

## Phonon mediation of solid state photoreaction: Photodimerization of *o*-methoxy cinnamic acid<sup>†</sup>

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**Abstract.** The solid state photodimerization reaction of *o*-methoxy cinnamic acid is shown to be mediated by a lattice phonon. The phonon participation, in this case, is through a mode softening and not through strong exciton-phonon coupling as is generally observed. Raman phonon spectroscopy suggests that the reaction is heterogeneous. Infrared spectroscopy has been used to study the internal vibrations of the reactant and the product.

**Keywords.** Solid state photoreaction; phonon mediated reaction; mode softening; spectroscopic studies of photoreactions; *o*-methoxy cinnamic acid.

### 1. Introduction

We have used the laser Raman phonon spectroscopic technique to study the crystalline state photoreaction in a number of systems (Misra and Prasad 1982; Ghosh and Misra 1985, 1987). It has been shown that strong exciton-phonon coupling is involved in the photodimerization reaction of 2,6-dimethyl-*p*-benzoquinone (Misra and Prasad 1982) and *p*-formylcinnamic acid crystals (Ghosh and Misra 1985). We have now extended our studies to the photodimerization reaction of *o*-methoxy cinnamic acid (MCA). MCA when irradiated in the crystalline state, dimerizes to give (1 $\alpha$ , 2 $\alpha$ , 3 $\beta$ , 4 $\beta$ )-2,4-bis(*o*-methoxyphenyl)-1,3-cyclobutanedicarboxylic acid, a centrosymmetric cyclobutane derivative (Cohen *et al* 1964) and the reaction is considered to be topochemically controlled. To study the role of the lattice phonon in this reaction and to see if the reaction is homogeneous or heterogeneous at the molecular level, we have used laser Raman phonon spectroscopy sampled as a function of reaction progress. Electronic absorption spectroscopy has been used to determine the extent of reaction progress. Intramolecular vibrations of the monomer and the dimer have been studied by infrared spectroscopy and this has been used to study the mechanism of the reaction.

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## 2. Experimental

MCA samples purchased from Aldrich, USA, were purified by repeated crystallization from spectro-grade methanol (Merck). Purified MCA was taken in a Petri dish covered with a quartz plate and was irradiated by a 500 W xenon lamp. For our set up, almost complete dimerization of the sample was achieved in  $\sim 50$  h of irradiation. Samples were taken out at different stages of reaction-progress and studied.

The UV absorption spectra were run in a Shimadzu UV VIS 210 A spectrophotometer. The emission spectra were run in a Perkin-Elmer MPF 44A spectrofluorimeter. The infrared spectra were recorded in a Perkin-Elmer 783 IR spectrophotometer. The Raman spectra were recorded on a Spex Ramalog 1403 spectrophotometer and excited with 5145 Å line of  $\text{Ar}^+$  laser.

## 3. Results and discussion

### 3.1 Study of internal vibrations of reactant and product by infrared spectroscopy

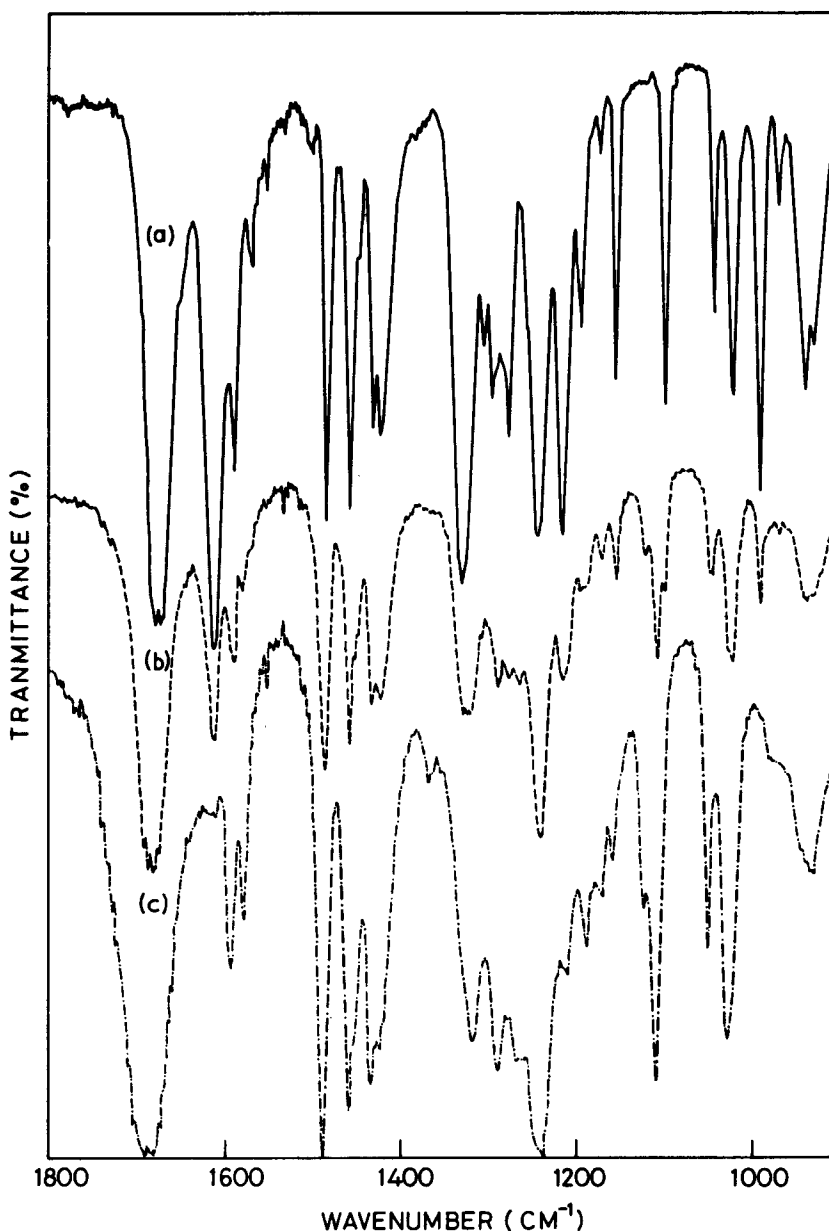
The infrared spectra of MCA crystals at different stages of reaction progress in KBr pellets are shown in figure 1. The aliphatic C=C stretching mode at  $1621\text{ cm}^{-1}$  is intense in the monomer. With the extent of dimerization the intensity of this band decreases and this band disappears in the dimer crystal. Also the HC=CH *trans*-vibrations at  $992\text{ cm}^{-1}$  show similar behaviour. Disappearance of this olefinic double bond supports cyclobutane ring formation. Some cyclobutane ring vibrations such as cyclobutane ring stretching at  $1109\text{ cm}^{-1}$ , do indeed appear in the infrared spectrum of the dimer crystal. The observed IR bands of the monomer, partially dimerized and dimer crystals are listed in table 1 and partial assignment of the bands is made.

### 3.2 Electronic spectral change with progress of reaction

The progress of the dimerization reaction of MCA was monitored by electronic absorption spectroscopy. The monomer in methanol solution at room temperature has two broad absorption bands with maxima at 270 and 315 nm. With reaction-progress the intensity of the 315 nm band decreases in intensity and disappears when the reaction is almost complete. This is shown in figure 2.

MCA shows fairly strong fluorescence emission in the crystalline state but no phosphorescence is observed. In figure 3, low temperature (77 K) emission spectra of MCA crystals at different stages of the reaction are shown. The monomer fluorescence is structured and shows three distinct band maxima at 371, 384 and 405 nm (figure 3a) with a number of humps in-between. In the partially dimerized crystal, the emission loses its structure and a broad band with  $\lambda_{\text{max}}$  at 396 nm is observed (figure 3b). There is, however, no change in the spectral position. When the dimerization reaction is almost complete, the fluorescence emission broadens further and the band maxima shifts to 380 nm (figure 3c).

This spectral behaviour is similar to that observed in the case of the thermal rearrangement reaction of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate crys-



**Figure 1.** Infrared absorption spectra of MCA crystals in KBr pellet (a) monomer, (b) partially dimerized, and (c) dimer.

tals (Swiatkiewicz and Prasad 1982). Such broadening and shift of the emission band on progress of the reaction may be either due to a homogeneous internal strain field created by the photoreaction process where the photodimers formed are randomly distributed as a solid solution in the monomer lattice or it may arise from an intermediate structure formed before completion of dimerization. In view of the heterogeneous mechanism of the reaction, as revealed by Raman phonon spectra

**Table 1.** Infrared bands observed in monomer, partially dimerized and dimer forms of MCA.

Monomer	Part dimer	Dimer	Assignment
372	365	–	M C–O–C stretching
	380		M
458 ( <i>sh</i> )			M
469 ( <i>s</i> )	469 ( <i>ms</i> )		
	480 ( <i>sh</i> )	480 ( <i>sh</i> )	D
	538 ( <i>w</i> )	538 ( <i>w</i> )	D
565 ( <i>s</i> )	567 ( <i>ms</i> )	569 ( <i>ms</i> )	
	592 ( <i>sh</i> )	592 ( <i>sh</i> )	D Cyclobutane ring bending
595 ( <i>s</i> )	595 ( <i>ms</i> )	595 ( <i>ms</i> )	
	645 ( <i>w</i> )	646 ( <i>ms</i> )	D Cyclobutane ring deformation
696 ( <i>s</i> )	696 ( <i>ms</i> )		M
	730 ( <i>sh</i> )	730 ( <i>sh</i> )	D Cyclobutane ring deformation
757 ( <i>vs</i> )	753 ( <i>vs</i> )	750 ( <i>vs</i> )	
779 ( <i>s</i> )	776 ( <i>w</i> )		M
	790 ( <i>w</i> )	792 ( <i>ms</i> )	D C–C skeletal stretching
849 ( <i>w</i> )	849 ( <i>w</i> )	849 ( <i>w</i> )	
877 ( <i>s</i> )	877 ( <i>w</i> )		M
932 ( <i>sh</i> )	936 ( <i>ms, b</i> )	930 ( <i>ms</i> )	
940 ( <i>s</i> )			
971 ( <i>ms</i> )	969 ( <i>vw</i> )	969 ( <i>sh</i> )	
992 ( <i>vs</i> )	992 ( <i>ms</i> )		M HC=CH trans
1023 ( <i>s</i> )	1023 ( <i>ms</i> )	1029 ( <i>s</i> )	C–H bending
1043 ( <i>s</i> )	1045 ( <i>ms</i> )	1049 ( <i>ms</i> )	
1099 ( <i>vs</i> )	1099 ( <i>sh</i> )		M
	1108 ( <i>ms</i> )	1109 ( <i>vs</i> )	D Cyclobutane ring stretching
	1121 ( <i>sh</i> )	1122 ( <i>sh</i> )	D
1154 ( <i>vs</i> )	1154 ( <i>w</i> )	1159 ( <i>w</i> )	C–Ph ring stretching (ethylenic)
1172 ( <i>w</i> )	1170 ( <i>w</i> )	–	
1195 ( <i>ms</i> )	1190 ( <i>w</i> )	1188 ( <i>w</i> )	
1218 ( <i>vs</i> )	1215 ( <i>w</i> )	1210 ( <i>w</i> )	
1246 ( <i>vs</i> )	1241 ( <i>s</i> )	1241 ( <i>s</i> )	C–O stretching
–	1265 ( <i>w</i> )	1265 ( <i>w</i> )	D OH in plane bending
1279 ( <i>ms</i> )	1279 ( <i>w</i> )		
	1289 ( <i>w</i> )	1289 ( <i>ms</i> )	D
1297 ( <i>ms</i> )	1297 ( <i>sh</i> )	–	
1306 ( <i>ms</i> )	1306 ( <i>sh</i> )	–	
1331 ( <i>vs</i> )	1322 ( <i>s</i> )	1318 ( <i>s</i> )	Carbonyl O–H out of plane bending
1421 ( <i>s</i> )	1421 ( <i>s</i> )	1423 ( <i>sh</i> )	Carbonyl O–H in plane bending
1431 ( <i>ms</i> )	1431 ( <i>ms</i> )	1436 ( <i>ms</i> )	
1458 ( <i>vs</i> )	1458 ( <i>s</i> )	1458 ( <i>s</i> )	C=C ring stretching (aromatic)
1485 ( <i>vs</i> )	1487 ( <i>vs</i> )	1489 ( <i>vs</i> )	C=C ring stretching (aromatic)
1569 ( <i>w</i> )			M
	1578 ( <i>w</i> )	1579 ( <i>ms</i> )	D
1590 ( <i>ms</i> )	1590 ( <i>ms</i> )	1592 ( <i>ms</i> )	C=C symmetric stretching of benzene ring
1612 ( <i>vs</i> )	1612 ( <i>s</i> )	–	C=C stretching (aliphatic)
1675 ( <i>vs</i> )	1685 ( <i>vs</i> )	1689 ( <i>vs</i> )	C=O stretching

Abbreviations: *sh*–shoulder, *s*–strong, *ms*–medium strong, *vs*–very strong, *w*–weak, *vw*–very weak, *b*–broad.

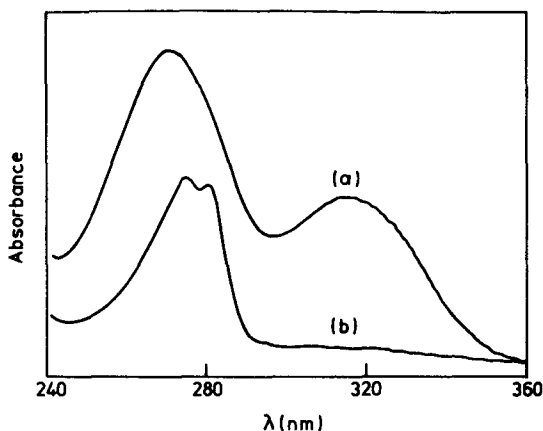


Figure 2. Electronic absorption spectra of MCA in methanol at room temperature (a) monomer, (b) dimer.

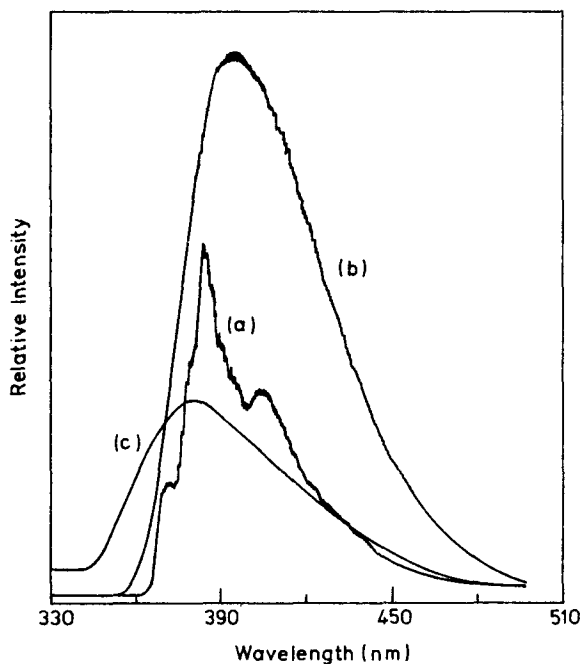
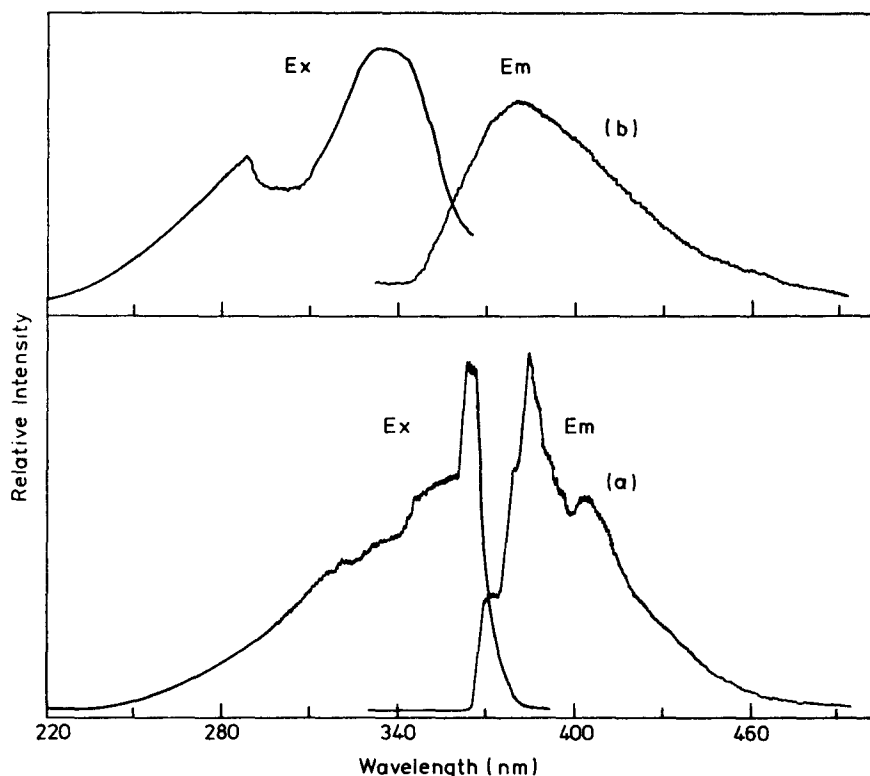


Figure 3. Emission spectra of MCA crystals at 77 K (a) monomer, (b) partially dimerized, and (c) dimer.

discussed below, the fluorescence spectral behaviour is likely to be due to some intermediate structure formation before phase separation of the product and the reactant occurs. Otherwise the fluorescence emission characteristic may represent the initial stage of reaction when concentration of the product is low and the reaction mechanism is homogeneous. Raman spectroscopy may fail to provide information about the initial stage of reaction when the product concentration is low.

In figure 4 we show the emission and fluorescence excitation spectra of monomer and dimer crystals. It is observed that the origin of the excitation and the emission



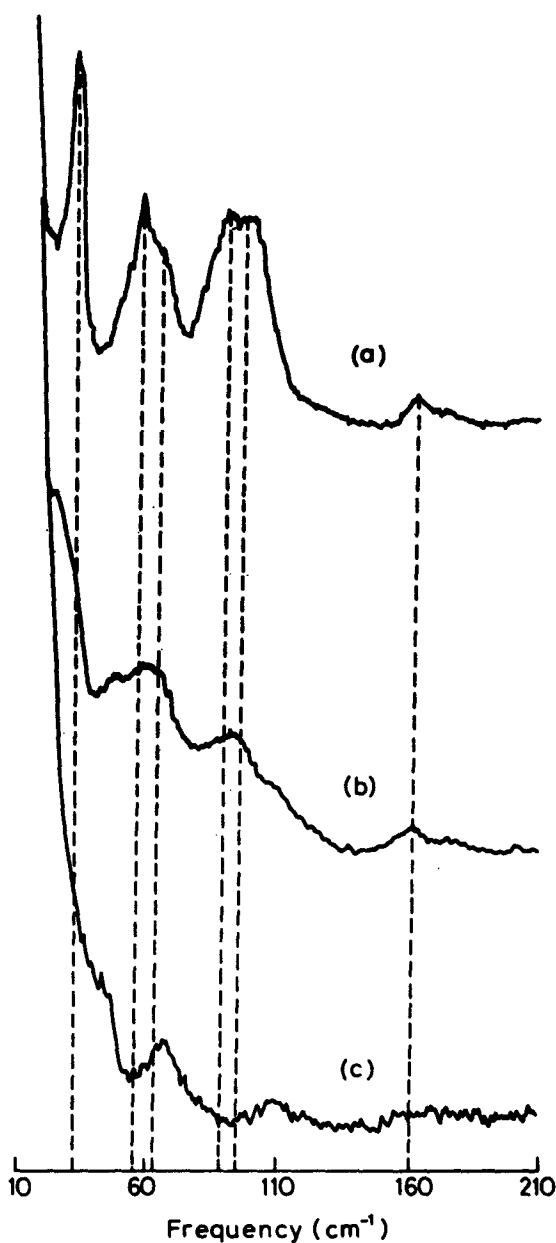
**Figure 4.** Overlap of emission and excitation spectra of (a) monomer, and (b) dimer crystal of MCA.

overlap in both the cases. This absence of significant Stokes' shift suggests that exciton-phonon coupling is weak in this case. This observation is different from our earlier observation in photodimerization reaction of 2,6-dimethyl-*p*-benzoquinone and *p*-formylcinnamic acid.

### 3.3 Raman phonon spectral change during reaction-progress

The phonon spectra of MCA at different stages of reaction progress are shown in figure 5. In the monomer, spectral bands are observed at 32.5, 57.5, 65, 89, 95.5 and 160  $\text{cm}^{-1}$ . With progress of the reaction, the sharp monomer phonon band at 32.5  $\text{cm}^{-1}$  in (a) shifts to lower frequencies (27  $\text{cm}^{-1}$  in (b)) and finally disappears in the dimer spectrum. We believe that this is not due to rise in the Rayleigh background. This has been checked using some chemically stable systems as was done by Dwarkanath and Prasad (1980). We thus conclude that the experimental observation suggests softening of the 32.5  $\text{cm}^{-1}$  phonon mode with reaction. It is suggested that the reaction is mediated by this phonon.

The soft mode theory of structural phase transition was introduced by Cochran (1959). The basic idea of mode softening is that one of the normal lattice modes becomes unstable due to phonon-phonon interaction and its frequency decreases with temperature. The restoring force softens unless the phonon condenses into the lattice to cause a structural phase transition. Mode softening also produces large



**Figure 5.** Raman phonon spectra of MCA crystals (a) monomer, (b) partially dimerized, and (c) dimer.

amplitude displacements which are analogues of molecular collisions in the gas phase and thus can assist reactivity. Dwarkanath and Prasad (1980) first showed that in the thermal rearrangement reaction of methyl *p*-(dimethyl-amino) benzenesulphonate into *p*-(trimethylammonium) benzenesulphonate zwitterion, a particular phonon frequency at  $27\text{ cm}^{-1}$  shifts to a lower frequency and finally merges into the Rayleigh wing as the temperature is raised and the reaction

progresses. Eyster and others (Eyster and Prohofsky 1977) applied the method of mode softening to the nonthermal  $B \rightarrow A$  conformation change in the DNA double helix. The change can be brought about by reducing the polar nature of the solvent. The effect of decreasing the dielectric shielding on electrostatic interaction between regions of unbalanced charge and on the Van der Waals' interaction between atoms does cause the mode to soften. It now appears that photoexcitation of the crystal may also bring about similar effect. Observation of soft mode mediation in the solid state photoreaction is new.

The other features of phonon spectra show that in the partially dimerized crystal (figure 5b), the monomer phonon bands lose their intensity and new phonon bands appear at 49, 68 and  $110\text{ cm}^{-1}$ . When the reaction is almost complete, the monomer phonon bands disappear and a new phonon spectrum is observed (figure 5c) with bands at 49, 68,  $110\text{ cm}^{-1}$ . The appearance of segregated phonon spectra in the partially dimerized crystal suggests that the reaction is heterogeneous in character in the final stage and the reactant and the product form separate lattices.

Thus we conclude that in the crystalline state photodimerization reaction of *o*-methoxycinnamic acid, the phonon participation is through a mode softening and not through strong exciton-phonon coupling as is generally observed.

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