

INFRARED SPECTROSCOPY OF THE DIFFERENT TYPES OF SECOND ORDER STRUCTURAL PHASE TRANSITIONS IN MOLECULAR CRYSTALS.

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ABSTRACT

This paper is devoted to the study of second order structural phase transitions in molecular crystals by means of infrared spectroscopy. The experimental results obtained from the molecular crystal of chloranil, sym-triazine and malononitrile are given and analysed.

Infrared spectroscopy results are reported for chloranil and, in particular, near the phase transition point. The temperature dependence of linewidths ($\delta \Delta \nu_1$) of exciton bands, are found to be described by a $(T_c - T)^\beta$ law in the low

temperature phase with a critical exponent β approximately equal to 0.5. In the case of sym-triazine, the splitting $\delta(\Delta \nu)$ of the exciton components is studied as a function of temperature and can be described by $(T_c - T)^\beta$ law with critical exponent β of approximate value of 0.36. This splitting can be considered as an order parameter of Landau's theory. Infrared spectroscopy is reported for malononitrile crystal. The sudden disappearance of the doublet structure at the III - II transition is in agreement with a phase transition from a monoclinic to a triclinic structure. In the vicinity of the second order phase transition at $T_c = 141$ K, the variation of the splitting $\delta(\Delta \nu)$ as a function of $(T_c - T)^\beta$ gives a critical exponent β of the order parameter of 0.5 above and below the transition point. Experimental results show that the variation of the exciton structure as on function of temperature can be considered as an order parameter allowing a second order phase transition to be characterized.

KEYWORDS: Molecular crystal, order parameter, structural phase transition, vibrational exciton

INTRODUCTION

Infrared spectroscopy of vibrational excitons is a technique of study, particularly adapted to study the second order structural phase transitions observed in molecular crystals.

Indeed, phase transitions are characterized by the evolution of the physical sizes which can extremely differ from one crystal to the other. We can have unit cell scissoring, the rotation of molecules, etc. Thus, in infrared spectroscopy, the observable effects are varied. One can note the variation of the splitting of components of the exciton structure, the modification of the profile and disarticulation in frequency of the infrared absorption bands. The development of the physical size makes it possible to classify these phase transitions.

The structural phase transitions are related to a change of crystalline structure (change of group of crystallographic space losing some symmetry elements). This change of symmetry (Landau, et al., 1967) associates the very fertile concept order parameter. This order parameter concept makes it possible to classify the structural phase transitions generally distinguished as follows:

Structural phase transitions from order - disorder

Displaceable structural phase transitions.

In the present paper we will mainly present the exciton structure of infrared waves of some molecular crystals and show the variation of the exciton structure as on function of temperature can be considered as an order parameter allowing a second order phase transition to be characterized.

1. DIFFERENT TYPES OF PHASE TRANSITIONS IN MOLECULAR CRYSTALS

1.1 Structural Phase Transitions: order - disorder

In this category of structural phase transitions the loss of symmetry originates from an ordering of the position or of the orientation of the atoms, ions or molecules of the crystal molecules. The structural phase transitions, order - disorder, with the intervention of molecular orientation are generally found in molecular crystals. An example is the structural phase transition of cyclohexane at $T_c = 186.3$ K (Moulehiawy, 1983). Structural phase transitions, order - disorder, are generally of the first order.

1.2 Displaceable structural phase Transitions

The displaceable structural phase transitions are characterized by a modification from crystalline structure related to a very weak atoms, ions or molecules displacement. A priori, this displacement can originate either from a translation, or from a rotation, or again from a deformation of the unit cell.

The elastic oscillations associated with the oscillations of the low amplitude atoms or molecules around their balances position are quantified under the name of phonons. These phonons are broadcast in the crystal with an angular frequency

ω and with a wave vector k . For a displaceable structural phase transition, the order parameter generally corresponds to a soft phonon or 'soft mode' which is characterized by a frequency ω which moves towards zero when the temperature moves towards T_c in the low phase temperature. The displaceable structural phase transitions could be controlled by a soft optical phonon or by a soft acoustic phonon.

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2. EXCITONS STRUCTURE OF THE ABSORPTION INFRARED BANDS OF SOME MOLECULAR CRYSTALS PRESENTING DISPLACEABLE PHASE TRANSITIONS.

2.1. Displaceable structural phase transitions controlled by a soft optical phonon: the case of the chloranil molecular crystal.

The brute formula chloranil molecule $C_6Cl_4O_2$ is plane and belongs to the specific group of D_{2h} symmetry. The crystal presents a second level phase transition at $T_c = 91K$ highlighted by NQR (Nuclear Quadripolar Resonance) (Richardson, 1963). The high and low phase temperatures of the crystal belong both to the monoclinic system and have the same space group. The phase transition is characterized by a loss in translation symmetry along the c axis of the crystal in the low temperature.

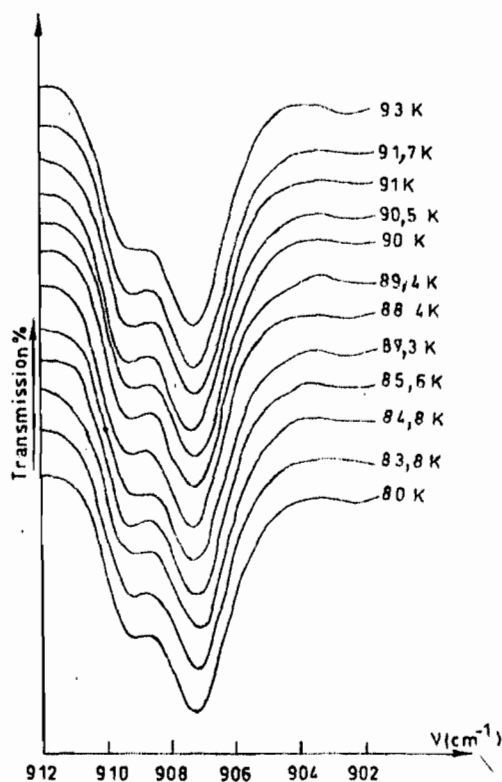


Figure 1: Temperature dependence of the B_{3u} band of solid chloranil

It is obvious that the vibrations modes B_{3u} are not sensitive to the rotation φ which, on the contrary, affects the vibration modes B_{2u} . This rotation φ poses a discontinuity to the transition, which confers on to the latter a slight first order character observed by some authors (Terauchi et al, 1975 and Yoshihara et al, 1983). The modes of vibration B_{3u} are only sensitive to the θ rotation (order parameter of the transition in the theory of Landau) and can consequently confirm the character of the second order phase transition of chloranil crystals.

The analysis and the interpretation of the infrared spectra based on the calculation of network energy (Djeteli et al., 1999) reveal that the separation of the energy levels of the bands B_{3u} in accordance with the rotation θ of the molecules influences mid-height width of the high frequency component. This, thus explains the mid-height width of this component according to an analytical law of the form $A(T_c - T)^\beta$ and confirms that this mid-height width can be taken as spectroscopic parameter characteristic of the second order phase transition of the chloranil crystal.

The experimental study is mainly devoted to the evolution with the temperature and the immediate T_c environment, and with two classes of infrared bands B_{3u} and B_{2u} .

The B_{3u} class absorption bands present a couple structure more or less resolved in the two crystalline phases. They are characterized by a width variation at mid-way height ($\delta(\Delta\nu_{1/2})$) of the high frequency component according to an analytical law of the form $\Delta(\delta_{1/2}) = A(T_c - T)^\beta$, β varying from 0.45 to 0.5 (Le Roy et al., 1990 and Djeteli et al., 1999). No variation of the width with mid-way height of the low frequency component was observed (Figs 1 and 2).

The absorption bands of B_{2u} class present a simple structure in both phases. One observes a low discontinuity of the width with mid-way height of these bands to the phase shift.

Many authors highlighted not only one rotation (θ) around the perpendicular axis to the plan of the molecule but also a rotation (φ) around the axis passing through oxygen atoms (Baudour et al, 1981).

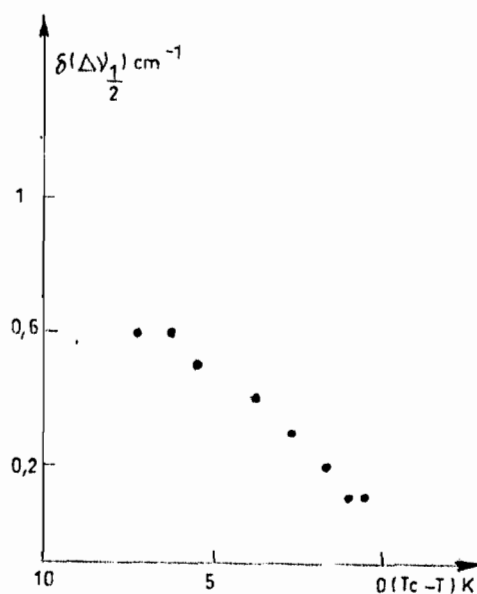


Figure 2: Linewidth of the upper excitation band as function of $(T_c - T)$

2.2. Displaceable structural phase transitions controlled by a soft acoustic phonon: the case of the molecular sym-triazine crystal

The brute sym-triazine formula 1, 3, 5, $C_3H_3N_3$ crystallizes in ambient temperature in the rhomboedric system space group $D_3^h(R\bar{3}c)$ with two molecules in unit cell.

The molecular crystal presents a second order phase transition at $T_c = 198 K$ highlighted by diffraction of x-rays. The crystal passes from a rhomboedric high temperature phase to a space group monoclinic (C_2^h), low temperature phase with two molecules per unit cell. The phase transition is characterized by the elastic strain of the unit cell which induces a rotation of the molecules of ten degrees around the c_1 axis parallel to the axis b of the crystal. The component e_5 of the tensor of deformation thus generates a soft acoustic phonon, and is snuffed like a parameter of a principal nature. In our experimental study, we followed the evolution according to the temperature of two bands of vibration belonging to the

classes of symmetry E' and E'' and respectively located at 1172 cm^{-1} and 1035 cm^{-1} in the phase high temperature. These two bands are characterized by a structure of couples in the low temperature phase whereas only one band is observed in the high temperature phase. This couple appears at $T_c = 196 \text{ K}$ and is as solved as the temperature is low.

For the two bands, the instantaneous frequency deviation in both sub-levels varies according to the temperature in the low phase temperature following an analytical law of form $A(T_c - T)^\beta$, β varying from 0.23 to 0.36 (Le Roy et al., 1988).

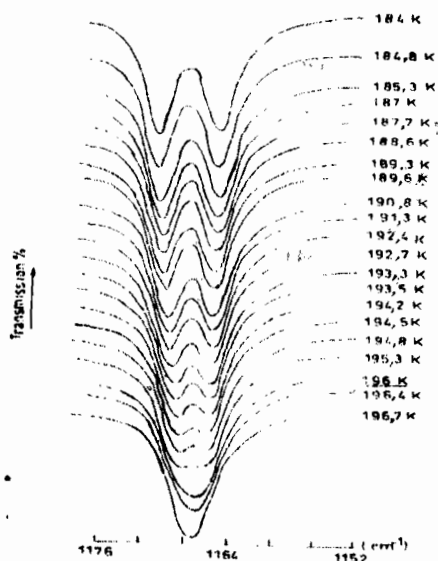


Figure 3: Temperature dependence of E' band of solid triazine

The variation observed between the value of β of the theory of Landau on second order phase transitions and those obtained for sym-triazine, explains the weak character of the first order observed by some authors (Smith et al., 1978 and Raich et al., 1980). This is illustrated by the presence of the invariant order 3 in the analytical expression of the free energy.

The analysis and the interpretation of the infrared spectra based on the calculation of network energy (Djeteli et al., 1999) show that the reorientation of the molecules around the axis C_2 of the monoclinic system parallel to the axis b of the sym-triazine molecular crystal affects the instantaneous frequency deviation of the sub-levels in the low temperature phase, which confirms the choice of the instantaneous frequency deviation of the sub-levels as order parameter.

We conclude that for the $T < T_c$ temperature in the monoclinic phase, the parameter of a corresponding nature is cancelled by undergoing a discontinuance. Finally for $T > T_c$, there is a split of the order on along distance which justifies the disappearance of the structure of the bytes.

2.3. Transition of re-entering displaceable structural phases controlled by a soft acoustic phonon: the case of the malononitrile molecular crystal

The malononitrile is one of the rare molecular crystals presenting a succession of second level phase transition with an intermediate lower symmetry phase. The raw malononitrile molecule formula $\text{CH}_2(\text{CN})_2$ crystallizes at an ambient temperature in monoclinic system with the space group of $P2_1/n - C_5$. The crystal presents two second level phase transitions at $T_{c1} = 294.7 \text{ K}$ and $T_{c2} = 141 \text{ K}$.

The high temperature phases (I) and low temperature (IV) are of the same structure. The intermediate phase is triclinic with the special group $P_1 (C_1)$. The transition from phase monoclinic

Figures 3 and 4 show the excitons structures of the infrared spectra from the band E' to

1172 cm^{-1} at low temperature, on the one hand, and the evolution of the instantaneous frequency deviation of both sub-levels according to the temperature, on the other hand.

To characterize the transition, we have chosen as order parameter the variation in frequency of both sub-levels. Fig 4 shows that the order parameter follows an analytical law of the form $\Delta\nu = \Delta\nu_0(T_c - T)^\beta$, characteristic of a transition from second order phase.

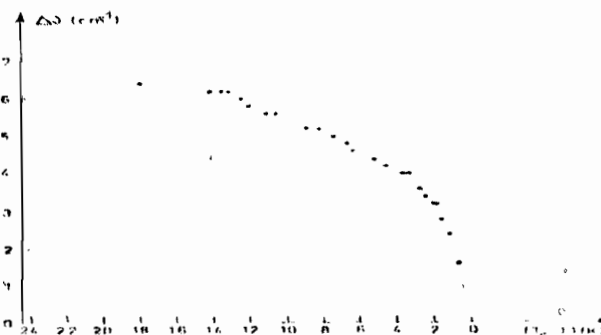


Figure 4: Splitting of the E' band as a function of $(T_c - T)$

is characterized by a rotation θ in phase opposition of two immediate neighbour molecules and other pattern molecules coupled around the axis b to the monoclinic unit cell. Both phase transitions ($T_{c1} = 294.7 \text{ K}$ and $T_{c2} = 141 \text{ K}$) are

controlled by a soft optical phonon of wave vector k from the center of the zone of Brillouin in the high temperature phase.

The malononitrile used in our experiments was obtained commercially and purified by crystallization and sublimation.

Thin crystalline films of about $10 \mu\text{m}$ were prepared by a slow crystallization of the liquid between two windows of KBr or AgCl . The sample holder was mounted in a liquid nitrogen cryostat. The temperature was automatically controlled throughout the range $80 - 300 \text{ K}$ with a precision of 0.5 K .

The infrared spectra were recorded on a Perkin - Elmer model 125 spectrometer used with a resolution better than one wave number.

In the experimental part, we have studied the excitons structure of the infrared absorption bands of the malononitrile molecular crystal, at several temperatures in a given phase, on the one hand, and at several temperatures in the immediate vicinity and on both sides of the transition temperature on a range of 10 K on the other hand.

The infrared absorption bands respectively located at 1395 , 916 and 582 cm^{-1} (Phase IV), this structure is preserved at $T > T_{c2} = 141 \text{ K}$ (Fig 5).

These bands are characterized by the variation of the instantaneous frequency deviation ($\Delta\nu$) of the components according to an analytical form law $(T_c - T)^\beta$ in phases IV and III with β close to 0.5 (Fig 6).

Furthermore, a brutal disappearance of the excitons structure of the absorption bands is observed when $T_c = 260 \text{ K}$. This result is characteristic of a first order phase transition as highlighted by some authors (Dove et al., 1983).

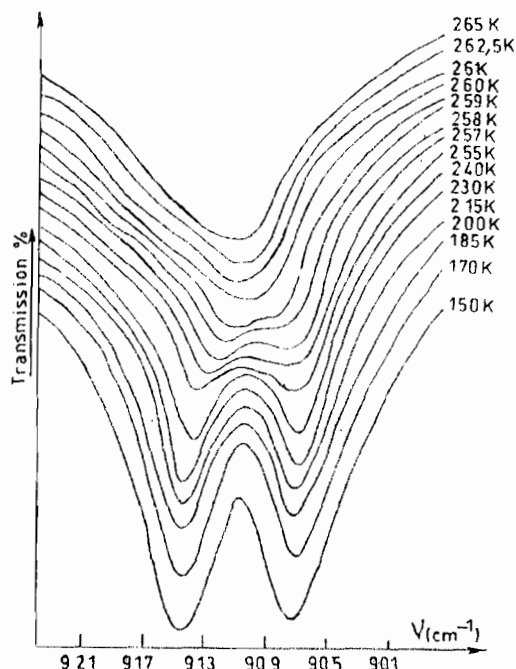


Figure 5: Excitation structure of the 916 cm^{-1} band close to $T_c = 141\text{ K}$.

The analysis and the interpretation of these results (Benkhail, 1990) in the model of the vibrational excitons and the theory of Landau show that the malononitrile molecular crystal presents a succession of phase transitions:

monoclinic \rightarrow triclinic \rightarrow monoclinic \rightarrow monoclinic, with a phase reappearance at $T_{c2} = 141\text{ K}$. The intermediary phase (phase III) is made up of two phases of different structures, with a first level phase transition at $T_c = 260\text{ K}$.

CONCLUSION

The significant parameter of the theory of the vibrational excitons is the resonant transfer of energy between two identical molecules, one being in its excited state and the other in its basic state. The study of the two molecule system illustrates this resonant transfer of the vibrational excitation (Djeteli et al., 2001). This experimentally illustrates the variation of the separation of the structure of bytes (Le Roy et al., 1988, Guerin et al., 1993 and Le Roy et al., 1993) the mid height width (Le Roy et al., 1990 and Djeteli et al., 1999) or the bands dislocation into frequency. The analysis and the interpretation of this vibration make it possible to characterize the phase transition.

Thus, the interpretation of the infrared spectra enables us to better know the properties of the molecular crystal: molecular movements, symmetry and phase shift (Le Roy et al., 1990, Le Roy et al., 1988, Le Roy et al., 1993 and Le Roy et al., 1995). It proves to be of great use in research on surface phenomena and particularly the characterization of absorbed species. It then results that the interpretation of many optical properties of the condensed stuff in molecular physics requires the use of the concept of the vibrational excitons.

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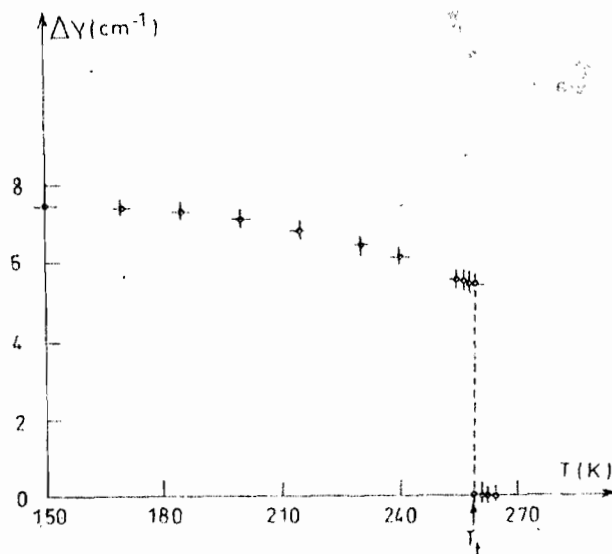


Figure 6: Splitting of the A_1 band near 916 cm^{-1} as function of temperature in phases III and II.

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