature-independent relaxation of the orientational coordinate $\frac{1}{2}(R_x^2 - R_y^2)$, and is introduced in the spirit of the pseudospin–phonon treatments of coupled systems, as can be found in ref. [14]. Assumption (6) is consistent with previous treatments [12] that have assumed that the phonon–phonon damping is negligible compared to the damping due to phonon–reorientation coupling.

These assumptions lead to

$$\sum_l D_{il} G_{l2} = -\delta_{i2}, \quad i, l = 1, ..., 5 \ , \tag{7}$$

where

$$\mathbf{D} = \begin{bmatrix} 0 & i\omega & 0 & 0 & 0 \\ -i\omega & \omega_-^2 & 0 & g^*(15) & g^*(17) \\ 0 & 0 & 1 & i\omega & 0 \\ 0 & g(15) & -i\omega & \omega_R^2 & 3g(57) \\ 0 & g(17) & 0 & 3g(57) & 2g(77) - i\omega/\gamma \end{bmatrix} . \tag{8}$$

Here $\omega_R^2 = 2\mathcal{B}a/\hbar^2 + (c/I)\langle R_x^2 + R_y^2\rangle$. Similar relationships are obtained for $G_{lj}, j \neq 2$. The correlation functions are determined from eq. (7). For example, the phonon–phonon correlation function in the high-temperature limit, $k_B T \gg \hbar\omega$, is given by

$$\phi_{22} = (2k_B T/\omega)\,\mathrm{Im}(D^{-1})_{22} \ . \tag{9}$$

An examination of eqs. (8) and (9) shows that the above method of calculating ϕ_{22} gives the same results as Onsager's phenomenological equations of motion [14].

The mean-field parameters a, b, c, A and C, as introduced above, can be determined approximately from a fit of the limited Raman data on the librational modes of the low- and high-temperature phases [1], and the observed molecular orientation angle and lattice strain [3–5]. Thermal expansion is taken into account. We follow the mean-field treatment [8] by assuming that the entire temperature dependence of the orientational potential can be accounted for with the temperature dependence of the quadratic coefficient a, i.e. $a = a_0(T - T_0)$. The results are: $a_0 = 12.9\ \mathrm{cm^{-1}/K}$, $b = -3.11 \times 10^3\ \mathrm{cm^{-1}}$, $c = 3.53 \times 10^4\ \mathrm{cm^{-1}}$, $A = 1.28 \times 10^4\ \mathrm{cm^{-1}}$, $C = -1.82 \times 10^4\ \mathrm{cm^{-1}}$, and $T_0 = -759$ K. In determining these phenomenological parameters, we have arbitrarily assumed that $\omega_x > \omega_y$ for the librational frequencies in the low-temperature phase. The effective elastic constant for the TA mode propagating along $[k_x 00]$ and polarized along [001], defined by $c_- \equiv \rho\omega_-^2/k_x^2$, has the value $2.30 \times 10^{10}\ \mathrm{dyn/cm^2}$.

The orientational potential predicted for s-triazine on the basis of this fit is a single anharmonic well centered at $R_x = R_y = 0$, rather than three distinct wells oriented about the three-fold crystal axis. Thus, instead of tunnel splittings of librational ground states, one observes in the high-temperature phase a doubly degenerate librational excited state and a single ground state [18]. The present model is thereby a modification of the usual pseudospin system for which tunneling modes are appropriate.

In the long-wavelength limit the translation–translation correlation response ϕ_{22} dominates the inelastic neutron cross section [13]. The phonon–phonon correlation function calculated using eq. (9), with the values $\hbar\omega = 9.3\ \mathrm{cm^{-1}}$ and $\gamma/\hbar = 3.1 \times 10^{-4}\ (\mathrm{cm^{-1}})^{-1}$, are shown in fig. 1 for the same range of temperatures as the transverse acoustic phonon groups of ref. [7]. Good agreement in the relative intensities and the temperature dependence of the peak frequencies is found except for the case $T = 205$ K. This represents the measurement closest to the transition temperature, $T_c = 198$ K.

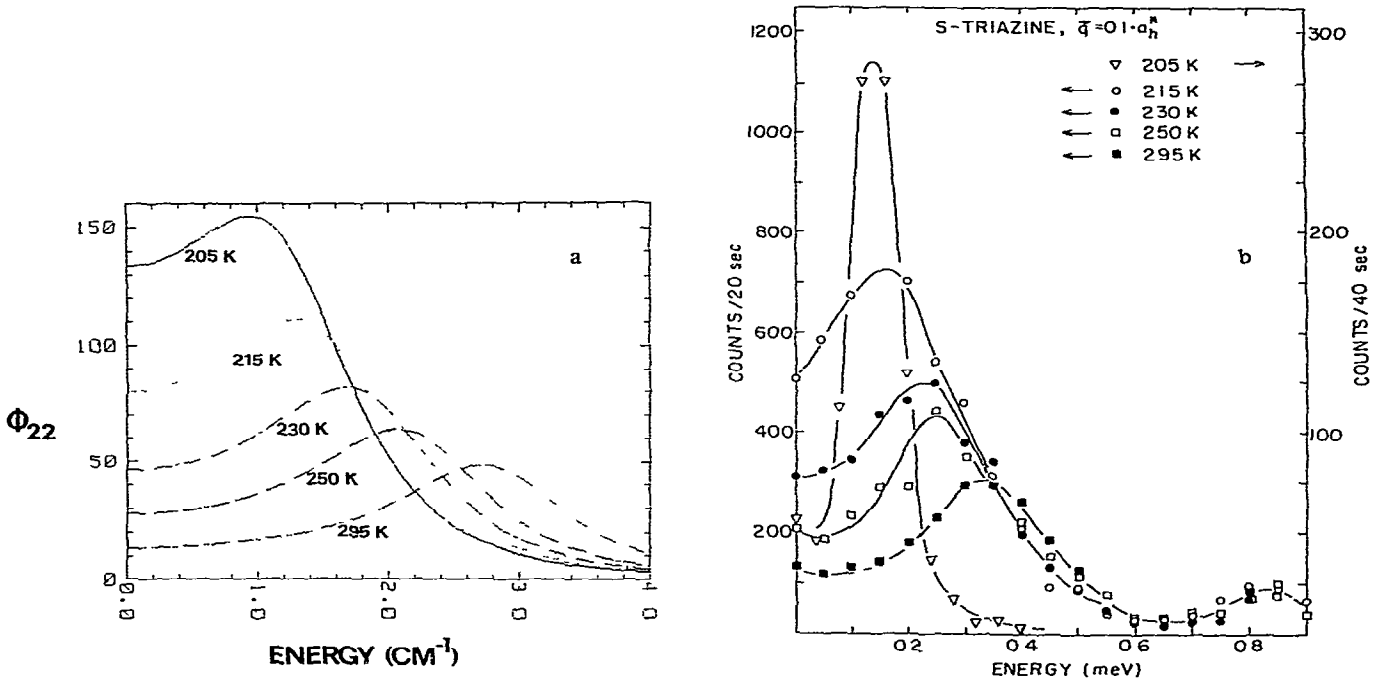

Fig. 1. (a) Calculated spectra of the phonon–phonon correlation functions for $\hbar\omega_- = 9.3$ cm^{-1} and $\gamma/\hbar = 3.1 \times 10$ (cm^{-1})$^{-1}$ for transverse acoustic phonons with k along [100], polarized essentially along C_h. (b) Phonon groups for transverse acoustic modes in s-triazine for the $[\xi 00]_{TA}$ mode, polarized along C_h, at temperatures of 205 K (▽, right-hand axis) and 215 (○), 230 (●), 250 (□) and 295 (■) K (left-hand axis). The weak peak at ≈0.8 meV is the "Bragg tail". Taken from ref. [7].

The failure of the present theory to provide a fit of the phonon groups close to the transition could be taken as evidence of critical behavior [11,19] ‡. The libron–libron and "spin"–"spin" correlation functions can be calculated in the same manner as the phonon–phonon correlations and are found to have roughly the same shapes but are considerably reduced in intensity.

The present theory does provide an adequate description of the structural transformation away from the immediate neighborhood of the transition. Near the phase transition the present treatment, based on a mean-field approach, breaks down. Further experimental investigations in the critical region seem to be worthwhile for that reason. Because of the dependence of the coupling coefficients $g(kjj')$ on the molecular moment of inertia, I, a comparative study of the isotope effect with $C_3N_3D_3$ might shed additional light on the details of the coupling mechanisms between the molecular rotations and translations.

‡ Preliminary Brillouin and Rayleigh scattering data further reinforce this interpretation [20].

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