Disorder and molecular-flexibility model for the ferroelastic phase transition in phenothiazine

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The $Pbnm \rightarrow P2_1/n$ ferroelastic phase transition in phenothiazine has been studied using experimental intermolecular energy functions of the form $-A/r^6+Be^{-Cr}$ and a quadratic term for intramolecular distortion energy. A change of the molecular dihedral angle during the phase transition is found and a low-frequency mode that could be responsible for it has been identified. A split-molecule disorder model has been applied and predicts by free-energy arguments a first-order order-disorder phase transition at a temperature that is in good agreement with experiment. The phase transition under pressure is also studied and the calculated p-T phase diagram also agrees with experiment.

I. INTRODUCTION

Phenothiazine ($C_{12}H_8SN$) is an interesting three-ring-membered molecular material that displays a ferroelastic phase transition, a rather unusual fact among neutral molecules. The phase transition between the $P2_1/n$ monoclinic low-temperature phase[1] (LTP) and the $Pbnm$ high-temperature phase[2] (HTP) takes place at 251 K and atmospheric pressure.[3] By applying pressure in the HTP, the transition to the monoclinic phase is also induced, raising the transition temperature [332 K for 2.2 kbar (Ref. 4)].

The HTP has four molecules located at mirror planes with $z=0.25$ and $z=0.75c$ (see Fig. 1) and x-ray,[1] Brillouin-scattering,[5] and proton magnetic relaxation[6] experiments suggest that this phase is disordered with respect to these special positions. The LTP structure ($a=5.808$, $b=7.783$, $c=20.74$ Å, $\beta=94.9°$, $Z=4$, at 120 K) is not known experimentally, although the small heat of transition[3] suggests a weak first-order transition and very small structural changes through the transition. Large molecular reorientations are found from NMR work[7] near the transition point. Also, optical measurements[3] indicate a gradual change of 4° in the molecular orientation for the LTP as it approaches the transition point, in agreement with NMR results.

The most complete information about the nature of the phase transition comes from Raman and ultrasonic measurements. Raman-scattering work[8] shows a B_{2g} librational mode (band 3 in Ref. 8), around an axis perpendicular to the molecular best plane, which softens incompletely at the transition point (14 cm^{-1} at T_c) and that might be related to the transition mechanism. Another low-frequency mode A_g, which is rather insensitive to temperature in the range from 90 to 300 K (band 2, 26.6 cm^{-1} at 90 K), has been attributed a molecular internal deformation character and it is expected that it also might play a role in the phase transition. The changes of the Raman frequencies across the phase transition are small, pointing also to small structural changes.

Ultrasonic measurements[9,10] reveal that the C_{55} elastic constant in the HTP softens linearly on approaching T_c. This elastic constant is related to the B_{2g} shear strain e_{13}, the order parameter in the transition from orthorhombic to monoclinic unit cell. The B_{2g} symmetry is that corresponding to the change from $Pbnm$ to $P2_1/n$ space groups in a continuous transition model, therefore it is deduced that this phase transition also has a certain second-order character. However, the relative importance of both the Raman "soft mode" and the shear strain has not been established from the experimental point of view.

Several studies of the phase transition within the Landau theory framework have been made in the past,[5,9,10] where models including coupling coefficients, either between e_{13} and the B_{2g} optical mode coordinate or between e_{13} and the totally symmetric e_{33} strain (proper ferroelastic transition) have been proposed to explain the discontinuous character of the phase transition.

In summary, from all the experimental facts, it can be deduced that the transition has a weak first-order behavior with some symptoms of a displacive type, although the exact transition mechanism is unknown yet. Piezo-Raman experiments[11] are currently carried out in order to find a possible coupling between the soft-mode optical mode and the shear-strain acoustic branch.

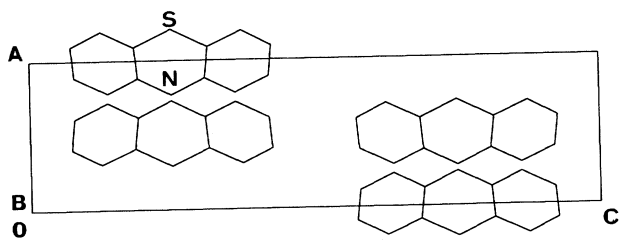

FIG. 1. View of the orthorhombic phase unit-cell contents along the **b** direction.

Another puzzling aspect of the transition is the role of ferroelastic domains, their symmetries and dynamics.[21]

We have proposed in a recent work[12] an atom-atom model of the form $-A/r^6+Be^{-Cr}$ for studying the structure and lattice dynamics of phenothiazine. The calculated orthorhombic structure showed a good agreement with the experimental one. Also, we have found an unstable B_{2g} optical mode whose displacement pattern agrees well with the experimental evidence. We were also able to find a calculated monoclinic $P2_1/n$ crystal structure, differing from the orthorhombic one mainly in a molecular reorientation of about 4°. The lattice modes calculated for this structure are stable and show a good agreement with the Raman spectra. An acoustic branch related to the C_{55} elastic constant was also found to soften when the shear strain e_{13} tends to zero.

In a later paper,[13] we have analyzed the discontinuous character of the phase transition and the role of the optical soft mode and the shear strain in the transition mechanism using the Landau theory where the coefficients of the polynomial expansion were calculated from our potential model of the form $-A/r^6+Be^{-Cr}$. We have found strong couplings between the optical-mode coordinate and the shear strain on one hand, and between the shear strain e_{13} and the totally symmetric e_{33} strain, on the other hand. Nevertheless, according to our results, these couplings do not explain the discontinuity of the transition, whose origin remains unknown. An important result is that the orthorhombic structure is energetically stable against a pure e_{13} deformation and that it is the cooperative contribution of the optical-mode normal coordinate that makes the monoclinic structure energetically favorable.

So far, our model has considered the molecules as rigid and we have treated that HTP as an ordered structure. In this work, we extend our study in order to include molecular flexibility effects to analyze the role of band 2 (Ref. 8) in the phase transition. We also mean to explore a possible order-disorder character of the phase-transition character in order to explain the discontinuous first-order transition.

II. MOLECULAR FLEXIBILITY

A rigid-molecule model, where the molecular lattice dynamics can be expressed in terms of translational and rotational coordinates is strictly applicable in those systems which show a large frequency gap between internal and external crystal modes. If the frequency of the low-frequency free-molecule modes is comparable to that of the lattice modes, the latter have both internal and external components and a complete lattice-dynamical treatment including molecular internal degrees of freedom is called for. For large planar molecules, the out-of-plane butterfly vibrational modes show smallest frequencies, for instance, in the case of the similar aromatic molecule of anthracene it is as small as 100 cm^{-1}.[14] In phenothiazine, the S and N atoms located at the mirror plane in the central ring break the π-electron conjugation between both sides of the molecule, which deviates from a planar structure. It has been argued[8] that this loss of planarity may soften the butterfly mode around the S-N axis and therefore, band 2 in the observed Raman spectra for the crystal might correspond essentially to this internal mode, with some mixing with the lattice modes.

From x-ray crystal structure analysis[2] of the HTP crystalline state, the experimental value for the molecular dihedral angle θ—folding of both benzene rings about the S-N axis—is $\theta=158.5°$, whereas the corresponding value for the free molecule obtained by the measurement of the Kerr constant in benzene solution is $\theta=150°\pm7$.[15] The Raman-frequency value of the free-molecule butterfly mode has also been measured in the vapor phase as 49 cm^{-1},[15] much lower that in the anthracene case, as expected. This value is, however, higher than the observed one for band 2 in the crystalline state, indicating a considerable softening of the butterfly mode by effect of the crystalline field if the assignment made for band 2 is correct.

A. Method of calculation

Our previous work[12,13] assumed a crystal potential-energy model as a sum of intermolecular atom-atom energy contributions in the form $V(r)=-A/r^6+B\exp(-Cr)$ where A, B, and C are constants, empirically adjustable and depending on the kind of the atoms involved in the pair interaction. In our case, the parameter values for each kind of atom were taken from the literature.[16–18] The parameters A and C for mixed interactions were obtained from the geometric and arithmetic mean combination rules, respectively, and the mixed B parameters were chosen so that the minimum of the mixed potential-energy curve corresponds to the arithmetic mean of the minima of the energy curves of the involved interacting atoms. This potential model has been validated by several statical and lattice-dynamical calculations,[12,19] within the rigid-molecule approximation, for the different polymorphic forms of phenothiazine. In this work we have included molecular deformation in the following simplified way. We have added an extra internal molecular degree of freedom, assuming that the molecule is composed of two rigid parts which can rotate about the central S-N axis, thus changing the molecular dihedral angle. In this way, we can introduce the coupling of the low-frequency butterfly mode to the lattice modes and study its influence on the system behavior.

The extended crystal potential-energy model maintains the same intermolecular atom-atom potential parameter set and introduces an intramolecular energy contribution in the form $V(\theta)=1/2\,k_\theta(\theta-\theta_0)^2$, where k_θ and θ_0 are the force constant for the butterfly mode, and the equilibrium dihedral angle respectively, both in the free-molecule state.

B. Results

The program WMIN (Ref. 20) was used to calculate the frequency of the butterfly mode for the isolated molecule and the value of k_θ was adjusted so that the calculated value corresponds to the observed value of 49 cm^{-1}.[15] Given that the experimental value of θ_0 has a large uncertainty, we have preferred to choose the value of θ_0 so that

the calculated dihedral angle for the energy-minimized *Pbnm* orthorhombic structure coincides with the experimental one. The obtained value for the equilibrium angle is $\theta_0 = 153°$, within the experimental uncertainty and less than the crystal value, indicating that the molecule flattens in the high-temperature structure due to the crystalline field.

Then, we have proceeded to get the theoretical LTP structure also by energy minimization starting at the HTP structure and relaxing all crystal structure parameters compatible with the $P2_1/n$ crystal symmetry. The resulting unit-cell parameters are $a = 5.825$, $b = 7.710$, $c = 20.85$ Å, $\beta = 93.9°$, and the obtained dihedral angle in the monoclinic phase is $\theta = 161°$, i.e., according to this calculation, the molecule would flatten about 2.5° during the HTP→LTP transition. In the minimization process, the molecule rotated an angle of 7.5° around an axis perpendicular to the molecular plane.

At this equilibrium configuration, we have calculated the lattice frequencies in the center of the Brillouin zone, $\mathbf{q} = \mathbf{0}$, also using the WMIN program and including the intramolecular normal coordinate. In Table I we show the experimental Raman frequencies for the low-temperature phase at 90 K (Ref. 8) together with the 14 calculated Raman-active ones classified according to the C_{2h} point-group representations. We also show the percentage contribution of the internal component in the eigenvector of each mode, which gives us an idea of the mixing of the lattice modes with the intramolecular one.

We can see that the agreement between calculation and experiment is satisfactory and that, in general, the internal component of the mode eigenvectors is small except for bands 10 and 11, 55.7 and 52.0%, respectively, which clearly derive from the splitting of the butterfly free-molecule 49-cm^{-1} mode, because of the crystal field. The first important result is that the butterfly mode raises its frequency in the crystal state and therefore band 2 is not predominantly an internal mode, as already pointed out by us in our previous work.[12] Nevertheless, the internal mode character of band 2, claimed in Ref. 8, has indeed some foundation if we notice that the internal contribution to the polarization vector (8.3%) is the highest after bands 10 and 11, in spite of having a very low frequency. This fact allows us to support the hypothesis that band 2 could have some role in the phase transition. According to our results, the A_g totally symmetric band 2 would be responsible for the change of the molecular dihedral angle from one phase to the other, whereas the cooperation of both the B_{2g} band 3 and shear strain in the HTP would produce structural symmetry change for the transition from the orthorhombic *Pbnm* to the monoclinic $P2_1/n$ crystal structures.

TABLE I. Calculated and experimental frequencies at 90 K (Ref. 8) and calculated internal character of the Raman-active modes in the low-temperature phase of phenothiazine at zero pressure.

		exp (cm^{-1})	cal	int (%)
(1)	B_g	22.9	24.9	1.0
(2)	A_g	26.6	23.3	8.3
(3)	A_g	34.3	32.1	4.0
(4)	B_g	39.9	33.4	0.0
(5)	A_g	47.4	45.1	5.4
(6)	B_g	59.7	48.9	4.4
(7)	A_g	65.7	54.1	1.1
(8)	B_g	78.3	77.3	4.2
(9)	A_g	91.5	87.2	0.8
(10)	A_g	94.1	96.8	55.7
(11)	B_g	100.5	85.7	52.0
(12)	A_g	107.5	125.8	4.7
(13)	B_g	108.1	104.5	4.7
(14)	B_g		124.3	10.0

One could argue that band 3 has also an important internal component of about 4.0%, nevertheless this mixing with the internal normal coordinate is not present in the corresponding HTP B_{2g} mode, as it is forbidden by symmetry reasons. Thus from the low-frequency modes in the high-temperature phase only A_g (band 2) bears an appreciable internal component.

III. DISORDER MODEL

A calculation of lattice modes in the orthorhombic phase using the same procedure gives an unstable pattern similar to that found within the rigid-molecule model,[12] where we have found that the mirror position corresponds to an energy maximum and that there is an energy double well centered at the symmetry plane. We proposed in that work that the stabilization of the HTP could be reached *via* anharmonic terms where both minima of the double well would be accessible to the given molecule—dynamical disorder—or a statical disorder situation where each molecule chooses either minimum in an average *Pbnm* structure. A lattice-dynamical calculation of the thermal motion amplitude in the LTP at T_c has shown that it was large enough to allow the transition from one minimum to the other. In the following we have tried to model this possible disorder in the HTP, which is also supported by different experimental evidences,[5,6,22] in order to see whether the order-disorder mechanism of the phase transition could explain the features which still remain to be understood.

We have assumed a split-molecule, two-site disorder model, first developed for charge-transfer crystals,[23,24] by considering a molecule obtained from the superposition of both sites with an occupancy of a half. The two distinct positions arise from rotating the molecule a certain disorder angle off the mirror plane in opposite directions around an axis perpendicular to the molecular plane, according to the soft-mode eigenvector pattern. To simplify the model we have neglected molecular deformation, considering the molecules as rigid though disordered. If the disorder is random, the crystal lattice energy calculated using this molecule as the asymmetric unit would be coincident with the energy of the disordered crystal (see Ref. 24 for details).

Using this procedure to model the disorder in phenothiazine we have calculated next the crystal energy as a function of the disorder parameter by crystal-energy minimization with respect to cell parameters and translations and rotations of the average molecule considered as

rigid, i.e., keeping fixed the disorder angle in the minimization process. We have carried out this calculation, first imposing the monoclinic $P2_1/n$ symmetry on the variables and then, minimizing according to the orthorhombic *Pbnm* space-group symmetry. In this way, we have obtained two energy states as a function of the disorder parameter θ_d (rad), which correspond to both crystal phases and that are displayed in Fig. 2.

We can see in Fig. 2 that both curves cross over at about 0.0421 rad (2.4°) of the disorder angle. For the lower angles, the monoclinic configuration is energetically favorable and for higher angles, the orthorhombic has less energy. Of course, this stability picture would correspond to the behavior of the real system at $T=0$, where the true structure is the absolute minimum level, i.e., an ordered monoclinic phase. At finite, but low temperatures, we can see from Fig. 2 that the monoclinic energy levels can be more easily excited whereas for high temperatures the orthorhombic levels are more favorable. Therefore, this model must predict a phase transition at a certain temperature.

The relevant thermodynamical quantity to study the relative stability of both phases is the free energy, calculated as $F=-kT\ln Z$, where Z is the partition function for each phase: $Z=\sum_i \exp(-E(\theta_d)/kT)$. Here, i runs over all energy levels of the corresponding crystal phase. In our case, both energy states adjust very well to a parabolic function $E(\theta_d)=a+b\theta_d^2$, with $a_M=-21.685$ and $b_M=180.78$ kcal/mol for the monoclinic level and $a_0=-21.599$ and $b_0=132.40$ kcal/mol for the orthorhombic one. From this expression, the free energy can be easily calculated as

$$F=a-kT\ln[\tfrac{1}{2}\sqrt{(\pi/b)}(kT)^{1/2}]\ ,$$

assuming there is a continuity of energy levels.

Figure 3 shows the calculated free-energy curves for both phases, whose crossing point, $T_c=275$ K, corresponds to the transition temperature predicted by the model, in very good agreement with the experiment (251 K). From the slope change in the free-energy curves at the crossing point we can get an estimation of the LTP→HTP entropy and heat of transition, $\Delta S=\frac{1}{2}k\ln(b_M/b_0)$ and $\Delta Q=\Delta S T_c$. The calculated

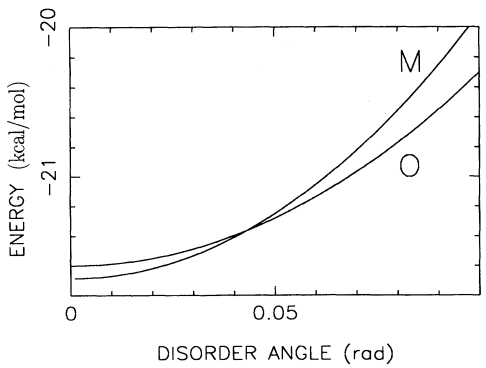

FIG. 2. Calculated monoclinic (M) and orthorhombic (O) energy levels (kcal/mol) as a function of disorder angle (rad) at zero pressure.

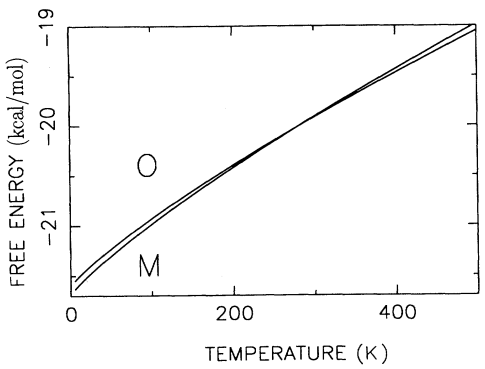

FIG. 3. Calculated free-energy curves (kcal/mol) for the monoclinic (M) and orthorhombic (O) configurations vs temperature (K) at zero pressure.

values are 0.31 cal $K^{-1}mol^{-1}$ and 77.4 cal mol^{-1} (assuming $T_c=251$ K), respectively, which are in semiquantitative agreement with the experimental values[3] of 0.17 cal $K^{-1}mol^{-1}$ and 47.8 cal mol^{-1}. We can calculate also the thermodynamical average for the disorder angle, $\langle\theta_d\rangle=(kT/\pi b)^{1/2}$, which yields a value of 0.373 rad (2.1°) for the orthorhombic phase at room temperature.

It is crucial to notice that we have assumed energy levels as a function of a disorder parameter, also in the monoclinic LTP. In fact, if we assume a single ordered state for the monoclinic phase, the corresponding energy curve in Fig. 2 would be a horizontal straight line at $E(\theta_d=0)=-21.685$ kcal/mol, and the monoclinic phase would be more favorable at all temperatures. Nevertheless, it is possible to reconcile this fact with the hypothesis of an order-disorder LTP→HTP transition if we regard the split-molecule model just as a molecular probability distribution function. For small disorder angles in the LTP this split-molecule would simply be a way to represent a single-peaked and narrow orientational distribution in an ordered crystal structure and it would not correspond to real disorder. The increase of the disorder parameter merely implies that the single-peaked probability distribution broadens and when the disorder angle is large enough the phase transition takes place and we would have a double-peaked distribution which can be related to genuine disorder.

This picture agrees quite well with the mechanism we proposed above for the phase transition, where the librational thermal motion in the HTP becomes larger as the temperature increases and when it is large enough to overcome the double-well barrier of the crystal energy, a phase transition to a disordered HTP phase would take place.

IV. PRESSURE EFFECTS

In a recent work,[4] the Raman spectra of the phenothiazine crystal under pressure were measured up to 20 kbar. By application of pressure to the orthorhombic phase, a phase transition is observed in which band 3 shows a partial softening and band 2 shows very little variation with pressure. The behavior of these bands

with pressure in the pressure-induced transition is very similar to their dependence with temperature through the transition point for the temperature-induced transition,[8] and so it is concluded that the phase obtained under pressure is the same as the monoclinic low-temperature phase LTP, although the stronger intensity of band 2 seems to suggest that there is a larger change in the molecular orientation accompanying the phase transition under high pressure. Also, from the shifts of the Raman bands it is inferred that the change in the molecular conformation in the phase transition under high pressure may be larger than that at atmospheric pressure. In summary, a monoclinic to orthorhombic p-T phase-transition diagram seems to appear, where the transition temperature raises for increasing pressure. One can justify the fact that $dTc/dp > 0$ from the Clausius-Clapeyron equation $dTc/dp = \Delta V/\Delta S$ where ΔV and ΔS are the increase of volume and entropy during the phase transition. In our case, the energy-minimized orthorhombic cell is 0.53% larger than the corresponding monoclinic one. Unfortunately, the experimental cell volume values[1] for both phases correspond to very different temperatures (120 and 300 K).

We have also studied in this work the influence of pressure on the phase transition in order to find out whether our disorder model is able to reproduce the actual phase transition behavior under pressure correctly. We have introduced pressure in our potential-energy model by simply adding an extra energy term pV to the energy-minimization process and in this way we can get the equilibrium crystal configuration at a given pressure. As a first check of whether an applied pressure favors the orthorhombic to monoclinic transition we have considered our split-molecule disorder model with a disorder angle for which the orthorhombic energy level is energetically lower than the monoclinic one. Then, we have carried out minimization processes under different pressures and we have found that for large enough values, the minimization evolves towards the $P2_1/n$ monoclinic structure, which becomes energetically stable under pressure. From the structural parameter shifts, we find that the monoclinic structure found under pressure is the same as the LTP at atmospheric pressure in agreement with the experimental evidence.

This successful result encouraged us to perform more systematic calculations in order to study the variation of the transition temperature with pressure. For this purpose, we have repeated the calculations, now at 2.5 kbar. By minimization under pressure we have obtained the monoclinic and orthorhombic energy levels as a function of disorder parameter, which also fit very well to a parabolic law $E(\theta_d) = a + b\theta_d^2$, with $a_M = -22.003$, $b_M = 210.56$ kcal/mol for the monoclinic level and $a_0 = -21.889$, $b_0 = 160.76$ kcal/mol for the orthorhombic one. For these values, the crossover angle shifts to a larger value of 2.7°, favoring the monoclinic structure, as already discussed.

Then, we proceeded to calculate the free-energy curves for both structures and to obtain the transition temperature, which turned out to raise up to 420 K. This calculated value shows a worse agreement with the experimental one of 340 K than in the study at zero pressure. We believe that this fact can probably be due to the assumption of molecular rigidity for our disorder model. Molecular deformation effects under pressure must be important and a more elaborate model taking into account molecular flexibility and disorder simultaneously would be desirable in order to calculate the phase diagram under pressure more precisely. Nevertheless, our simplified model describes correctly the qualitative behavior of the phase transition of phenothiazine under pressure.

It is rather interesting to compare the obtained value for the transition temperature under pressure with that predicted by the Clausius-Clapeyron equation. If we get an estimation of the volume change during the transition from the difference between the orthorhombic (942 Å^3, $Z=4$) and monoclinic (937 Å^3, $Z=4$) energy-minimized unit-cell volumes and using the calculated value for the entropy of transition (0.308 cal K^{-1} mol^{-1}) we find that if the calculated transition temperature at zero pressure is 275 K, it should be 421 K at 2.5 kbar, in excellent agreement with the value obtained from the free-energy curves.

Lastly, we have carried out some calculations using the flexible molecule model in the monoclinic phase under pressure in order to get an idea of changes induced in the structural parameters. For instance, at 20 kbar, the minimized cell parameters are $a = 7.257$, $b = 20.25$, $c = 5.658$ Å, and $\beta = 95.5°$, which represents a decrease of 11.4% in the cell volume with respect to the zero-pressure calculation. The molecular rotational tilt from the mirror position is now 10.1°, larger than at zero pressure, in agreement with experimental results. The molecule flattens under pressure, as the calculated dihedral angle at 20 kbar is 167.1°. We have also calculated the dihedral angle for the orthorhombic energy minimized structure at 20 kbar, which is 163.2°. These last two values give us an estimation of 3.9° for the change in the molecular conformation angle in the phase transition at 20 kbar, larger than the corresponding value at atmospheric pressure, also in agreement with experimental evidence.

We also show in Fig. 4, the calculated frequency using the flexible molecule model of some selected modes,

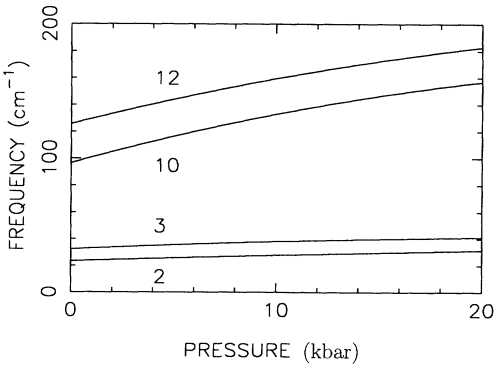

FIG. 4. Calculated pressure variation (kbar) of the frequencies (cm^{-1}) of bands 2, 3, 10, and 12 of the monoclinic phase of phenothiazine.

bands 2, 3, 10, and 12, in the LTP as a function of pressure. The frequency increase with pressure is in good agreement with experiment,[4] except for band 3, which changes much more in the experiment than in the calculation. It is known that soft modes are very sensitive to small structural changes, hence this discrepancy which goes beyond the limitations of our approximate model.

V. CONCLUSIONS

The adoption of a model which takes into account molecular flexibility through the normal coordinate of the butterfly lowest internal mode has allowed us to determine the role of molecular deformation in the phase transition. There is a change in the molecular dihedral angle accompanying the transition, which increases with pressure. We have found that the polarization vector for the low-frequency A_g band 2 has an important intramolecular deformation component, which can be responsible for this change in the phase transition.

A split-molecule model has also been considered to simulate disorder. We have been able to predict a phase transition based on free-energy arguments and the predicted transition temperature agrees well with experiment. From this model, a mechanism for the phase transition has been proposed where the thermal-motion molecular probability distribution of the low-temperature ordered phase broadens as the temperature raises, turning into a two-site double-peaked distribution in the phase transition.

This disorder model predicts a first-order phase transition as the slopes of the free energy curves of both phases at the transition temperature are different.

Pressure effects are also correctly reproduced by this model, where the transition temperature increases with pressure although a more elaborated model, in which both disorder and molecular flexibility were taken into account at the same time, would be necessary in order to establish the phase diagram. The structural changes of the phenothiazine crystal under pressure have been studied at 20 kbar and the results also agree with experimental evidence.

We intend in the nearest future to carry out molecular-dynamics calculations in phenothiazine with the aim of reproducing the phase transition in the simulation and to establish the statical or dynamical nature of the disorder.

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