Research Paper Electronics

# All-Optical Ultrafast Switching in Cytochrome c Protein

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**ABSTRACT**

The dynamics of ultrafast all-optical switching in oxidized state of Cytochrome c ( ) has been theoretically analyzed based on the principle of nonlinear intensity –induced excited state absorption to achieve high contrast and fast switching. The transmission of probe laser beam at 490nm corresponding to the peak absorption of the S1 state through Cytochrome c molecule is switched by a pulsed pump laser beam at 532nm that excites molecule from the ground state. Switching characteristics are shown to be sensitive to the variation of pump pulse width, peak pumping intensity, absorption cross-section of the singlet state at probe wavelength 490nm, relaxation time of the first excited state

**KEYWORDS** All-optical switching; oxidized Cytochrome c

**Introduction**

Nonlinear optical properties of organic molecules have been the subject of a large number of theoretical and experimental investigations during the last decade due to the prospect of their use in photonic devices. Among several new organic molecules, porphyrins have deserved special attention, because of their potential usefulness in photonic devices. Cytochrome c (Cyt c), a Fe-porphyrin which is one of the most intensively investigated redox proteins, acts as an electron carrier in the respiratory chain. Cyt c is observed in two different oxidation states, ferric ( $Fe^{3+}$ ) and ferrous ( $Fe^{2+}$ ) , which possess different optical properties.All-optical switching was observed in Bacteriorhodopsin and other photosensitive proteins such as Photoactive yellow protein, Phototropins, Protorhodpsin, however usually protein dynamics are in millisecond and microsecond. Recent investigation using ultrafast transient absorption spectroscopy in oxidized Cyt c ( $Fe^{3+}$ ) demonstrated change in electronic structure occurs in the fs and ps regimes when the heme group is excited .The three-energy-level diagram of oxidized Cyt c was used to model the population dynamics as a function of the laser pulse time-evolution. The molecules in the ground-state S0 which has population density n0 can be excited to S1 which has population density n1, with a rate that depends on the ground-state absorption cross-section, σ01 (λ), and two-photon absorption (2PA) cross-section. From S1, molecules can relax back to the ground-state with a relaxation time σ1n (λ), or be promoted to another excited-state, Sn which has population density n2, whose absorption cross-section is σ1n. Once in this state, the system may relax back to the first excited-state with a time described by τn1.In this paper, we investigate all-optical switching in oxidized Cyt c in detail based on the principle of nonlinear intensity -induced excited state absorption to achieve high switching contrast and low switching time. The transmission of probe laser beam at 490nm corresponding to the peak absorption of the S1 state through Cyt c molecule is switched by a pulsed pump laser beam at 532nm that excites molecule from the ground state. The switching characteristics have been analyzed using the rate equation approach. The effect of various parameters such as pump pulse width, peak pumping intensity, absorption cross-section of the singlet state at probe wavelength 490nm, relaxation time of the first excited state on switching characteristics has been analyzed in detail. The proposed designs would be useful in all-optical information processing due to high switching contrast, small size, simple digital operation and flexibility.The absorption spectrum of oxidized cytochrome c can be represented by the time dependent rate equations approach in terms of population densities that describe the transition between three states . We consider a medium containing Cyt c molecules exposed to a light beam of intensity $I'_m$, which modulates the population densities of different states through the excitation and de-excitation processes. These light induced population changes can be described by the rate equations in the operator form in terms of the photo induced and thermal transitions of different levels as

(2)

$$\frac{dN}{dt} = \dot{O}\,N$$

$$\dot{O} = \begin{bmatrix} -W_{01}(\lambda) & 1/\tau_{10} & 0 \\ W_{01}(\lambda) & -(W_{1n}(\lambda) - 1/\tau_{10}) & 1/\tau_{n1} \\ 0 & W_{1n}(\lambda) & -1/\tau_{n1} \end{bmatrix}$$

**And the transpose of the population vector N is given by:**

$$\tilde{N} = (n_{s0} + n_{s1} + n_{s2}) \quad (3)$$

This cumulative process will reflect in the total transmittance of the beam trough the sample length (z). Therefore, after simplifying the equation, the intensity transmitted through the sample, during the interaction with the femtosecond-pulse laser, is given by:

$$\frac{dI}{dz} = -\sigma_{01}\, In_{s0}(t) - \sigma_{1n}\, In_{s1}(t) \quad (4)$$

In this case where the 2PA process is negligible, the nonlinear effect in the sample is related to the excited states transitions. At this condition, the time evolution of the absorption coefficient for each wavelength, α (λ,t) can be calculated using the following equation:

$$\alpha(\lambda, t) = N\left[\sigma_{01}(\lambda) n_{s0}(t) + \sigma_{1n}(\lambda) n_{s1}(t)\right] \quad (5)$$

is excited-state absorption cross-section and is ground state absorption cross-section. N is the number of molecules per $cm^3$. Thus using the population densities given in equation (2), the nonlinear absorption coefficient can be obtained from equation (5).

We consider a modulating pump laser pulse given by,

$$I'_m = I'_{m_0} \mathrm{Exp}\left(-C\left(\frac{t-t_m}{\Delta t}\right)^2\right) \quad (6)$$

Where C= 4 log [2] is the pulse profile parameter, Δt is the pulse width and $t_m$ is the time at which the pulse maxima occurs.

The all optical switching characteristics, namely, the probe transmission intensity as a function of time have been obtain by solving rate equations for the intermediate states through computer simulations using equations (1), (5) and (6).

To analyze two input logic gates configurations, two pump laser pulses have been considered such that the four input combinations (0,0), (0,1), (1,0) and (1,1) in terms of phase differences of their peaks are given by,

$$I'_{m1} = I'_{m_0}\left[\mathrm{Exp}\left(-C\left(\frac{t-t_{m1}}{\Delta t}\right)^2\right) + \mathrm{Exp}\left(-C\left(\frac{t-t_{m2}}{\Delta t}\right)^2\right)\right] \quad (7)$$

$$I'_{m2} = I'_{m_0}\left[\mathrm{Exp}\left(-C\left(\frac{t-t_{m2}}{\Delta t}\right)^2\right) + \mathrm{Exp}\left(-C\left(\frac{t-t_{m3}}{\Delta t}\right)^2\right)\right] \quad (8)$$

Where $I'_{mo}$ is the peak pumping intensity, $t_m$, $t_{m1}$, $t_{m2}$ and $t_{m3}$ are the times at which the respective pulse maxima occur, c is the pulse profile parameter and $\Delta t$ is the pulse width.

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**Results and Discussion**

**All-Optical Switching in Pump and Probe Configuration**

The optical switching characteristics, namely the probe beam transmitted intensity as a function of time have been obtained by computer simulation using equations (1) to (7). The parameters used in the computation are **$\sigma$01=4.1×10$^{-17}$** cm$^2$ , $\sigma$1n=3.5× 10$^{-17}$ cm$^2$, **$\sigma$01p=2.5× 10$^{-17}$** cm$^2$, **$\sigma$1np=4.5× 10$^{-17}$** cm$^2$ , **$\tau$10=2.7ps, $\tau$n1=300fs where $\sigma$01p and $\sigma$1np are ground and first excited state absorption cross-section at probe wavelength [5, 10]. The concentration of** Cyt c in water has been considered to be 65μM with thickness of 2mm .Fig. 2 shows that the switch on/off time and percentage modulation (i.e. variation in the normalized transmitted intensity of the probe beam ($I_{Pout}/I_{Pin}$) when it is on and off) increases as peak pumping intensity increases and saturates after a certain value. For instance for $I'_{mo}$=10 GW/cm$^2$ and 30 GW/cm$^2$, the transmittance gets modulated by 20.9% and 40.0% respectively whereas for $I'_{mo}$=10 GW/cm$^2$, switch on and off time is 1.12ps and 0.06ps and for $I'_{mo}$ =30 GW/cm$^2$, switch on and off time is 1.48ps and 0.1ps nearly.

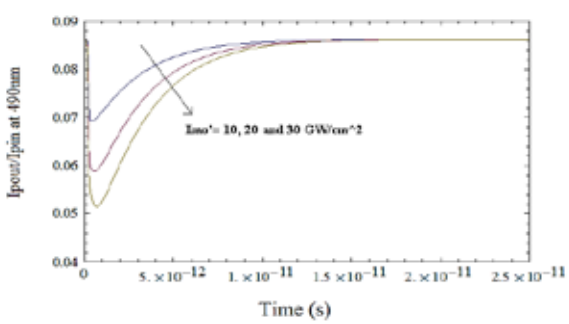



Fig. 2: Variation of normalized transmitted intensity of the probe laser beam ($I_{Pout}/I_{Pin}$) at 490nm with time for different peak pump intensity ($I'_{mo}$) values for $\Delta t$=120fs, l=2mm, tm=225fs The percentage modulation and switch on/off time can also be increased by increasing the pulse width shown in fig 3. For instance, for $\Delta t$=90fs, the switch off and on time is 0.025ps and 4.05ps respectively, whereas for $\Delta t$=140fs, the off and on time is 0.05ps and 5.025ps respectively. The percentage modulation for these pulses 14.01% and 20%.

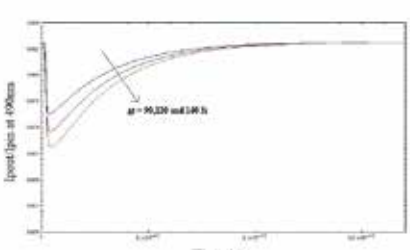



Fig 3: Variation of normalized transmitted intensity of the probe laser beam ($I_{Pout}/I_{Pin}$) at 490nm with time for different values of pump pulse widths for, l=2mm, tm=225fs, $I'_{mo}$ = 10 GW/cm$^2$

Figure 4 shows the effect of variation in the relaxation time of the first excited state .As relaxation time increases both switching time and percentage modulation of probe laser beam increases. An increase in relaxation time results in a slower decay from first excited state to the ground state thereby increasing the population of the first excited state. This results in increase in the absorption of probe laser beam. For $\tau_1$=1.7ps, the switch off and on time is 0.375ps and 4.125ps respectively, resulting in 16.6% modulation of probe laser beam while for $\tau_1$=2.7ps, the switch off and on time is 0.437ps and 5.5ps respectively, resulting in 16.86% modulation of probe laser beam.

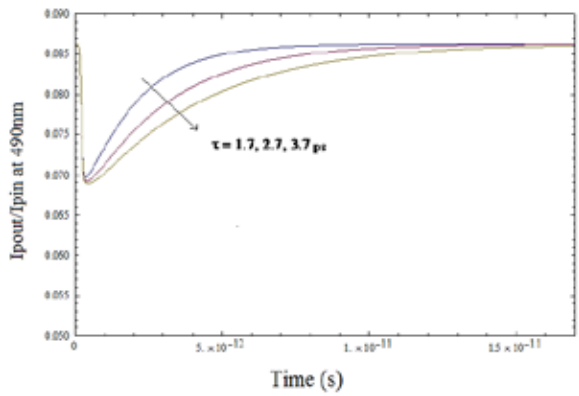



Fig 4: Variation of normalized transmitted intensity of the probe laser beam ($I_{Pout}/I_{Pin}$) at 490nm with time for different relaxation time of the first excited state for $\Delta t$=120fs, l=2mm, tm=225fs, $I'_{mo}$ = 10 GW/cm$^2$

Figure 5 shows the effect of variation in the normalized transmitted intensity of the probe beam with time, for different $\sigma_{1np}$ values .As $\sigma_{1np}$ increases, the percentage modulation increases, as this result in increase in absorption of the probe laser beam. For $\sigma_{1np}$=3.5 ×10$^{-17}$cm$^2$, the switch off and on time is 0.375ps and 5.75ps respectively, resulting in 8.23% modulation of probe laser beam while for $\sigma_{1np}$=4.5 ×10$^{-17}$cm$^2$, the switch off and on time is 0.5125ps and 6.625ps respectively, resulting in 17.8% modulation of probe laser beam.

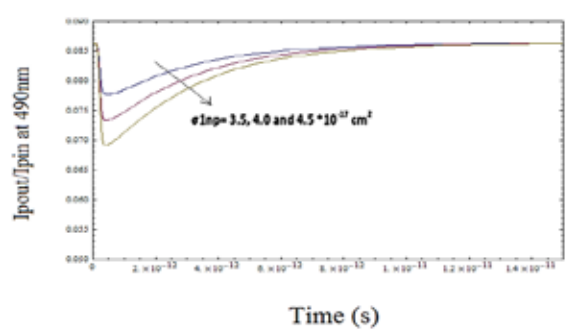



Fig 5: Variation of normalized transmitted intensity of the probe laser beam ($I_{Pout}/I_{Pin}$) at 490nm with time for different absorption crossection (probe) values of first excited state for $\Delta t$=120fs, l=2mm, tm=225fs, $I'_{mo}$ = 10 GW/cm$^2$.

**Non-Linear Absorption Dynamics in Single Laser Pulse**

The simulation of transient transmittance verses time during a single laser pulse is based on above equations (1-6). In this calculation, the pulse duration is set as 120fs and four excitation intensities are adopted. The result in Fig 6 shows saturable absorption (SA) process. So, when input intensity is at (a) 100 GW/cm$^2$ (b) 200 GW/cm$^2$ (c) 300 GW/cm$^2$ (d) 400 GW/cm$^2$ the transmission increase with the excitation intensity increasing and decrease with the excitation intensity decreas-

ing during a single laser pulse. So, the increase in the transmittance, as shown in the graph, is because the population of the ground state S0 is promoted to the first excited state S1, which has absorption cross-section smaller than that of the ground state.

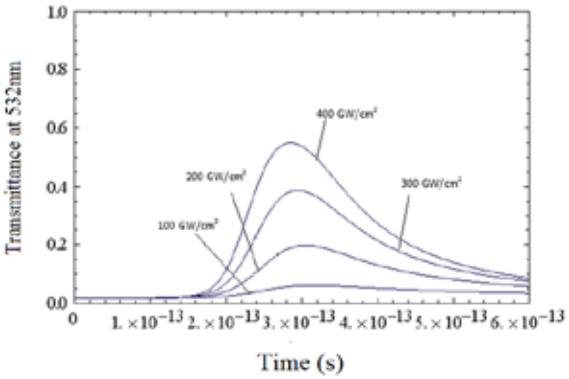



Fig 6: Transient transmission at 532nm versus time during single laser pulse with a width of 120fs under four different excitation intensities (a) 100GW/cm$^2$ (b) 200GW/cm$^2$ (c) 300GW/cm$^2$ (d) 400 GW/cm$^2$

However, the big increase on the on the Transmittance is most occasioned by the population that goes to the higher excited state Sn, in this state, the population does not absorb any light . Because this state (Sn) has short lifetime (300 fs), the population in this state goes to zero just after the 120 fs pulse passed. This population returns to S1 and keep there until the time of this state 2.7 ps.

**Conclusion**

All-optical femtosecond switching in oxidized Cytochrome c was analyzed in detail based on its singlet-state dynamics to achieve it with high switching contrast and low switching time. The effect of various parameters such as pump pulse width, lifetime of the first singlet state, absorption cross-section of the singlet state at probe wavelength 490nm and peak pumping intensity on the switching have been analyzed in detail. Earlier protein dynamics has been shown to function in millisecond-microsecond regime but by the use of Cyt c logic gate operation is in the femtosecond regime. The proposed designs would be useful in all-optical information processing due to high switching contrast, small size, simple digital operation and flexibility.

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