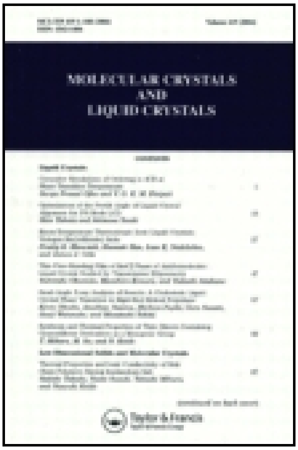

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Dynamics of Reactions in molecular Solids

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Version of record first published: 17 Oct 2011.

To cite this article: Paras N. Prasad & Jacek Swiatkiewicz (1983): Dynamics of Reactions in molecular Solids, Molecular Crystals and Liquid Crystals, 93:1, 25-39

To link to this article: http://dx.doi.org/10.1080/00268948308073513

Mol. Cryst. Liq. Cryst., 1983, Vol. 93, pp. 25–39
0026-8941/83/9304–0025/$18.50/0

Printed in the United States of America

DYNAMICS OF REACTIONS IN MOLECULAR SOLIDS

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Abstract The dynamics of several thermal and photochemical reactions in the solid-state are investigated by laser Raman spectroscopy, electronic spectroscopy and a rigid-body motion analysis of the thermal parameters of x-ray diffraction studies. Raman phonon spectroscopy along with electronic emission spectroscopy is used to identify the reaction mechanism. The possibility of occurence of any lattice and/or molecular intermediate is examined, by Raman spectroscopy of both phonons and intramolecular vibrations. The new concept of phonon-assisted reaction is tested by examining the role of an overdamped oscillation in a thermal reaction and that of a strong electron-phonon coupling in a photochemical reaction.

INTRODUCTION

Crystal engineering is a term which has widely been used in recent years in relation to solid state reactions[1,2]. This term emphasizes the prospect which the solid state reactions offer for the synthesis of novel monomeric and polymeric materials by a highly selective reaction pathway. The technique, widely used in the past, has been x-ray diffraction which yields space and time averaged results. Consequently, the details of reaction dynamics is lost in such averaging. In order to formulate dynamic requirements for reactivity in condensed phase, space-resolved and time-resolved studies of reactivity are needed. The spectroscopic studies, discussed in this paper, can conveniently be used for the study of dynamics of reaction.

The investigation utilizes mainly the approach of phonon spectroscopy, introduced recently by us[3-7], to derive information on reaction dynamics. Phonons are low frequency co-operative lattice vibrations of a solid and, therefore, probe the lattice interactions and dynamics directly. Phonons can be observed as optical transitions in the Raman spectra and in the electronic spectra (in the latter as a phonon side band). Some information regarding averaged librational and translational phonon motions can also be obtained from the rigid-motion analysis of the thermal parameters of x-ray diffraction studies.

This paper presents the study of dynamics of several thermal as well as photochemical reactions in solids. The experimental techniques used are electronic spectroscopy and laser Raman spectroscopy in conjunction with the thermal parameters of the x-ray diffraction studies. The presentation consists of the following parts: (A) Probes for the reaction mechanism; (B) Existence of any lattice and/or molecular intermediates; (C) Role of low frequency molecular motions; and (D) Selected examples of reactions.

A. PROBES FOR THE REACTION MECHANISM

The Raman phonon spectra, monitored as a function of the reaction progress, can conveniently be used to determine if a reaction occurs by a homogenous mechanism or by a heterogeneous mechanism[6]. The basic principle of this method is that the phonons are particularly sensitive to the organization of the aggregate on the molecular level and thus probe the immediate (local) structure of a given site. In the case of a homogeneous reaction, a solid solution forms between the reactant and the product.

The phonon spectra, in such a case, should show a monotonic change accompanied by broadening of the transitions as the reaction progresses. In the case of heterogeneous reaction, the phonon spectrum of the product superimposes on that of the reactant, and their relative intensities change with the advancement of the reaction. In the case where the reaction proceeds through an intermediate crystalline phase, a different phonon spectrum will be observed with the reaction in progress. Raman spectroscopy is applicable to all solid state reactions. Unfortunately, it is limited in its sensitivity, and is very useful in probing the conversion of > 1%.

In cases where the reactant and/or the product show electronic emission under the reaction conditions, the emission spectra can also be used to derive information on the reaction mechanism[7]. A homogeneous mechanism will create a homogeneous internal strain field as the reaction proceeds. This strain field will give rise to a shift of the emission maximum and a broadening of the spectral profile. Emission spectroscopy is highly sensitive and more suitable for the very initial stage of the reaction. The limitations of emission spectroscopy are the lack of detailed information regarding the chemical nature of the rearrangement, its dependence on the crystal quality, and the complication due to energy transfer. Therefore, emission spectroscopy can provide valuable information regarding the mechanism of the process at the initial state (< 1%) where the Raman method is not sensitive. After the initial state and throughout the conversion range (≥ 1%), Raman spectroscopy is the preferred technique for the investigation of the reaction.

B. EXISTENCE OF ANY LATTICE AND/OR MOLECULAR INTERMEDIATES:

A solid state reaction may involve a lattice intermediate or a molecular intermediate or both. The possibility of a lattice intermediate is more when a reaction is intermolecular in nature. Examples of such reactions are intermolecular rearrangements, and intermolecular aggregation (such as polymerization). The use of the technique of laser Raman spectroscopy permits us to investigate the possible existence of both types of intermediates. The reason is that, in the same experimental arrangement, we can obtain both the Raman phonon spectra and the intramolecular vibration spectra as a function of the reaction progress. The Raman phonon spectra are used as probes to investigate the occurrence of any lattice intermediates. The intramolecular vibrations give information on the existence of any molecular intermediates.

C. ROLES OF LOW FREQUENCY MOLECULAR MOTIONS:

Recently, we have introduced the new concept of phonon-assisted reaction[3,4]. In other words, a reaction in the solid state can be assisted by these low frequency cooperative molecular motions. The concept of the phonon-assisted chemical transformation bears a direct analogy to that of a phonon-assisted physical transformation in solid. Important phonon interactions can be divided in two categories: (i) Anharmonic phonon-phonon interactions and (ii) electron-phonon interactions.

One manifestation of the anharmonicity is the shift of phonon frequencies to lower values at higher temperatures[8]. This shift is also accompanied by a broadening (or damping) of the phonon transitions at higher temperatures. In some cases the shift behavior, called mode softening[9], leads to an overdamped oscillation where the amplitude of the motion along the soft-mode coordinate is large. In many systems such as a mode-softening creates a lattice instability which gives rise to a phase transition[9]. In a reactive system, large amplitude displacements, owing to mode-softening, are analogs of molecular collisions in a gas phase. Thus the mode-softening can be expected to assist in reactivity. This possibility has led us to propose the new concept of phonon-assisted reactions[3]. The role of phonon mode-softening in a thermal reaction can easily be investigated by Raman spectroscopy if the soft mode is a Raman-active optical mode. The mode softening can be observed as a gradual shift of the phonon frequency to the zero value accompanied by a rapid broadening of the transition with the increase of temperature. Some information about the co-ordinate of the soft mode can be derived from the thermal motion anisotropy observed in the thermal parameters of the x-ray diffraction studies.

The electron-phonon interaction arises because the electronic potential is a function of intermolecular separation[10]. Therefore, it is modulated by the intermolecular displacements occuring in a phonon motion. The electron-phonon interactions can give rise to phase-transitions such as metal-insulator transitions. Electron-phonon interactions can also assist photochemical reactions in solids[4]. Photochemical aggregation reactions, such as dimerization or polymerization reactions, can be assisted by the occurence of strong electron-phonon interaction in the reactive electronic state[4]. This strong electron-phonon interaction creates a local lattice-deformation in the reactive (excited) electronic state. The deformation traps the electronic excitation and, at the same time, it may provide a local preformation of the product lattice if the distortion is along the reaction co-ordinate. Both these features assist a photochemical aggregation reaction. Depending on the strength of the electron-phonon coupling one may observe the formation of a polaron or an excimer. The formation of a polaron does not lead to the loss of the identity of the monomer[4] in the excited state, but simply the excitation is localized by local lattice-deformation. The excimer formation requires a severe distortion of the local structure which leads to an excited state dimer. It may also be pointed out, that the polaron mechanism is a purely dynamic effect which can occur even in a defect-free lattice. In contrast, the excimer formation can occur either by a dynamic effect due to strong electron-phonon coupling or by a static effect due to sites deformed by the presence of defects.

The information on the formation of a polaron or an excimer is derived from the low temperature electronic absorption and emission spectra of the reactive crystals. The strong electron-phonon coupling in the reactive state manifests itself as a very strong phonon-side band in the liquid helium temperature spectra[10].

D. SELECTED EXAMPLES OF REACTIONS

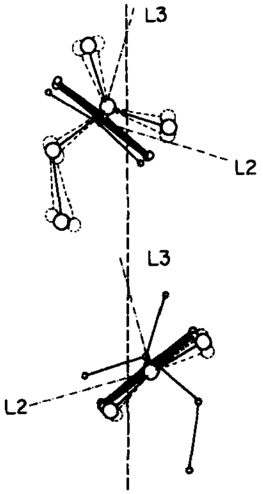
1. Thermal Rearrangement of Methyl-p-dimethylaminobenzene sulfonate.

Methyl-p-dimethylaminobenzene sulfonate (as MSE) undergoes a thermal rearrangement[11] in the solid state to form the product p-trimethylammonium benzene sulfonate (abbreviate as ZWT).

The reaction is intermolecular which involves the migration of an ester methyl group from the oxygen atom of a MSE molecule to the nitrogen atom of the neighboring molecule in the b crystallographic direction along which the molecules are stacked. The reaction is greatly accelerated when temperature is raised above room temperature.

The Raman spectroscopic study of the reaction progress shows no evidence of any lattice or molecular intermediate. During the conversion, a simple superposition of the phonon spectra of MSE and ZWT is observed[3]. Therefore, a heterogeneous mechanism is found for the conversion range sensitive to the Raman spectroscopy. This thermal reaction requires a co-operative intermolecular transformation. Both the thermal nature and the co-operative transformation make this reaction suitable to test the applicability of the model of a phonon-assisted reaction which involves mode softening. A temperature dependence study of the Raman phonon spectra reveals a mode-softening behavior for the 27 cm^{-1} phonon mode[3].

For further confirmation of the mode-softening and a possible identification of the molecular nature of the over-damped mode, we used the rigid-body motion analysis of the thermal parameters of the room temperature x-ray diffraction study. A thermal-motion analysis (TMA) program was used to calculate the components of the librational (L) and the translational (T) tensors with a least-square fit of the published thermal parameters[11] of all non-hydrogen atoms of the molecule. The librational frequencies were calculated by the method of Cruickshank[12], using the appropriate eigenvalues of the L-tensor and the corresponding moments of inertia. Figure 1 shows the results of this calculation.



	L1	L2	L3
AMPLITUDE DEG	8.5	3.5	2.8
LIBRATION FREQUENCY CM^{-1}	23.5	63.0	37.6
LATTICE MODES OBS. IN RAMAN	18	61.5	44

FIGURE 1. The projection of two neighboring molecules of MSE, in the plane containing the b-axis as the verticle axis. The phonon frequencies and amplitude calculated from the thermal parameters are displayed along with the frequencies observed in the Raman spectra.

The amplitude of libration along the L_1 axis is the largest. The corresponding librational frequency calculated by Cruickshank's formula is 23.5 cm^{-1}. On the other hand, the frequency of the 27 cm^{-1} soft mode at room temperature is 18 cm^{-1}. Considering the simplifying assumptions involved in the use of Cruickshanks formula, the agreement between the two values is reasonable. In other words, L_1 libration appears to be the soft-mode.

Figure 1 also shows the orientation of the two neighboring molecules of the stack along the b-axis along with their librational principal axes. The L_1-axis is perpendicular to the b-axis. The dashed lines refer to the methyl sulfonate group and the neighboring dimethyl amino group positions during the L_1 libration. It can be seen that during this libration the two reactive groups come close to each other. Therefore, a mode softening of the L_1 libration can assist this rearrangement reaction. We conclude from this thermal motion analysis in combination with the temperature effect on the Raman phonon spectra, that this reaction is phonon-assisted.

2. Thermal Rearrangement of Dimethyl-3,6-dichloro-2,5-dihydroxyterephthalate.

The thermal rearrangement of dimethyl-3,6-dichloro-2,5-dihydroxyterephthalate leads to the conversion of the yellow crystal (Y) to a white crystalline isomer (W). The two forms in the solid state differ both in the conformation of the carboxymethyl group and the nature of the hydrogen bond[13]. For this reason, the two forms have been classified as the chemical isomers. The conversion rate is highly dependent on the temperature. A search for any lattice or molecular intermediate by Raman study of this rearrangement reveals that when the Y-isomer crystals is converted to the W-isomer crystal at high temperature, the modes associated with the hydrogen-bond in the W-isomer do not show up immediately[7]. Once the crystal is cooled and left for some time, these modes appear. This observation suggests that, in the conversion of the Y-isomer to the W-isomer, the development of the intermolecular hydrogen bond is probably the last process involved in the rearrangement mechanism[7].

Because the crystals of the Y-isomer, fortunately, emit at the conversion temperature, both the electronic emission spectra and the Raman phonon spectra were used to investigate the reaction mechanism[7]. The emission spectra were recorded as a function of time at 383°K and results are shown in Figure 2.

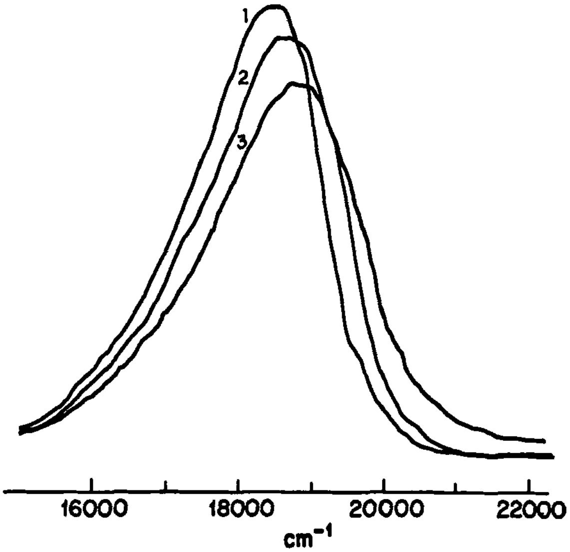


FIGURE 2. The emission spectra of the Y-isomer single crystal, monitored as a function of time, after raising the temperature of the crystal to 383 K. The spectra 1, 2, and 3 were obtained after 5, 100, and 175 minutes respectively.

The results of the emission studies were interpreted as follows[7]. During the initial phase of rearrangement, the reaction creates a homogeneous internal strain-field, which gives rise to the shift of the emission maximum and a broadening of the spectral profile. (c.f. curves 1 and 2 in Figure 2) This homogeneous internal strain may arise either from the formation of the W-isomer randomly distributed as a solid solution in the Y-isomer lattice, or from an intermediate structure which converts to the W-isomer later. As the rearrangement, at this stage, is too small to be probed by Raman spectroscopy, we cannot conclusively establish the exact nature of the rearrangement. In either case, the results of the study indicate that the rearrangement, at this initial state, involves a homogeneous mechanism. The distortion of the reactant lattice, created by further rearrangement, is severe enough to break the lattice and crack the crystal. However, despite the crystal fracture, the emission spectra show that the strain created within the reactant lattice still exists. (c.f. curves 2 and 3) Perhaps, a small phase separation of the W-isomer product may already occur at the state of the rearrangement. The process of phase separation of the W-isomer is evident when the Raman phonon spectroscopy becomes adequately sensitive to the conversion. At this conversion, the observed phonon spectra are found to be superposition of the unperturbed phonon bands of the Y-and the W-isomers which indicate a heterogeneous behavior. Therefore, the thermal rearrangements of the Y-isomer in the solid state is homogeneous only at the very initial state, which is not detectable by the sensitivity limit of Raman phonon spectroscopy.

We used the rigid motion analysis of the thermal parameters in conjunction with the Raman phonon spectra to make assignments of the phonon bands. The temperature dependence study of the phonon spectra of the Y-isomer did not show any phonon mode-softening. In this case, our study suggests that the rearrangement is defect-controlled, and not phonon-assisted.

3. Photodimerization of 2,6-Dimethylbenzoquinone.

The solid state photodimerization of 2,6-dimethyl-p-benzoquinone has been suggested to yield an oxetan type dimer as opposed to a cage dimer[14]. Our Raman study of this reaction supports the formation of an oxetan[4]. The Raman phonon spectra, obtained as a function of the advancement of the photodimerization, show that at the initial stage of the reaction, it proceeds by a homogeneous mechanism[4]. As the concentration of the product increases with the reaction progress, the lattice distortion leads to the product phase separations. The reaction then turns heterogeneous.

In order to investigate the phonon-assistance of the photodimerization process, the electron-phonon coupling in the photoreactive state ($^1n_\pi{*}$) was studied[4]. The electronic absorption spectra of the monomer crystal were obtained[8] at cryogenic temperatures. At 6 K, a sharp zero-phonon transition at 19952 cm^{-1} is accompanied by a strong phonon side band which appears to fit into a progression of a 65 cm^{-1} phonon. This study is interpreted in terms of a selective and strong electron-phonon coupling with a specific phonon mode which gives rise to the formation of a polaron. It, therefore, is in support of the concept of a phonon-assisted photodimerization process in the crystalline phase. A selective and strong electron-phonon coupling with a specific phonon, the co-ordinate of which is the reaction co-ordinate, can create a lattice distortion bringing the reactant molecules in a configuration to initiate the photoreaction (preformation of a dimer configuration).

4. Four-center Type Photopolymerization.

Four-center type photopolymerization in the crystalline state describes the reaction of a group of compounds containing a conjugated diolefinic group[19]. By photopolymerization, the crystal of the monomer is converted into crystals of linear polymer containing cyclobutane rings. Two specific compounds of this class are 2,5-distyryl pyrazine (abbreviated as DSP) and 1,4-bis(β-pyridyl-2-vinyl) benzene (abbreviated as P2VB). Two crystalline modifications of DSP are known, of which only the α-form is photoreactive. Both α-DSP and P2VB are isomorphic. In the past, the crystal packing has been used to demonstrate the application of topochemical principles which utilizes a static lattice picture and relates the reactivity to the separations of the reactive centers. The distance between the reactive double bonds of the neighboring molecules in α-DSP is 3.939 Å. This value for P2VB is shorter (3.910Å). Therefore, one would expect P2VB to be more reactive than α-DSP. Comparing the quantum yields listed by Hasegawa[15], the contrary is observed. This failure may be because the dynamic nature of the lattice is not considered.

The emphasis of our study was to examine if the differences in their reactivities could be related to the differences in the electron-phonon interaction in the excited states. It should, however, be worth mentioning that our Raman phonon study of the photopolymerization of α-DSP has revealed a heterogeneous mechanism[5]. Figure 3 compares the electronic absorption and emission spectra of α-DSP and P2VB. The absorption spectra of α-DSP consist of considerably broad bands (FWHH > 100 cm^{-1}) compared to those of the P2VB.

This width is not due to disorder, because the phonon spectra of α-DSP, at this temperature, reveals a highly ordered lattice. We, therefore, conclude that this large width is due to a strong electron-phonon coupling in α-DSP. Hence, the photopolymerization in α-DSP is assisted by a strong electron-phonon coupling. In contrast, the electron-phonon coupling in the reactive excited state of P2VB is not so strong.

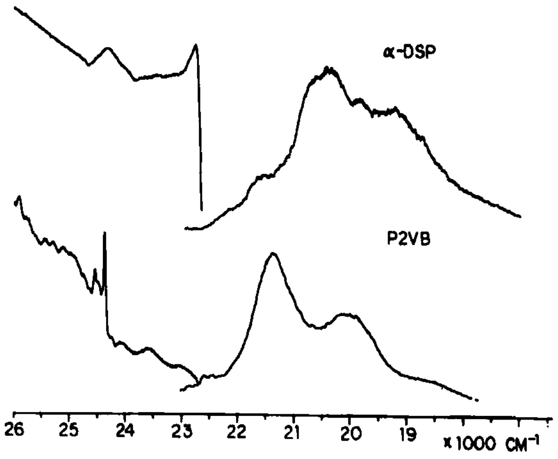


FIGURE 3. Electronic absorption and emission spectra of α-DSP and P2VB at 4.2 K are compared.

Comparing the emission spectra, both α-DSP and P2VB show broad excimeric emission. Therefore, the photopolymerization in both cases appear to be preceded by excimer formation. The occurrence of strong electron-phonon coupling in α-DSP (as inferred from the absorption spectra) suggests that the excimer formation is due to intrinsic dynamic process of local lattice relaxation because of this strong coupling with phonons. In the absence of such strong electron-phonon coupling in P2VB, we assign the excimer formation in this case to arise from the presence of defects. Therefore, the photopolymerization in α-DSP is assisted by the intrinsic process of strong electron-phonon coupling. In contrast, the photopolymerization in P2VB is suggested to be defected controlled.

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ACKNOWLEDGMENT

This work was supported by NIH Grant #1R01 GM 2735703.

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