Research Article

Detailed Photoisomerization Dynamics of a Green Fluorescent Protein Chromophore Based Molecular Switch

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With density-functional-based nonadiabatic molecular dynamics simulations, *trans*-to-*cis* and *cis*-to-*trans* photoisomerizations of a green fluorescent protein chromophore based molecule 4-benzylidene-2-methyloxazol-5(4H)-one (BMH) induced by the excitation to its S_1 excited state were performed. We find a quantum yield of 32% for the *trans*-to-*cis* photoisomerization of BMH and a quantum yield of 33% for its *cis*-to-*trans* photoisomerization. For those simulations that did produce *trans*-to-*cis* isomerization, the average S_1 excited state lifetime of *trans*-BMH is about 1460 fs, which is much shorter than that of *cis*-BMH (3100 fs) in those simulations that did produce *cis*-to-*trans* isomerization. For both photoisomerization processes, rotation around the central C2=C3 bond is the dominant reaction mechanism. Deexcitation occurs at an avoided crossing near the S_1/S_0 conical intersection, which is near the midpoint of the rotation.

1. Introduction

Molecules with the ability to undergo photoisomerization under radiation would have potential applications in molecular switches and other molecular devices. Photoisomerization mechanisms of stilbene [1–3], fulgide [4–6], diarylethene [7–9], and azobenzene [10–14], together with their derivatives [15–19], have been widely studied during the last two decades. Despite their appealing features as effective molecular switches, azobenzene derivatives and above photochromic compounds are just examples of a whole family of compounds capable of performing controlled isomerization reactions. The discovery of new or alternative photoswitch types could expand the applicability of the switch concept to different and increasingly complex molecular environments.

The chromophore of the green fluorescent protein, as a biomolecule from jellyfish *Aequorea victoria*, has been widely used as a genetically encoded noninvasive fluorescence marker in bioimaging [20]. Recently, several studies have revealed that the green fluorescent protein chromophore and its different modifications undergo photo-induced Z/E isomerization under radiation [21–26], which offer them

the opportunity to be molecular switches. Through investigation of several spectral modification of synthetic chromophore analogues of wild-type green fluorescent protein, Voliani et al. [21] found that *cis*-to-*trans* photoisomerization should be a general mechanism of green fluorescent protein chromophores whose efficiency can be modulated by the detailed mutant-specific protein environment. Using femtosecond fluorescence upconversion spectroscopy and quantum chemical calculations, Rafiq et al. [22] investigated two green fluorescent protein chromophore analogs and proposed a multicoordinate relaxation mechanism. Oxazolone analogs, as well-known intermediates in the synthesis of green fluorescent protein derivatives, have attracted relatively little attention in terms of their photoswitching ability. Very recently, several oxazolone analogs of the green fluorescent protein chromophore were synthesized and predicted to be good candidates for molecular switches by Blanco-Lomas et al. [27].

To furnish a deeper and detailed mechanistic understanding of the photoisomerization reaction of those green fluorescent protein chromophore based molecular switches, semi-classical nonadiabatic molecular dynamics simulations were

performed for a molecule 4-benzylidene-2-methyloxazol-5(4H)-one (BMH, named as 2e in [27]) in our group. We found that the average lifetime of the S_1 excited state in *trans*-BMH is about 1450 fs, much shorter than that of *cis*-BMH (3100 fs), which is in good agreement with the experimental result [27].

This paper is organized as follows. Our semiclassical nonadiabatic molecular dynamics simulation method is briefly reviewed in Section 2. The detailed results and discussions are represented in Section 3, followed by a conclusion in Section 4.

2. Methodology

Our nonadiabatic molecular dynamics simulation method was named semiclassical electron-radiation-ion dynamics (SERID), which has been described in detail elsewhere [28, 29]. We only briefly review it under below.

To obtain the evolution equations of electrons and nuclei, we postulate a mixed classical-quantum action [30–32] $S = \int dt L$, where

$$L = \frac{1}{2} \langle \Psi_e | \left(i\hbar \frac{\partial}{\partial t} - \mathcal{H}_e \right) | \Psi_e \rangle + \text{h.c.} + \frac{1}{2} \sum_{k\alpha} M_k \left(\frac{dX_{k\alpha}}{dt} \right)^2 - U_{\text{rep}}. \quad (1)$$

$\mathcal{H}_e$ is the electronic Hamiltonian, $|\Psi_e\rangle$ is the electronic state, “h.c.” means “Hermitian conjugate,” k labels a nucleus with spatial coordinates α , and U_{rep} is the repulsive interaction between nuclei and ion cores. As shown in [32], if one makes the usual time-dependent effective-field approximation and employs a nonorthogonal basis, extremalization of this action leads to the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi(t) = \mathbf{S}^{-1} \cdot \mathbf{H} \cdot \psi(t) \quad (2)$$

and to the equation of motion for the nuclei

$$M \frac{d^2 X}{dt^2} = -\frac{1}{2} \sum_n \psi_n^\dagger \cdot \left(\frac{\partial \mathbf{H}}{\partial X} - i\hbar \frac{\partial \mathbf{S}}{\partial X} \frac{\partial}{\partial t} \right) \cdot \psi_n + \text{h.c.} - \frac{\partial U_{\text{rep}}}{\partial X}. \quad (3)$$

The Hamiltonian matrix $\mathbf{H}$, overlap matrix $\mathbf{S}$, and repulsive potential U_{rep} are obtained from the density-functional-based parameterizations of Frauenheim and coworkers [33, 34].

The results of [14, 35–44] calculated with SERID method have provided a clear demonstration of the following features of simulations based on Ehrenfest dynamics: (1) electronic transitions are automatically observed at an avoided crossing near a conical intersection in configuration space predicted by Teller [45, 46], with energy released to molecular vibrations; (2) these transitions occur rapidly, over a time interval of ~ 2 femtosecond, during which the nuclei do not move appreciably.

TABLE 1: Optimized geometrical parameters of *cis*-BMH and *trans*-BMH, calculated with our SERID method and B3LYP/6-311G(d,p) implemented in Gaussian 03 software package. The lengths are in Å and the dihedral angles and bond angles are in degrees.

	SERID	B3LYP/6-311G(d,p)
<i>cis</i>		
C1C2C3C6	180.0	180.0
C3C2C1C5	0.0	0.0
C1C2H12C3	180.0	180.0
C1C2C3	127.0	129.9
C2C1C5	122.9	123.5
C2C3N21	127.6	129.4
C2–C3	1.37	1.35
C1–C2	1.45	1.45
C3–N21	1.42	1.40
<i>trans</i>		
C1C2C3C6	0.1	0.0
C3C2C1C5	0.1	0.0
C1C2H12C3	180.0	180.0
C1C2C3	130.8	134.3
C2C1C5	124.6	125.4
C2C3N21	119.0	120.3
C2–C3	1.37	1.36
C1–C2	1.45	1.45
C3–N21	1.43	1.41

In the present work, we have made a little change in the procedure that should lead to better results for the quantum yields. By simply placing an electron in the lowest unoccupied molecular orbital (LUMO) and a hole in the highest occupied molecular orbital (HOMO) in the beginning of nonadiabatic simulations, we focus exclusively on the S_0 - S_1 excitation, as in other excited state molecular dynamics simulations [47, 48]. However, we still allow deexcitation to occur automatically at an avoided crossing near a conical intersection, since we found that deexcitation was already nearly complete in our present simulations.

3. Results and Discussion

We optimized the *cis* and *trans* structures of BMH in the ground state, starting from 300 K through reducing the nuclear velocities by a factor of 0.9997 after each time step of 0.01 fs until the total molecular kinetic energy was less than 10^{-7} eV. The optimized geometries of *cis* and *trans* BMH are presented in Figure 1, with their geometrical parameters summarized in Table 1. We also optimized both structures with B3LYP/6-311G(d,p) implemented in Gaussian 03 software package [49]. Both results are in good agreement with each other. The electronic energy of *cis*-BMH is 0.11 eV lower than that of *trans*-BMH in our SERID calculation, agreeing well with the energy difference (0.13 eV) obtained with B3LYP/6-311G(d,p) method. Both results confirm that *cis*-BMH is more stable than its *trans* isomer. Starting from its optimized geometry, each molecule was then heated to 300 K

FIGURE 1: Optimized geometries of (a) *trans* and (b) *cis* structures of BMH calculated with SERID. All atoms are labelled.

FIGURE 2: Time dependence of (a) orbital energies from HOMO – 1 to LUMO + 1 and (b) LUMO-HOMO energy gap in BMH for the *trans*-to-*cis* isomerization. 0.06 eV is the minimum value of the LUMO-HOMO energy gap in this simulation.

(via random velocities resulting in this temperature) and then allowed to equilibrate and move in the electronic ground state for 10000 fs. The initial conditions for various simulations were then sampled from the configurations during the last half of this 10000 fs interval.

3.1. *trans*-to-*cis* Photoisomerization of BMH. Starting from the first excited state of *trans*-BMH with different initial conditions, 90 simulations have been performed, 29 of which resulted in *trans*-to-*cis* isomerization. So the quantum yield of this reaction in our calculation is about 32%. For the 29 simulations which did produce *trans*-to-*cis* isomerization, the average S_1 lifetime of *trans*-BMH is about 1460 fs. A detailed discussion of the isomerization mechanism in a representative simulation with a 1740 fs S_1 lifetime is presented below.

BMH molecule is excited to the S_1 excited state at time $t = 0$ fs. To compare the results before and after the excitation, the results before 0 fs are also presented in Figures 2–7 below. Time dependence of the four orbital energies nearest the initial HOMO-LUMO gap are displayed in Figure 2. As we can see, after the excitation at 0 fs, only the HOMO and LUMO energy levels are affected evidently. The energy gap between HOMO and LUMO orbitals, as shown in Figure 2(b), decreases continuously from 2.55 eV to 0.06 eV until 1739 fs.

After about 1810 fs, the energy gap between HOMO and LUMO returns to about 2.66 eV and then vibrates around this new value until the end of our simulation. Electron occupations for the four orbitals presented in Figure 2(a) after the excitation are shown in Figure 3. As we can see, BMH deexcites to its ground state at about 1740 fs in 4 fs interval; nearly all electrons return to their ground state. The lifetime of the S_1 excited state in *trans*-BMH is thus about 1740 fs.

Variations of geometry for BMH are displayed in Figures 4–7. As displayed in Figure 4, dihedral angle C1C2C3C6 vibrates around 0° before the excitation at 0 fs, after the excitation, which increases continuously from -27° to about 73° at 1740 fs when BMH returns to the ground state. After the deexcitation at 1740 fs, the rotation around C2=C3 bond continues. Dihedral angle C1C2C3C6 reaches 180° (the optimized value for dihedral angle C1C2C3C6 in *cis*-BMH) at about 2040 fs and then vibrates around this new value, which can demonstrate that the molecule arrives at its *cis* geometry in about 2040 fs. Atomic distance between H20 and N21 displayed in Figure 7(c) can be another confirmation for the final *cis* geometry. After the excitation at 0 fs, the distance between H20 and N21 decreases continuously from about 4.4 Å to 2.2 Å until 2040 fs and then vibrates around this value until the end of our simulation. Other two dihedral

FIGURE 3: (a) Evolution of electron occupations in BMH from HOMO - 1 to LUMO + 1 for the *trans*-to-*cis* isomerization. (b) Details of Figure 3(a) from 1720 to 1760 fs.

FIGURE 4: Time dependence in BMH of (a) C1C2C3C6 dihedral angle, (b) C3C2C1C5 dihedral angle, and (c) C1C2H12C3 dihedral angle for the *trans*-to-*cis* isomerization. All labels are defined in Figure 1.

angles C3C2C1C5 and C1C2H12C3 are also displayed in Figure 4. During the whole simulation, C3C2C1C5 vibrates around 0°. That is, there is no evident rotation around C1-C2 bond. C1C2H12C3 also does not vary evidently during the whole simulation and keeps on vibrating around 180°, which demonstrates that H12 atom stays nearly in a plane with atoms C1, C2, and C3 all the time.

Three bond angles in BMH during the *trans*-to-*cis* isomerization are presented in Figure 5. As we can see, during the whole simulation, C1C2C3 bond angle keeps on vibrating around 125°, while C2C1C5 bond angle keeps on staying around 121°. C2C3N21 vibrates around 119° (the optimized C2C3N21 value in *trans*-BMH) before the excitation at 0 fs

and then stays around 128° (the optimized C2C3N21 value in *cis*-BMH) after the deexcitation at 1740 fs.

Time dependence of five bond lengths in BMH is shown in Figures 6 and 7. As shown in Figure 6, after the excitation at 0 fs, C2=C3 bond is weakened, increasing from 1.37 Å to 1.47 Å and then returning to 1.37 Å after the deexcitation at 1740 fs. On the other hand, other two bond lengths presented in Figure 6, C1-C2 and C3-N21, are shortened from 1.47 Å to 1.40 Å and from 1.43 Å to 1.37 Å after the excitation at 0 fs, respectively. After the deexcitation at 1740 fs, both bond angles, C1-C2 and C3-N21, return to their initial values before the excitation. Time dependence of other two carbon-carbon bonds, C3-C6 and C1-C4, which are connected with

FIGURE 5: Time dependence in BMH of three bond angles: (a) C1C2C3, (b) C2C1C5, and (c) C2C3N21 for the *trans*-to-*cis* isomerization. All labels are defined in Figure 1.

FIGURE 6: Time dependence in BMH of (a) bond length C2-C3, (b) bond length C1-C2, and (c) bond length C3-N21 for the *trans*-to-*cis* isomerization. All labels are defined in Figure 1.

C2=C3 and C1-C4, respectively, are displayed in Figure 7. As we can see, after the excitation at 0 fs, C3-C6 was also shortened, decreasing from 1.46 Å to 1.43 Å, and returning to 1.46 Å after the deexcitation at 1740 fs. The C1-C4 bond length

increases from 1.41 Å to 1.45 Å at 0 fs and comes back to 1.41 Å after 1740 fs.

For the representative *trans*-to-*cis* isomerization of BMH discussed above, lifetime of the S_1 excited state in

FIGURE 7: Time dependence in BMH of (a) bond length C3-C6, (b) bond length C1-C4, and (c) atomic distance H20-N21 for the *trans*-to-*cis* isomerization. All labels are defined in Figure 1.

FIGURE 8: (a) Orbital energies from HOMO - 1 to LUMO + 1 and (b) LUMO-HOMO energy gap in BMH as a function of time for the *cis*-to-*trans* isomerization.

trans-BMH is about 1740 fs, while the *cis* geometry is arrived in about 2040 fs. Rotation around C2=C3 bond is the dominant reaction mechanism. Deexcitation occurs near the midpoint of the rotation, due to an avoided crossing near the S_1/S_0 conical intersection.

3.2. *cis*-to-*trans* Photoisomerization of BMH. On the basis of 60 simulations, 20 of which did produce *cis*-to-*trans* isomerization, we find a quantum yield of 33% for *cis*-to-*trans* isomerization of BMH induced by the excitation to its S_1 excited state, which is only a little larger than that of *trans*-to-*cis* isomerization of BMH. For the 20 simulations which did produce *cis*-to-*trans* isomerization, the average S_1 lifetime of *cis*-BMH is about 3100 fs. In order to provide the detailed

cis-to-*trans* reaction mechanism, a single representative simulation with a 3545 fs S_1 lifetime is discussed below.

Time dependence of orbital energies from HOMO - 1 to LUMO + 1 and energy gap between LUMO and HOMO in BMH during the *cis*-to-*trans* photoisomerization are shown in Figure 8. For comparison, the results of orbital energies and LUMO-HOMO energy gap before the excitation are also displayed in this figure. As we can see, after the excitation at 0 fs, only HOMO and LUMO energies are strongly affected by the nuclear motion. The LUMO-HOMO energy gap decreases from 2.7 eV to about 0.5 eV in 2000 fs, increases to about 2.0 eV at about 2500 fs, and decreases again to the minimum value of 0.119 eV in this simulation at 3543 fs. After 3600 fs, the LUMO-HOMO energy gap increases to about

FIGURE 9: (a) Electron occupancies in BMH from HOMO - 1 to LUMO + 1 for the *cis*-to-*trans* isomerization. (b) Details of Figure 9(a) from 3530 to 3560 fs.

FIGURE 10: Geometry of BMH at 3543 fs in our *cis*-to-*trans* isomerization simulation, which is near a S_1/S_0 conical intersection. Bond lengths are in angstroms, and bond angles and dihedral angles are in degrees.

2.7 eV and vibrates around this value until the end of this simulation.

Variations of electron occupancies in the orbitals from HOMO - 1 to LUMO + 1 during the *cis*-to-*trans* photoisomerization are displayed in Figure 9. Details of the electron occupancies between 3530 and 3560 fs are also shown in this figure. As we can see, after the excitation at 0 fs, BMH stays in the first excited state until the deexcitation occurring at 3543 fs, which is corresponding to an avoided crossing near the S_1/S_0 conical intersection, as shown in Figure 8.

The geometry of BMH at 3543 fs is displayed in Figure 10. At this point, C1C2C3C6 dihedral angle is equal to 92.5°, near the midpoint of the rotation. Bond length C2=C3 is equal to 1.47 Å, much longer than the ordinary C=C bond length. Other geometrical values, such as bond lengths and bond angles, are also presented in this figure.

Variations of geometry during the *cis*-to-*trans* photoisomerization of BMH are presented in Figures 11–14. Time dependence of three dihedral angles in BMH, C1C2C3C6, C3C2C1C5, and C1C2H12C3, is shown in Figure 11. As shown in this figure, after the excitation at 0 fs, dihedral angle C1C2C3C6 increases from 180° to about 240° in 900 fs, stays around 240° between 900 fs and 2100 fs and then changes the rotation direction, and decreases dramatically from 240° to 0°. When BMH arrives at an avoided crossing near the S_1/S_0 conical intersection at 3543 fs, the value of C1C2C3C6

reaches 92.5°, as shown in Figure 10. C1C2C3C6 arrives at 0° (the optimized C1C2C3C6 value in *trans*-BMH) at 3623 fs and then vibrates around this new value until the end of our simulation. This new C1C2C3C6 value (0°) can be a demonstration that the molecule arrives at its *trans* geometry in about 3623 fs. Atomic distance between H20 and N21 presented in Figure 14(c) can be another confirmation for the final *trans* geometry, which does not vary evidently before 3000 fs but increases continuously from about 2.2 Å to 4.4 Å (the optimized distance between H20 and N21 in *trans*-BMH) in subsequent 600 fs and then vibrates around this value until the end of our simulation. As can be seen in Figure 11(b), dihedral angle C3C2C1C5 stays around 180° before BMH returns to its ground state at 3545 fs. But due to the energy redistribution among the molecule after deexcitation, BMH starts and keeps on rotating around C1–C2 bond until the end of our simulation. Similar results have been found in photoisomerization of stilbene and azobenzene [14, 40]. C1C2H12C3 also does not vary evidently during the whole simulation and keeps on vibrating around 180°, which can demonstrate that H12 atom stays nearly in a plane with atoms C1, C2, and C3 all the time.

Time variations of three bond angles, C1C2C3, C2C1C5, and C2C3N21, are shown in Figure 12. As we can see, C1C2C3 keeps on vibrating around 125° during the whole simulation, while C2C1C5 stays around 120°. For C2C3N21, it vibrates

FIGURE 11: Time dependence in BMH of (a) C1C2C3C6 dihedral angle, (b) C3C2C1C5 dihedral angle, and (c) C1C2H12C3 dihedral angle for the *cis*-to-*trans* isomerization. All labels are defined in Figure 1.

FIGURE 12: Time dependence in BMH of three bond angles (a) C1C2C3, (b) C2C1C5, and (c) C2C3N21 for the *cis*-to-*trans* isomerization. All labels are defined in Figure 1.

around 128° before the excitation at 0 fs and decreases slowly to about 119° (the optimized value of C2C3N21 in *trans*-BMH) when deexcitation occurs at 3543 fs.

Figure 13 displays the time dependence of three bond lengths in BMH. After the excitation at 0 fs, C2=C3 is

weakened, increasing from $1.35 \text{ \AA}$ to $1.46 \text{ \AA}$ and returning to $1.35 \text{ \AA}$ after the deexcitation at 3545 fs. Two other bonds shown in Figures 12(a) and 12(b), on the other hand, are shortened after the excitation at 0 fs. C1–C2 decreases from $1.46 \text{ \AA}$ to $1.40 \text{ \AA}$ after 0 fs and goes back to $1.46 \text{ \AA}$ after 3545 fs.

FIGURE 13: Time dependence in BMH of bond lengths (a) C2-C3, (b) C1-C2, and (c) C3-N21 for the *cis*-to-*trans* isomerization. All labels are defined in Figure 1.

FIGURE 14: Time dependence in BMH of (a) bond length C3-C6, (b) bond length C1-C4, and (c) atomic distance H20-N21 for the *cis*-to-*trans* isomerization. All labels are defined in Figure 1.

C3-N21 decreases from 1.43 Å to 1.38 Å after the excitation and returns to its initial value after the deexcitation. Bond lengths C1-C4 and C3-C6, as shown in Figure 14, are also affected by the excitation and deexcitation. C1-C4 increases

from 1.41 Å to 1.45 Å after 0 fs and returns to its initial value after deexcitation. Bond length of C3-C6 decreases from 1.46 Å to 1.43 Å after the excitation and then returns to its initial value 1.46 Å after the deexcitation at 3545 fs.

4. Conclusions

With density-functional-based nonadiabatic molecular dynamics simulations, *trans*-to-*cis* and *cis*-to-*trans* photoisomerizations of a green fluorescent protein chromophore based molecule 4-benzylidene-2-methyloxazol-5(4H)-one (BMH) induced by the excitation to its S_1 excited state were performed. We find a quantum yield of 32% for the *trans*-to-*cis* photoisomerization of BMH and a quantum yield of 33% for its *cis*-to-*trans* photoisomerization. In those simulations that did produce *trans*-to-*cis* isomerization, the range of calculated S_1 lifetimes was 700–4000 fs, with a mean value of 1450 fs. For the finished *cis*-to-*trans* isomerization, the range of calculated S_1 lifetimes was 1200–7000 fs, with a mean value of 3100 fs. The S_1 lifetime of *cis*-BMH is much larger than that of *trans*-BMH, agreeing well with the experimental result [27].

For the simulation shown in detail, lifetimes of the *trans*-BMH and *cis*-BMH are 1740 fs and 3545 fs, respectively. The whole *trans*-to-*cis* isomerization is finished in about 2040 fs, while whole time needed for *cis*-to-*trans* isomerization is about 3623 fs. For both photoisomerizations, rotation around the central C2=C3 bond is the dominant reaction mechanism; deexcitation occurs at an avoided crossing near the S_1/S_0 conical intersection, which is near the midpoint of the rotation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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