Z-Scan and Degenerate Four Wave Mixing Studies in Metal Complexes of Quinoxaline-2-Carboxalidene-2-Aminophenol

Abstract

Degenerate four wave mixing experiments were carried out in solutions of various metal complexes of Quinoxaline-2-Carboxalidene-2-Aminophenol (QAP). 532 nm radiation from a Q-switched Nd:YAG laser operating in the nanosecond region is used for the sample excitation. Figure of merit of third order nonlinearity (F), Third order susceptibility ($\chi^3$) and Second hyperpolarizability $\langle \gamma \rangle$ of these samples were measured in different solvents using DFWM technique. The nonlinear absorption coefficient ($\beta_{eff}$) and imaginary part of susceptibility tensor [Im($\chi_{eff}^3$)] of these samples were measured using z-scan technique. The measured nonlinear parameters are explained as due to the combined effect of nonlinear absorption, oscillator strength and resonance effects at the wavelength of excitation. The optical limiting nature of these samples were also studied and it is observed that Ni and Co QAP’s are very good candidates for device applications.
1 Introduction

Nonlinear optical processes in π-electron organic systems have attracted considerable interest because their understanding has led not only to compelling technological promise but also to new phenomena, new theoretical insights and new materials and devices [1]. The π-electron excitation occurring on the individual molecular units is the basic origin of the observed non-resonant nonlinear optical coefficients, which are often unusually large in magnitude. As shown by theory and experiments, ‘many body correlation effects’ determine the sign, magnitude and frequency dependence of these nonlinear optical parameters and this level of understanding helps us for the development of new NLO materials with many useful properties.

In recent years the research in this field is focused on high performance NLO materials with technological applications and considerable progress has been achieved towards the realization of the same. Many challenges in material synthesis have been met so far and this has resulted in various methods for ultra-structure synthesis and the discovery of entirely new materials exhibiting high thermal, mechanical and chemical stability. Semiconductors, conjugated polymers, liquid crystals, dyes, fullerenes, charge transfer complexes, organometallics, biomaterials, nanocomposites etc. are different class of materials with varying degree of NLO behaviour and several new compounds are being studied for their applications in various fields [2-15]. Out of the large number of compounds with varying degree of NLO behaviour, as mentioned earlier organic compounds like Porphyrins, Phthalocyanines etc. with large number of delocalized π-electrons have got a great deal of attention because of their architectural flexibilities, large nonlinear optical susceptibilities and ease of fabrication [16-17]. Different types of structural modifications can considerably modify the nonlinear optical properties of various organic compounds and the structural modifications include peripheral and axial substitutions to the molecules, complex formation with different metal atoms etc. [18-20]. The metal substitution can be effective in improving the nonlinear optical
Investigations of nonlinear response through the polarisable valance electrons. With the motivation to develop an understanding of the effect of metal ion substitution on the nonlinear behaviour of organic compounds, we have studied the effect of different metal ions on the second hyperpolarizability of the compound, Quinoxaline-2-Carboxalidene-2-Aminophenol (QAP).

Quinoxaline-2-Carboxalidene-2-Aminophenol (QAP) is an organic compound derived from the well known class of compounds named Schiff bases. Schiff's bases are organic compound containing the azomethine group (-RC=N-) and are usually formed by the condensation of a primary amine with an active carbonyl compound. Metal complexes of schiff bases represent an important and interesting class of nonlinear optical material and there are reports on the NLO properties of various Schiff base compounds in different forms [20-22]. There are various methods by which we can synthesis the Schiff's base. The preparation and isolation of the free base ligand followed by copmplexation with a metal ion has traditionally been the usual method for the preparation of metal ion complexes of Schiff' bases.

4.2 Experimental
The experimental part of the present study is divided into two sections viz. sample preparation and Degenerate Four Wave Mixing

4.2.1 Sample Preparation
The samples used for the present study were prepared by the method explained below

4.2.1.1 Preparation of Quinoxaline-2-Carboxaldehyde
For the synthesis of the base compound Quinoxaline-2-Carboxaldehyde we have used the reported procedure in the literature [23-24]. Treatment of D-glucose with O-phenylenediamine in the presence of hydrazine hydrate and acetic acid on a boiling water bath under carbon dioxide atmosphere gave the compound 2-(D-arabinotetrahydroxybutyl) quinoxaline. Oxidation of this
compound with sodium metaperiodate in water in the presence of acetic acid at laboratory temperature gives the compound Quinoxaline-2-Carboxaldehyde. The product thus obtained is isolated by extraction with ether and purified by re-crystallization from petroleum ether. The structure of Quinoxaline-2-Carboxaldehyde is as shown below [25].

Fig 4.1 Structure of quinoxaline-2-carboxaldehyde

4.2.1.2 Preparation of Quinoxaline-2-Carboxalidene-2-aminophenol (HQAP)

The ligand Quinoxaline-2-Carboxalidene-2-aminophenol (HQAP) was prepared by mixing an ethanolic solution of Quinoxaline-2-Carboxaldehyde and 2-aminophenol. The solution was refluxed for one hour. The ligand separated out was filtered and dried in vacuum over anhydrous calcium chloride. The structure of HQAP thus obtained is as shown below [25].

Fig. 4.2 Structure of HQAP
4.2.1.3 Preparation of metal complexes

The metal complexes of Quinoxaline-2-carboxaldehyde-2-aminophenol were prepared by the following procedure. An ethanolic solution of the Schiff base (HQAP) was mixed with the corresponding metal salt solution. The solution was refluxed for two hours. The volume of the resulting solution was then reduced by evaporation and the solution was cooled in a freezer for about one hour. The crystalline complexes separated out was filtered, washed with ether and dried in vacuum over anhydrous calcium chloride. Fig. 4.3 shows the structure of the metal complexes thus obtained [25].

![Fig. 4.3 Schematic structure of QAP Complexes](image)

The samples thus obtained are dissolved in highly purified, spectroscopic grade solvents and the absorption spectra are recorded using a UV/VIS/NIR spectrophotometer (Jasco V-570). In all experiments, sample solutions are taken in 1-mm quartz cuvettes. Fresh solutions are prepared for each measurement to avoid any complications arising from photodegradation.
## 4.2.2 Degenerate Four Wave Mixing

Detailed theory and experimental setup of degenerate four wave mixing were discussed in chapter 2. We employ the standard back scattering geometry for making the measurements. Radiation at 532 nm from a Q-switched Nd:YAG laser is used as the source of excitation. One of the advantages of DFWM experiment is that by suitably choosing the polarizations of interacting beams we can select different components of third order susceptibility tensor [26-27].

This property is exploited to avoid thermal contribution occurring in experiments with nanosecond pulses. In the present experiment, polarizations of the interacting beams were so chosen that measurements gave only electronic response. The two pump beams were vertically polarized and the probe beam was horizontally polarized. The polarization of the phase conjugate beam is same as that of pump beam. The angle between the pump and probe beams is ~$8^0$ and the phase conjugate signal counter propagating to the probe is separated by using a beam splitter. The energy of the phase conjugate signal as well as the pump beams were measured by using a dual channel energy ratio meter Rj-7620 and Rjp-735 pyroelectric probes (Laser Probe International, USA).

The values of the second hyperpolarizability $\gamma$ were calculated using the following equations

\[
\chi_s^{(3)} = \chi_{\text{ref}}^{(3)} \left[ \frac{(I/I_0^3)}{(I/I_0^3)_{\text{ref}}} \right]^{1/2} \left( \frac{n_0}{n_{\text{ref}}} \right)^2 \left( \frac{l_{\text{ref}}}{l} \right) \left( \frac{\alpha l \exp(\alpha l/2)}{1 - \exp(-\alpha l)} \right) \tag{4.1}
\]

and

\[
\langle \gamma \rangle = \frac{\chi^{(3)}}{L^4 N} \quad ; \quad L = \frac{n^2 + 2}{3} \tag{4.2}
\]
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where 'n' is the refractive index 'l' is the length of the sample, 'α' is the linear absorption coefficient and 'I' is the intensity. For a solution of non-interacting particles, the effective \( \chi^{(3)} \) assuming a pairwise additive model [28] is given by

\[
\chi^{(3)}_{\text{solution}} = L^4 \left[ N_{\text{solvent}} \gamma_{\text{solvent}} + N_{\text{solute}} \gamma_{\text{solute}} \right]
\]

where \( N_{\text{solute}}, N_{\text{solvent}} \) are the number densities of molecules of the solute and the solvent respectively. For dilute solutions with \( N_{\text{solute}} = (A \times C)/M \), we may write

\[
\chi^{(3)}_{\text{solution}} = \chi^{(3)}_{\text{solvent}} + \frac{L^4 \gamma_{\text{solute}} A x C}{M}
\]

where 'A' being the Avagadro's number, 'M' being the molecular weight and 'C' the concentration of the solute in g/ml. For lower concentrations the \( \chi^{(3)} \) of the solution follows a linear relationship with respect to the concentration of the solute. \( \chi^{(3)} \) may have both real and imaginary components originating from the solute as well as solvent. The real part is responsible for the nonlinear refraction whereas the imaginary part is responsible for nonlinear absorption, SA, TPA or ESA. The real part can be positive or negative. The figure of merit, independent of concentration, \( F \) is defined as \( \chi^{(3)}/\alpha \). We have taken the value of \( \chi^{(3)} \), for the reference sample CS\(_2\) as \( 2.73 \times 10^{-13} \) esu [29]. \( L \) is the local field correction factor and \( N \) is the number density of the solute molecules in solution. The \( \chi^{(3)} \) contribution from solvent is taken to be zero, as it is negligibly small in comparison to the solute.

4.2.2.1 Calibration

For the measurements of the nonlinear parameters using degenerate four wave mixing technique the experimental setup has to be standardized using a nonlinear optical material. Carbon disulphide (CS\(_2\)) is used as the standard material because of its completely non-resonant Kerr nonlinearity due to orientational response. Fig. 4.3 shows the log-log plot of optical phase conjugate signal intensity against pump beam
intensity for CS$_2$ when polarization of the probe beam was orthogonal to the pump beam. The graph obtained is a straight line with slope 2.98 which is very close to the theoretical value 3 showing the cubical dependence of phase conjugate signal against the pump beam intensity.

![Graph](image)

**Fig. 4.4 log-log plot of OPC signal against pump beam intensity**

4.2.3 Z-Scan

The detailed theory of the z-scan measurements was explained earlier in this thesis. Here also we have used the standard open aperture z-scan technique developed by Sheik Bahae *et. al.* [30], for evaluating the nonlinear optical parameters of the samples. Radiation at 532 nm from a Q-switched Nd:YAG laser were used for the excitation. The samples were taken in 1 mm quartz cuvette and scanned across the focus a lens of 20 cm focal length by using a micrometer translation stage. This configuration gives a Raleigh range of 1.36 mm so that the thin sample approximation condition is satisfied for the measurements carried out here. The input and output energies were measured by using a duel channel energy ratio meter (Rj-7620, Laser Probe International, USA) with pyroelectric detector heads (Rjp-735)
4.3 Results

Fig. 4.5 and 4.6 show the absorption spectra of the samples used for the present study. Fig. 4.5 shows the absorption spectrum of 0.1 mM solution of the samples in Dimethyl Formamide (DMF) and Fig. 4.6 represent the same in chloroform (0.25 mM). From the absorption spectra it is clear that in DMF, Nickel Quinoxaline-2-Carboxalidene-2-aminophenol [Ni(QAP)\textsubscript{2}], Cobalt Quinoxaline-2-Carboxalidene-2-aminophenol [Co(QAP)\textsubscript{2}] and Manganese Quinoxaline-2-Carboxalidene-2-aminophenol [Mn(QAP)\textsubscript{2}] shows two absorption bands. But in the case of Copper Quinoxaline-2-Carboxalidene-2-aminophenol [Cu(QAP)\textsubscript{2}] the low energy absorption band is missing. In all these samples the high energy absorption bands extend from 300 to 450 nm region and they are known as the Soret band or S-band. The low energy bands called (Q-bands) are having slightly different ranges. The red shift in the absorption bands (Q-band) in these metal QAP’s is found to be proportional to the atomic number of the central metal atom present. But in chloroform, only Ni(QAP)\textsubscript{2} shows two absorption bands. All the other samples show only high energy band. This clearly shows that the solvent induces chemical changes in the samples under investigation and this is reflected in the measured values of NLO parameters.
4.3.1 Degenerate Four Wave Mixing

The experiments were carried out with freshly prepared samples in spectroscopic grade solvents DMF and Chloroform. The Degenerate Four Wave Mixing (DFWM) experiments carried out in these samples shows a cubical dependence of the phase conjugate signal over the pump signal.

Fig. 4.7 log-log plot of \( \text{Co(}Q\text{AP)}_2 \)

Fig. 4.8 log-log plot of \( \text{Cu(}Q\text{AP)}_2 \)

Fig. 4.9 log-log plot of \( \text{Mn(}Q\text{AP)}_2 \)

Fig. 4.10 log-log plot of \( \text{Ni(}Q\text{AP)}_2 \)
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Figure 4.7 to 4.11 shows the phase conjugate signal verses input intensity of these samples in DMF. The concentration of the samples was kept at 0.1 mM. Similarly Fig. 4.12 to 4.16 shows the log-log plots obtained with DFWM experiments in these samples in chloroform. In this case the concentration of the samples used are 0.25 mM.

Fig. 4.11 log-log plot of different QAP's in DMF

Fig. 4.12 log-log plot of Co(QAP)$_2$ in CHCl$_3$

Fig. 4.13 log-log plot of Cu(QAP)$_2$ in CHCl$_3$
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A slope of 3 in the log-log plots between the pump and phase conjugate signal indicates the third order nature of the process involved as well as the absence of saturation of nonlinearity in the measurements. The straight line graphs
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obtained in all these experiments are fitted by using a cubical function defined by Eq. 2.40 in chapter 2.

There are several processes, which can influence the degenerate four wave mixing experiments. Two photon absorption (TPA) is one among them. If TPA is present in the samples the slope of the straight line obtained in the log-log plot between the pump intensity and the optical phase conjugate signal (OPC) should be 5 instead of 3 [31-32]. All the samples studied here gives plots with slope 3 and hence the presence of TPA contribution to the measurements can be ruled out. Since the experiments were done with samples dissolved in spectroscopic grade solvents, it is possible to evaluate the microscopic molecular property viz. second hyper polarizability $\gamma$. Measured values of third order susceptibility ($\chi^{(3)}$), Figure of merit (F), Extinction coefficient ($\varepsilon$) and Second hyper polarizability $\gamma$ are given in the table 4.1 and 4.2 given below. For the calculation of the Figure of merit (F) of a nonlinear optical material we have used the relation

$$F = \frac{\chi^{(3)}}{\alpha}$$ (4.5)

where $\alpha$ is the linear absorption coefficient of the sample. The extinction coefficient will be given by [33]

$$\varepsilon = \frac{\alpha N_A x 10^{-3}}{\ln(10)}$$ (4.6)

where $\sigma$ is the absorption cross section and $N_A$ is the Avogadro number. From the extinction coefficient $\varepsilon$ we can calculate the oscillator strength of the molecule. It is a very important parameter, which can heavily influence the second hyper polarizability $\gamma$ [34-36] and is related to the extinction coefficient by the following relation.

$$f = \left(\frac{1}{n}\right) \times 4.319 \times 10^{-9} \int \varepsilon dv$$ (4.7)
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#### Table 4.1 Extinction coefficient, Third order susceptibility, Figure of merit and Second hyper polarizability of different QAP's measured in Dimethyl formamide

<table>
<thead>
<tr>
<th>Sample in DMF (0.1 mM)</th>
<th>Linear Absorption Coefficient $\alpha$ (cm$^{-1}$)</th>
<th>Extinction coefficient $\varepsilon \times 10^3$ ltr cm$^{-1}$ mol$^{-1}$</th>
<th>Third order Susceptibility $\chi^{(3)}$ (x $10^{-13}$ esu)</th>
<th>Figure of Merit $F$ (x $10^{-13}$ esu-cm)</th>
<th>Second Hyper polarizability $\langle \gamma \rangle$ (x $10^{-30}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (QAP)$_2$</td>
<td>1.054</td>
<td>4.579</td>
<td>12.65</td>
<td>12.00</td>
<td>6.42</td>
</tr>
<tr>
<td>Cu (QAP)$_2$</td>
<td>0.136</td>
<td>0.591</td>
<td>2.54</td>
<td>18.65</td>
<td>1.29</td>
</tr>
<tr>
<td>Mn (QAP)$_2$</td>
<td>0.183</td>
<td>0.795</td>
<td>3.08</td>
<td>16.85</td>
<td>1.56</td>
</tr>
<tr>
<td>Ni (QAP)$_2$</td>
<td>0.708</td>
<td>3.074</td>
<td>11.40</td>
<td>16.10</td>
<td>5.78</td>
</tr>
</tbody>
</table>

#### Table 4.2 Extinction coefficient, Third order susceptibility, Figure of merit and Second hyper polarizability of different QAP's measured in Chloroform

<table>
<thead>
<tr>
<th>Sample (in chloroform)</th>
<th>Linear Absorption Coefficient $\alpha$ (cm$^{-1}$)</th>
<th>Extinction coefficient $\varepsilon \times 10^3$ ltr cm$^{-1}$ mol$^{-1}$</th>
<th>Third order Susceptibility $\chi^{(3)}$ (x $10^{-13}$ esu)</th>
<th>Figure of Merit $F$ (x $10^{-13}$ esu-cm)</th>
<th>Second Hyper polarizability $\langle \gamma \rangle$ (x $10^{-30}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (QAP)$_2$</td>
<td>0.113</td>
<td>0.195</td>
<td>10.55</td>
<td>93.74</td>
<td>2.04</td>
</tr>
<tr>
<td>Cu (QAP)$_2$</td>
<td>0.082</td>
<td>0.142</td>
<td>04.98</td>
<td>60.85</td>
<td>0.96</td>
</tr>
<tr>
<td>Mn (QAP)$_2$</td>
<td>0.073</td>
<td>0.126</td>
<td>07.32</td>
<td>100.49</td>
<td>1.41</td>
</tr>
<tr>
<td>Ni (QAP)$_2$</td>
<td>1.5379</td>
<td>2.672</td>
<td>53.12</td>
<td>34.54</td>
<td>10.25</td>
</tr>
</tbody>
</table>
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Table 4.1 and 4.2 shows the NLO parameters calculated in various QAP’s in DMF (0.1 mM) and Chloroform (0.25 mM) respectively by using the DFWM technique. From the table 4.1 we can see that in DMF the Figure of merit of all these samples are more or less same. Out of the four QAP’s studied here Co (QAP)₂ gives the lowest value of Figure of merit and highest value for second hyper polarizability. The largest value of Figure of Merit calculated is in Cu (QAP)₂. In chloroform the maximum and minimum values of figure of merit is obtained in Mn (QAP)₂ and Ni (QAP)₂ respectively. But the maximum and minimum values of second hyper polarizability is in Ni (QAP)₂ and Cu (QAP)₂.

4.3.2 Z-Scan

Fig. 4.13 to 4.16 shows the open aperture z-scan curves obtained with 0.25 mM solutions of these samples in chloroform. All these samples show similar behaviour. The nonlinear absorption coefficient ($\beta_{\text{eff}}$) in these samples can be calculated using the model suggested by Sheik Bhahe et.al. [37] explained in chapter 3. The imaginary part of the nonlinear susceptibility ($\text{Im} \chi_{\text{eff}}^3$) can be calculated from $\beta_{\text{eff}}$ using the expression

$$\text{Im}(\chi_{\text{eff}}^3) = \frac{\lambda \varepsilon_0 n^2 c \beta_{\text{eff}}}{4 \pi}$$

(4.8)

Fig. 4.13 Open aperture z-scan curve of 0.25 mM Ni (QAP)₂ in chloroform

Fig. 4.14 Open aperture z-scan curve of 0.25 mM Mn (QAP)₂ in chloroform
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Fig. 4.15 Open aperture z-scan curve of 0.25 mM Cu (QAP)$_2$ in chloroform

Fig. 4.16 Open aperture z-scan curve of 0.25 mM Co (QAP)$_2$ in chloroform

Table 4.3 gives the NLO parameters, nonlinear absorption coefficient ($\beta_{\text{eff}}$) and the imaginary part of the nonlinear susceptibility ($\text{Im}\chi_{\text{eff}}^3$) calculated using the open aperture z-scan measurements carried out in these samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption Coefficient $\alpha$ (cm$^{-1}$)</th>
<th>$\beta_{\text{eff}}$ (m/GW)</th>
<th>$\text{Im}\chi_{\text{eff}}^3 \times 10^{-17}$ m$^2$V$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (QAP)$_2$</td>
<td>1.538</td>
<td>4.578</td>
<td>10.73</td>
</tr>
<tr>
<td>Co (QAP)$_2$</td>
<td>0.113</td>
<td>3.415</td>
<td>8.00</td>
</tr>
<tr>
<td>Cu (QAP)$_2$</td>
<td>0.0818</td>
<td>3.315</td>
<td>7.77</td>
</tr>
<tr>
<td>Mn (QAP)$_2$</td>
<td>0.0730</td>
<td>1.515</td>
<td>3.55</td>
</tr>
</tbody>
</table>
4.4 Discussion

We have studied the nonlinear optical behaviour of four different metal QAP's by using the DFWM and Z-Scan techniques. The usefulness of these samples to protect the light sensitive instruments from intense light radiations has been studied using the optical limiting technique. The second hyperpolarizability \( \langle \gamma \rangle \) of a material depends on many factors. \( \pi \)-electron conjugation length \([38,39]\), Oscillator Strength \([36, 40-41]\), Metal substituents in the molecule \([40, 42-45]\) , Dimensionality of the molecule \([46-49]\), Axial and peripheral substituents \([50-56]\) etc. are the important parameters determining the Second hyperpolarizability \( \langle \gamma \rangle \) values of a material. The \( \langle \gamma \rangle \) values measured can have a cumulative contribution from these parameters.

The metal atoms present in various QAP's plays a very important role in the nonlinear as well as spectroscopic properties of the samples studied here. For example, from the absorption spectra in DMF we can see that the redshifts of peak wavelength of Q-bands in these samples are proportional to the atomic number of the metal present in the complex. Here we consider only the influence of metal ions on the third order NLO properties of these samples. The effect of metal ions in the NLO properties of compounds like Phthalocyanines, Porphyrins etc. are well known and the mechanism of interaction which leads to the modification of the nonlinear behaviour is really interesting since it will give greater insights into the NLO properties of this class of compounds \([38, 40, 43, 57, 58]\). Metal substitution, on many occasions, improves the magnitude of nonlinear optical response through the polarisable valance electrons. Among a number of metal ions transition metal with incompletely filled d-shells have been found to be very effective in enhancing the third order nonlinear properties. \([38,40]\). From the tables 4.1 to 4.3 we can observe that in QAP's also the NLO properties are modified by the nature of the metal ion present. As mentioned earlier, several mechanisms can have cumulative effects in the measured second hyperpolarizability \( \langle \gamma \rangle \) values of a NLO material. One of the major
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reason for the observed large value of second hyperpolarizability $\gamma$ of Ni and Co QAP's in DMF can be attributed to the larger oscillator strength of these compounds. The second hyperpolarizability $\gamma$ values of the same set of samples, given in table 4.2, measured in Chloroform confirms our observation in DMF. In this case, Ni (QAP)$_2$ which is having the largest value of extinction coefficient $\varepsilon$ has got the maximum value for oscillator strength defined by the equation 4.7 and hence the largest value for the second hyperpolarizability $\gamma$.

The $\pi$-electrons present in the system get perturbed by the metal ions and this in turn affect the spectral features of the material by the introduction of low lying charge transfer (CT) states in the HOMO-LUMO gap through charge transfer mechanisms. The charge transfer mechanism means the interaction of the valance electrons of the metal ions with $\pi$-electrons of the complex molecular system and the CT mechanism include metal-ligand, ligand-metal and metal-metal CT processes. The location of the CT states depends on the overlap between the orbitals and separation between filled and unfilled states [59]. This can also contribute to the measured values of second hyperpolarizability.

Dimensionality of the molecule is another important factor contributing to the nonlinear properties of the materials [50]. Out of the samples studied here Co (QAP)$_2$ is having tetrahedral structure. Ni (QAP)$_2$ and Cu (QAP)$_2$ are having square planar geometry [60]. When the dimensions of the molecules are increased the effective conjugation length available for an electron to respond to applied optical field decreases and consequently the magnitude of $\gamma$ values decreases [61]. For example, Kumar et al. [62] have measured $\chi^{(3)}$ values of basket handle porphyrins and observed a decrease in third order nonlinearity due to the deviation from planarity of molecules.
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Resonance is another important process, which influence the nonlinear properties of materials. A salient feature of resonant nonlinearity is the considerable enhancement in the magnitude of nonlinear coefficients with respect to nonresonant quantity [50]. In most of the experimental situations a combination of a weak resonant and a background nonresonant nonlinearity is observed instead of a completely resonant or completely nonresonant nonlinearity. A fundamental drawback of resonant nonlinearity is its slow response [63]. But its advantage is its enormously large magnitude. A large number of resonant transitions, such as electronic, vibrational and rotational transitions are possible in macromolecules with large number of $\pi$-electrons. Each of these transitions may produce resonance effects. The relative strength of different transitions varies over several orders of magnitude [50]. From the absorption spectra (Fig. 4.5 and 4.6) we can see that at the wavelength of excitation there are some resonance effects. This resonance effect is more prominent in Ni (QAP)$_2$ in chloroform. Compared to the second hyperpolarizability $\chi^{(3)}$ values of the samples other than Ni (QAP)$_2$ large value for $\chi^{(3)}$ in this sample when taken in chloroform may be due to the resonance enhancement. The low figure of merit of this sample in this case is an indication of this effect. Therefore the observed large value of Ni and Cu QAP's has a combined effect of several processes, out of which the combined effect of nonlinear absorption, large oscillator strength and resonance effects are the major contributors to the second hyperpolarizability of these molecules. This observation is well supported by the nonlinear absorption coefficient $\beta_{\text{eff}}$ and imaginary part of nonlinear susceptibility $\text{Im}(\chi^{(3)})$ values obtained with the z-scan technique given in table 4.3.

To explain nonlinear absorption under nanosecond excitation, we suggest a five level model involving the states $S_0, S_1, S_2, T_1$ and $T_2$ as shown in Fig. 4.17 Here $S_n$ and $T_n$ are the singlet and triplet states respectively where $n = 0, 1$ or 2 and every electronic energy level involves many vibronic sublevels. When interacting with a laser pulse at 532 nm, atoms get excited from the $S_0 (\nu=0)$ to the upper vibrational
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The level of $S_1$. Here $v$ corresponds to the vibrational quantum number. Through the nonradiative decay within picosecond time scales, they can relax to the lowest vibrational level of $S_1$ ($v=0$). Since QAP's have very low fluorescence the transition from $S_1$ ($v=0$) to $S_0$ can be neglected. The occurrence of the $S_2 \leftrightarrow S_1$ transition does not appreciably deplete the $S_1$ state, as the $S_1 \leftrightarrow S_2$ decay also takes place within picoseconds. However the cross section of the $T_1(v=0) \leftrightarrow S_1(v=0)$ intersystem crossing is large, leading to a strong triplet – triplet absorption $T_2 \leftrightarrow T_1$. Here we assume that the intersystem crossing [64] is fast compared with the laser pulse width (9 ns) and virtually all the atoms excited from $S_0$ reach the first excited triplet state $T_1$. Therefore under nanosecond pulse excitation, the nonlinear absorption observed here is a consequence of $T_2 \leftrightarrow T_1$ absorption [$T_2 \leftrightarrow T_1(v=0)$]

![Five level energy diagram](image)

Fig. 4.17 Five level energy diagram for metal QAP's. $S_n$ ($n = 0,1,2$): Singlet levels; $T_n$ ($n = 1, 2$): Triplet levels
The nonlinear absorption coefficient ($\beta_{\text{eff}}$) and the imaginary part of the nonlinear susceptibility ($\text{Im}\chi_{\text{eff}}^{3}$) calculated in these samples shows that $\text{Ni (QAP)}_2$ is having the best nonlinear optical parameters.

### 4.5 Optical Limiting

The nonlinear absorption seen in these samples reveals that they can be used as potential optical limiters. Therefore, the optical limiting behaviour of these samples was investigated and Fig. 4.17 to 4.21 represents the optical limiting graphs generated from the z-scan curves given earlier. For being used as a good optical limiter, a number of important requirements should be met by the nonlinear material. Fast response, high damage threshold and an excited state absorption cross-section larger than the ground state absorption cross-section are the most important among them [65]. It is well known that materials which are having excited state absorption cross section larger than the ground state absorption cross section are better optical limiters and they can respond to both fast and slow laser pulses via the ($S_2 \leftarrow S_1$) and ($T_2 \leftarrow T_1$) transitions respectively.

![Fig. 4.17 Optical limiting in 0.25 mM Ni (QAP)$_2$ in chloroform](image1)

![Fig. 4.18 Optical limiting in 0.25 mM Co (QAP)$_2$ in chloroform](image2)
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Fig. 4.19 Optical limiting in 0.25 mM Cu (QAP)$_2$ in chloroform

Fig. 4.20 Optical limiting in 0.25 mM Mn (QAP)$_2$ in chloroform

Fig. 4.21 Optical limiting in 0.25 mM Ni, Co, Cu and Mn (QAP)$_2$ in chloroform
Investigations of nonlinear .......... 

From these graphs it is clear that all the QAP samples studied here show better optical limiting at the excitation wavelength of 532 nm. Out of the four samples the optical limiting in Ni (QAP)₂ is really commendable because it shows the highest degree of limiting. It is a potential candidate for device applications at the wavelength of excitation considered in the present studies.

4.6 Conclusions
Degenerate Four Wave Mixing (DFWM), Z-Scan and optical limiting studies have been carried out in certain selected metal complexes of QAP’s at 532 nm under nanosecond excitation. For the DFWM measurements the polarization of the interacting beams were so chosen that electronic response is obtained. Third order susceptibility, figure of merit of third order nonlinearity and nonlinear absorption coefficient of these samples are calculated. The measured nonlinear parameters of these samples are explained as due to the combined effect of nonlinear absorption, oscillator strength and resonance effects at the wavelength of excitation. It is observed that Ni (QAP)₂ and Co (QAP)₂ are promising NLO materials and their importance in the context of device applications is confirmed by the optical limiting studies carried out in these samples.
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