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Low Energy Phase Transitions in Molecular Crystals and Raman Spectroscopy: The Case of Benzil

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Low Energy Phase Transitions in Molecular Crystals and Raman Spectroscopy

The Case of Benzil

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(*Received August 4, 1975*)

The low-energy phase transition discovered by Esherick and Kohler in solid benzil has been studied by Raman spectroscopy as a function of temperature and pressure. Some of the frequency shift curves exhibit a discontinuity in their slopes at the transition point, but the most striking feature is the continuous increase of the intensity of a Raman line lying at 47 cm^{-1} when decreasing temperature or increasing pressure, followed by an intensity jump of the same line at the transition. Starting from these observations, a mechanism for the phase transition is proposed.

Until now, work on phase transitions in molecular crystals have been mostly devoted to the study of transitions of the destructive-reconstructive type, which imply large molecular displacements accompanied by a high transformation energy. For this type of transitions, it is not easy to discover a simple geometric transformation according to which one phase corresponds to the other one (translation[1] or molecular change of orientation[2]).

On the other hand, in the case of low-energy phase transitions ($\Delta S <$ 0.5 e.u.) through which single crystals are generally not destroyed, molecular rearrangements will be progressive and of small amplitudes. A systematic study of such phase transitions in molecular solids should lead to a better understanding of the mechanisms which are involved.

This is the reason why we first studied thiourea in which four phase transitions have been observed at atmospheric pressure.[1] In the temperature range of these phase transitions, the Raman spectrum exhibits little change. Schrader *et al.*,[3] have only observed weak frequency discontinuities on two of the external mode frequencies, whereas Bandy *et al.*,[4] did not see any

discontinuity at all. However, in the same temperature range, we observed a progressive evolution of the relative intensities of several intermolecular modes.[5]

In the case of benzil, Esherick and Kohler[6] described a low energy phase transition at 84 K. We have studied the low-frequency Raman spectrum of this compound as a function of temperature and pressure, in order to see whether the same phenomenon as in thiourea could be observed and whether it could give a clue as to what concerns the transition mechanism.

Benzil single crystals were grown from a saturated solution in ethyl alcohol at room temperature. A selected crystal was placed inside a three-window high pressure cell[7] in which the pressure transmitting medium is gaseous helium. This crystal which was fastened without any stress on the output optical window was excited along its three-fold axis with a Spectra Physics 164 Argon laser beam at 514.5 nm; the incident power was 60 mW. Raman spectra were analysed by means of a PH1 Coderg double monochromator spectrometer. Pressure measurements were performed by means of a manganin coil placed inside a connected pressure vessel. Low temperatures were obtained by circulating liquid nitrogen through an outer jacket and temperature was regulated by means of a Thermocoax resistance.

The frequency shifts of the external modes of benzil have been studied from 77 K up to room temperature as a function of pressure up to 4 Kbar. Figure 1 shows the observed shifts as a function of pressure at 102 K. It can be seen that for the modes lying at approximately 40, 60 and 170 cm^{-1} the

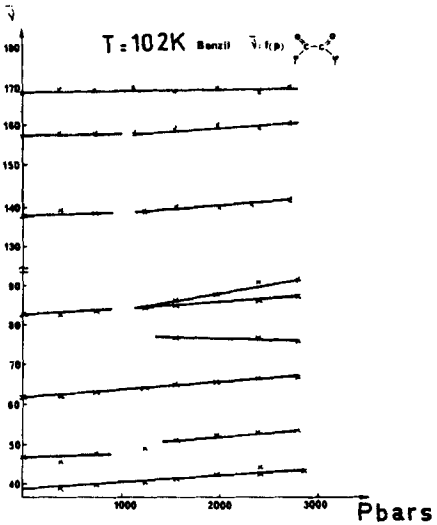

FIGURE 1 Isothermal frequency shifts of Raman modes in benzil at 102 K.

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frequency shift curves can be represented by plain straight lines. As to what concerns the four modes lying respectively at 47, 82, 140 and 160 cm^{-1}, it can be observed that the corresponding frequency shift curves exhibit a slope change around 1050 bars. It is to be noticed that, when decreasing pressure, the two modes lying respectively at 76 and 86 cm^{-1} at 2800 bars disappear in the vicinity of the former pressure.

The same features have been observed during experiments performed at constant pressure as a function of decreasing temperature. For instance, at 640 bars, the slope change takes place at 95 K.

We assign this break in the slopes of some frequency shift curves to the onset of the phase transition described† by Esherick and Kohler and studied later by Chan and Nelson[8] by zero-field magnetic resonance.

From the transition points we determined ($T = 95$ K, $P = 640$ bars and $T = 102$ K, $P = 1050$ bars), together with the value given by Esherick and Kohler, we can determine the slope dT/dP of the transition curve, that is:

$$\frac{dT}{dP} = (1.7 \pm 0.2)\ 10^{-7}\ \text{K/Pascal}$$

Starting from Esherick and Kohler's evaluation for the enthalpy increment at the transition:

$$\Delta H \leq 0.04\ \text{cal/g},$$

and using Clapeyron equation, we can deduce that the molar volume ΔV is given by:

$$\Delta V \leq 7 \times 10^{-2}\ \text{cm}^3.$$

This corresponds to:

$$\frac{\Delta V}{V} \leq 8 \times 10^{-4},$$

which is very low indeed.

On Figure 2, we have represented three low frequency Raman spectra of crystalline benzil which were recorded in different temperature-pressure conditions. These spectra illustrate the most striking feature of the transition. For instance, decreasing temperature from room temperature at atmospheric pressure, we first observe a spectrum analogous to that which is reported on Figure 2a: the line lying at 40 cm^{-1} does not present any apparent shoulder on its high frequency side. From 150 K and lower, a shoulder at 47 cm^{-1} grows on the 40 cm^{-1} line (Figure 2b). At the phase transition, the intensity of the shoulder suddenly increases as is represented on Figure 2c.

† 1 bar = 10^5 Pascal.

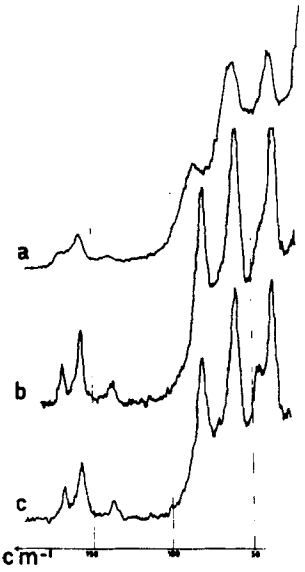

FIGURE 2 Low frequency Raman spectra in benzil. (a) $T = 293$ K, $P = 2090$ bars; (b) $T = 102$ K, $P = 1$ bar; (c) $T = 77$ K, $P = 1$ bar.

It is to be noticed that this intensity jump accompanies the slope changes described above.

This continuous growing of a Raman line in the high temperature phase followed by this intensity jump led us to fancy a speculative mechanism for the low-energy phase transition of benzil.

We have already said that in the case of thiourea, the phase transitions were accompanied by changes in the relative intensities of some Raman external modes. Goldsmith and White[2] have showed that, in phases I and V of thiourea, the molecular positions differ by their orientations with respect to the crystalline axes of the unit cell (and also by a slight translation of their centres of gravity). Furthermore, Calvo[9] has showed that a continuous change of molecular orientations with respect to the crystalline axes from phase I to phase V could explain his dielectric data. So, we tentatively concluded that such a molecular change of orientation would generate relative intensity changes in external Raman modes.

So we tried to apply such a model to the case of benzil. We had to look for an orientational change which preserves the crystalline symmetry but modifies some of the polarizability crystalline tensor elements.

Now, Brown and Sadanaga[10] describes for the high temperature phase of benzil a structure the space group of which is $P3_{1,2}21$. In such a structure, the molecular binary axis is also a symmetry element for the unit cell. So,

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only a change of orientation of the benzil molecule around its binary axis, or a molecular deformation preserving its C_2 symmetry, is compatible with an overall symmetry conservation, and moreover can explain the intensity change which is experimentally observed. A careful examination of the Raman spectrum in the internal mode region did not reveal any abnormal frequency change in the considered temperature range. This led us to think that the most probable deformation taking place in the post-transition process is a progressive change of orientation of the molecule as a whole around its binary axis. This, of course, would lead to a modification of some polarizability elements, which in turn could explain the change of intensity we observe in the Raman spectra.

As temperature is lowered, we observe a continuous increase of the intensity of the 47 cm^{-1} line. According to our model, this means that the molecules undergo a continuous change of orientation around its binary axis. It is obvious that such a process cannot go on indefinitely and that at some time the crystalline structure will not be able to accommodate such a molecular configuration change. At that point, steric hindrance will be such as to force some molecules to slide aside. This, of course, will destroy the former space group and will generate the new one. It is to be noticed that this sliding process, once generated, will tend to go on. This could explain the drastic increase of the angle between the two optic axes in the low temperature phase just below the transition as observed by Esherick and Kohler.[6]

Such a mechanism is almost continuous and the transition could only be revealed by a change of crystal symmetry, without exhibiting dramatic changes in thermodynamic functions. In order to check our tentative mechanism, dielectric and heat capacity measurements are in process.

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