



## INFRARED SPECTRA OF CHARGE TRANSFER COMPLEXES OF PROTEOGLYCAN

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### ABSTRACT

The FTIR spectra of charge transfer complexes of an important biomolecule called proteoglycan (PG) with acceptors such as TCNQ, TCNE, DDQ, chloranil and iodine have been studied. Proteoglycan-TCNQ shows features corresponding to strongly ionic nature of complex and stacks of  $\text{TCNQ}^-$  and  $\text{TCNQ}^=$  ions. Proteoglycan-chloranil spectrum shows oscillations in the density of states along chloranil stacks. Proteoglycan-TCNQ, proteoglycan-chloranil and proteoglycan-iodine (I<sub>2</sub>) spectra reveal forbidden indirect transitions across the band gaps while proteoglycan-TCNE forbidden direct transition.

**Key words:** Proteoglycan, Charge transfer complexes, Infrared spectra, Nature of transition, Gaussian distribution

### INTRODUCTION

Proteoglycan is an important molecule which is combination of protein and polysaccharides. Proteoglycan has a branched core structure. The branches are polypeptide chains. Each polypeptide chain has sub-branches made up of glycosaminoglycans. If the polysaccharides are dominant in proteoglycan in content, it is called proteoglycan [1]. If protein content dominates, it is called glycoprotein. Here we study proteoglycan. It has structure suggested in Little's model of high temperature superconductivity [2]. Therefore, we selected proteoglycan in the present study.

### EXPERIMENTAL DETAILS

Proteoglycan was a white powder obtained from Sigma chemical company, USA. Proteoglycan was mixed with acceptors such as TCNE (tetracyano-p-ethylene), DDQ (2,3-dichloro-5,6-dicyano-pbenzoquinone), TCNQ (7,7,8,8-tetracyano-p-quinodimethane), Chloranil (2,3,5,6-tetrachloro-p-benzoquinone) and iodine (I<sub>2</sub>) in 1:1 molecular weight proportion. The mixtures were grinded in a mortar till the CT (charge transfer) complexes were formed. These CTCs (charge transfer complexes) were further grinded with 95% of dry spectrograde KBr powder till dispersed homogeneously. Circular discs which were semitransparent prepared using a die and a manual compressing machine. The discs were placed in a dark chamber of spectrophotometer.

### RESULTS AND DISCUSSION

The FTIR spectrum of proteoglycan is shown in Figure 1. The material is transmitting in the range of  $1800\text{cm}^{-1}$  to  $3000\text{cm}^{-1}$ , which shows that it does not have any band gap in IR (infrared) range. Various vibrational bands particularly corresponding to outer periphery of large molecule of proteoglycan are observed in FTIR (fourier transform infrared spectroscopy) spectrum. No background absorption has developed indicating that it is an insulator. The FTIR spectrum of proteoglycan-TCNQ is also shown in Figure 2. Here TCNQ being a large molecule as compared with other acceptors used in the present study. It forms segregated stacks and absorbs being  $\text{TCNQ}^-$  or  $\text{TCNQ}^=$  radical-ions. No bands of proteoglycan are pronounced in IR range. Bands of  $\text{TCNQ}^-$  and  $\text{TCNQ}^=$  dominate the full IR spectrum which shows presence of TCNQ stacks and ionic nature of the compound. The spectrum is

similar to those of hemoglobin-TCNQ and myoglobin-TCNQ where TCNQ goes into the cavity of hemoglobin in the place of diphosphoglycerate enzyme. The bands of  $\text{TCNQ}^-$  and  $\text{TCNQ}^=$  dominate the spectra of hemoglobin-TCNQ and myoglobin-TCNQ. Here a similar spectrum is observed indicating that TCNQ goes into the cavity of proteoglycan molecules. The IR spectrum is mainly governed by the vibrational levels of  $\text{TCNQ}^-$  and  $\text{TCNQ}^=$  organic radical-anions. This special interaction is due to  $\pi$ -character of TCNQ.

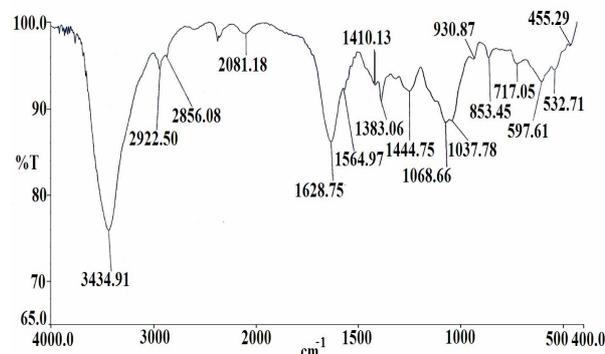


Fig. 1 The FTIR spectrum of proteoglycan only

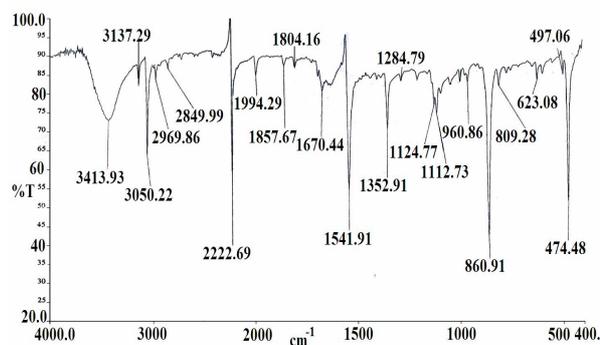
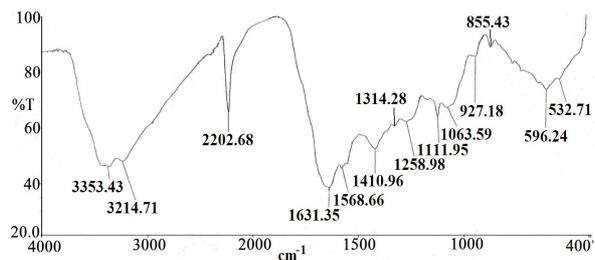


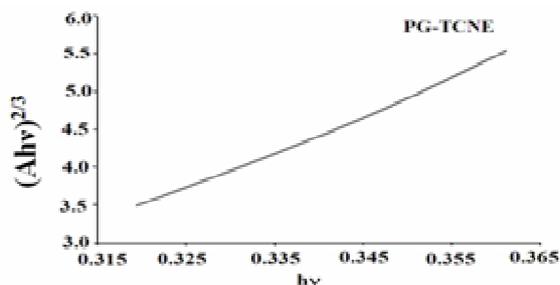
Fig. 2 FTIR spectrum of proteoglycan-TCNQ charge transfer complex.

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The FTIR spectrum of proteoglycan-TCNE is shown Figure 3. Here TCNE interacts as an acceptor with various vibrational levels of proteoglycan. The spectrum is different from that of proteoglycan alone. There is development of absorption in the range of  $3000\text{cm}^{-1}$  to  $1800\text{cm}^{-1}$ . This can be ascribed to electronic transition across the band gap as found normally in all CT complexes. The nature of transition is analyzed to be a forbidden direct transition [3, 4] obeying  $Ah\nu = B(h\nu - E_g)^{3/2}$  with a graph of  $(Ah\nu)^{2/3}$  vs  $h\nu$  which shown in Figure 4. Other background absorptions developed around  $1630\text{cm}^{-1}$  and  $596\text{cm}^{-1}$  can be assigned to imperfect nesting. When imperfect nesting occurs, a distorted and asymmetric triangular distribution is observed.



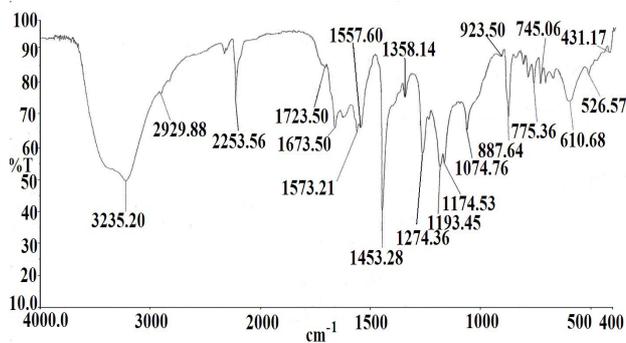
**Fig. 3** The FTIR spectrum of proteoglycan-TCNE charge transfer complex.



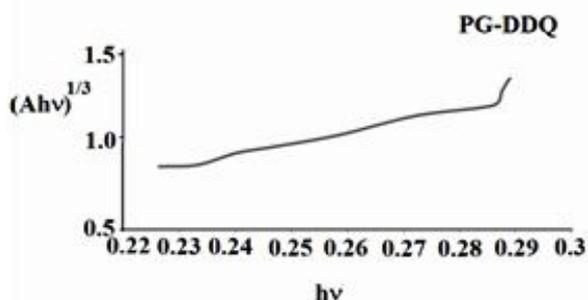
**Fig. 4** The nature of transition of proteoglycan-TCNE charge transfer complex

The Other important compound is proteoglycan-DDQ whose spectrum is shown in below figure 5. A nature of transition range is found in a small range of  $2800\text{cm}^{-1}$  to  $2000\text{cm}^{-1}$ . The absorption in this range is analyzed and it is found that it is a forbidden indirect transition obeying  $Ah\nu = B(h\nu - E_g \pm E_p)^3$  by plotting  $(Ah\nu)^{1/3}$  vs  $h\nu$  Figure 6. Apart from this, two Gaussians, one broad and other sharp are observed in the mid-IR range of  $1000\text{cm}^{-1}$  to  $1800\text{cm}^{-1}$ . Both the Gaussians are fitted which obey  $\alpha = \alpha_0 \exp(-(k-k_0)^2/2m^2)$  where  $\alpha_0$  is maximum value of absorption,  $k_0$  is the central wave number and  $m^2$  is the second moment of the distribution. These fits are shown in which  $\ln\alpha$  vs  $(k-k_0)^2$  are plotted as in figure 7 and figure 8. The proteoglycan-chloranil shows a completely different spectrum shown in figure 9. Here the transition across the band gap leads to development of absorption in the range of  $3000\text{cm}^{-1}$  to  $1750\text{cm}^{-1}$ . The transition is found to be of forbidden indirect type upon analysis and fitted as shown in figure 10 i.e. it obeys  $Ah\nu = B(h\nu - E_g)^3$ . Rest of the spectrum of proteoglycan-chloranil complex shows repeated structures below  $1700\text{cm}^{-1}$ . Three repeated structures with only little damping are observed. These structures can be assigned to the oscillations in the density of states. The shape of each structure is governed by square-root singularity unique for one-dimensional systems of lattice vibrations. There is strong electron-phonon interaction through which these lattice vibrations become infrared active. The system acts as a

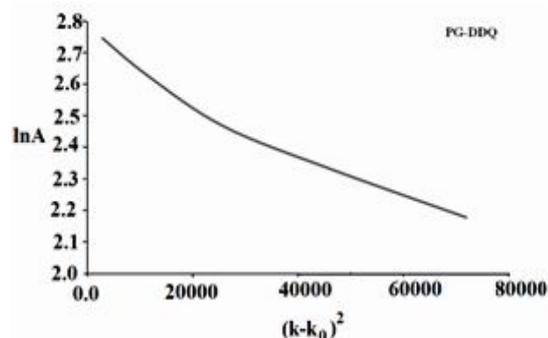
molecular multivibrator. This is a special state in molecular electronics. Multivibrator has non-sinusoidal periodic structures. Here it is also a non-sinusoidal type vibration. This is found in other chloranil complexes too. It is not know why chloranil complexes many times reveal oscillations in the density of states. Biolytin-chloranil, hemoglobin-chloranil and myoglobin-chloranil have also similar property [5].



**Fig. 5** The FTIR spectrum of proteoglycan-DDQ charge transfer complex



**Fig. 6** The nature of transition in proteoglycan-DDQ charge transfer complex



**Fig. 7** Broad Gaussian Fitted in mid-IR range in proteoglycan-DDQ charge transfer complex

The FTIR spectrum of proteoglycan-iodine is shown as below figure 11. It shows a range in which transition across a band gap occurs and two broad Gaussians in other lower frequency ranges. The nature of transition is analyzed to obey  $Ah\nu = B(h\nu - E_g \pm E_p)^3$  revealing a forbidden indirect type transition which shown in figure 12. There are weak and a broad Gaussian distribution in absorption around  $1380\text{cm}^{-1}$  and  $595\text{cm}^{-1}$ . Also there is comparatively stronger gaussian band around  $595\text{cm}^{-1}$ .

Both of these Gaussian bands are fitted by plotting  $\ln A$  vs  $(k-k_0)^2$  which are shown in Figure 13 and Figure 14.

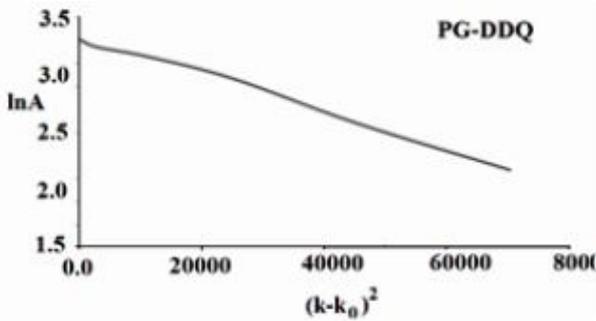


Fig. 8 Sharp Gaussian Fitted in mid-IR range in proteoglycan-DDQ charge transfer complexes

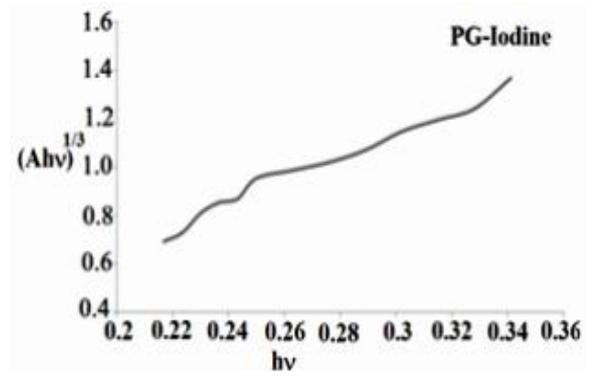


Fig. 12 Nature of transition of proteoglycan-iodine charge transfer complex

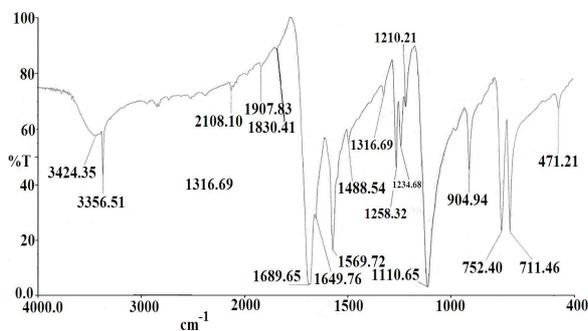


Fig. 9 The FTIR spectrum of proteoglycan-Chloranil charge transfer complex

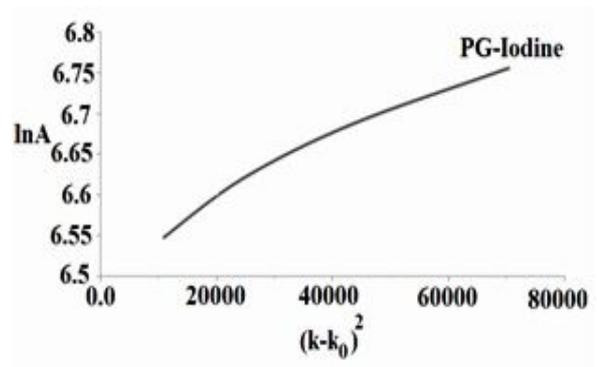


Fig. 13 Gaussian band fitted around  $1380\text{ cm}^{-1}$  of proteoglycan-iodine charge transfer complex

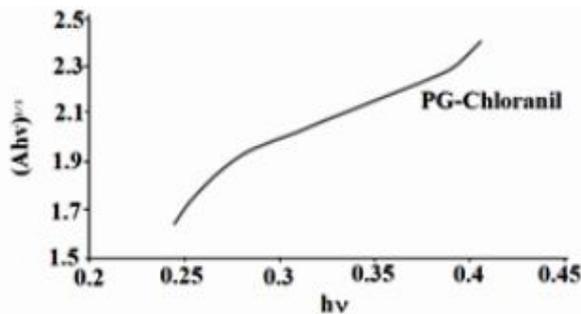


Fig. 10 The nature of transition of proteoglycan-Chloranil charge transfer complex

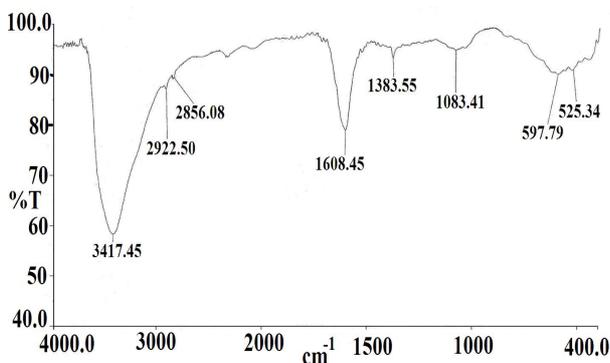


Fig. 11 The FTIR spectrum of proteoglycan-iodine charge transfer complex

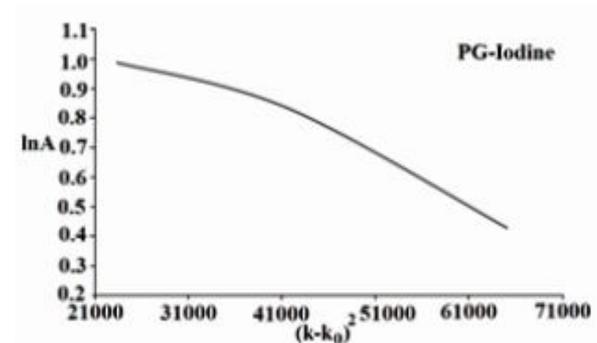


Fig. 14 Gaussian band fitted around  $595\text{ cm}^{-1}$  of proteoglycan-iodine charge transfer complex

Table - 1 Parameter of gaussian distribution in the different proteoglycan complexes.

Name of the complex	$\alpha_{\text{max}}$ (%) Peak value	$K_{\text{max}}$ ( $\text{cm}^{-1}$ ) Central wave number	FWHM ( $\text{cm}^{-1}$ )
PG-DDQ			
(1)	84.412	1392.5	301
(2)	73.24	1032.25	408.5
PG-I <sub>2</sub>			
(1)	96.928	1102	510
(2)	92.496	455.56	276.27

**Table - 2** Nature of transitions in proteoglycan charge transfer complexes.

Name of the complex	Absorption function	Values of band gap(eV) (Forbidden direct)
PG-TCNE	$A_{hv} = \beta(h\nu - E_g)^{3/2}$	0.32 eV
PG-DDQ	$A_{hv} = \beta(h\nu - E_g \pm E_p)^3$	0.23 eV
PG-Chloranil	$A_{hv} = \beta(h\nu - E_g \pm E_p)^3$	0.25 eV
PG-I <sub>2</sub>	$A_{hv} = \beta(h\nu - E_g \pm E_p)^3$	0.21 eV

**CONCLUSION**

Proteoglycan forms charge transfer complexes with organic acceptors and iodine. The spectra of CTCs are very much different from the spectrum of proteoglycan alone which shows

presence of charge transfer interaction. Four complexes reveal transition across a band gap in IR range and subsequent (resultant) development of absorption. Proteoglycan–TCNQ spectrum reveals absorptions due to TCNQ<sup>-</sup> and TCNQ<sup>•-</sup> ions and therefore indicates ionic nature of the complex. Proteoglycan–chloranil shows oscillations in the density of states with repeated structures which are almost undamped.

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