

Photo isomerization probability calculation of azo-benzene

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ABSTRACT

Probability of the photo isomerization of azo-benzene can be calculated by using Stimulated Raman Adiabatic Passage (STIRAP) method, one of the time evolutionary state-space calculations used in excited state modeling. By setting 4 bounded states and using transition dipole moment driven from quantum simulation, we can get probability of the trans → cis photo isomerization of the azo benzene according to light intensity, light polarization angle, and time. According to our computation, we are assuming that light intensity and the angle of the light only affect the rising time of the probability, but do not confine the maximum probability itself.

1. INTRODUCTION

Azo-benzene liquid crystal elastomer (LCE) is well known for their photo deformation effect, causing 20% contraction in 300nm wavelength of light, and go back to original shape in 400nm wavelength of light.(Finkelmann 2001)(Harris 2005) This kind of large deformation is caused by photo isomerization (transition from trans state to cis state) of the azo-dye, which lowers nematic-isotropic transition temperature of the LCE, and induces large bending in LCE structure. The rate of the cis state in azo-benzene is the key factor in predicting lowered nematic-isotropic transition temperature of the LCE, and for this reason, estimating population rate of the azo-benzene is the key factor in predicting deformation of the azo-benzene LCE.(Corbett 2006) In order to build up physically reliable and accurate formulation for predicting photo isomerization of azo-benzene, we introduced Stimulated Raman Adiabatic Passage (STIRAP) method into our calculation.(Bergmann 1998)(Coulston 1992)(Ficek 1986)(Kurkal 2001) In this paper, we will show overall calculation method for predicting photo-isomerization of azo-benzene, and their calculation result.

2. METHODOLOGY

2.1 Photo-Isomerization Mechanism

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According to Bookmann and Eric's first principle calculation, energy trajectory of azo-benzene isomerization usually passes intersection of the excited state and ground state, usually referred as conic point in Fig. 1.(Ciminelli 2004)(Diau 2004)(Weingart 2011) As shown in Fig. 2, excited state of the azo-benzene molecule starts rotational movement along N-N atom axis, and change their C-N-N-C dihedral angle. When azo-benzene reaches conic point, azo-benzene molecule fall down to ground state and changes into cis state or goes back to original state.

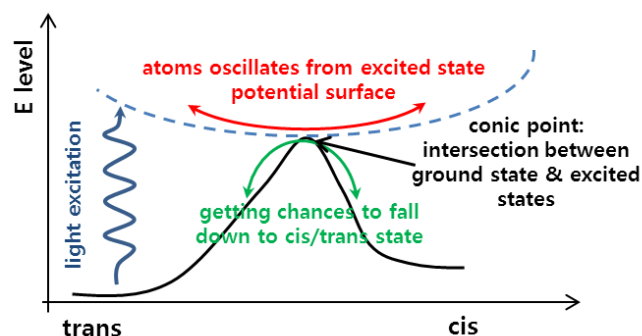


Fig. 1 Energy diagram of the photo-isomerization of azo-benzene

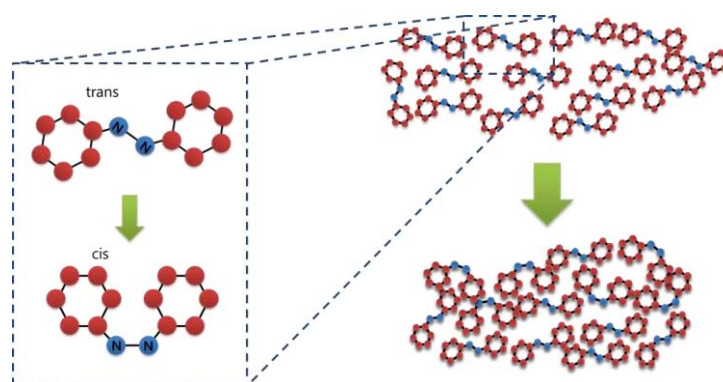


Fig. 2 photo-isomerization of azo-benzene, molecular overview

2.2 STIRAP formulation

STIRAP method is one of the state space control algorithm, solving extended set of a time dependent Schrödinger equation as shown in Eq. (1)-(2). By solving the STIRAP equation numerically, we can calculate time evolutionary change of the trans: cis population ratio. Same as the notation in Fig. 3, we set 4 bounded states for calculating photo-isomerization of azo-benzene. In main STIRAP equation Eq. (3), ρ_{11} and ρ_{22} indicate population rate of trans and cis state respectively. ρ_{33} and ρ_{44} indicates excited population rate of the trans azo-benzene and conic point azo-benzene. Total sum of the population rate is normalized into 1, and index form of the STIRAP equation for photo-isomerization of azo-benzene is described as follow:

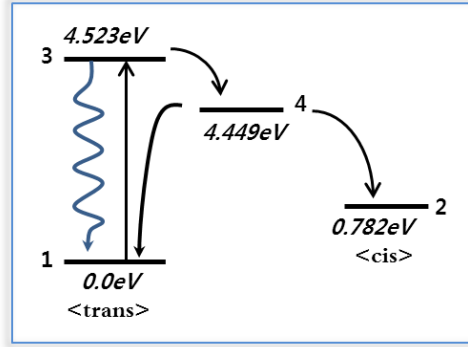


Fig. 3 bound state modeling of trans \rightarrow cis azo-benzene isomerization

$$i\hbar \frac{d}{dt} \Psi \psi_j^* = [\hat{H}_0 + \hat{H}_{inter}] \Psi \psi_j^* \quad (1)$$

$$\Psi = [\psi_1 \quad \psi_2 \quad \psi_3 \quad \psi_4]^T \quad (2)$$

$$\psi_n = c_n |n\rangle = c_m \phi_m \exp(-i\omega_n t)$$

$$\begin{bmatrix} \dot{\rho}_{11} \\ \dot{\rho}_{22} \\ \dot{\rho}_{33} \\ \dot{\rho}_{44} \\ \dot{\rho}_{13} \\ \dot{\rho}_{31} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 2r_{31} & 2k_{41} & \frac{i}{2\hbar}(\varepsilon \cdot d_{13})\exp(-i\omega t) & -\frac{i}{2\hbar}(\varepsilon \cdot d_{13})\exp(i\omega t) \\ 0 & 0 & 0 & 2k_{42} & 0 & 0 \\ 0 & 0 & -2(r_{31} + k_{34}) & 0 & -\frac{i}{2\hbar}(\varepsilon \cdot d_{13})\exp(-i\omega t) & \frac{i}{2\hbar}(\varepsilon \cdot d_{13})\exp(i\omega t) \\ 0 & 0 & 2k_{34} & -2(k_{41} + k_{42}) & 0 & 0 \\ \frac{i}{2\hbar}(\varepsilon \cdot d_{13})\exp(i\omega t) & 0 & -\frac{i}{2\hbar}(\varepsilon \cdot d_{13})\exp(i\omega t) & 0 & i\omega - (r_{31} + k_{34}) & 0 \\ -\frac{i}{2\hbar}(\varepsilon \cdot d_{13})\exp(-i\omega t) & 0 & \frac{i}{2\hbar}(\varepsilon \cdot d_{13})\exp(-i\omega t) & 0 & 0 & i\omega - (r_{31} + k_{34}) \end{bmatrix} \begin{bmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \\ \rho_{44} \\ \rho_{13} \\ \rho_{31} \end{bmatrix} \quad (3)$$

$$\omega = (E_3 - E_1) \hbar^{-1}$$

In Eqn. (3), d_{13} , k_{34} , means transition dipole moment of the trans state azo-benzene and oscillation of the excited state energy surface. k_{41} , k_{42} means oscillation frequency of the conic point, and each of them predicts ratio of the population change from conic point to trans or cis state. All of the frequency and transition dipole moment is calculated by Gaussian package. Epsilon is referred as polarized electric field of light, and can be derived from the following equation of photon density n_ω .

$$\frac{\vec{\varepsilon}_0^2 / 8\pi + \vec{B}^2 / 8\pi}{2} \cong \frac{\vec{\varepsilon}_0^2}{8\pi} \cdot d\omega \quad (4)$$

$$\frac{\vec{\varepsilon}_0^2}{8\pi} \cdot d\omega = 2\hbar\omega n_\omega \frac{dk}{(2\pi)^3} \quad (5)$$

$$\vec{\varepsilon}_0^2 = \frac{8\hbar\omega^3}{\pi c^3} n_\omega \cdot d\omega \quad (6)$$

$$\vec{\varepsilon}_0^2 = \int_{-\infty}^{\infty} d\tilde{\omega} \frac{8\hbar\tilde{\omega}^3}{\pi c^3} \cdot n_\omega \delta(\omega - \tilde{\omega}) \quad (7)$$

$$|\vec{\varepsilon}_0| = \left(\frac{8\hbar\omega^3}{\pi c^3} \cdot n_\omega \right)^{\frac{1}{2}} \quad (8)$$

In Eqn. (4) we simply normalized electro-magnetic energy of the light into the combination of electric field of light and derivative of light angular frequency. By connecting Eqn. (4) with photon clustered light energy term (Eqn. (5)), and apply spatial frequency and angular frequency relation ($dk = 4\pi k^2 d\omega$), we can get electric field vector of light according to the derivation of light angular frequency. Assuming that light is mainly formed with monochromatic frequency of photons and integrate Eqn. (6) over whole range of angular frequency, we can get absolute amount of electric field of light in light as shown in Eqn. (8).

3. DATA RESULT

We calculated time derivative population change of the photo-isomerization of azo-benzene ($\frac{dn_{cis}}{dt}$), and parameterized them according to different light intensity n_ω and light polarization angle θ . The parameterized data plot is stated in Fig. (4):

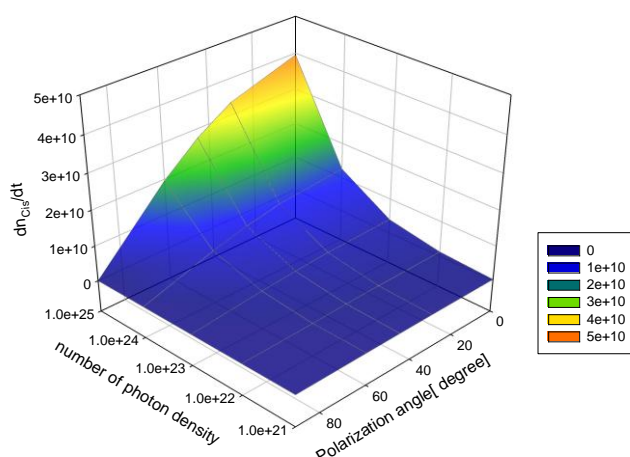


Fig. 4 time derivative trans→cis population transfer rate of azo-benzene.

By parameterizing light intensity and polarization angle, we formulated correlational function of the time derivative trans→cis ratio:

$$\frac{dN_{cis}}{dt} = \cos(\theta) \cdot \frac{n_\omega^{0.4994}}{10^{0.8997}} \quad (9)$$

4. CONCLUSION

We calculated trans→cis population change of the azo-benzene with STIRAP method. As shown in Fig. (5), we found that photon density and angle of the light only

affects the rising time of the population ratio of the cis state azo-benzene. Based on the Eqn. (9), we are expecting that we can predict the population ratio of the azo-benzene in photo-reactive LEC and predict exact nematic-isotropic transition temperature.

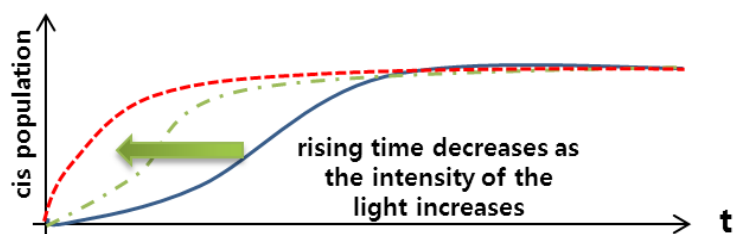


Fig. 5 time evolutional change in cis population

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