Chapter 6

Ultrafast Nonlinear Optical Absorption in Cytochrome-c Protein and its Application to All-Optical Logic Gates

6.1 Introduction

As discussed in section 1.1 of Chapter 1, cytochrome-c (cyt-c) is another important photoactive protein that has received considerable attention for various applications due to its unique properties and advantages. Several applications have been proposed with cyt-c that include memory devices, biomolecular photodiodes, switches, biosensors, charge storage devices and optoelectronic and chemophotonic logic gates [Choi et al. (2001, 2002), Deonarine et al. (2003), Zhu et al. (2009), Lee et al. (2010, 2015)]. Efficient integration of cyt-c protein with graphene, nanoparticles and semiconductor QDs has been shown to enhance its photocurrent response and optical properties for hybrid nano-biosystems based biotechnological and biomedical applications. Recently, fs spectroscopic characterization of ESA dynamics in cyt-c has revealed SA and RSA at different wavelengths for its application in optical limiting and photodynamic therapy [Andrade et al. (2003, 2004), Boni et al. (2010)]. RSA has been observed below 520 nm, while SA occur around 530 nm. These SA and RSA characteristics are based on ESA and are necessary to understand the NLO response of this protein in detail.

Hence, in this Chapter, a detailed theoretical analysis of ultrafast wavelength-dependent SA and RSA characteristics with cyt-c based on singlet-state dynamics has been undertaken. These NLA characteristics have also been optimized to design various fs AOL gates. Theoretical simulations are in good agreement with reported experimental results. Further, the effect of pulse intensity and pulse width, absorption cross-section, pulse frequency and life time of the excited states has also been studied in detail.

6.2 Theoretical Model

To analyze ultrafast NLA characteristics of cyt-c, the simplified three-level energy level diagram that involves the singlet states has been considered as shown in Figure 6.1.
Figure 6.1  Simplified three level energy diagram to describe the NLA in fs regime. Solid and dashed arrows indicate the absorptions and relaxations respectively.

The excitation and de-excitation can be described by the following rate equations for different energy states;

Rate of change of population in $S_0$ state,

$$\frac{dN_0}{dt} = -\frac{\sigma_0 I N_0(t)}{hv} + \frac{N_1(t)}{\tau_1} - \frac{\beta I^2 N_0(t)}{2hv}$$  \hspace{1cm} (6.1)

Rate of change of population in $S_1$ state,

$$\frac{dN_1}{dt} = \frac{\sigma_0 I N_0(t)}{hv} - \frac{\sigma_1 I N_1(t)}{hv} - \frac{N_1(t)}{\tau_1} + \frac{N_2(t)}{\tau_2} + \frac{\beta I^2 N_0(t)}{2hv}$$  \hspace{1cm} (6.2)

Rate of change of population in $S_2$ state,

$$\frac{dN_2}{dt} = \frac{\sigma_1 I N_1(t)}{hv} - \frac{N_2(t)}{\tau_2}$$  \hspace{1cm} (6.3)

The transmitted intensity through the sample during the interaction with the fs laser pulse is given by,

$$\frac{dl}{dt} = -\sigma_0 I N_0(t) - \sigma_1 I N_1(t) - \beta I^2$$  \hspace{1cm} (6.4)

The gaussian modulating excitation laser pulse is expressed by the following equation:

$$I = I_0 \frac{\omega_0^2}{\omega^2(z)} \exp\left(-c \frac{t^2}{\tau_p^2}\right) \exp\left(-\frac{2r^2}{\omega^2(z)}\right)$$  \hspace{1cm} (6.5)

where $\omega(z) = \omega_0 \{1+(z/z_0)^2\}^{1/2}$, $c = 4\ln2$ is the pulse profile parameter. Other symbols are their usual meanings.

Two single laser pulses have been considered to analyze two input AOL gates which are as
follows:

\[ I_1 = I_0 \frac{\omega_0^2}{\omega^2(z)} \left[ \exp \left( -c \left( \frac{t - t_{m1}}{\tau_p} \right)^2 \right) + \exp \left( -c \left( \frac{t - t_{m2}}{\tau_p} \right)^2 \right) \right] \exp \left( - \frac{2r^2}{\omega^2(z)} \right) \] (6.6)

and

\[ I_2 = I_0 \frac{\omega_0^2}{\omega^2(z)} \left[ \exp \left( -c \left( \frac{t - t_{m3}}{\tau_p} \right)^2 \right) + \exp \left( -c \left( \frac{t - t_{m2}}{\tau_p} \right)^2 \right) \right] \exp \left( - \frac{2r^2}{\omega^2(z)} \right) \] (6.7)

Pulse peaks are represented by the times \( t_{m1}, t_{m2}, \) and \( t_{m3} \).

### 6.3 Results and Discussion

NLA characteristics have been computed through computer simulations using above theoretical model, considering the experimental conditions and spectroscopic parameters reported for cyt-c, with \( \sigma_0 = 4.2 \times 10^{-17} \) cm\(^2\) at 460 nm, concentration 0.2 µM, sample length 2 mm and radius of the beam waist as 20 µm [Andrade et al. (2003, 2004), Boni et al. (2010)]. We consider a laser pulse of pulse energy ~10 nJ and 120 fs pulse width to excite the sample from a wavelength tunable optical parametric amplifier pumped at 775 nm by Ti:Sapphire laser with a chirped pulse amplifier [Boni et al. (2010)].

The variation of transmittance with time at different wavelengths in the visible region at peak input pulse intensity \( I_0 = 2.64 \times 10^{10} \) W/cm\(^2\) is shown in Figure 6.2. The NLA behavior switches from SA to RSA at lower wavelengths. The absorption spectrum of the ground and the excited-state \( S_1 \) reported experimentally by Boni et al. (2010) clearly shows that for lower wavelengths in the range 450-520 nm, the absorption cross-section (\( \sigma_1 \)) of the \( S_1 \) state is higher than that of the ground-state absorption cross-section (\( \sigma_0 \)). Whereas, in the range 520-600 nm, the reverse holds true [Boni et al. (2010)]. Hence, in the range 450-520 nm, RSA takes place and between 520-600 nm SA. At 520 nm, \( \sigma_0 \approx \sigma_1 \approx 4.2 \times 10^{-17} \) cm\(^2\), hence, the transmittance is nearly constant with time.
Figure 6.2 Variation of transmittance with time for different wavelengths with a 120 fs single laser pulse at $I_0 = 2.64 \times 10^{10}$ W/cm$^2$.

The effect of pulse intensity on the variation of transmittance with time is shown in Figure 6.3 (a) and (b) at 460 and 530 nm. At 460 nm, transmittance decreases with increase in $I_0$ due to higher ESA, which results in continuous increase in the population of $S_0$ and $S_1$ states, as is evident from the corresponding variation in the normalized population density, as shown in Figure 6.3 (c). This leads to RSA with increased percentage modulation as shown in Figure 6.3 (a). 19% modulation with switch off/on time of 190 and 210 fs is achieved at $I_0 = 4.5 \times 10^{10}$ W/cm$^2$. At 530 nm, the transmittance and percentage modulation increase with increase in $I_0$ due to strong absorption as the ground-state absorption cross-section ($\sigma_0$) is larger that results in increase in the population of $S_1$ state, also evident from the corresponding variation in normalized population density of different states shown in Figure 6.3 (d) that leads to SA (Figure 6.3 (b)). At $I_0 = 85 \times 10^{10}$ W/cm$^2$, 35% modulation with switch off/on time of 160 and 200 fs is achieved.
Figure 6.3  Effect of intensity on transmittance with time at 120 fs laser pulse (a) at 460 nm, (b) at 530 nm, and (c) and (d) corresponding variations in normalized population density of different states with time, respectively at different $I_0$ values.

The effect of variation of pulse width on NLA characteristics at 460 nm is shown in Figure 6.4. On increasing the pulse width, the percentage modulation increases due to larger ESA. As expected, the RSA characteristics become more symmetric for larger $\Delta t$ values as compared to $\tau_1$.

Figure 6.4  Variation of transmittance with time for different laser pulse width values at $I_0=4.5\times10^{10}$ W/cm$^2$. 
The effect of excited-state life-time ($\tau_2$) on the RSA characteristics at $I_0 = 4.5 \times 10^{10}$ W/cm$^2$ is shown in Figure 6.5 (a). An increase in $\tau_2$, results in increase in switch off/on time and decrease in percentage modulation as the molecules are retained for longer time in the $S_n$ state resulting in lower population buildup of the $S_1$ state, shown in Figure 6.5 (b) and (c). This leads to lower absorption and hence lower percentage modulation. At lower value of $\tau_2$, molecules relax back faster to the $S_1$ state from the higher $S_n$ state as shown in Figure 6.5 (d). Hence, at $\tau_2 = 0.5$ fs, maximum percentage modulation (~24%) is achieved with faster switch off/on time of 175 and 200 fs respectively.

**Figure 6.5** Variation of transmittance with time for different $\tau_2$ values (a) at 460 nm and (b-d) are the corresponding variations in normalized population density of different states with time.
Figure 6.6  Variation of transmittance with time for different values of $\sigma_1$ at pulse width of 120 fs and $I_0 = 4.5 \times 10^{10}$ W/cm$^2$.

ESA cross-section values have been shown to vary 21% from its original value, obtained by the theoretical fitting of the experimentally reported Z-scan data [Boni et al. (2010)]. Hence, for device optimization the variation in ESA cross-section is important. The effect of ESA cross-section values on NLA characteristics at 460 nm has been shown in Figure 6.6. It is clear from the variation that the percentage modulation increases on increase in ESA cross-section values at 460 nm. At $\sigma_1 = 46 \times 10^{-17}$ cm$^2$, 19% modulation can be achieved. Similar behavior can be achieved at other wavelengths.

To estimate the maximum bit rate possible with the SA and RSA characteristics in cyt-c protein, the effect of pump pulse frequency on the SA and RSA characteristics at 460 nm (solid lines) with $I_0 = 7.0 \times 10^{10}$ W/cm$^2$, $\tau_p = 50$ fs and $\sigma_1 = 46 \times 10^{-17}$ and at 530 nm (dashed lines) with $I_0 = 95 \times 10^{10}$ W/cm$^2$ and $\tau_p = 50$ fs is shown in Figure 6.7. For 460 nm, the optimum pulse separation is 235 fs with 19% modulation that leads to bit rates ~ 4.2 Tbits/sec, whereas for 530 nm the optimum pulse separation is 200 fs with 33% modulation that leads to 5 Tbits/sec repetition rates.


**Figure 6.7** Optimal pulse frequencies for RSA and SA at 460 and 530 nm, respectively.

### 6.4 Application of Results: Design of All-Optical Logic Gates

The wavelength dependent SA and RSA characteristics have been used to theoretically design fs AO NOT, OR, AND and the universal logic gates. For this, two single laser pulses (Equations 6.6 and 6.7) have been considered. NOT and the universal NOR and NAND logic gates have been designed by utilizing the RSA characteristics at 460 nm with $I_0 = 3.5 \times 10^{10}$ W/cm$^2$. However AND and OR logic gates can be designed by utilizing the SA characteristics at 530 nm with $I_0 = 75 \times 10^{10}$ W/cm$^2$ as shown in Figure 6.8 (a).

**Figure 6.8** Design of fs AOL gates.
For the universal AO NOR logic gate, the output is low when either one or both the pulses are incident on the sample and is high when both pulses are absent (Fig. 6.8 (a)). The same configuration also results in an AO NAND logic gate with solid line as a threshold. In this case the output is low only when both the pulses are present and is high for all other cases. Similarly, AND and OR logic gates can be designed as shown in Figure 6.8 (a).

6.5 Conclusion

NLA dynamics of cyt-c protein in fs regime has been analysed in detail at different wavelengths. It is clear from the analysis that ultrafast SA and RSA in cyt-c is at lower pump intensities (~GW/cm²) compared to other organic molecules such as copper-phthalocyanine thin films (~TW/cm²) [Roy and Yadav (2011)]. In comparison to bR protein, although the switch on/off time (~0.2 ps) is same, but percentage modulation is lower at the same order of intensity. The peak pulse intensity values used in the present analysis (~10¹⁰ W/cm²) are below the experimental values (~10¹¹ W/cm²) used in the transient spectroscopic analysis of cyt-c in the fs regime. Although, experimental ultrafast spectroscopic characterization studies have demonstrated SA and RSA behavior, the present study provides a detailed theoretical analysis for optimization of SA and RSA and highlights important insights necessary for designing all-optical devices for practical implementation. Cyt-c films with high photo and thermal stability at different pH values (6.0-10) have been fabricated for bioelectronic devices [Choi et al. (2001)]. The strong conjugation of cyt-c with Au nanoparticles, Au-TiO₂ nanocomposites, ZnO-MAA nanoparticles and CdSe/ZnS quantum dots has been used for photocurrent generation and sensing [Zhu et al. (2009), Alwarparan et al. (2010), Lee et al. (2010), Li et al. (2011) Simsikova et al. (2013)]. Hence, NLO absorption properties of cyt-c can also be tailored by integrating it with metal nanoparticles and semiconductor quantum dots to meet device specifications. The designs are the first application of cyt-c based sub-ps AOL gates and show the applicability of cyt-c for ultrafast AO information processing.