

Raman phonon spectroscopic study of solid state photoreaction in 7-bromo coumarin crystals

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Abstract The photodimerization reaction in 7-bromo coumarin (7BC) in the crystalline state has been studied by Raman phonon spectroscopy. Monotonic red shift of the phonon bands and nonappearance of any new phonon bands on reaction progress suggest that the mechanism is homogeneous and the reactant and the product form solid solution. Broadening of the phonon band suggests that the reaction lattice becomes disordered with the increase of product concentration. Significant overlap between the electronic absorption and emission bands indicates that the exciton-phonon coupling is not very strong in the monomer lattice. Softening of a specific phonon mode with the progress of reaction observed in the Raman spectrum suggests that the reaction is phonon mediated through this mode softening. In the reaction, formation of cyclobutane ring through the $>C=C<$ of the pyrone moiety is established by infrared and Raman spectroscopy.

Keywords Crystalline state photoreaction, Raman phonon spectroscopy, 7-Bromo coumarin

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1. Introduction

Crystalline state photoreaction in organic materials has gained much interest recently. This relatively new field of research can be dated from the initial landmark studies of Schmidt and his associates [1]. The unique feature of solid state reaction is that they provide a degree of control that is not available either in the gas or liquid phase. The correspondence between the molecular packing in the reactant crystal and the steric configuration of the product obtained in the solid state photoreaction is well established [1–3]. The α form of the crystal in which the distance between the reacting double bonds of neighboring molecules is $\sim 3.7\text{\AA}$ gives a centrosymmetric dimer. The product dimer is mirror symmetric when the crystal is β packed *i.e.* lattice having one axial length $\leq 4.2\text{\AA}$. The γ form of the crystal where double bonds of neighboring molecules are more than 4.2\AA , results in no photoreaction. 7-bromo coumarin (7BC) is one of the substituted coumarins that is highly photoreactive (yield 90%) in the crystalline state and gives *syn* head to head dimer as the only product [4]. The molecular structure of the

monomer and the dimer of 7BC are shown in Figure 1. Irradiation in the crystals of unsubstituted coumarins in its

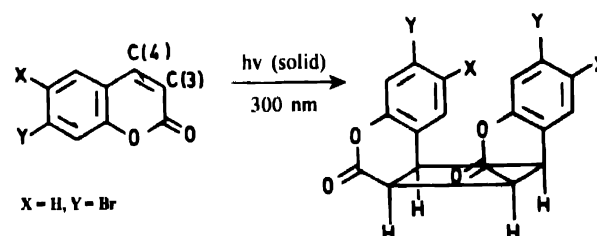


Figure 1. Molecular structure of the monomer and the dimer of 7BC.

stable modification, results in no photodimerization reaction [5]. On the other hand, bromo substitution at the 6 or 7 positions engineers the molecules to adopt β' stack packing mode in the lattice and the crystal becomes photoreactive [4]. Thus, it is evident that β steering ability of the bromo group plays an important role in solid state photoreaction.

Raman phonon spectroscopy has been established as a useful technique to study the reaction mechanism and dynamics of solid state photoreactions [6–8]. In some early

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works [9–13], laser Raman phonon spectroscopy has been successfully used by this group to show that the solid state photoreactions are mediated by lattice phonon. Phonon participation in such reactions occurs either through strong exciton-phonon coupling or through softening of a specific phonon mode in excited state of the crystals. In this article, Raman phonon and electronic absorption and emission spectroscopy have been used to study the photoreaction mechanism and dynamics in 7BC crystal.

2. Experimental

The 7BC sample was obtained from Prof. K. Venkatesan, I.I.Sc., Bangalore, India as a generous gift and was used without further purification.

Crystals of 7BC were taken in a petri dish covered with a cut-off filter (cut-off for $\lambda < 295$ nm) and irradiated using a 200 W high pressure mercury lamp. The sample was turned periodically to provide uniform exposure and was taken out at different stages of the reaction progress for spectroscopic study.

UV absorption and emission spectra were recorded on a Shimadzu UV-VIS scanning absorption spectrophotometer (Model UV-2101PC) and Hitachi fluorescence spectrophotometer (model F-4500) respectively. The infrared absorption spectra were run on a Nicolet FTIR spectrophotometer (Model Magna 750). Raman spectra were recorded using a Spex double monochromator (Model 1403) with gratings having 1800 grooves/mm. We used the 5145Å line of Spectra Physics (Model 2020-5) argon ion laser as Raman excitation source. Spex Datamate 1B was used for spectrometer control, data acquisition and analysis.

3. Results and discussion

3.1. Study of internal vibrations of the reactant and the product by infrared and Raman spectroscopy :

As the positions of IR absorption and Raman scattered bands of a molecule are in general extremely sensitive to the molecular structure, infrared absorption and Raman spectroscopy have been used to characterize the monomer and the dimer molecules. The infrared spectra of the monomer, partially dimerized and the dimer crystals of 7BC are shown in Figure 2. Raman spectra of the monomer and the partially dimerized crystal of 7BC, are shown in Figure 3. The dimer crystal of 7BC shows poor Raman scattering. Partial assignment of the observed infrared and Raman bands is presented in Table 1. As seen from Figure 2(a), the infrared band due to C=C stretching mode of pyrone moiety appears at 1554 cm^{-1} with moderate intensity. The intensity of this band decreases with the progress of reaction [Figure 2(b)] and finally disappears when the reaction is complete [Figure 2(c)]. This observation indicates that the double

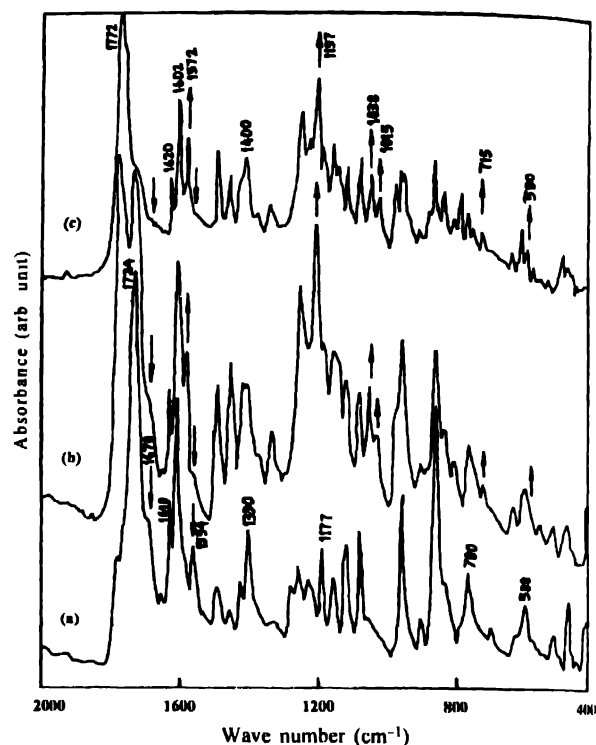


Figure 2. Infrared spectra of (a) monomer, (b) partially dimerized and (c) dimer of 7BC in KBr pellet at 300 K.

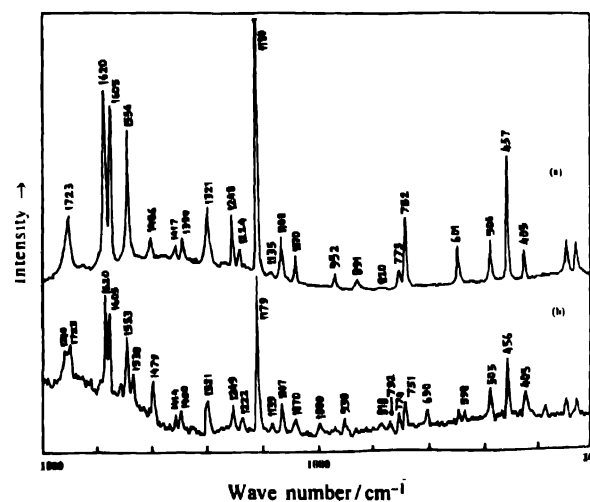


Figure 3. Raman spectra of (a) monomer and (b) partially dimerized 7BC in the crystalline state at 300 K.

bond between C(3) and C(4) is used to form the cyclobutane ring in photodimerization reaction. The corresponding Raman band is at 1556 cm^{-1} . The strong Raman band at 1620 cm^{-1} in the monomer crystal is due to C=C stretching vibration of the aromatic ring. In the Raman spectrum of the dimer crystal, the band attributed to C=C stretching of the pyrone moiety should vanish. Unfortunately, due to poor scattering, it was not possible to record the dimer spectrum. The partially dimerized crystal's spectrum shows that the relative intensity of the C=C stretching mode of pyrone moiety as

Table 1. Infrared bands (in KBr pellet) of the monomer and the dimer and Raman bands (in polycrystals) of the monomer and partially dimerized crystals of 7BC in cm^{-1}

Monomer		Dimer	Partially dimerized	Tentative assignment
IR ν/cm^{-1}	Raman ν/cm^{-1}	IR ν/cm^{-1}	Raman ν/cm^{-1}	
---	405 (ms)	---	405 (w)	
455 (ms)	457 (s)	458 (ms)	456 (ms)	$\beta(\text{C}-\text{C})$
500 (w)	506 (ms)	506 (w)	505 (w)	
---	---	555 (w)	---	D :
---	---	580 (w)	579 (vw)	D : Cyclobutane ring bending
588 (ms)	---	589 (ms)	---	
---	601 (ms)	---	598 (w)	
620 (w)	---	618 (w)	---	
---	---	---	690 (w)	D :
---	---	715 (w)	---	D : Cyclobutane ring deformation
---	---	736 (w)	---	D :
750 (ms)	752 (ms)	749 (ms)	751 (ms)	
780 (ms)	773 (w)	776 (ms)	774 (w)	
---	---	---	792 (w)	D C-C Skeletal stretching
818 (w)	820 (vw)	820 (ms)	818 (vw)	
848 (vs)	---	850 (s)	---	
888 (w)	891 (w)	890 (w)	---	
---	---	940 (s)	930 (w)	D
948 (s)	952 (w)	950 (s)	---	
965 (w)	---	966 (s)	---	
---	---	1015 (ms)	1000 (w)	D : Cyclobutane ring stretching
---	---	1038 (s)	---	D :
1068 (s)	1070 (ms)	1069 (s)	1070 (vw)	
1105 (s)	1108 (ms)	1107 (s)	1107 (w)	
1138 (s)	1135 (vw)	1130 (s)	1139 (w)	$\beta(\text{C}-\text{H})$
1177 (s)	1180 (vs)	1176 (s)	1179 (s)	$\beta(\text{C}-\text{H})$
---	---	1197 (vs)	---	D
1220 (ms)	1224 (w)	1220 (s)	1222 (w)	
1245 (ms)	1248 (ms)	1241 (vs)	1249 (ms)	
1264 (ms)	---	---	---	M :
1322 (w)	1321 (ms)	1325 (ms)	1321 (ms)	
---	---	1363 (ms)	---	D :
1390 (s)	1390 (w)	1400 (s)	1400 (w)	
1412 (ms)	1417 (w)	1412 (s)	1414 (w)	
1444 (w)	---	1445 (s)	---	
1479 (ms)	1486 (w)	1486 (s)	1479 (ms)	
---	---	---	1538 (ms)	D :
1554 (s)	1556 (s)	---	1553 (ms)	M : $\nu(\text{C}=\text{C})$ Pyronic ring
---	---	1572 (s)	1569 (w)	D :
1599 (vs)	1605 (vs)	1602 (vs)	1605 (s)	$\nu(\text{C}=\text{C})$ aromatic
1618 (s)	1620 (vs)	1620 (ms)	1620 (s)	$\nu(\text{C}=\text{C})$ aromatic
1670 (s)	---	---	---	$\nu(\text{C}=\text{C})$ pyronic ring
1724 (vs)	1723 (s)	1772 (vs)	1723 (s)	$\nu(\text{C}=\text{O})$
---	---	---	1740 (sh)	$\nu(\text{C}=\text{O})$

vs→ very strong; ms→ medium strong; s→ strong; w→ weak; vw→ very weak; sh→ shoulder; M→ monomer; D→ dimer

compared to aromatic $\text{C}=\text{C}$ stretching mode decreases. The infrared band at 1670 cm^{-1} in the monomer crystal disappears in the dimer spectrum. Therefore, this band must be associated with the $>\text{C}=\text{C}<$ vibration in the pyrone moiety. As seen from Figure 2, some new bands appear in the dimer spectrum. The bands at $580, 715$ and 1015 cm^{-1} are assigned as cyclobutane ring bending, deformation and stretching vibration respectively. The corresponding Raman bands for cyclobutane ring bending and ring stretching vibration are recorded at 579 and at 1000 cm^{-1} respectively. All these confirm that 7BC crystal photodimerizes through cyclobutane ring formation. The lactone carbonyl bond freed from hydrogen bonding absorbs near 1725 cm^{-1} in the solid state. The observed 1724 cm^{-1} band in the monomer spectrum of infrared is the $\text{C}=\text{O}$ stretching mode of lactone. In the monomer Raman spectrum, this band appears at 1723 cm^{-1} . With progress of reaction, this band continues to shift to the higher wavenumber [Figure 2(b)] region and appears at 1772 cm^{-1} when the reaction is complete. This shift is due to loss of conjugation on dimerization.

3.2. Electronic spectral change with the progress of reaction :

The electronic absorption and emission spectra of monomer 7BC at room temperature in solid state are shown in Figure 4(a). The absorption spectrum shows two broad bands with λ_{max} at 290 and 329 nm . The emission band is observed with λ_{max} at 405 nm . As shown in Figure 4(a) there is a considerable overlap near the electronic origin of absorption and emission spectra. This suggests that the exciton-phonon coupling is not very strong in the monomer lattice.

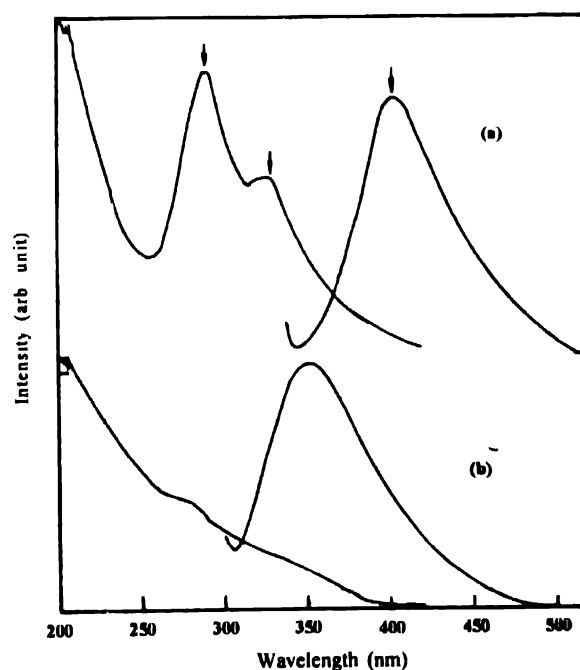


Figure 4. Electronic absorption and emission spectra of 7BC (a) monomer and (b) dimer in the solid state at 300 K .

On reaction progress, the intensity of the absorption bands continues to decrease. The absorption band observed at 329 nm disappears in the dimer spectrum and the monomer band at 290 nm shows a blue shift with diminished intensity in the dimer. The blue shift of electronic absorption bands on dimerization is a general observation in cinnamic acid and its derivatives. This has been attributed to loss of conjugation on dimerization [9,14]. On dimerization, the emission band of 7BC shifts to higher energy (λ_{max} 354). The absorption and emission spectra of dimerized 7BC crystal are shown in Figure 4(b).

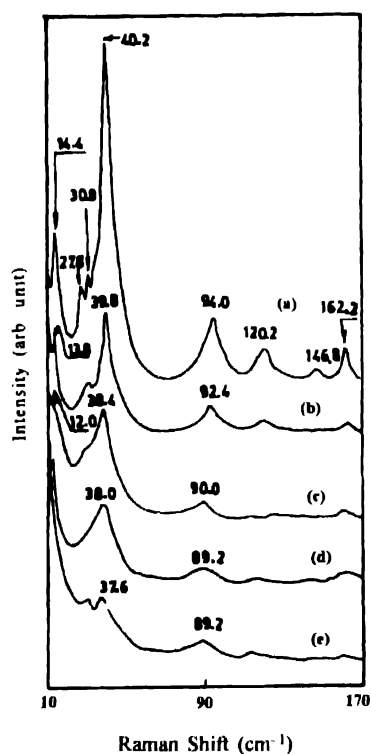


Figure 5. Raman phonon spectra of 7BC crystals with reaction progress at 300 K [Mono crystal irradiated for : (a) 0 hour, (b) 0.5 hour, (c) 5 hour, (d) 10 hour and (e) 14 hour]

3.3. Raman phonon spectral change with progress of reaction :

The Raman phonon spectra as a function of the advancement of the reaction are shown in Figure 5. In the monomer crystal spectrum [Figure 5(a)], eight sharp distinct phonon bands appear at 14.4, 27.8, 30.8, 40.2, 94.0, 120.2, 146.8 and 162.2 cm^{-1} . With the progress of reaction, the phonon bands shift to lower wavenumbers in a monotonic fashion and this trend continues until the reaction is almost complete. No new phonon band appears. This suggests that the reaction is homogeneous, the reactant and the product form solid solution and the product does not segregate out to form a separate lattice. This is in contrast to the case of 6-bromo coumarin [13] where the product forms separate lattice.

In the later stage of the reaction, however, as the dimer concentration increases significantly, the lattice becomes disordered and the phonon bands become broad and weak.

The other feature of this spectral evolution is that as the reaction proceeds, the shifts of the phonon bands are neither equal nor parallel with their intensity. The intensity of the strongest band at 40.2 cm^{-1} is drastically reduced compared to the fall of intensity of the band at 94.0 cm^{-1} . The intensity of the lowest phonon band at 14.4 cm^{-1} is less diminished. Also the shift of the 40.2 cm^{-1} band is by 1.8 cm^{-1} only at the reaction stage shown in Figure 5(c) whereas the corresponding shift of the 14.4 cm^{-1} band is 2.4 cm^{-1} and it disappears in the Rayleigh wing in the next reaction stage. 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 Dwarakanath and Prasad [7]. This indicates softening of this low wavenumber phonon mode on photoexcitation of this crystal. Such type of behaviour was observed in the photodimerization of 7-methoxy coumarin [12]. One of the normal lattice modes becomes unstable due to phonon-phonon interaction and its wavenumber decreases with certain perturbation (such as change in temperature, dielectric shielding *etc.*). The restoring force softens unless the phonon condenses into the lattice to cause a structural phase transition [15]. Mode softening also produces large amplitude displacement of molecules which are analogous to molecular collisions in the gas phase and thus can assist photoreactivity.

4. Conclusion

We conclude that in the crystalline state, photodimerization reaction of 7BC is phonon mediated and the phonon participation is through softening of a specific phonon mode in the excited state of the crystal and not through the exciton-phonon coupling.

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