



Laser Raman Spectroscopy: Application to Solid State Photoreaction In Organic Crystals

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Abstract

Laser Raman Spectroscopy has been used to study the crystalline state photoreaction in organic materials. It is shown that in many such cases the reaction is mediated by lattice phonons. Phonon participation in solid state photoreaction occurs either through a strong exciton-phonon coupling and polar on formation or through softening a low frequency phonon mode in the electronic excited state of the crystal. Some dimerization and polymerization reactions are discussed to emphasize the thesis.

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INTRODUCTION:

The reactivity of organic materials in the crystalline state when photo irradiated, depends on molecular packing arrangement in the lattice. The study of phonons provides information about the dynamic aspects of such reactions. According to Schmidt's "topochemical principle" the center to center distance between the reactive groups is to be less than 4.2Å for the reaction to occur. However, this upper limit is not very restrictive because of non availability of data in the range 4.2 - 4.7Å [1]. The another criterion is the parallelism of reactive double bonds. Though in many cases the potentially reactive groups are separated by a critical distance and the reacting double bonds are parallel, large number of solid state photoreactions show apparent violation of topochemical principle which suggests that topochemical principle is insufficient to account for many solid state reactions. Consideration of the orbital overlap rather than parallel double bond separation has been used to explain solid state photo reactivity [2, 3].

Phonon participation in solid state photoreactions are shown to occur through strong exciton phonon coupling or through a mode softening. In such reaction a strong exciton phonon coupling may result in the

molecule. This deformation can localize excitation. Furthermore, a local conformation which is precursor to the photodimer lattice to created by strong exciton-phonon coupling. The manifestation of strong exciton-phonon coupling in electronic spectra is the lack of fine structure and large Stokes' shift between the absorption and emission maxima or appearance of phonon side bands and line broadening.

In most of the order-order transitions, the structural distortions are characterized by an unstable or soft mode whose frequency goes towards zero value as the temperature approaches the phase transition temperature. In structural phase transitions the restoring force which opposes displacement goes to zero as the mode softens resulting in large amplitude displacement. In solid state photoreactions this large amplitude displacement can assist the reaction to occur by bringing molecules in favourable configuration. Solid state photoreactions in ortho methoxy trans cinnamic acid [4] and 7 methoxy coumarin [5] are the cases where mode softening is observed.

Raman phonon spectroscopic study gives information about reaction mechanism. If the difference between the phonon frequency of host pure crystal and impurity pure crystal is

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smaller than the phonon band width of the host, amalgamation of phonon results [6-9] which manifests as a monotonic shift of the phonon frequencies with increasing impurity concentration. Such a mechanism has been suggested for solid state photo polymerization of several diacetylenes [10-12]. Localized impurity bands also appear along with pure host bands when the perturbation caused by the impurity is large. In solid state photoreaction this situation gives segregated phonon spectra and the reaction mechanism is said to be heterogeneous. In some cases reaction mechanism is homogeneous in the initial stages and becomes heterogeneous as product concentration increases [13, 14].

Cohen has put forward the concept of "reaction cavity." emphasizing the role of nearest neighbours [15, 16]. The neighbours exert some 'pressure' on the wall of the cavity leading to some distortions. Those reactions which involve minimum change of the surface of reaction cavity are energetically favoured. This concept is very useful in predicting the product where more than one product is topochemically permitted.

The creation of an excited molecule by localized excitation introduces a local instability in the lattice configuration which may lead to large molecular displacements. The lattice instability helps go drive one molecule close to its neighbour promoting excimer and exciplex formation. Relaxation of this excimer or exciplex may result in ground state dimer.

EXPERIMENTAL

2, 6 Dimethyl p-Benzoquinone and 7 MC crystals were taken in petri-dish covered with a quartz plate and were photo irradiated by turning around periodically to ensure uniform exposure with HBO 200 watt high pressure mercury lamp. Other samples were taken in a pyrex container where the crystals were dispersed in an inert solution and 500 watt Xenon lamp (oriel) was used as irradiation source.

The UV absorption spectra were run on a Shimadzu UV-VIS 210A spectrophotometer and the emission spectra were recorded on a Perkin-Elmer MPF 44A spectrofluorimeter. Raman spectra were obtained using as Spex double monochromator model 1403 and the 5145Å line of Spectra Physics, Model 2020-5 Argon Ion Laser as the Raman excitation. Spex

Datamate 1B was used for spectrometer control data acquisition and analysis.

SPECIFIC SYSTEMS

(i) Dimerization of 2, 6 Dimethyl p-Benzoquinone:

In this crystal the nearest neighbour monomer geometry controls the interaction of two double bonds $>C=C<$ and $>C=O$ leading to an oxetan or a cage dimer. IR spectrum suggests that oxetan is the primary photoproduct.

From the phonon spectra as a function of reaction progress it is found that the monomer bands show significant shift on dimerization. Two new bands appear which gain in intensity with reaction progress and finally broad band having a little structure is observed. This suggests that in at low concentration the product form solid solution in the monomer lattice but as the reaction proceeds the product segregates out and forms its own lattice.

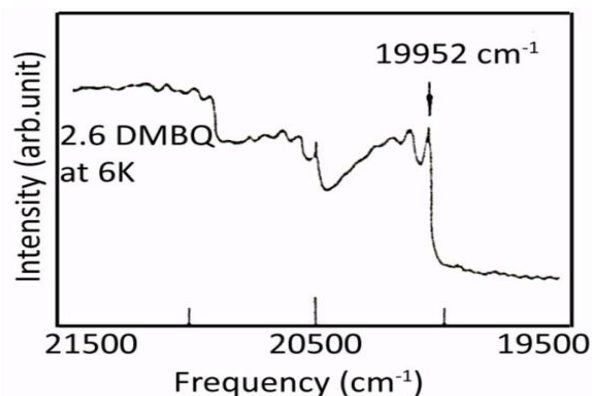


Fig. 1. Electronic absorption spectra of 2, 6 dimethyl p-benzoquinone crystal at 6K.

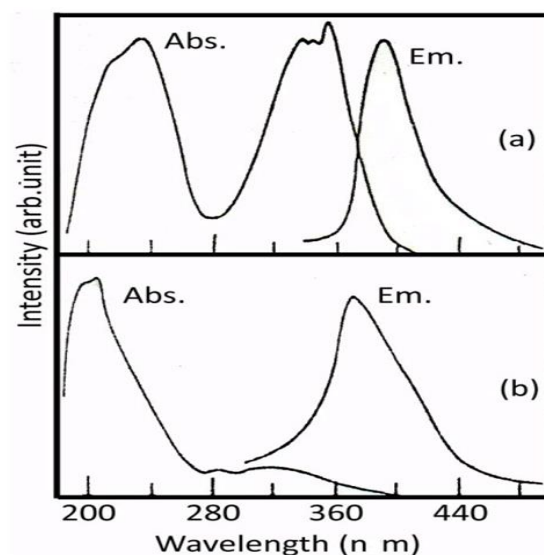


Fig. 2. Electronic absorption and emission spectra of (a) monomer and (b) dimer of 7-MC in solid film at 300K.



Electronic absorption spectra of 2, 6 Dimethyl p-benzoquinone at 6K is shown in fig.1. A zero phonon transition at 19952 cm^{-1} is observed with prominent phonon side bands which fit into a progression of 65 cm^{-1} phonon corresponding to one of the observed phonon bands at 62 and 67 cm^{-1} in the Raman spectrum. These observations indicate that in this reaction strong exciton-phonon coupling with a specific phonon mode results in the formation of polaron. This provides a local conformational change in the lattice is a precursor to the photoproduct lattice.

(ii) Dimerization of 7-Methoxy coumarin:

In 7-Methoxy coumarin (7MC) apparent violation of Schmidt's topochemical criteria is observed. Here the reactive double bonds of two nearest neighbour 7 MC molecules in the lattice are rotated by 65° with respect to each other [17], The symmetrical head-tail dimer is the only photoproduct [18].

The blue shift of the broad absorption band with $A_{\text{max}} = 354\text{ nm}$ with dimerization is due to the loss of conjugation. Considerable overlap between emission and absorption spectra as shown in fig.2 suggests that exciton phonon coupling is rather weak in this crystal.

The Raman phonon spectra (fig.3) show that the 19.8 cm^{-1} bands gradually shifts to lower frequency on reaction progress and finally disappears in the Rayleigh wing and all other phonon bands broaden appreciably with no significant shift in frequency. So the photoreaction is assisted by softening of this phonon mode. The 19.8 cm^{-1} is likely to arise from librational motion of monomer molecules around Lz axis and this may bring the reactive double bonds of the molecular pair in a favourable configuration for the reaction to occur.

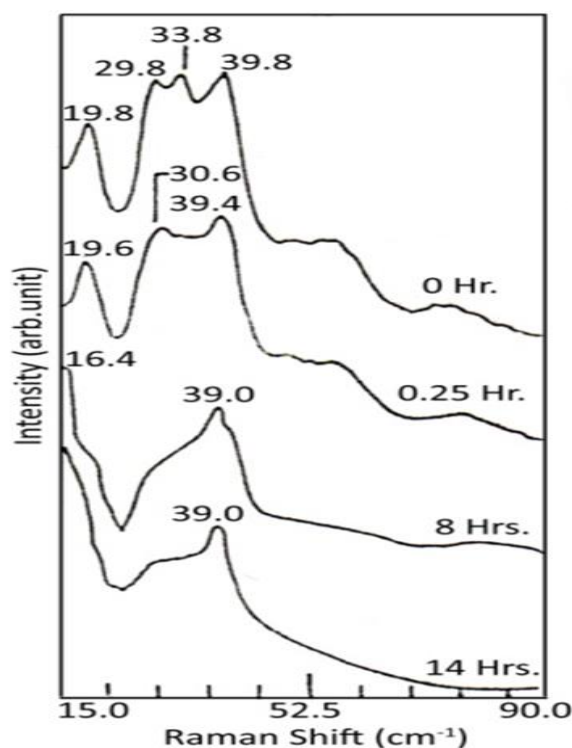


Fig. 3. Raman phonon spectra of 7-MC crystal with reaction progress at 300K.

(iii) Polymerization of dimethyl ester of α, α' dicyano p-phenylene diacrylic acid:

The molecule contains two unsaturated centers. Here four center type polymerization occurs on photo irradiation.

The electronic excitation and emission spectra of monomer and polymer are shown in fig.4.

The monomer emission peaks are at 462 and 497 nm. The excitation peaks are at 363 and 394 nm. The large Stoke's shift is a clear indication of exciton phonon coupling caused by strong lattice distortion in the excited state and the photoreaction is likely to be phonon mediated.



Raman phonon spectra with reaction progress are given in fig.5. In initial stages with reaction progress the intensity of the bands decrease and the bands shift towards higher wave numbers. So the reaction mechanism is homogeneous in the initial stages. Progressive broadening of phonon spectra with reaction suggest increasing lattice disorder and the absence of any phonon bands after 14h of irradiation indicates amorphous nature of polymer.

(iv) Polymerization of diethyl ester of p-phenylene diacrylic acid:

The photoproduct is a high molecular weight polycrystalline powder as evidenced from 20 cm^{-1} shift of $\text{C} = \text{O}$ stretching mode on polymerization [19].

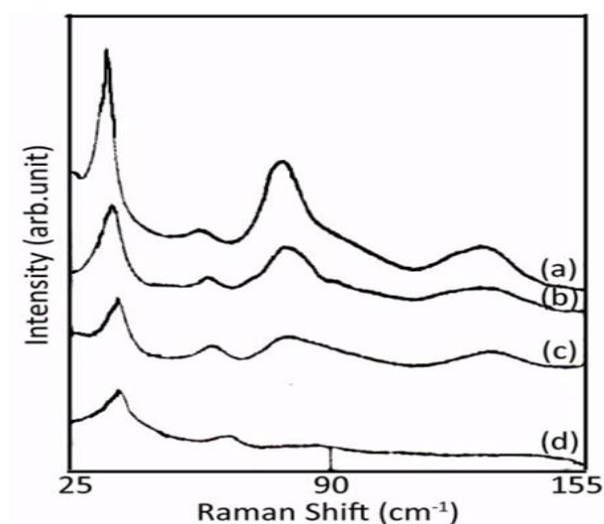


Fig. 4. Electronic excitation and emission spectra of (a) monomer (b) polymer of p-CPAME at 77K.

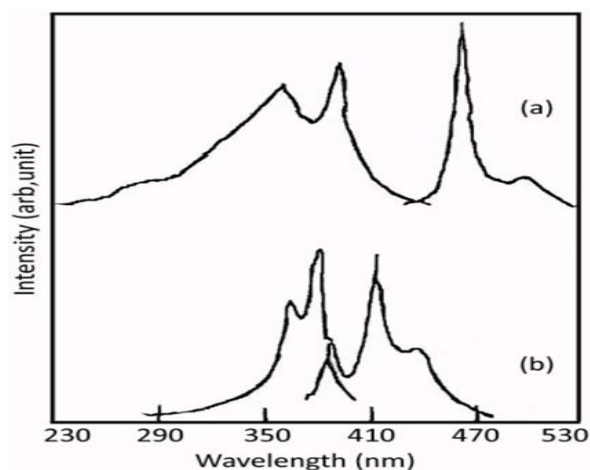


Fig. 5. Raman phonon spectra of p-CPAME polycrystals with reaction progress. a \rightarrow d are in the increasing order of reaction. (Exposed for a: 0 min., b: 120 min., c: 240 min., d: 360 min).

The emission and the excitation spectra of the monomer and the polymer crystal at 77K are shown in Fig. 6. It is observed that the emission spectrum of the monomer is well structured with (0,0) band at 362 nm and strong vibrational peaks. The exciton-phonon coupling is weak in the monomer lattice as evidenced from the appearance of fine structures in the emission spectrum and overlapping between emission and excitation spectra. So the lattice phonon is unlikely to play any significant role in this polymerization reaction.

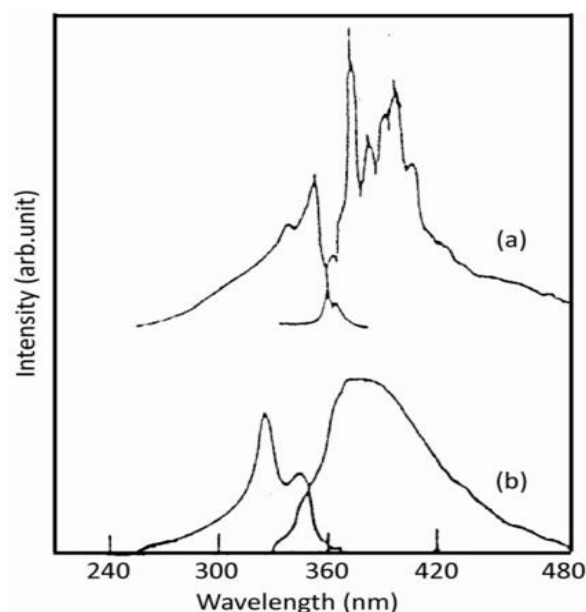


Fig. 6 Electronic excitation and emission spectra of (a) monomer (b) polymer of p-PDAEt at 77K.

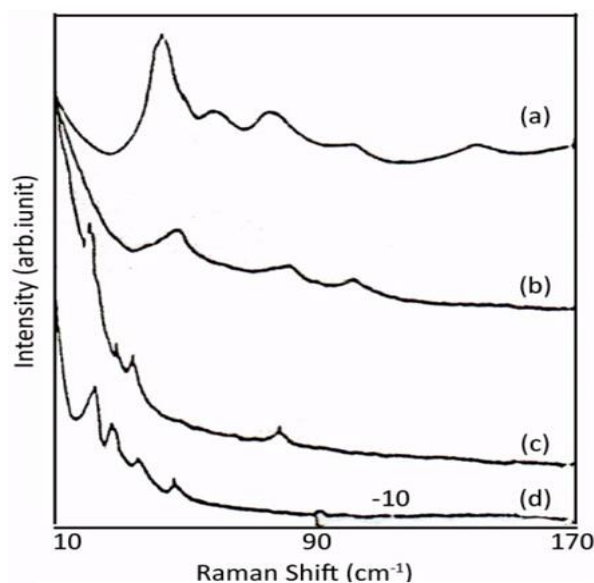


Fig. 7 Raman phonon spectra of p-PDAEL polycrystals with reaction progress. A \rightarrow d are in the increasing order of reaction. (Exposed for a: 0 min., b: 60 min., c: 12min. d: 180 min).



The Raman phonon spectra at different reaction stages are shown in fig.6. Frequency shifts and broadening of phonon modes in the initial stages point to the homogeneous nature of initial reaction mechanism and also to some lattice disorder originating from oligomer formation. In the later stages, phase separation between the reactant and the product is confirmed by the appearance of new sharp bands. This sharp feature indicates that the final polymer lattice is highly ordered.

CONCLUSION:

This article focuses on the role of phonon motion in deriving the dynamic concept of reactivity and the mechanism of solid state photoreaction. Phonon participation in such reactions may occur through strong exciton-phonon coupling or through a mode softening. In some reactions lattice phonon does not influence reactivity significantly. The reaction mechanism may be homogeneous or heterogeneous depending on solid solution formation or phase separation respectively. In many cases mixed behaviour is also observed.

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