# Laser Raman spectroscopic study of photoreaction dynamics in p-chloro cinnamic acid crystal

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**Abstract.** Raman phonon spectroscopy has been used to study photodimerization reaction in p-chloro cinnamic acid (pCCA) crystal. The β-form of the crystal yields the 4, 4'-dichloro-β-truxinic acid dimer. Six distinct low frequency phonon bands are observed in the pCCA monomer crystal. On reaction progress, these bands show a monotonic shift to lower frequencies and broaden out. Finally, in the dimer crystal the phonon spectrum shows two weak broad bands. These results suggest that the reaction is homogeneous in the initial stages and, as the product concentration increases, the lattice becomes highly disordered. The reactant and the product were characterised by infrared and Raman spectroscopy. The disappearance of aliphatic C=C bond stretching vibration and appearance of cyclobutane ring deformation and cyclobutane ring-breathing vibrations on reaction confirm photo-dimerization by cyclobutane ring formation. The large Stoke's shift between the absorption and emission band suggest strong exciton–phonon coupling in the monomer lattice. This reaction seems to be phonon-mediated.

**Keywords.** Solid state photoreaction; phonon-mediated reaction; mode softening; p-chloro cinnamic acid crystal.

## 1. Introduction

The photoreaction in organic crystals is known to be topochemically controlled and the reactivity and the stereochemistry of the product depend on the arrangement of the molecules in the lattice (Cohen and Schmidt 1964; Schmidt 1964, 1971). Like many cinnamic acid derivatives, p-chloro cinnamic acid (pCCA) also undergo photodimerization reaction in the crystalline state (Schmidt 1964) and this reaction is also thought to satisfy the topochemical principle. In recent years a large number of photoreactions in organic crystals have been reported which do not conform to this principle. In some photodimerization reactions, reacting double bonds of the molecular pair are either nonparallel (Patel et al 1980; Theocaris et al 1984; Hasegawa et al 1984; Gnanaguru et al 1985; Bhadbhade et al 1984) or their separation is beyond the accepted topochemical limit of 4·2 Å (Gnanaguru et al 1984; Nakanishi and Hasegawa 1985). Molecular motions in the lattice is, therefore, thought to influence their photoreactivity. The influence of orientational flexibility of the reactive molecules and the influence of their environment in the crystal in the photoreaction have been

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considered (Murthy *et al* 1987). Indeed many crystalline state reactions have been confirmed to be mediated by lattice phonons (Misra and Prasad 1982; Ghosh and Misra 1985; Misra 1989). In earlier communications (Ghosh and Misra 1986, 1988) it was shown that the photodimerization reaction in *o*-methoxy cinnamic acid crystal is mediated by softening of a specific phonon mode in the excited state of the crystal. Photoreaction in *p*-CCA crystal may as well be phonon-mediated and in the present investigation we have attempted to examine this aspect of the problem by laser Raman spectroscopy. In this paper we report our experimental results.

## 2.  Experimental

*p*CCA samples purchased from Aldrich, USA, were purified by repeated crystallization from glacial acetic acid.

    Purified *p*CCA was taken in a petri dish covered with a quartz plate and was irradiated using a 200 W high pressure mercury lamp. Samples were taken at different stages of reaction progress and studied.

    The UV absorption spectra were run on a Shimadzu UV–VIS 210A spectro-photometer. The emission spectra were run on a Perkin–Elmer MPF 44A spectro-photometer. The infrared spectra were recorded on a Perkin–Elmer 783 IR spectro-photometer. Raman spectra were obtained using a Spex double monochromator model 1403 and the 5145 Å line of Spectra Physics, Model 2020-5 Argon Ion Laser as the Raman excitation source. Spex Datamate 1B was used for spectrometer control, data acquisition and analysis.

## 3.  Results and discussion

*p*CCA crystal belongs to the space group $P2_{1/a}$ with four molecules in the unit cell (Schmidt 1964). The lattice parameters are $a = 32.0$ Å, $b = 3.87$ Å, $c = 6.56$ Å, $\beta = 83°$ and $d = 1.460$. Crystals grown from acetone solution are of the $\beta$-form with two nearest neighbour molecules along the *b*-axis being related by mirror symmetry. The contact distance of the aliphatic C=C bonds between them is the *b*-axis distance of 3.87 Å. Photoirradiation of the crystal yields mirror symmetric dimer 4, 4'-dichloro-$\beta$-truxinic acid (Cohen *et al* 1964). The structures of the monomer and the dimer molecules are shown in figure 1.
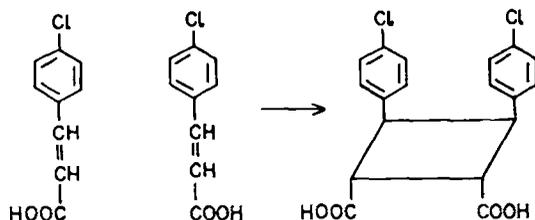


**Figure 1.**   Chemical structure of the monomer molecular pair of *p*CCA and the photoproduct 4, 4' dichloro $\beta$-truxinic acid.

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

The infrared absorption spectra and Raman spectra of the $p$CCA monomer and the dimer crystal are shown in figures 2 and 3 respectively. The intense aliphatic C=C stretching mode at $1620\,cm^{-1}$ in the monomer decreases in intensity with reaction progress and finally disappears in the dimer spectrum. This suggests photodimerization by cyclobutane ring formation. Also cyclobutane ring breathing vibrations at $1095\,cm^{-1}$ and ring deformation vibrations at 672 and $745\,cm^{-1}$ appear in the dimer spectrum. The observed infrared and Raman bands in the monomer and the dimer are listed and their partial assignment is presented in table 1. As shown in the table few other monomer bands disappear in the dimer. These bands are likely to be associated with the C–H bond attached to the aliphatic $\rangle$C=C$\langle$ bonds which form the cyclobutane ring on dimerization. Thus monomer 875 and $985\,cm^{-1}$ bands may be out-of-plane modes whereas 1335 and $1352\,cm^{-1}$ bands may represent deformation modes of this C–H bond. The stretching mode of this bond is difficult to identify as this falls in the O–H stretching frequency range of this crystal. In the monomer crystal, the $p$CCA molecules form strongly hydrogen-bonded dimers and the O–H stretching modes form a broad absorption region in the infrared with many submaxima in the $2500-3050\,cm^{-1}$ region (figure 2). This broadness may arise from the interaction of these modes with the low frequency hydrogen-bond stretch or from a series of hydrogen bonds of different discrete lengths (Bellamy 1975). In cinnamic acid crystals, the O–H deformation is observed at $950\,cm^{-1}$. We have tentatively assigned the medium strong $942\,cm^{-1}$ band to this mode in $p$CCA crystal.
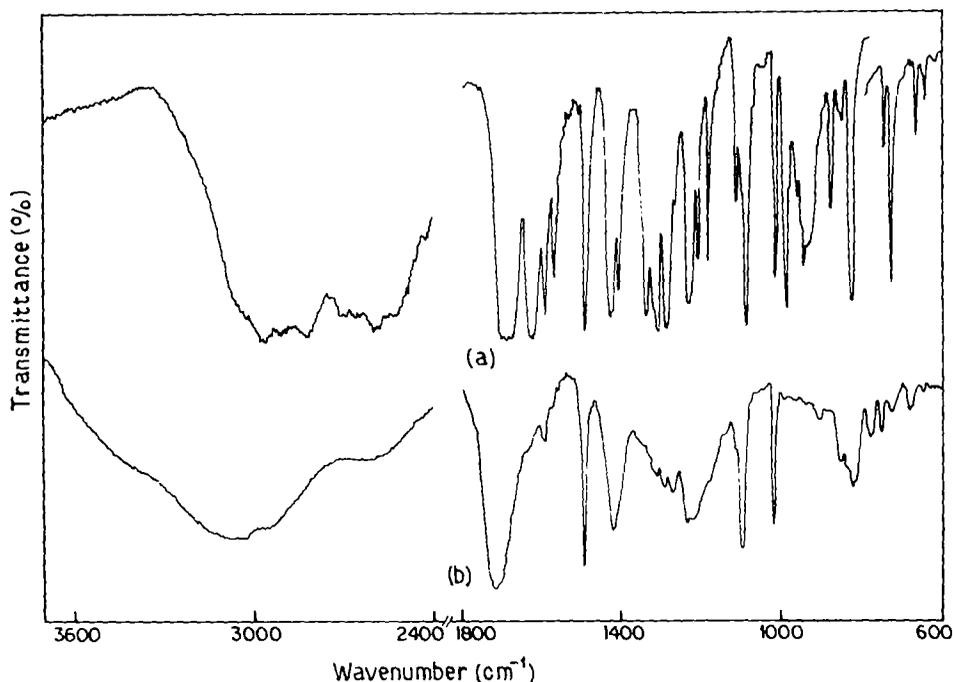


**Figure 2.** Infrared spectra of (a) monomer and (b) dimer of $p$CCA in solid state (in KBr pellet) at 300K.
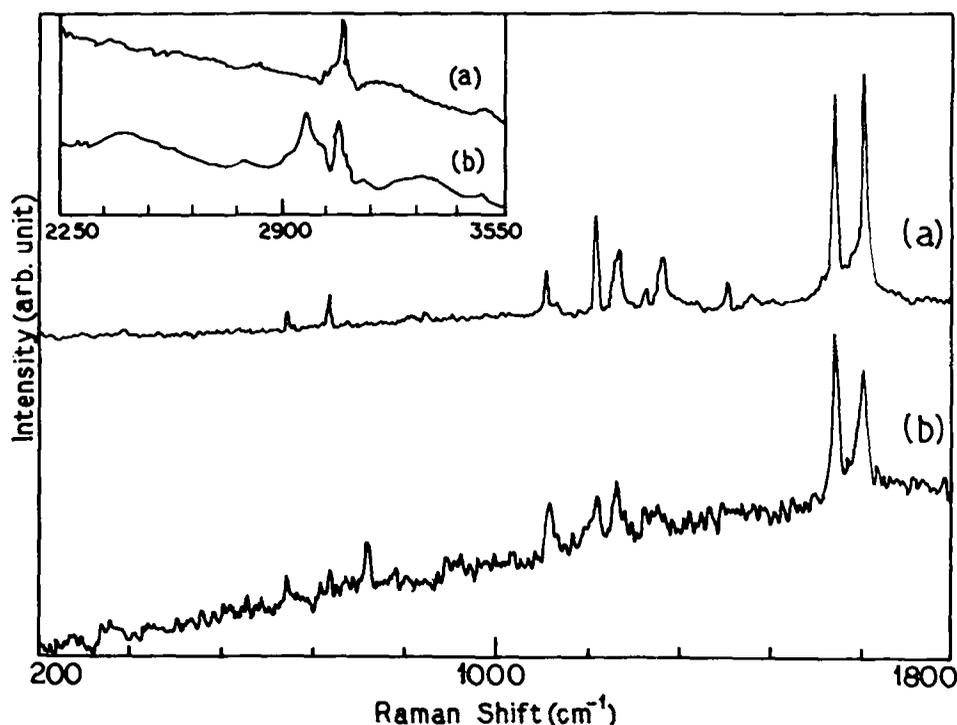
**Figure 3.** Raman spectra of the (a) monomer and (b) dimer of $p$CCA in the crystalline state at 300K. The inset shows the 2250–3550 cm$^{-1}$ spectral range.

**Table 1.** Infrared and Raman bands of monomer and dimer crystals of $p$CCA. IR spectra as KBr pellets; Raman spectra of crystals.

| Monomer | | Dimer | | |
|---|---|---|---|---|
| Infrared | Raman | Infrared | Raman | Tentative assignment |
| | 278 (w) | | | |
| | | | 327 (w) | D |
| | 347 (w) | | | |
| | | 425 (w) | | D |
| 375 (w) | | | | |
| 450 (w) | | | | |
| | | 470 (w) | | D |
| 495 (ms) | | | | |
| | | 510 (w) | | D |
| 550 (w) | | | | |
| | 635 (w) | | 634 (w) | |
| 645 (w) | | | | |
| 658 (w) | | | | |
| | | 672 (w) | | D: Cyclobutane ring deformation |
| | 707 (ms) | | 708 (ms) | |
| 718 (ms) | | 720 (w) | | |
| 738 (w) | 739 (w) | | | |
| | | 745 (w) | | D: Cyclobutane ring deformation |
| | | 775 (w) | 778 (ms) | D: C–C skeletal stretching |

*(continued)*

**Table 1.** (*continued*)

| Monomer | | Dimer | | |
| Infrared | Raman | Infrared | Raman | Tentative assignment |
| --- | --- | --- | --- | --- |
| 820(s) | | 820(ms) | 824(w) | |
| 845(w) | | 850(w) | | |
| 875(ms) | 876(w) | | | C–H out of plane mode (aliphatic) |
| | | 900(w) | | |
| 942(ms) | | | | O–H deformation out of plane |
| 985(s) | | | | C–H out of plane mode (aliphatic) |
| 1012(s) | | 1015(s) | | |
| 1085(vs) | 1086(s) | | | |
| 1100(vw) | | 1095(s) | 1095(s) | D: Cyclobutane ring stretching |
| 1110(ms) | | 1110(vw) | | |
| 1178(s) | 1176(s) | | 1176(s) | |
| 1205(s) | | | | |
| | 1215(s) | | 1214(s) | |
| 1230(s) | | 1235(w) | | |
| 1260(w) | 1261(w) | 1270(w) | | |
| 1282(s) | | 1290(w) | | |
| | 1293(s) | | | |
| 1306(s) | | 1310(w) | | |
| 1318(sh) | | | | |
| 1335(s) | | | | C–H deformation (aliphatic) |
| | 1352(s) | | | C–H deformation (aliphatic) |
| 1405(s) | 1407(ms) | | | |
| 1425(s) | | 1420(s) | | Aromatic ring |
| | 1449(w) | | | |
| 1490(vs) | | 1495(vs) | | Aromatic ring |
| 1565(s) | | | | |
| 1590(vs) | 1592(s) | 1592(w) | 1593(s) | Aromatic skeletal breathing |
| 1620(vs) | | | | C=C stretch (aliphatic) |
| | 1644(s) | | 1643(s) | Aromatic ring |
| 1700(vs) | | 1715(vs) | | C=O stretch |
| | | | 2450(b) | |
| 2530(b) | | | | |
| 2600(b) | | 2620(b) | | |
| 2700(b) | | | | |
| 2820(b) | | | | O–H stretch |
| 2970(b) | | 2950(b) | 2970(s) | |
| 3050(b) | 3077(s) | 3080(b) | 3077(b) | |
| | | | 3350(b) | |
| | | 3440(b) | | |

Abbreviations: D-dimer, *sh*-shoulder, *s*-strong, *ms*-medium strong, *vs*-very strong, *vw*-very weak, *b*-broad.

The 1700 cm$^{-1}$ monomer band is, by all means, the C=O stretching mode. In the photodimer, this frequency increases to 1715 cm$^{-1}$ possibly due to the disruption of the strong hydrogen bonds on reaction and their replacement by weaker association. This is also reflected in the O–H stretching modes. The broad infrared bands around 2970 cm$^{-1}$ shift to higher frequencies and a new broad band also appears at 3440 cm$^{-1}$. In the Raman spectrum (figure 3, inset) the monomer crystal shows only one weak band at 3077 cm$^{-1}$ whereas in the photodimer crystal, in addition to some weak broad bands, a new band is observed at 2970 cm$^{-1}$.
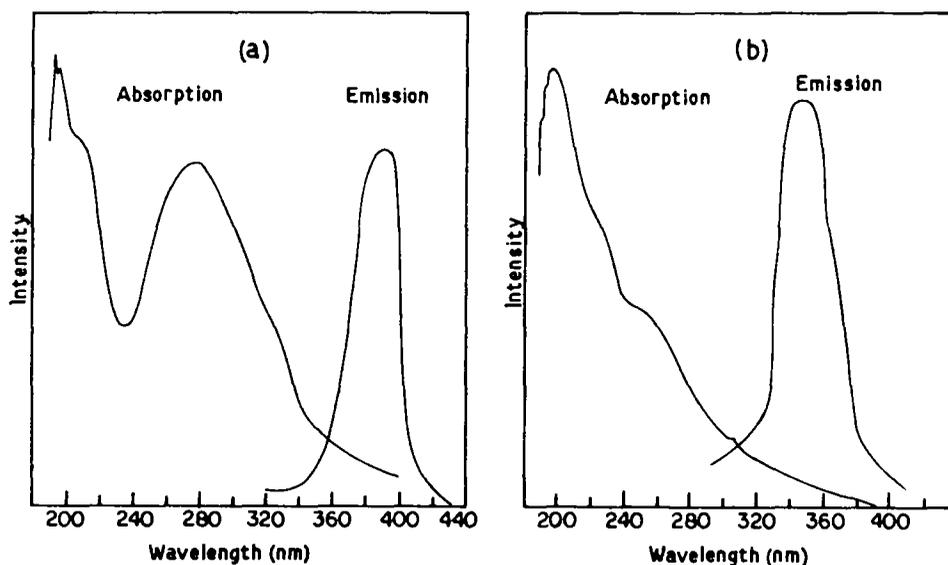
**Figure 4.** Electronic absorption and emission spectra of (a) monomer, and (b) dimer of pCCA in the crystalline state at 300K.

### 3.2 *Electronic spectral change with reaction progress*

Electronic absorption spectroscopy has been used to monitor the progress of the photodimerization reaction in the pCCA crystal. In the solid film of the monomer, broad absorption bands are observed at 194 and 276 nm. With progress of the reaction, the intensity of the 276 nm-band decreases and a new band starts developing at 250 nm. The band observed at 276 nm disappears in the dimer spectrum and the monomer 194 nm-band shows a slight red shift in the dimer.

pCCA shows strong fluorescence in the crystalline state at 300 K. The broad emission band with $\lambda_{max}$ at 392 nm shifts to higher energies with progress of reaction and in the dimer crystal it is observed at 358 nm. In figure 4, the absorption and emission spectra of the monomer and the dimer are shown. As shown in figure 4a there is significant Stokes' shift between $\lambda_{max}$ (absorption) and $\lambda_{max}$ (emission) in the monomer crystal. Such large Stokes' shift and broad structureless absorption and emission bands suggest strong exciton–phonon coupling in the monomer lattice. This reaction, therefore, may be phonon-mediated. Such observations are quite general in cinnamic acid derivatives (Ghosh and Misra 1985, 1987).

### 3.3 *Raman phonon spectral change with reaction progress*

It is now well-established that a phonon probe can efficiently distinguish between homogeneous and heterogeneous mechanisms (Misra and Prasad 1982; Misra 1989). In a homogeneous reaction, the reactant and the product form a solid solution and amalgamation of the phonon results. Phonon frequencies, in this case, show a monotonic shift as reaction proceeds. If, on the other hand, the reaction is homogeneous, the reactant and the product form separate lattices and segregated phonon spectra result. Phonon spectra may also reveal if there is a phonon mode softening (Ghosh and Misra 1988) with progress of the reaction.
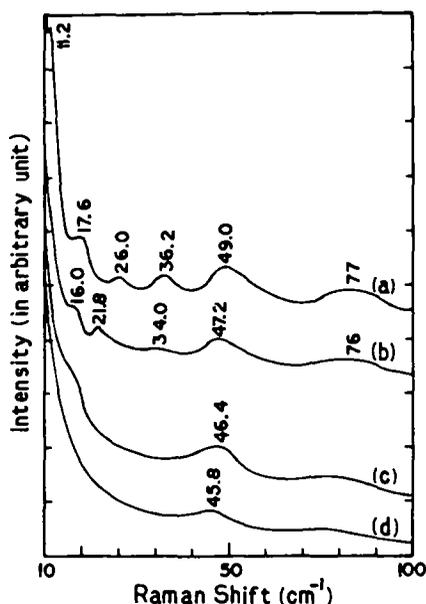
**Figure 5.** The Raman phonon spectra of pCCA crystal with reaction progress at 300K. (a→d: in increasing order of dimerization).

In figure 5, we show the Raman phonon spectra of pCCA crystal as reaction proceeds. In the monomer crystal six distinct low frequency phonon bands are observed at 11·2, 17·6, 26·0, 36·2, 49·0 and 77 cm$^{-1}$. As the reaction proceeds, these bands show a monotonic shift to lower frequencies. A phonon band at 11·2 cm$^{-1}$ disappears in the Rayleigh wing and other bands are observed at 16·0, 21·8, 34·0, 47·2 and 76·0 cm$^{-1}$. As reaction progresses further, as shown in figure 4c, the bands broaden appreciably and the spectra appear structureless. Further shift to lower frequencies, however, can be identified from the 46·4 cm$^{-1}$ band. In the extensively dimerised crystal, a diffuse phonon spectrum is observed. That no new phonon band is observed on photoreaction suggests that the product does not form any separate lattice. The reaction is homogeneous in the initial stages but as the product concentration increases, the lattice becomes progressively disordered.

**Acknowledgement**

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