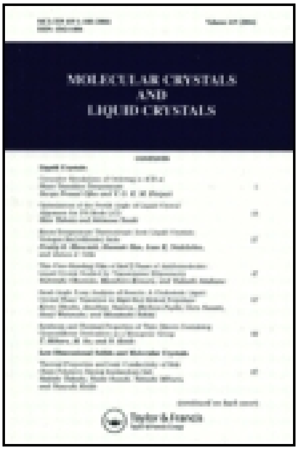

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MOLECULAR MOTIONS IN ORGANIC CRYSTALS

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ABSTRACT The piezomodulation spectroscopy of molecular crystals is discussed with particular reference to its application to lattice dynamics and its extension to the understanding of the motions of the molecules in crystals through their displacement by the strain. Results arising from the investigation of the proposed triclinic intergrowth phase in anthracene and the triboluminescence of acenaphthene are presented.

INTRODUCTION

The problem set by lattice dynamics is the understanding of the motions of molecules and atoms in a crystal and the consequences of those motions. To understand this requires the somewhat formidable task of obtaining the potential energy function of the lattice. While the formal theory has been quite well developed,[1] its application has normally been most successful in the study of crystals composed of atoms or quite small molecules. Molecular crystals present useful systems for study in spite of the apparently complicated nature of the molecular basis for the solids. This obtains because these crystals are largely held together by Van der Waals forces and are not complicated by extensive chemical bonding between the basis units themselves.

The determination of a useful set of interatomic potentials[2] has made it possible to perform useful calculations of the lattice energy. These have proven particularly effective in the calculation of the lattice dynamics of hydrocarbons. However, extension to more complicated molecules such as halogenated hydrocarbons has been more problematic. Much still remains to be learned about the lattice potentials of molecular crystals.

One of the major goals of lattice dynamical calculations is to obtain as complete a picture as possible of the motions of the molecules in the crystal. This is equivalent to determining the complete dispersion curves for the phonons. From the macroscopic point of view, it is important to determine the elastic constants such that both internal and external strains can be found. The two viewpoints are not, of course, independent.

Lattice dynamical theory is most commonly formulated in the harmonic approximation. However, many of the most interesting properties of crystals, such as phase transitions, arise from the anharmonicity of the lattice. This confronts lattice dynamical theory and subsequent calculations with a more difficult task.

The experimental approaches to the study of lattice dynamics are varied. Classical techniques are those such as calorimetry or various transport properties such as thermal conductivity. As usual, spectroscopy is expected to provide a more microscopic probe. The techniques range from the fairly common, such as Raman and infra-red spectroscopy, to the much less frequently used Brillouin and neutron scattering.

The techniques mentioned thus far are indirect since the motions of the molecules in the crystals must be inferred. A caveat must be made since with the increasingly shorter times of measurement being developed, it may be possible to obtain a more direct observation of these motions. The most powerful and common technique is solid state magnetic resonance spectroscopy. The limitation here is that the motions cannot be too rapid. With synchrotron radiation sources, it is possible to conceive of doing X-ray crystallography and observing more momentary positions of molecules but this is far from being accomplished.

PIEZOMODULATION SPECTROSCOPY

Recently, we have introduced a new spectroscopy for organic molecular crystals. It is based on the recognition that strain may be regarded as a manifestation of acoustic phonons and that these phonons may couple with other vibrations of the crystal. Put in a more analytical form:

$$e_{\alpha\beta} = \lim_{q_\beta \to 0} Q_\alpha(q,j)q_\beta$$

The piezomodulation spectroscopy employs a periodic stress applied to the crystal. The resulting optical signal is synchronous to the driving stress. By using this approach the crystals are kept in the elastic regime and the stress can be well clarified.

In recent theoretical studies[3] we have shown that the piezomodulation spectroscopies are capable of providing a great deal of information on the lattice dynamics of molecular crystals. Of particular use is the ability to apply the stress uniaxially. These spectroscopies are divided into two natural groups. These are the scattering and dipole allowed spectroscopies. The information obtained from them with the piezomodulation experiment are different but complementary.

Strain modulation of transition dipole processes, characterized by piezoreflection, provides measurement of two properties which relate directly to the motion of molecules in crystals. First, the experiment provides a method of determining the internal strains. The application of an external stress causes an external strain, **e**, which describes the deformation response of the lattice. These external strains provide no description of the adjustments made by the contents of the unit cells to the deformation. These changes are given by the internal strains, **W.**[1] They are of obvious interest in the understanding of intermolecular interactions since they describe the relative displacement of the molecules. The two may be related together by $\boldsymbol{\gamma}$, the appropriate coupling tensor:

$$\mathbf{W} = \boldsymbol{\gamma} : \mathbf{e}$$

The piezoreflection signal at a given frequency, $\xi_{\mathbf{b}}(\omega)$, takes a particularly simple form when the stress is along the b-axis of a monoclinic crystal:[3,4]

$$\xi_{\mathbf{b}}(\omega) = \Delta R(\omega)/R = 1\text{-}n^2(\omega)(4\pi n)^{-1} R_{22,\alpha\beta} \cdot e_{\alpha\beta}$$

$$\text{where: } R(\mathbf{q},\omega) = (\partial\,[\alpha(\omega)]^{-1}/\partial\,\mathbf{W}): \; + 4\pi\partial\,T(\mathbf{q})/\partial\,\mathbf{e}$$

The last expression is a form of the elasto-optic tensor which is particularly suited for this application. The two terms in the right side of the equation have different dependencies. The first involves the frequency dependence of the free molecule polarizability, $\alpha(\omega)$, while the second displays the wavevector dependence of the dipole-dipole interaction, T. The frequency dependent term is that which involves the internal strain and thereby shows how the internal strain will affect the bandshape of the piezoreflection signal. It is through this analysis of the shape of the piezoreflection response that the internal motions can be deduced. The procedure will be similar to that in crystal structure determination wherein a trial geometry is used to calculate the piezoreflection response and that result is compared to the measurement.

The piezoreflection data can also be used to determine the fraction of the applied mechanical energy that is "stored" by each mode through determination of the area under the piezoreflection response for a given mode.[3] This information may also be related to the motion of the molecules in the crystal.

In the piezoraman experiment the anharmonicity of the lattice can be explored. Here the information relates to the intermolecular interactions more than it does directly to the motions of the molecules themselves. Of course, they are closely related. The expression for the piezoraman signal is:

$$\chi_{jj'}(\omega) \simeq - \sum_{j'',j'''} \chi_{jj''}(\omega)\,\phi_{\alpha\beta,j''j'''}\,\chi_{j'''j'}(\omega)$$

The ϕ represents the coupling between the optical phonons arising from the strain. If the lattice is harmonic the coupling term would not exist and, therefore, there would be no piezoraman signal. So on the most primitive level, i.e., the presence or absence of signal, some assessment of the nature of the lattice potential can be made.

Since phase transitions are a manifestation of anharmonicity of the lattice, the piezoraman experiment can be used to explore these interesting phenomena. They are of additional interest since they also involve relative motions of molecules in the lattice. Strong distortion of the expected piezoraman response, which normally will appear to resemble a derivative, can be expected if a phase transition can be induced by strain over a given temperature range.

We report here initial results of studies of two phenomena which are related to the motions of molecules in crystals. The first is an investigation into the monoclinic to triclinic phase transition of anthracene. The second is a study of the anisotropy of triboluminesence from acenaphthene crystals.

PHASE TRANSITION OF ANTHRACENE

Anthracene has been reported to undergo a topotactic monoclinic to triclinic phase transition.[5] The triclinic phase appears to be an intergrowth which is induced by a shear resulting from a stress approximately normal to the (001) face. The phase has been identified through electron diffraction measured with an electron microscope.

In later work, Gramaccioli et al.[6] performed lattice dynamical calculations to determine the packing energies and lattice vibrational frequencies for both phases of anthracene. For the monoclinic crystal, correlation with respect to symmetry and energy can be made to the polarized Raman measurements made by Suzuki et al.[7] The two bands at 65 and 70 cm^{-1} are of interest since they are predicted to show the greatest shifts upon change of phase. The lower frequency band is predicted to shift approximately 10 cm^{-1} to the red and the higher 20 cm^{-1} to the blue. In the triclinic system the two transitions are totally symmetric while of the two, only the 70 cm^{-1} is A_g in the monoclinic crystal. The consequence of the symmetry in the monoclinic lattice is that the two bands can be cleanly separated by polarized Raman spectroscopy. Suzuki et al. have demonstrated this experimentally by showing that the 65 cm^{-1} but not the 70 cm^{-1} band is seen in the (ab) polarization configuration and the converse is seen for the (aa) geometry.

The piezomodulated Raman experiment can be used to further investigate this proposed phase transition. If the triclinic phase is strain induced, it may be expected to show structure in the 55 cm^{-1} region of the piezomodulation spectrum. Otherwise, the response will be expected to sharply peak around 70 cm^{-1} for the (aa) geometry.

The experiment was performed in a uniaxial configuration using apparatus described previously.[4] The modulation frequency was 200 Hz. The anthracene crystal was mounted such that the stress was along the a-axis. For the (aa) scattering geometry the incident light must be polarized parallel to the a-axis and the analyzer has the same polarization. The result is shown in Fig. 1 for the measurement at ambient temperature. The bandshape is not quite as derivative-like as expected and it is strongly skewed toward the low frequency region with some scatter at higher energy. Examination of the red side of the response shows that it lacks the distinct peak that is observed at 71 cm^{-1}. In Fig. 2 the spectrum taken after approximately one hour of modulation is shown. The change in the bandshape is quite evident with almost no derivative-like response seen but

FIGURE 1. (Left side) Piezomodulated Raman spectra of anthracene crystal at 300K.

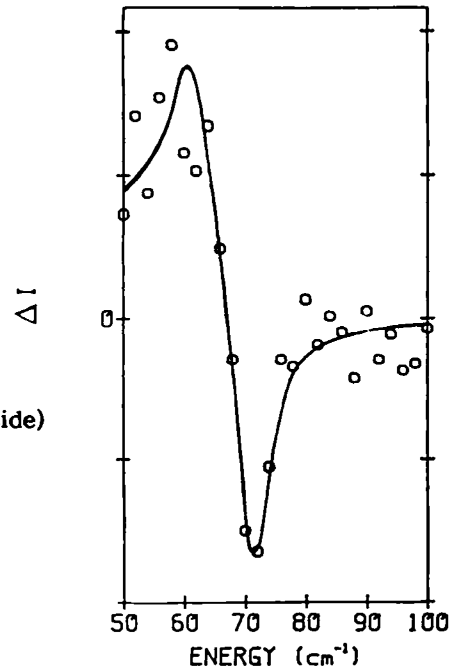
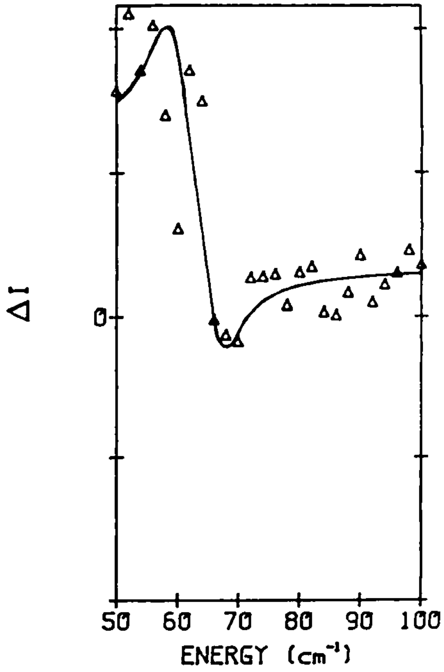


FIGURE 2. (Right side) Piezomodulated Raman spectra of anthracene crystal after one hour of modulation.



with the activity in the 55 cm^{-1} region still intense. Somewhat more intensity is observed at higher frequency also.

These results, although preliminary, support the presence of the triclinic phase in the monoclinic "host". While the strain of approximately 10^{-4} should be within the elastic regime of the crystal, it is obvious that after a time some relaxation, probably due to fatigue, occurs. The development of structure in the region where the shifted frequency is expected is in agreement with the expectation of the calculations as is the blue shift of the 70 cm^{-1} band. A problem arises when it is realized that the response characteristic of the monoclinic crystal is greatly diminished. This may be rationalized by considering that the size of the beam of about 50 square microns could be sampling a region where the triclinic phase is preponderant.

TRIBOLUMINESCENCE OF ACENAPHTHENE

Phase changes have been associated with numerous other phenomena. One of the most interesting is the emission of light which can occur during the phase transition. Since these transitions are induced by either temperature or pressure changes, the actual process is either one of pyroluminesence or triboluminesence. Neither of these processes are well understood. Two types of emission are observed: (1) that characteristic of the ambient gas, or (2) that characteristic of the crystal itself. The latter, which we shall refer to as intrinsic emission, may involve rearrangement and, in some cases, reaction of the molecules in the lattice.

Most of the characterization to date has been on powders or aggregates of crystals[8] because study of the single crystal is difficult. However, investigation of single crystals is necessary. A question of interest is whether an anisotropy in the emission can be observed and, if it exists, what its characteristics are.

We report here a preliminary investigation into these questions. To avoid complications in the initial part of the study, a crystal that does not undergo a phase transition was selected. Because of its ready and intense triboluminesence, acenaphthene, an orthorhombic crystal, was chosen.

The crystals studied were grown from methanol and were mounted similarly to the piezoraman measurements. The PZT piezoceramic used to apply the stress was driven at 250 Hz at 1500 V peak to peak. An RCA 1P28 photomultiplier tube, biased at 800 volts, was placed in front of the crystal. The photocurrent was monitored by a Kiethley electrometer whose output was sent to a strip chart recorder. These parameters were held constant for all of the experiments subsequently described.

In one set of experiments, the crystals were mounted such that the stress was in the [011] direction. The projections of the four molecules in the unit cell onto (011) are shown in Fig. 3. Emission was observed from the crystal only after a DC bias of 500 volts was applied. The pulse arising from this is shown on the right hand side of Fig. 4.

In the other set of experiments, the crystals were studied with the stress along [010].

In this case a pulse of light was observed with no bias but in the same elapsed time observed in the previous case. A typical example is shown in Fig. 4. Close visual inspection did not show sign of cracks in either set of experiments.

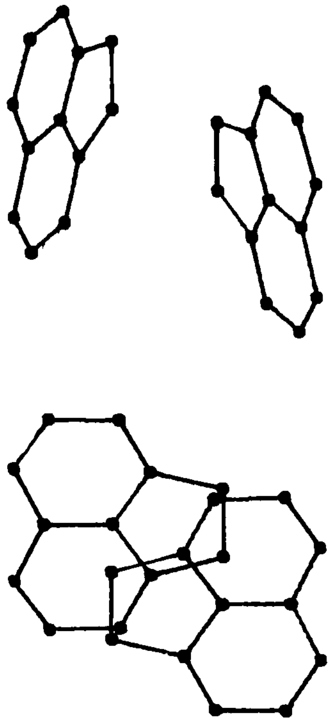


FIGURE 3. Projection of acenaphthene onto (011).

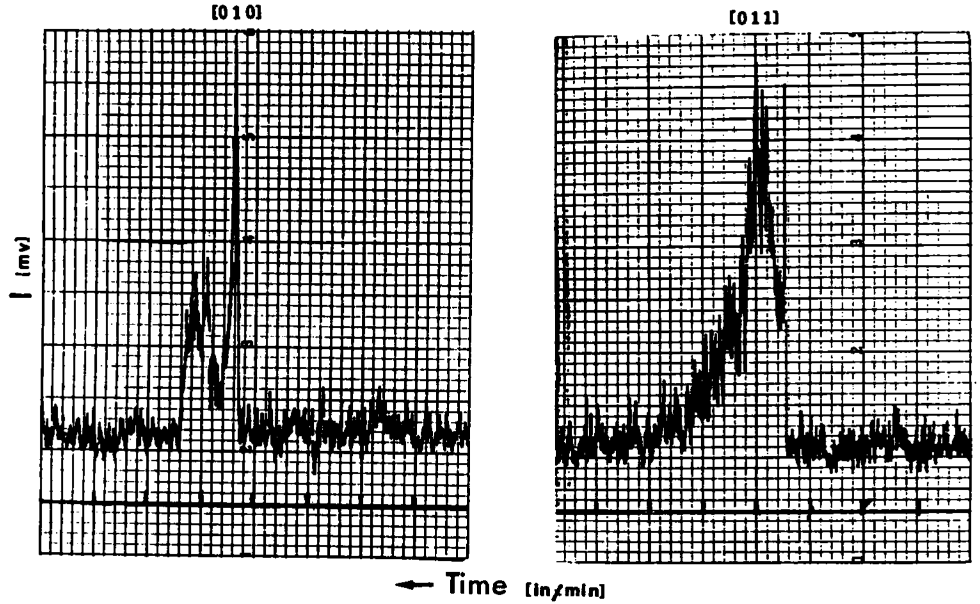


FIGURE 4. Left graph shows TL intensity of an acenaphthene crystal with stress along the b-axis. Right graph shows TL intensity of an acenaphthene crystal with stress along [011].

CONCLUSIONS

The piezomodulation experiments lend support to the presence of a triclinic intergrowth phase of anthracene. The change of samples' piezoraman response after approximately an hour of modulation is in accord with the model for the transition. The length of time involved would indicate that some fatigue of the sample is involved. Since the strain is within the elastic regime and the two bands under investigation are differently polarized, no great perturbation of the monoclinic 70 cm^{-1} band would be expected in this experiment. The fact that it is greatly altered argues that the stress needed to induce the proposed triclinic phase is not great.

In the case of the triboluminesence, quite different dependencies are observed. A strong static stress had to be applied to the acenaphthene crystal along [011] to observe emission while no such stress was required for the [010] direction. The intensity of the emission was essentially the same in both cases. Without the availability of elastic constants for the crystal, it is impossible to categorically claim that the triboluminesence response is anisotropic.

The piezomodulation experiment can be quite useful in the study of those solid state phenomena where the relative motion of molecules may be of importance. The uniaxial stress applied to the crystal is the perturbation which affects these motions of the molecules in the crystal.

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