Chapter 2
All-Optical Switching in LOV2 Phototropin with CW Pump Beam Excitation*

2.1 Introduction

As discussed in section 1.5 of Chapter 1, the transmission of a weak cw probe laser beam at the peak absorption wavelength of an excited state passing through LOV2 phototropin sample can be modulated by varying the cw pump laser beam intensity at the peak absorption wavelength of the ground state, which varies the population of the excited state. These spatial light modulation characteristics are based on nonlinear intensity-induced excited-state absorption and are necessary to understand the rnonlinear optical response of LOV2 phototropin.

In this Chapter, a detailed theoretical analysis of all-optical light modulation characteristics of LOV2 phototropin considering its L-state dynamics has been presented using rate equation approach. A probe laser beam at 660 nm, corresponding to the peak absorption wavelength of L-state is shown to be modulated by a cw pump laser beam at 442 nm which corresponds to the peak absorption wavelength of initial D-state. The effects of various parameters such as the normalized small signal absorption coefficient, rate constants of intermediates, absorption cross-section values of initial D-state and excited L-state on the modulation characteristics have also been studied. Further, the modulation characteristics have been used to design an all-optical spatial light modulator and all-optical logic gates including all-optical NOT and two input universal NOR and

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NAND logic gates by considering the transmission of the probe beam as output and two pump beams as inputs.

2.2 Theoretical Model

To analyze all-optical light modulation in LOV2 phototropin in a wide range of pump intensities, the typical simplified photocycle of LOV2-WT depicting all possible states and transitions has been considered as shown in Fig. 1.3 in Chapter 1 [Swartz et al. (2001)].

A detailed theoretical analysis of all-optical light modulation of a weak cw probe laser beam at 660 nm, corresponding to the absorption peak of the L-state (Light activating state) by a modulating pump laser beam at 442 nm that corresponds to the absorption maximum of the initial D-state (Dark state), has been conducted.

2.2.1 Theoretical Model for LOV2-WT

We first consider wild type (WT) LOV2 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 that can be described by the rate equations in the following form [Roy et al. (2001, 2002, 2004), Singh and Roy (2002, 2003 a, b), Roy and Kulshrestha (2006, 2007)],

\[
\frac{dN_D}{dt} = -\psi_{DL} \sigma_D I_m N_D + (\psi_{LD} k_{LD} + I_m \sigma_L) N_L + (k_{SD} + I_m \sigma_S) N_S \\
\frac{dN_L}{dt} = \psi_{DL} \sigma_D I_m N_D - (\psi_{LD} k_{LD} + \psi_{LS} k_{LS} + I_m \sigma_L) N_L \\
\frac{dN_S}{dt} = \psi_{LS} k_{LS} N_L - (k_{SD} + I_m \sigma_S) N_S
\]

(2.1)

(2.2)

(2.3)

where $\sigma_i$, $i = D, L$ and $S$ are absorption cross-sections of the three states; $I_m$ is the photon density flux of the modulation laser beam i.e. ratio of the intensity $I'_m$ to the photon energy $h \nu$. $\psi_{DL} = 0.88$ is the quantum efficiency for the formation of the L-state and $\psi_{LD} = \psi_{LS} = 0.5$ are the transition probabilities for the transitions $L \rightarrow D$. 
and \( L \rightarrow S \), respectively [Swartz et al. (2001)]. The rate constants \( k_{LD}, k_{LS} \) and \( k_{SD} \) represent transitions from \( L \rightarrow D, L \rightarrow S \) and \( S \rightarrow D \), respectively.

The light-induced population densities in the various levels at steady state are given by

\[
N_i = N_D I_m P \left( I^{-1}_m P \frac{I_m^{-1} P}{\psi_{DL} \sigma_D} \right)
\]

where

\[
N_D = N_j X
\]

is the population density in D-state.

\[
P = \psi_{LD} k_{LD} + \psi_{LS} k_{LS} + I_m \sigma_L
\]

\[
Q = k_{SD} + I_m \sigma_S
\]

\[
X = \left[ 1 + \frac{\psi_{DL} I_m \sigma_D}{P} \left( \frac{I + \psi_{LS} k_{LS}}{Q} \right) \right]
\]

and

\[
N = N_D + N_L + N_S
\]

is the total number of active LOV2 molecules.

We consider the transmission of a weak cw probe laser beam of intensity \( I_p \) \((I_p \ll I_m)\) at 660 nm corresponding to the peak absorption of the L intermediate in the LOV2 photocycle, modulated by absorption due to excitation of the molecules by the cw laser beam at 442 nm. As \( \sigma_{dp} = \sigma_{sp} = 0 \) at the probe wavelength, the absorption coefficient of the probe beam can be written as

\[
\alpha_p(I_m) = N_L(I_m) \sigma_{lp}
\]

where subscript \( p \) denotes the value at probe wavelength.
The propagation of the probe beam through the LOV2 sample is governed by,

\[ \frac{dI_p'}{dx} = -\alpha_p(I_m)I_p' \]  

(2.11)

where \( x \) is the distance in the medium. Assuming a thin LOV2 sample, the effect of propagation of the pump beam has been neglected.

The modulation characteristics can be computed by integrating Eq. (2.11). The result in the form of normalized transmitted probe intensity (NTPI) is given by

\[ \frac{I_{pout}}{I_{pin}} = \exp\left(-\frac{\beta \psi_{DL} I_m \sigma_D}{X \frac{P}{P}}\right) \]  

(2.12)

where the small-signal absorption coefficient is given by

\[ \beta = N \sigma_{lp} L. \]  

(2.13)

### 2.2.2 Theoretical Model for LOV2-C39A

In LOV2-C39A mutant, replacement of Cysteine\(^{39}\) with alanine eliminates the light induced photochemical reaction of LOV2. Absence of Cysteine\(^{39}\) precludes the formation of LOV2 S-state. Hence, the L-state of LOV2-C39A mutant decays back to the ground state with a time constant of 72 \( \mu \)s, which is more than one order of magnitude longer than LOV2-WT, as shown in Fig. 2.1 [Swartz et al. (2001)].

The population densities of different states of LOV2-C39A mutant through the excitation and de-excitation processes can be described by the rate equations in the following form [Roy et al. (2001, 2002, 2004), Singh and Roy (2002, 2003 a, b)],

\[ \frac{dN_D}{dt} = -\psi_{DL} \sigma_D I_m N_D + (k_{LD} + I_m \sigma_L)N_L \]  

(2.14)

\[ \frac{dN_L}{dt} = \psi_{DL} \sigma_D I_m N_D - (k_{LD} + I_m \sigma_L)N_L \]  

(2.15)

where \( \sigma_i \), \( i = D \) and \( L \) are absorption cross-sections of the D- and L-states, respectively; \( I_m \) is the photon density flux of the modulation laser beam i.e. ratio of
the intensity $I_m$ to the photon energy $hv$. $\Psi_{DL} = 0.88$ is the quantum efficiency for the formation of the L-state [Swartz et al. (2001)]. The rate constants $k_{LD}$ represents transition from L→D state.

The light-induced population densities in the various levels at steady state are given by

$$ N_i = \frac{N_D I_m}{(k_{LD} + I_m \sigma_L)} \left( I_m^{-1} (k_{LD} + I_m \sigma_L) \right) \left( \frac{1}{\Psi_{DL} \sigma_D} \right) $$

(2.16)

where

$$ N_D = N/X $$

(2.16)

is the population density in D-state,

$$ X = \left[ 1 + \frac{\Psi_{DL} I_m \sigma_D}{k_{LD} + I_m \sigma_L} \right] $$

(2.17)

and

$$ N = N_D + N_L $$

(2.18)

is the total number of active LOV2 molecules.

Fig. 2.1 Photocycle of LOV2-C39A mutant of phototropin from Avena sativa. The solid and dashed arrows represent the thermal and photoinduced transitions [Swartz et al. (2001)].
For this case, we consider the transmission of a weak cw probe laser beam of intensity $I'_p$ ($I'_p \ll I'_m$) at 660 nm corresponding to the peak absorption of the L intermediate in the LOV2 photocycle, modulated by absorption due to excitation of the molecules by the cw laser beam at 442 nm. As $\sigma_{dp} = 0$ at the probe wavelength, the absorption coefficient of the probe beam can be written as

$$\alpha_p(I_m) = N_{i_p} I_m \sigma_{ip}$$

where subscript $p$ denotes the value at probe wavelength. The propagation of the probe beam through the LOV2 sample is governed by,

$$\frac{dI'_p}{dx} = -\alpha_p(I_m) I'_p$$

where $x$ is the distance in the medium.

The modulation characteristics can be computed by integrating Eq. (2.20). The result in the form of normalized transmitted probe intensity (NTPI) is given by

$$\frac{I_{pout}}{I_{pin}} = \exp \left( -\frac{\beta}{X} \frac{\psi_{DL} I_m \sigma_D}{k_{LD} + I_m \sigma_L} \right)$$

where the small-signal absorption coefficient

$$\beta = N \sigma_{ip} L$$

2.3 Results and Discussion

The transmission characteristics, namely the variation of NTPI at 660 nm with $I'_m$ at 442 nm have been simulated using equations (2.1)-(2.22), for LOV2-WT and its mutant LOV2-C39A with the typical values of absorption cross-sections and rate constants reported in literature and as given in Table 2.1, with sample thickness $L = 2$ mm.

The transmission characteristics of LOV2-WT for different values of small-signal absorption coefficient $\beta$, are shown in Fig. 2.2. Increase in pump intensity $I'_m$ leads to increase in the population of the L-state and hence increased absorption of probe beam. It is evident that NTPI decreases considerably with increase in $I'_m$ and
saturates at higher pump intensities. The percentage modulation of the probe beam intensity in LOV2-WT for $\beta = 0.2$ and 5 at $I'_m = 50 \text{ kW/cm}^2$ is 11.85% and 95.73%, respectively. The probe beam gets completely switched i.e. 100% modulation in LOV2-WT at $I'_m = 50 \text{ kW/cm}^2$, for $\beta = 8$. This is due to the fact that the absorption cross-section of the ground state at probe wavelength $\sigma_{dp} = 0$.

Table 2.1 Rate constants and absorption cross-sections of the different intermediate states of LOV2-WT and LOV2-C39A [Swartz et al. (2001)].

<table>
<thead>
<tr>
<th>Rate constants</th>
<th>Values (s$^{-1}$)</th>
<th>Absorption cross-sections</th>
<th>Values (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LOV2-WT</td>
<td>LOV2-C39A</td>
<td>442 nm</td>
</tr>
<tr>
<td>$k_{LS}$</td>
<td>$2.5 \times 10^4$</td>
<td>$1.38 \times 10^4$</td>
<td>$\sigma_g$</td>
</tr>
<tr>
<td>$k_{LD}$</td>
<td>$2.5 \times 10^4$</td>
<td>$1.38 \times 10^4$</td>
<td>$\sigma_g$</td>
</tr>
<tr>
<td>$k_{SD}$</td>
<td>$1.42 \times 10^{-2}$</td>
<td>$1.38 \times 10^{-2}$</td>
<td>$\sigma_g$</td>
</tr>
</tbody>
</table>

Fig. 2.2 Variation of NTPI at 660 nm with $I'_m$ for LOV2-WT, for different values of $\beta$, for $\sigma_{ip} = 2.1 \times 10^{-17} \text{ cm}^2$.

Figure 2.3 shows the variation in the normalized population density of the different intermediates of LOV2-WT with $I'_m$. Initially, at lower values of $I'_m$, the
population of the S-state increases rapidly due to the shorter lifetime of the L-state that can be seen in a magnified view in the inset of Fig. 2.3. The population of the L-state is hence negligible. After a certain value of $I'_m$, the population of the S-state decreases due to the absorption of the modulation beam by the S-state itself, resulting in an increase in the population of the L-state. There is a slight increase in the population of the initial D-state also, as shown in Fig. 2.3.

![Graph showing population density variations](image)

Fig. 2.3 Variation of normalized population density with $I'_m$ for different intermediate states of LOV2-WT. Inset shows a magnified variation at smaller values of $I'_m$.

The kinetic and spectral characteristics of LOV2 can be altered by varying the pH value and addition or substitution of chemical groups, etc. [Swartz et al. (2001), Kay et al. (2003), Salomon et al. (2000)]. The effect of rate constant $k_{LD}$ on the NTPI characteristics of LOV-WT is shown in Fig. 2.4. It is evident that as $k_{LD}$ decreases, NTPI decreases resulting in an increase in the percentage modulation of the probe beam. This is due to the effect that an increase in the lifetime of the L-state increases the population of the L-state, which leads to increased absorption of the probe beam. Variation in $k_{LS}$ leads to a similar effect with NTPI saturating at lower pump intensities for lower values of $k_{LS}$ as shown in the inset of Fig. 2.4. Figure 2.5 shows the effect of absorption cross-section of ground D-state $\sigma_D$ on the transmission characteristics of probe beam at 660 nm for LOV2-WT. Higher values
of $\sigma_D$ lead to higher population of the L-state, which decrease the transmission of probe beam and hence increase the percentage modulation.

![Graph](image1)

Fig. 2.4 Variation of NTPI at 660 nm with $I'_m$ for LOV2-WT for different values of rate constant $k_pD$, for $\beta = 1$. Inset shows the corresponding variation for different values of rate constant $k_pS$, for $\beta = 1$.

![Graph](image2)

Fig. 2.5 Variation of NTPI at 660 nm with $I'_m$ for LOV2-WT for different values of absorption cross-section of initial D-state $\sigma_D$, for $\beta = 1$.
Variation of NTPI at 660 nm with $I'_m$ at 442 nm for different values of absorption cross-section of intermediate L-state $\sigma_L$ at pump beam wavelength is shown in Fig. 2.6. As $\sigma_L$ increases, NTPI decreases due to more absorption of the pump beam by intermediate L-state also, resulting in a lower percentage modulation of the probe beam.

Fig. 2.6 Variation of NTPI at 660 nm with $I'_m$ for LOV2-WT for different values of absorption cross-section of L-state $\sigma_L$, for $\beta = 1$.

Figure 2.7 shows the variation of NTPI at 660 nm with $I'_m$ at 442 nm, for LOV2-C39A for different values of $\beta$. In this case also, NTPI decreases as $I'_m$ increases and saturates after a certain value of $I'_m$. This saturation value of $I'_m$ in LOV2-C39A is comparatively lower than that in LOV2-WT. For LOV2-C39A, the percentage modulation for $\beta = 0.2$ and 5 at $I'_m = 1$ kW/cm$^2$ is 12.63% and 96.58%, respectively. The percentage modulation in LOV2-C39A is larger than that in LOV2-WT at comparatively lower values of $I'_m$ ($\sim 1$ kW/cm$^2$). The probe beam also gets completely switched i.e. 100% modulated in LOV2-C39A at $I'_m = 1$ kW/cm$^2$, for $\beta = 8$. Figure 2.8 shows the variation of normalized population densities with input pump intensity $I'_m$ at 442 nm. It is evident from Fig. 2.8 that as $I'_m$ increases population of the D-state decreases and population of L-state increases.
Fig. 2.7 Variation of NTPI at 660 nm with \( I_m \) for LOV2-C39A, for different values of \( \beta \).

Fig. 2.8 Variation of normalized population density with \( I_m \) for different intermediate states of LOV2-C39A.
The kinetic and spectral characteristics of LOV2-C39A can also be altered through various chemical and biotechnological techniques. Variation of NTPI at 660 nm with $I_m'$ for LOV2-C39A for different values of rate constant $k_{LD}$ is shown in Fig. 2.9. The NTPI decreases as $k_{LD}$ decreases as slower depopulation rate of L-state increases the absorption of the probe beam at 660 nm by L-state. Since, the initial D-state of LOV2 phototropin does not absorb probe beam at 660 nm i.e. $\sigma_{DP} = 0$, there is no optimization condition of kinetic and spectral parameters obtained for maximum percentage modulation in case of LOV2 phototropin, as reported in case of rhodopsin proteins where $\sigma_{DP} \neq 0$ [Sharma and Roy (2004a, b), Singh and Roy (2002), Sharma et al. (2005)].

![Fig. 2.9 Variation of NTPI at 660 nm with $I_m'$ for LOV2-WT for different values of rate constant $k_{LD}$ for $\beta = 1$.]
2.4. Applications of Results

2.4.1. Design of All-Optical Spatial Light Modulator

All-optical spatial light modulators (SLMs) find wide applications as input and output transducers for image amplification, time/space transformation, scratch pad memory, programmable detector masking and page composition for holographic and three-dimensional memories [Roy et al. (2000, 2001), Roy and Kulshrestha (2005), Sharma et al. (2005)].

The NTPI is high at lower values of pump intensity and becomes low at higher values. This switching mechanism can be utilized for the construction of a molecular spatial light modulator (SLM) that will mainly depend on the optics of probe (read) and pump (write) beams. In semiconductor, liquid crystal or photorefractive based SLMs, storage is achieved by the generation of photocarriers within the bulk due to the absorption of pump beam. These carriers diffuse or drift to regions of lower incident light intensity [Casasent (1977), Kirkby and Bennion (1986), Neff et al. (1990), Reddy (1991), Speiser and Orenstein (1988), Speiser et al. (1989), Roy et al. (2000)]. In contrast, in the present case, the excitation is localized in the molecules and the resolution depends on the focusing geometry i.e. spot sizes of the order of a few micrometers [Speiser and Orenstein (1988), Speiser et al. (1989)]. Typical SLM properties such as dynamic range and sensitivity can be estimated in the present case. Dynamic range can be defined as the ratio of NTPI through a sample of length \( L \) in the presence of the pump beam, to that in the absence of the pump beam as given in the following expression [Speiser and Orenstein (1988), Speiser et al. (1989), Roy et al. (2000)]

\[
\delta = \frac{\left( \frac{I_{\text{out}}}{I_{\text{pin}}} \right)_{I_m}^{I_m'}}{\left( \frac{I_{\text{out}}}{I_{\text{pin}}} \right)_{I_m=0}^{I_m'}}
\]  

(2.23)

and the sensitivity, which is defined as [Speiser and Orenstein (1988), Speiser et al. (1989), Roy et al. (2000)]

\[
S = - \left( \ln \delta \right) / I_m'
\]  

(2.24)
In LOV2 phototropin, the probe beam at 660 nm is only absorbed by the L-state as $\sigma_{dp} = \sigma_{sp} = 0$, which corresponds to the ideal case [Roy et al. (2000), Singh and Roy (2002), Singh et al. (2003), Sharma et al. (2003), Roy and Kulshrestha (2005)]. Hence, the variation of dynamic range with $I_m'$ for this case will be same as the variation of NTPI as plotted in Fig. 2.3. For LOV2-WT, $\delta = 0.53$ and $S = 1.26 \times 10^5$ cm$^2$/W, at $I_m' = 50$ kW/cm$^2$, for $\beta = 1$. For LOV2-C39A, variation of dynamic range with $I_m'$ will be same as the variation of NTPI with $I_m'$ as shown in Fig. 2.7 as LOV2-C39A also corresponds to the ideal case i.e. $\sigma_{dp} = 0$. For LOV2-C39A, estimated values of $\delta$ and $S$ are 0.51 and $6.73 \times 10^{-4}$ cm$^2$/W at $I_m' = 1$ kW/cm$^2$.

2.4.2. Design of All-Optical Logic Gates

The transmission characteristics of LOV2-WT at typical parameters can be used to design all-optical NOT, NAND and NOR logic gates by considering the NTPI as output and pump beam as combination of inputs [Roy and Kulshrestha (2005), Sharma and Roy (2004 a, b)]. The switching of the transmission characteristics from high (above threshold) to low (below threshold) at lower and higher input $I_m'$ values, respectively, correspond to the all-optical NOT logic gate as is evident from Fig. 2.10.

All-optical NAND logic operation can be obtained by considering two input intensities $I_{m1}' = I_{m2}' = 10$ kW/cm$^2$ and a threshold at 0.65 as shown in Fig. 2.10. The NTPI becomes high when either one or none of the input beams is present and becomes low when both the input beams are present. All-optical NOR logic gate can be designed by considering two input intensities $I_{m1}' = I_{m2}' = 20$ kW/cm$^2$. The NTPI becomes low when either one or both the input beams are present and becomes high when none of the input beams is present. The proposed design shows the applicability of the SLM characteristics of LOV2 phototropin for generating all-optical logic devices.
Fig. 2.10 Variation of NTPI at 660 nm with $I'_m$ for LOV2-WT for $\beta = 1$ and realization of all-optical NOT and two input universal NAND and NOR logic gates. Vertical and horizontal lines indicate input and output values for respective logic gates. Horizontal dashed line shows the threshold level.

2.5 Conclusion

In conclusion, a detailed analysis of all-optical light modulation of a cw probe laser beam at 660 nm by a cw pump laser beam at 442 nm, through recently discovered LOV2 phototropin and its mutant LOV2-C39A has been conducted. The present analysis highlights a number of advantages of LOV2 over other biomolecules such as bR, ppR and pR: (i) LOV2 has a simpler photocycle, (ii) high quantum efficiency, (iii) no overlap in the absorption spectra of the initial state and the excited-state at probe wavelength ($\sigma_{dp} = 0$), contrary to that observed in retinal proteins, hence 100% modulation can be achieved, (iv) since the absorption spectra of LOV2 exhibit RSA over a wide range (500 - 700 nm), with almost constant absorption by the L-state [Swartz et al. (2001)], the modulation characteristics would be similar for probe beams at different wavelengths in this range, leading to broadband switching and (v) as the properties of LOV2 can be tailored by physical,
chemical and genetic engineering techniques, all-optical light modulation in LOV2 can be optimized for fast response, high contrast and low power operation. The present analysis also shows the applicability of the above results to the design of all-optical spatial light modulator and all-optical logic gates that are the basic building blocks of information processing systems.