CHAPTER 3

FTIR SPECTRA OF CHARGE TRANSFER COMPLEXES OF RIBONUCLEIC ACID AND DEOXYRIBONUCLEIC ACID (RNA & DNA)
3.1 The study of FTIR spectra of CTCs of RNA

3.1.1 Introduction

Recent studies on d.c. and optical conductivity of DNA [1-6] inspired us to study spectroscopy of charge transfer complexes of RNA and DNA. Dipolar relaxation losses in DNA and magnetic properties of DNA-templated Co or Cu nanoparticle chains were also reported [7, 8]. In the present work we report study of FTIR spectra of CTCs of RNA. RNA is a big helical molecule with a cavity in the center. Small acceptor molecules of organic acceptors can go inside the cavity and interact with the units of RNA which are purines and pyrimidines. Recently we studied charge transfer complexes of purines and pyrimidines using FTIR spectroscopy of understand donor role of RNA and DNA. RNA is an electron donor because of donating character of adenine, guanine, thymine, cytosine and uracil. Organic acceptors such as TCNQ, TCNE, DDQ, chloranil and iodine were used to form CTCs with RNA.

3.1.2 Experimental detail

Pure RNA (ribonucleic acid) was obtained as a white powder from chemical company. TCNQ(7,7,8,8,-tetracyano-p-quinodimethane), TCNE (tetracyano-p-ethylene), DDQ(2,3,-dichloro-5,6-dicyano-p-benzoquinone),
chloranil (2,3,5,6-tetrachloro-p-benzoquinone) and iodine were also in pure form which work as electron acceptors. RNA and organic acceptor were taken in 1:1 molecular weight proportion and were homogeneously mixed with grinding for a long time using agate mortar and pastle. The colour changed upon formation of charge transfer complexes were further grinded with dry spectrograde KBr powder and the fine mixtures were used to form circular discs by a manually operated compressing machine. These round palates were placed in a dark chamber of Perkin Elmer single beam spectrophotometer.

The spectra in the range 400-4000cm\(^{-1}\) were recorded using this GXFTIR spectrophotometer having a resolution of 0.15cm\(^{-1}\), a scan range of 15,000-30cm\(^{-1}\), a scan time 30scansec\(^{-1}\), an OPD velocity of 0.20cmsec\(^{-1}\) and MIRTGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800-370cm\(^{-1}\). The spectra were recorded in purge mode.

### 3.1.3 Result and discussion

The FITR spectra of RNA in the full mid-IR range (400-4000cm\(^{-1}\)) is shown in figure 3.1.1. Apart from various rotational and vibration modes below 1800cm\(^{-1}\) the spectrum contains a featureless transmission or
abortion region between 2800cm\(^{-1}\) and 1800cm\(^{-1}\). This is an intermolecular band gap arising out of a gap in the dispersion relation of acoustic and optical phonon modes. Charge carrier is bound to various lattice vibrations.

Figure 3.1.1 The FTIR spectrum of ribonucleic acid

Such a gap between acoustic mode and optical mode and optical mode lies in the infrared range. There is a large distance between two neighboring macromolecules and therefore, coulomb repulsion between two electrons on neighboring molecules is very less. The intra-molecular bang gap is very large due to coulomb repulsion along a long straight or folded chain and therefore, such a gap lies in ultraviolet-visible range. This is the real electronic band gap along a chain molecule. Such effects are observed in β-caritene, stearic acid, α-keratin, etc. long chain molecules [9-
Such molecules have two band gaps— one in UV-visible range and the other in IR range.

The infrared gap is evaluated by the analysis of nature of transition. \( \alpha = A(h\nu - E_g)^r \) where \( r = \frac{1}{2}, \frac{3}{2}, 2, 3 \) or \( \alpha h\nu = A(h\nu - E_g)^r \) where \( \frac{1}{2}, \frac{3}{2}, 2, 3 \). For this \( (Ah\nu)^{1/2}, (Ah\nu)^{2/3}, (Ah\nu)^{1/3} \) and \( (Ah\nu)^2 \) are plotted against \( h\nu \) for straight line behavior. The best fit according to long range and scattering of data points is found by comparison of all of these graphs. \( (Ah\nu)^{1/3} \) vs \( h\nu \) is found to be the best fit and is shown figure 3.1.1b.

The band gap of RNA is about 0.252eV. This is the energy gap between acoustic branch and optical branch in the dispersion relation for lattice vibrations. Electron-phonon coupling is responsible for this gap to be explained as an electronic or polaronic band gap.
Apart from the above mentioned nature of transition, there is range between 1300 cm\(^{-1}\) and 700 cm\(^{-1}\) where a broad background gaussian is observed. The Gaussian distribution is fitted by plotting a straight line of \(\ln A\) vs \((k-k_0)^2\) where ‘A’ is absorption and ‘\(k_0\)’ is central wave number. This fitting is also shown in figure 3.1.1c.

![Figure 3.1.1c Fitting of Gaussian distribution in ribonucleic acid](image)

The physical significance of a Gaussian profile lies in delocalization of charge carriers. The full width or half-width of the gaussian is related with electron-phonon coupling constant. Larger the width, larger the coupling constant.

The FTIR spectra of RNA-TCNQ, RNA-DDQ and RNA-iodine are also shown figure 3.1.2a, 3.1.3a and 3.1.4a.
Figure 3.1.2a The FTIR spectrum of RNA-TCNQ charge transfer complex

Figure 3.1.3a The FTIR spectrum of RNA-DDQ charge transfer complex

Figure 3.1.4a The FTIR spectrum of RNA-iodine charge transfer complex
RNA-TCNQ spectrum contains a range of nature of transition between 3200cm\(^{-1}\) and 2000cm\(^{-1}\), which is featureless. It also contains a background gaussian in the range 400-1600cm\(^{-1}\). RNA-DDQ spectrum contains a range of nature of transition between 3000cm\(^{-1}\) and 2000cm\(^{-1}\) and a range of broad gaussian between 1700cm\(^{-1}\) and 400cm\(^{-1}\). RNA-iodine spectrum contains a nature of transition in the range 2000-3000cm\(^{-1}\) and a range of gaussian in 400-1750cm\(^{-1}\).

The nature of transition is analyzed as explained previously. \((Ahv)^{1/2}\) vs \(hv\) was found to be the best fit for RNA-TCNQ which is shown in figure 3.1.2b. This shows that a forbidden indirect transition of RNA in the same range becomes allowed in RNA-TCNQ.

![Figure 3.1.2b Allowed indirect transition in RNA-TCNQ charge transfer complex](image)
Thus the intermolecular distance reduces due to complexation with TCNQ. The band gap is 0.25eV and differs from 0.252eV in only RNA by only 0.02eV which is of the order of phonon energy. Thus a phonon is provided by TCNQ molecules. However, the nature of transition remains same in RNA-DDQ as in RNA which is verified by plotting \((Ahv)^{1/3}\) vs \(hv\) (figure 3.1.3 b). Thus, in RNA-DDQ the transition remains forbidden indirect with almost same band gap. Thus indirect transition of RNA with DDQ is very weak. The spectrum of RNA-iodine reveals direct forbidden transition verified by plotting \((Ahv)^{2/3}\) vs \(hv\) which is shown in figure 3.1.4b.
FIGURE 3.1.4b Forbidden direct transition in RNA-iodine

It has band gap of about 0.25eV. Here the effect of phonon is quenched and phonon is not involved in the transition of charge carrier.

There are gaussian distributions of RNA with TCNQ, DDQ and iodine complexes are observed in IR spectrum. The Gaussian distribution is described by \( A = A_0 \exp[-(k-k_0)/2m_2] \) where ‘\( A_0 \)’ is the maximum absorption, ‘\( k_0 \)’ is the central wavenumber and ‘\( m_2 \)’ is the second moment of the distribution. \( m_2 \) is related to the full-width at half-maximum (\( \omega \)) by \( m_2 = \omega^2/8\ln2 \). Thus the Gaussian distribution is fitted by plotting lnA vs (k-k_0)^2 which is a straight line with negative slope. These plots are shown for RNA-TCNQ, RNA-DDQ and RNA-iodine as figure 3.1.2c, 3.1.3c and 3.1.4c respectively.
The three gaussian parameters, namely absorption maximum, central wave number and the full-width at half maximum for these complexes and RNA only are shown in table I. It is easily observed that FWHM for CTCs is much larger than FWHM for only RNA. This shows that there is strong electron-phonon coupling in the CTCs of RNA.
The FTIR spectra of RNA-TCNE and RNA-chloranil are also shown in figure 3.1.5a and 3.1.6a. Both of RNA-TCNE and RNA-chloranil show allowed indirect transition similar to RNA-TCNQ which is fitted in figure 3.1.5b and 3.1.6b respectively. Thus TCNE and chloranil both furnish a phonon required in allowed indirect transition. A change of forbidden to allowed transition usually occurs when the intermolecular distance reduces. It should be noted that TCNQ, TCNE and chloranil are structurally symmetric molecules while DDQ and iodine (due to tri-iodide ions) are asymmetric molecules. Thus symmetric acceptor molecules lead to attractive indirect interaction between two neighboring RNA molecules.

The FTIR spectra of RNA-TCNE and RNA-chloranil contain very broad half-power beta density (flat peak) in rang 1050-400cm\(^{-1}\). This
background beta density follows $A = A_0 k^*^{1/2} (1-k^*)^{1/2}$ where $k^* = (k-a)/b$, ‘a’ being the initial point and ‘b’ being the base width of the peak. For this $A$ vs $k^*^{1/2}(1-k^*)^{1/2}$ is plotted for TCNE and chloranil complexes which shown in figure 3.1.5c and 3.1.6c.

Figure 3.1.5a The FTIR spectrum of RNA-TCNE charge transfer complex

Figure 3.1.6a The FTIR spectrum of RNA-iodine charge transfer complex
Figure 3.1.5b Allowed indirect transition fitted for RNA-TCNE charge transfer complex

Figure 3.1.6b Allowed indirect transition fitted for RNA-chloranil charge transfer complex

Figure 3.1.5c Half-power beta density fitted for RNA-TCNE charge transfer complex
Recently half-power beta densities were observed in many CTCs of biomolecules which were explained with polaron hopping [12, 13]. Beta density is based on Bernoulli a trial which corresponds to hopping and non-hopping of charge carriers. If a charge carrier hops, absorption increases and if it does not hop, absorption decreases. Small polaron formation is likely in most of the macromolecules. RNA is also a macromolecule. A charge moves almost freely between both ends of the molecule but carry a phonon cloud surrounding it. When it faces a large gap in real space between neighboring molecule, it is a form of a polaron at the end where intermolecular hopping occurs.
3.1.4 Conclusion

RNA forms CTCs with organic acceptors such as TCNQ, TCNE, DDQ, chloranil as well as with iodine. Band gap does not change much but nature of transition changes. In TCNQ, chloranil and TCNE complexes, the transition becomes allowed while in iodine complex the transition becomes direct from indirect and in DDQ complex nature of transition is unaffected. Also in TCNQ, DDQ, and iodine complex the gaussian band is retained with broadening while in TCNE and chloranil complex the gaussian band of RNA changes to beta density type which is associated with polaron hopping.

Table 3.1: Gaussian parameters of gaussian distributions observed in RNA and its charge transfer complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gaussian parameters</th>
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<tbody>
<tr>
<td></td>
<td>Absorption Maximum</td>
<td>Central wave</td>
<td>FWHM</td>
</tr>
<tr>
<td></td>
<td>(%)</td>
<td>number (cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
</tr>
<tr>
<td>RNA</td>
<td>42</td>
<td>1070</td>
<td>550</td>
</tr>
<tr>
<td>RNA-TCNQ</td>
<td>20</td>
<td>1100</td>
<td>1000</td>
</tr>
<tr>
<td>RNA-DDQ</td>
<td>20</td>
<td>1100</td>
<td>1040</td>
</tr>
<tr>
<td>RNA-Iodine</td>
<td>22</td>
<td>1080</td>
<td>1020</td>
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</table>
3.2 The study of FTIR spectra of CTCs of DNA

3.2.1 Introduction

DNA (deoxyribonucleic acid) is an important biomolecule and has been a subject of theoretical studies in early years [14-16]. Little proposed an excitonic mechanism of super conductivity in organic conductors [17]. Ladik and Bierman proposed possibility of super conduction in double stranded DNA [18]. Electronic structures and conduction properties of DNA were investigated at a later date [19-21]. Charge transfer and transport in DNA is also a subject matter of discussion [22, 23]. Photo induced charge separation recombination processes in synthetic DNA hairpins have been investigated [24].

D.C. conductivity was earlier found to be water induced [25]. Long-distance charge transport in duplex DNA was studied [26]. DC conductivity of λ-DNA was found to lie in semiconducting range i.e. of the order of $10^6 \Omega \text{cm}$ [27]. Physicists working on organic conductors have also found charge transfer along λ-DNA double helix [28]. Variable range hopping was found charge transport along DNA [29]. Insulating behavior was also observed [30]. Temperature dependence of hopping conductivity of DNA was studied [31]. A periodic nucleotide base-stack also showed
charge transport [32]. AC conductivity of a periodic DNA was studied [33]. Dipole relaxation losses in DNA due to water helix were studied [34]. Conductivity of DNA was also probed by conducting-atomic force microscopy [35]. Low-temperature conductivity of DNA was found to be very high [36]. Optical conductivity of wet DNA was also investigated [37]. Single molecule study of DNA was carried out [38]. Recently charge transfer excitons in DNA were reported [39]. Calf-thymas DNA films were studied for optical conductivity.

DNA complexes have also been studied recently. Ternary copper complexes for photo cleavage of DNA were studied [40]. Anthraquinone and its derivatives, chloranil and ethidium bromide [41-44] led to oxidative damage of DNA. However, organic donors like benzidine, arginine and lysine formed only molecular adducts or hydrogen bonded materials [45].

In the present studied, we carry out FTIR spectroscopic measurements on DNA and its charge transfer complexes with organic acceptors such as TCNQ, TNCE, DDQ, chloranil and KI-I\(_2\). This leads to oxidative damage but higher conductivity in complexes because of intercalation of acceptor molecules in DNA stacks. DNA-chloranil and DNA-KI-I\(_2\) were found to be semi-metallic on the basis of their infrared absorption edges.
3.2.2 Experimental details

Calf thymas DNA was obtained from Sigma-Aldrich chemical company as a white cotton-type fibrous material. It was mixed with organic acceptors such as TCNQ(7,7,8,8,-tetracyano-p-quinodimethane), TCNE( tetracyano-p-ethylene), DDQ (2,3,-dichloro-5,6-dicyano-p-benzoquinone), chloranil(2,3,5,6-tetrachloro-p-benzoquinone) and KI-I₂. Then the mixtures were grinded in an agate mortar with a pastle for 15-20 minutes till colours changed. The fine homogeneous powders were mixed with 95% spectrograde KBr powder and were again grinded. The mixtures were then compressed in circular die with a manually operated compressing machine to make semitransparent palates of circular shape. These round discs were placed in dark chamber of spectrophotometer.

3.2.3 Result and discussion

The FTIR spectrum of DNA (deoxyribonucleic acid) is shown in figure 3.2.1a. There is a range of 2950cm⁻¹ to 1800cm⁻¹ which corresponds to the electronic transition from valence band to conduction band. This interband transition is analyzed and the analytical graph is shown in figure 3.2.1b. All the graphs (Ahv)¹/₂, (Ahv)²/₃, (Ahv)¹/₃, (Ahv)² and (Ahv) vs hv were plotted and the best fit (Ahv)¹/₃ vs hv is shown in figure 3.2.1b. This
shows that $h\nu = B(h\nu - E_g \pm E_p)^3$ is the best fit for absorbance ‘a’. $E_g$ is found to be 0.3eV as shown as an intercept of line with the background absorption at 0.3eV. It was found in an earlier study [28] that the electrical conductivity is given by $\sigma = \sigma_0 \exp (-\Delta/2k_B T)$ and $\Delta = 0.3$eV for $\lambda$-DNA in a buffer environment. Thus our result of optical band gap agrees with this result. The site energy has a uniform distribution between $-\Delta/2$ to $+\Delta/2$ as reported elsewhere [29]. If R is the distance between an occupied site and a vacant site and if R smaller than ‘a’ (the distance between the nearest neighbor bases), the electrical conductivity has the usual temperature dependence of activated behavior. Thus our result also agrees with what is mentioned in study of variable range hopping [29]. $\Delta/2$ was reported to be 0.15eV.

![Figure 3.2.1 a The FTIR spectrum of calf thymus DNA](image)

Figure 3.2.1 a The FTIR spectrum of calf thymus DNA
The FTIR spectra of DNA-DDQ and DNA-TCNE are shown in figure 3.2.2a and 3.2.3a respectively. There is again a range of nature of interband transition in the spectra. There are threshold energies of excitons with phonon emission bands in the absorption edges as found in gallium phosphite [46]. In GaP, the exciton threshold energies lie in the UV-visible range. In DNA-DDQ and DNA-TCNE, these energies lie in the infrared range. These infrared excitons may be combination or pairing of electron-polaron and a hole polaron. They may be also called as excitonic bipolaron. The bipolaron to polaron dissociation occurs in this energy range. $E_B - 2E_p$ where $E_B$ is binding energy of a bipolaron and $E_p$ is polaron binding energy. The analysis shows that $(Ahv)^{1/3}$ vs $hv$ is the best fit
associated with forbidden indirect transition as it occurs in pure DNA. The Kinks as threshold energies are also seen with broad phonon emission bands in these graphs of analyses which shown in figure 3.2.2b & 3.2.3b respectively. GaP has electron-hole droplets or exciton liquid below 45K. The infrared excitons may also condense in liquid form at low temperatures. Thus there is possibility of exciton droplets in these CTCs of DNA. Electron-hole pairs or excitons form gas at room-temperature and can undergo a gas to liquid transition at low temperature. This can be studied with infrared stimulated luminescence which is also known in semiconductor physics [47].

![Figure 3.2.2a The FTIR spectrum of DNA-DDQ charge transfer complex](image)

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Figure 3.2.3a The FTIR spectrum of DNA-TCNE charge transfer complex

Figure 3.2.2b Forbidden indirect transition for DNA-DDQ charge transfer complex

Figure 3.2.3b Forbidden indirect transitions fitted for DNA-TCNE charge transfer complex
The FTIR spectra of DNA-chloranil and DNA-KI-I\textsubscript{2} are also shown in figure 3.2.4a and figure 3.2.5a respectively. These CTCs have shown even more interesting results. It is recently found that the absorption ‘a’ can be replaced by transmission $\tau$ in highly conducting compound in the analysis of absorption edge because whatever light is transmitted it all gets absorbed in a electrically conducting material. Thus $(\tau \hbar \nu)^{1/2}$, $(\tau \hbar \nu)^{2/3}$, $(\tau \hbar \nu)^{1/3}$ and $(\tau \hbar \nu)^2$ and $(\tau \hbar \nu)$ vs $\hbar \nu$ should be plotted for the analysis. This type of analysis was recently carried out for ternary CTCs of bis(diphenylglyoximato)Ni\textsuperscript{II} and four ternary complexes were predicted to be semi-metallic [48]. These CTCs show positive temperature coefficients of resistivity with negative activation energies like semi-metals [37]. Analysis of this type is carried out here for DNA-chloranil and DNA-KI-I\textsubscript{2} as shown in figure 3.2.4b & 3.2.5b respectively. $(\tau \hbar \nu)^{1/2}$ vs $\hbar \nu$ were found to be best fits indicating an allowed indirect transition in both of DNA-chloranil and DNA-KI-I\textsubscript{2} has also shown one more transition which is forbidden indirect type by the plot of $(A\hbar \nu)^{1/3}$ vs $\hbar \nu$ as shown in figure 3.2.5c. Thus DNA-KI-I\textsubscript{2} shows two band transport in which both DNA stacks and iodine chains may be conducting.

Finally, the FTIR spectrum of DNA-TNCQ is shown in figure 3.2.6. This shows a spectrum of TCNQ\textsuperscript{2-} ionic nature of the charge transfer
complex. TCNQ$^{2-}$ chains are bound by DNA stacks which form cationic stacks may be related with oxidative damage. In any case, purines and pyrimidines are giving rise to donating nature of DNA rather than working as an acceptor. The absorption spectrum is mainly governed by TCNQ$^{2-}$ stacks rather than DNA helix. The result for nature of transitions and values of band gaps are summarized in a table 3.2.

Figure 3.2.4 a FTIR spectrum of DNA-chloranil charge transfer complex

Figure 1.2.5 a The FTIR spectrum of DNA-KI-I$_2$ charge transfer complex
Figure 3.2.4b Allowed indirect transition fitted for DNA-chloranil charge transfer complex

Figure 3.2.5b allowed indirect transitions fitted for DNA-KI-K2 CTC at higher frequency

Figure 3.2.5c Forbidden indirect transitions fitted for DNA-KI-I2 at lower frequency
Figure 3.2.6 The FTIR spectrum of DNA-TCNQ charge transfer complex

### 3.2.4 Conclusion

DNA was found to be semiconducting with optical band gap of 0.3eV form its infrared transmission spectrum. The CTCs of DNA were found to be either semiconducting or semi-metallic. DNA-DDQ and DNA-TCNE were semiconducting with infrared excitons and with possibility of exciton droplets at low temperatures. DNA-chloranil and DNA-KI-I$_2$ were found to be semi-metallic having possibility of negative band gaps. DNA-TCNQ was found to be strongly ionic complex.
Table 3.2: Types of transition of DNA and its CTCs with its band gap

<table>
<thead>
<tr>
<th>Names of complexes</th>
<th>Absorption function</th>
<th>Nature of transition</th>
<th>Value of band gap $E_g$(eV)</th>
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<tr>
<td>DNA Ah $\nu = B(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>DNA-DDQ Ah $\nu = B(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>DNA-TCNE Ah $\nu = B(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
<td>0.28</td>
<td></td>
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<td>DNA-chloranil $\tau h \nu = B(h\nu - E_g)^2$</td>
<td>Allowed indirect</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>DNA-KI-I$_2$ $\tau h \nu = B(h\nu - E_g)^2$</td>
<td>Allowed indirect</td>
<td>0.25</td>
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<tr>
<td>DNA-chloranil Ah $\nu = B(h\nu - E_g)^3$</td>
<td>Forbidden indirect</td>
<td>0.218</td>
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</tbody>
</table>

Reference


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