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Predicting photoisomerization profile of the highly polymerized nematic azobenzene liquid crystal network: First principle calculation

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ABSTRACT

The cis profile of azobenzene is a key factor in predicting the photodeformation of the nematic azobenzene liquid crystal network (LCN). An *ab initio* based method for predicting the photoisomerization profile of azobenzene is developed by coupling the stimulated Raman adiabatic passage (STIRAP) method with non-linear Beers law, and compared with experimental data. Using this combined method, we calculate the photoisomerization profile of azobenzene with various light input conditions. We identify the cis profile of the nematic LCN structure evolves into a step-like decaying shape when the direction of polarized light is parallel to the nematic direction.

1. Introduction

An azobenzene-containing liquid crystal network (LCN) is well known for its photoresponsive deformation, wherein it undergoes contraction (about 20% of the total length along the nematic direction) when exposed to 300 nm wavelength of light and returns to its original shape on exposure to 400 nm wavelength of light [1–19]. As photo deformation of azobenzene LCN is affected by the trans–cis photoisomerization ratio of azobenzene [1,20,11,21–23], an accurate estimation of the isomerization ratio of azobenzene is crucial in predicting the photodeformation of the azobenzene LCN structure. Since while, many research groups have estimated the photoisomerization term of azobenzene as a product of quantum efficiency of the trans–cis reaction and light intensity profile [24,25], but did not concern the change of the light intensity due to the trans–cis population change of azobenzene. Although quantum efficiency is enough factor in estimating the photoisomerization ratio of azobenzene in static light intensity condition, merely multiplying quantum efficiency by the light penetration profile oversimplifies the photoisomerization profile, because light intensity dynamically changes as the trans–cis population changes, which is shown in Statman's experiment [20]. For this reason, we develop a new modeling approach considering both quantum excitation and photoisomerization feedback of azobenzene into light penetration. This modeling approach can be achieved by combining the stimulated Raman adiabatic passage (STIRAP) technique [26,27] with non-linear Beers law, which considers the change in the trans–cis population and the effect of light bleaching simultaneously.

2. Theoretical methods

2.1. STIRAP equation

The modeling approach is mainly divided into two parts: (1) stimulated Raman adiabatic passage (STIRAP) calculation for predicting the time derivative isomerization ratio of azobenzene, and (2) light penetration profile by using modified Beers law. For STIRAP calculations, we derived a correlation function for the photoisomerization reaction rate of azobenzene for a given light intensity and light input angle. By applying the correlation function to Statman's non-linear Beers law [20], we derived changes in the light penetration profile and isomerization profile of the azobenzene LCN structure with time. STIRAP is a state-space control method that predicts changes in each intermediate state of a photochemical reaction with time [26,27]. As the photoisomerization of azobenzene with second excitation (S_2) is the most efficient reaction path among others [28–30,23], we defined five states of the photoisomerization process, as shown in Figure 1. States 1 and 2 are the trans and cis ground states, and states 3 and 5 are the trans and cis excited states of the azobenzene, respectively. State 4 indicates the conic point, the intersection between the ground and excited states of azobenzene. Two different wavelengths (excitation for states 1 → 3, and 2 → 5) of light were considered in the calculation. Light of wavelength relevant to 1 → 3 triggers the *trans* → *cis* photoisomerization, whereas light of wavelength relevant to 2 → 5

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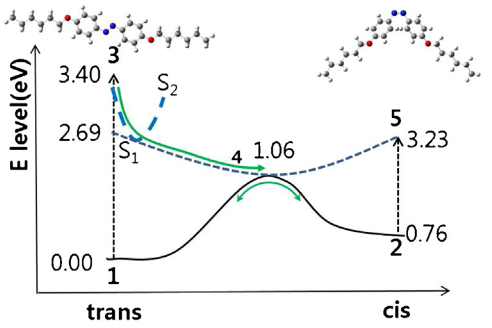

Figure 1. Schematic diagram for photoisomerization passage. Bold arrows in S_1 and S_2 states excitation path from trans to cis state.

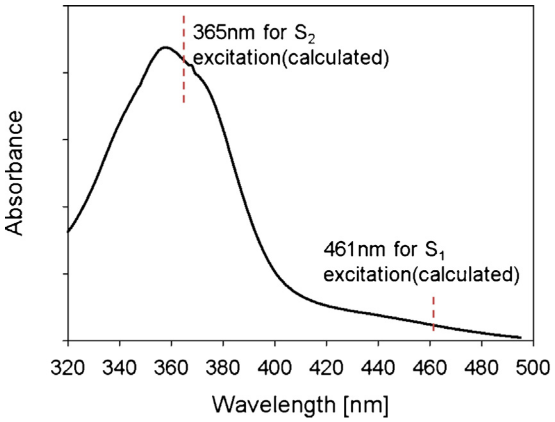

Figure 2. Trans state of the UV–vis spectrum (Cary 100, Agilent Tech.) of the A6ZA6 (Beam Co.) azobenzene monomer. S_2 excitation is 358 nm, and S_1 excitation is 440 nm for experiment.

stimulates the *cis* → *trans* photoisomerization. Light frequencies for each excitation, corresponding to wavelengths of 365 nm and 501 nm, were calculated by Gaussian 09 (TD B3LYP/6-311G*), and the target molecule for the calculation is an azobenzene unit with two side arms (—$(CH_2)_2$—) added on the both ends of the azobenzene. Calculated S_1, and S_2 level in trans state of azobenzene were compared with UV–vis spectrum data of A6ZA6 (Beam Co.) azobenzene monomer to verify the calculation result, as shown in Figure 2. Among trans state excitation levels calculated by Gaussian 09, we selected S_2 energy level as harmonic excitation from state (1 → 3). In case of cis state excitation (2 → 5), we choose lowest excitation energy level with non-zero oscillation strength which shows closest proximity to 450 nm wavelength of light. Relevant energy levels are summarized in Figure 1 (dashed lines with arrowheads from state 1–3 to state 2–5).

For the convenience of calculation, we neglected the phase difference of each state and assumed 2-electron excitation. As the surroundings of azobenzenes are mostly polymers with covalent bonding, we assumed that the electrons in azobenzene do not escape into the outer system. The main equations modified from the STIRAP equations are Eqs. (1)–(3), which are extended from resonance transitions in two level systems (Chapter 4.3 in Krainov and Reiss' Book [31]).

$$\frac{d\rho_{jj}}{dt} + 2(\nu_j+\gamma_j)\rho_{jj} - 2\sum_p(\nu_{pj}+\gamma_{pj})\rho_{pp} = \frac{i}{\hbar}\left[\sum_n V_{nj}\rho_{jn} - V_{jn}\rho_{nj}\right]$$

$$\omega_{jk} = \hbar^{-1}(E_j - E_k),\ \gamma_n = \sum_m \gamma_{nm},\ \nu_n = \sum_m k_{nm} \tag{1}$$

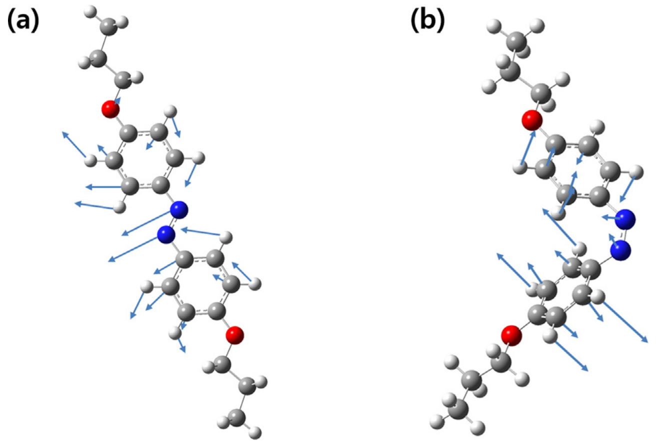

Figure 3. Oscillation frequency mode of azobenzene in (a) excited trans state and (b) conical state calculated by Gaussian 09.

$$\frac{d\rho_{jk}}{dt} + (\gamma_k + \nu_j + i\omega_{jk})\rho_{jk} = \frac{i}{\hbar}\left[\sum_n V_{nk}\rho_{jn} - V_{jn}\rho_{nk}\right] \tag{2}$$

$$\rho_{jk} = \Psi_j \cdot \Psi_k^* = c_{jk}\exp(i\omega_{jk}t)$$

$$V_{mn} = -\varepsilon \cdot d_{mn} = -\varepsilon_0 \cdot \cos(\omega_{mn}t) \cdot d_{mn} \tag{3}$$

where, ρ_{jj} represents each static state of azobenzene (j = 1, · · ·, 5), and ρ_{jk} indicates phase change in the excitation of azobenzene (jk = 13, 31, 25, 52). Ψ_j is the wave function of the electrons, and ω_{jk} is the excitation frequency from state j to state k. $\hbar$ is the reduced Planck constant, and ν_{jk} is the frequency of molecular change from state j to state k. γ_{jk} refers to the spontaneous radiation term of the excited states. d_{mn} is the transition dipole moment corresponding to each excitation (state 1 → 3, state 2 → 5). Total sum of the ρ_{jj} is normalized as 1, and all of the ν_{mn}, γ_{mn}, d_{mn}, and energy levels (E_j, E_k) were calculated by using the Gaussian 09 commercial software package. Right hand side of Eqs. (1) and (2) represents perturbation of Schrodinger equation caused by light, and left hand side of Eqs. (1) and (2) represents population transfer of the molecule due to the chemical reaction and radiation. Specific explanation of the STIRAP method is described in the Appendix H of Krainov and Reiss's Book [31].

As the main reaction passage for S_2 excitation is inversion type [23,29], we choose the frequency of which vibration mode in excitation is showing inversion (Figure 3a) as reaction rate through state 3 to state 4 (ν_{34}). In case of ν_{54}, we choose excitation frequency that shows rotational mode, as shown in Figure 3b. In case of conic point frequency (ν_{41}, ν_{42}), we used saddle point frequency mode.

Generally, conic point of excitation in different molecules are slightly skewed from saddle point of the ground state, so that reaction rates from conic point toward other minimum ground states are not always equal. However, in case of azobenzene monomer, there are reports saying that conic point of the excited state of an azobenzene molecule is quite flat to cover saddle point [32], meaning that there is high probability for excited electrons in an azobenzene molecule to fall into ground state through saddle point. Our CAS calculation (CASSCF(6,6)/6-31G) also indicates that molecule geometry of conic point of azobenzene is same as transition point of the azobenzene in ground state. For this reason, we regarded reaction frequencies in conic point as frequency in transition point. The coefficients γ_{31} and γ_{52} were calculated by transition dipole moment with using following equation, $\gamma_{jk} = 4\omega_{kj}^3|d_{jk}|^2/(3\hbar c^3)$, shown in the first chapter of Kranov and Reiss' Book [31]. ε_0 in Eq. (3) is the magnitude of the electric field vector of light, which can be transformed into a function of