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Letter

Unlocking the Double Bond in Protonated Schiff Bases by Coherent Superposition of S_1 and S_2

Massimo Olivucci,* Thierry Tran,* Graham A. Worth,* and Michael A. Robb*

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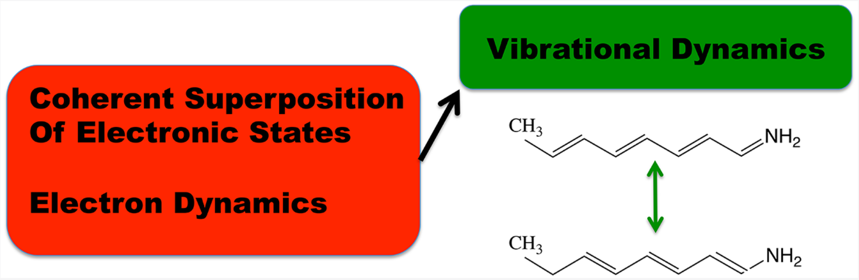

ABSTRACT: The primary event occurring during the E-to-Z photoisomerization reaction of retinal protonated Schiff base (rPSB) is single-to-double bond inversion. In this work we examine the nuclear dynamics that occurs when the initial excited state is a superposition of the S_1 and S_2 electronic excited states that might be created in a laser experiment. The nuclear dynamics is dominated by double bond inversion that is parallel to the derivative coupling vector of S_1 and S_2. Thus, the molecule behaves as if it were at a conical intersection even if the states are nondegenerate.

The "unlocking" of a double bond represents the truly primary event occurring during an E-to-Z double-bond photoisomerization reaction. Such an event has been widely investigated in photobiological C=C isomerizations employing both spectroscopic and computational methods. Past studies on the retinal protonated Schiff base chromophore (rPSB) of rhodopsin proteins show that the mechanism of the unlocking event remains substantially unchanged when investigated using minimal gas-phase models or in complex QM/MM models of the entire protein,[1] making rPSB an excellent target for fundamental studies.

As illustrated in Figure 1, according to the usual Born–Oppenheimer (BO) approximation picture, the C=C unlocking mechanism of rPSB starts at the Franck–Condon (FC) point on the first singly excited state (S_1) of the molecule. Because S_1 is a charge-transfer state relative to the ground state (S_0), the C=C bond is instantaneously *electronically* unlocked via photon absorption. The subsequent nuclear relaxation then leads in a ca. 20 fs time scale to an inversion of the single and double bond length alternation (BLA) along the conjugated chain to produce an *electronically and geometrically unlocked* C–C bond. This mechanism is supported by the comparison between the CASSCF(6,6)/6-31g* optimized bond lengths computed for the S_0 and S_1 equilibrium structures of the chromophore given in the Supporting Information (Figure S1) where we provide the equilibrium parameters of the rPSB model of Figure 2A.

Recently, it has been reported that, in certain rhodopsins (Figure 2B), the initial nuclear motion effectively decreases the energy gap between the S_1 and a nearby S_2 state which has a nonreactive diradical ($2A_g$) character rather than a reactive charge transfer ($1B_u$) character and thus could, in principle, alter the unlocking event. Indeed, the S_2 equilibrium structure (Figure S1) of our rPSB model is consistent with a fully delocalized π-system featuring geometrically semiunlocked C=C bonds and therefore is different from the inverted BLA seen in the S_1 equilibrium geometry. Such a theoretical/computational observation[2,3] indicates that the mixing of the S_1 and S_2 states may play a role in controlling the dynamics and, possibly, efficiency of the subsequent progression along the twisting nuclear mode (α) describing the actual isomerization event. While this mixing hypothesis is still under scrutiny,[4,5,1] it suggests that the modulation of the rPSB electronic structure via a spectroscopically induced S_2/S_1 mixing could provide a novel tool for the control of an important photobiological reaction.

Consistent with Figure 1, we normally assume that, as for other elementary photochemical reactions, photoisomerizations occur via sequential nuclear propagations along one or more potential energy surfaces connected by conical intersections (CoIns).[6−12] This picture begins to change when one uses laser pulses (e.g., extreme ultraviolet (XUV)) to create the initial

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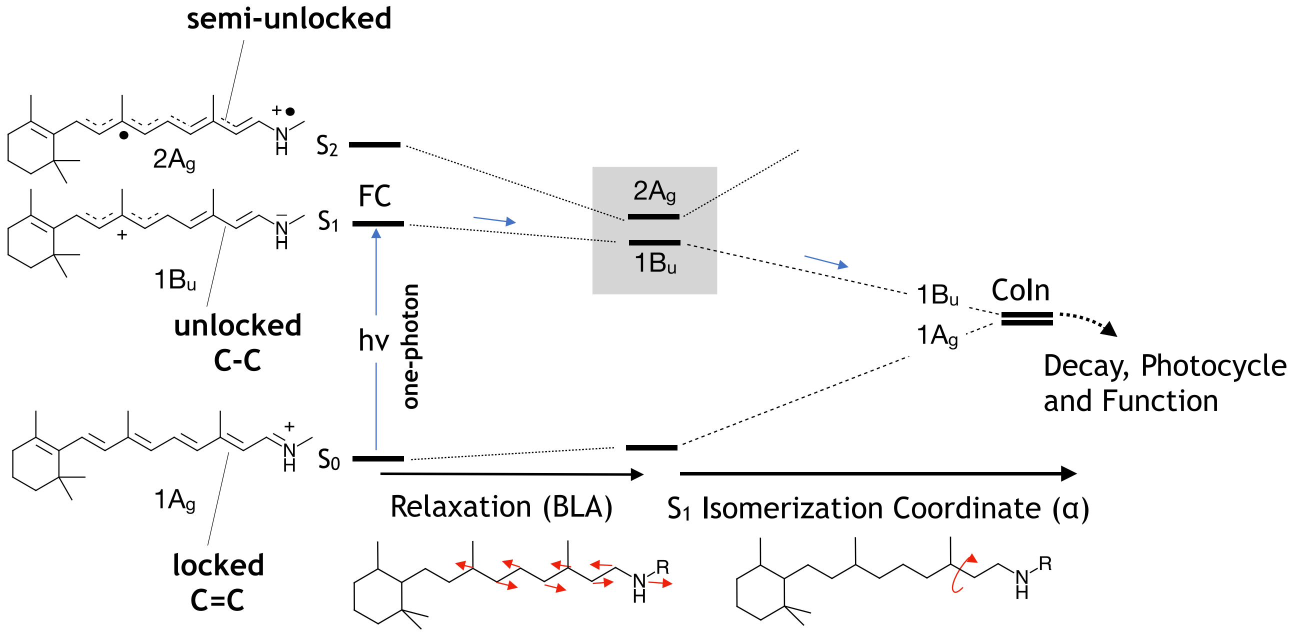

Figure 1. Schematic representation of the reaction coordinate for the rPSB photoisomerization. The Lewis formulas represent the electronic character of the ground state and first two singlet excited states. The conical intersection (CoIn) corresponds to a $1B_u/1A_g$ crossing delivering the chromophore to S_0. Notice during the initial BLA nuclear relaxation the $2A_g$ and $1B_u$ states transit in the vicinity of a $2A_g/1B_u$ CoIn, become nearly degenerate, and mix.

conditions in a reaction.[13−16] In this case, one excites a coupled manifold of electronic excited states, and the traditional idea of a potential energy surface is no longer valid. Rather the potential energy surface experienced by the nuclei is effectively time-dependent.[17] The resulting mechanism involves only the population of various electronic states and the amplitude of the various vibrational normal modes as a function of time. Furthermore, the electron and nuclear motion can occur asynchronously. (A theoretical study can be found in two recent papers[18,19] on the Benzene radical cation.)

The objective of both experimental and theoretical work is the electronic control of chemical reactivity. Thus, by creating a bespoke superposition of electronic states one may drive the reaction path by populating selected specific vibrational modes in a reaction coordinate. Experimentally, one may excite a superposition of states as the initial conditions,[13−16] or one may control reactivity by using a control pulse at a later time.[20] We will focus on the first aspect, and we shall demonstrate that by populating S_1 and S_2 differently at the FC point of rPSB one can modulate the mode corresponding to the initial, C=C unlocking part of the isomerization reaction (Figure 1) and therefore alter the BLA coordinate. To do so, we focus on the four-conjugated double bond model all-*trans* octa-3,5,7-trieniminium cation (Me-PSB4) displayed in Figure 2A.

Both the experiments and theoretical computations in this regime are challenging. The nonadiabatic dynamics computations to be discussed in this Letter were performed with the Quantum-Ehrenfest (Qu-Eh) method[22] which combines a CAS-CI formulation of the Ehrenfest method for the electronic motion,[23] implemented within a development version of Gaussian[24] and the Direct Dynamics variational Multi-Configuration Gaussian (DD-vMCG)[25] algorithm for nuclear dynamics as implemented in Quantics.[26,27] The initial electronic structure was chosen to be a coherent superposition of the S_1 and S_2 adiabatic states of the model rPSB, which was then propagated as a solution of the time-dependent Schroedinger equation in the Ehrenfest algorithm. The Ehrenfest propagation itself used a CAS(6,6)-CI in a 6-31G* basis. For the nuclear motion, we used 47 Gaussian wavepackets (gwp), which were chosen to span stretches, hydrogen-out-of-plane modes, bends, and torsions. Each initially unpopulated gwp is associated with an "excitation" of a normal mode from the ground-state wave function.

A feature of our implementation of the Ehrenfest method is that the full derivative coupling is included in the expression for the analytic gradient[23] so it should not be regarded as a mean field approach. The gradient (or force) that drives the nonadiabatic dynamics of a coherent superposition has 2 types of components: intrastate and interstate. The latter (off-diagonal gradients that arise from the mixing) are the derivative couplings and have the form $\langle \psi_I | \partial/\partial Q_i \hat{H}_e | \psi_{II} \rangle$ where the I and II are two adiabatic states and $\partial/\partial Q_i \hat{H}_e$ is the gradient operator for the *i*th normal mode. Thus, the dynamics that arises from the mixing of two states is very similar to the forces that act at a conical intersection where one force component is directed along the derivative coupling. Indeed, one may make a prediction about the course of the nuclear dynamics as a result of state mixing by computing the derivative coupling, as we shall presently show.

We now discuss the results obtained within the computational framework described above. More specifically, we present and compare the dynamics initiated at the FC point on either a pure S_1 state or a 50:50 superposition of the S_1 and S_2 states. We also have the results relative to a 75:25 superposition of S_1 and S_2. However, these lie nicely between the first two results; therefore, they are not discussed here but reported in the Supporting Information (Figure S3). We have used a sudden approximation to start our dynamics. Thus, we have ignored the rise and fall in the populations that would be included in a laser experiment. The nuclear motion problem needs the S_0 normal modes to define the initial conditions. These were computed at the DFT level of theory using a B3LYP optimized geometry in a 6-31G* basis. Finally, such computations are demanding in terms of

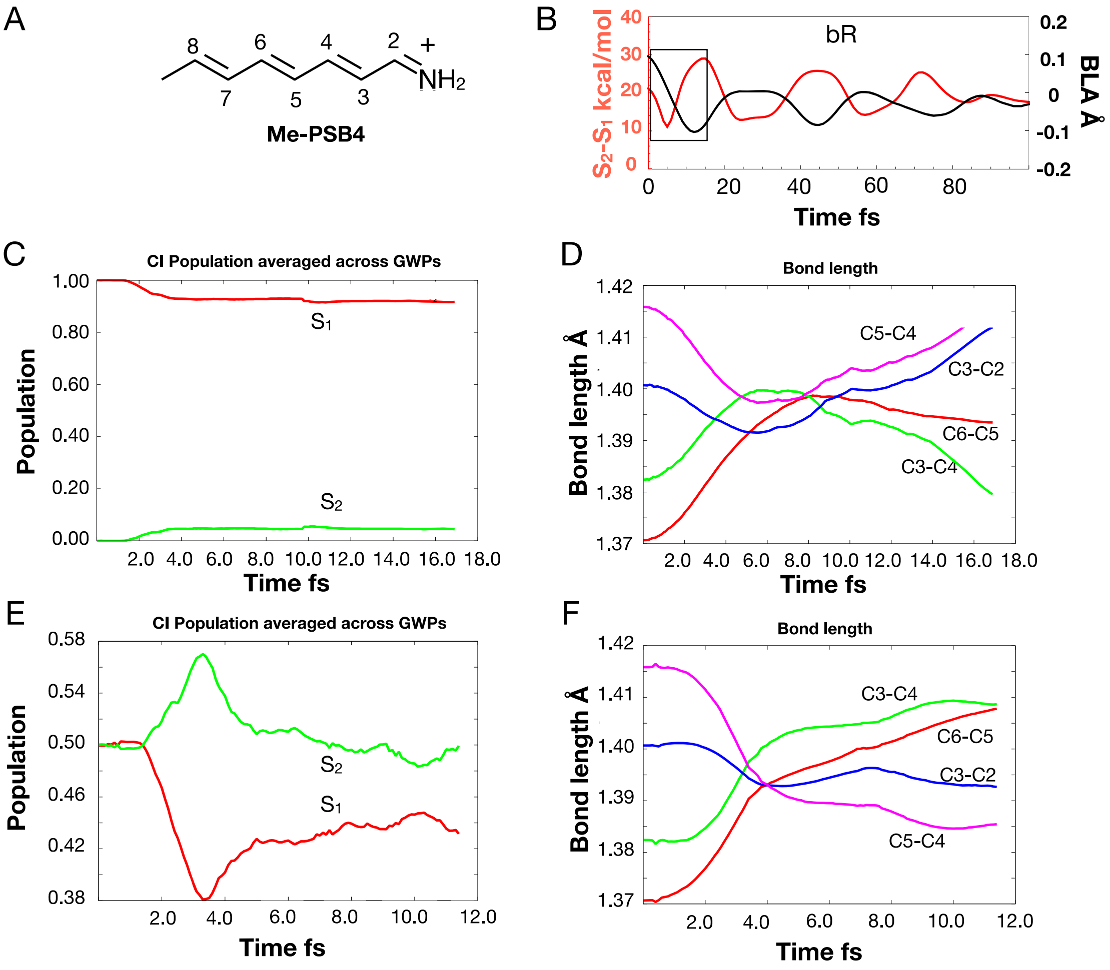

Figure 2. Relaxation dynamics. (A) The model chromophore structure adopted in the present work. (B) The semiclassical dynamics reported[2] for light-driven proton-pump bacteriorhodopsin (bR) showing oscillations in both the S_2−S_1 energy gap (red line) and BLA progression (black line). The first 15 fs related to the simulation reported in the present Letter and corresponding to the first single BLA period are framed. (C) Time-dependent adiabatic state population calculated with a Qu-Eh simulation started at FC point on S_1 (of course the chemical interpretation changes with time). The adiabatic state occupancy is averaged over 47 gwp (using gross populations).[21] (D) The corresponding relevant averaged single and double C−C bond lengths. (E) As for panel B but using 50:50 superpostion of S_1 and S_2 F. The corresponding progression of single and double C−C bond lengths. Note that the simulation time in panel F is slightly shorter than that in panel D.

computer time. Each step in the propagation of the 47 gwp needs 47 different CASSCF, gradient, and Hessian computations. We used a time-step of 0.1 fs. However, because our objective is to show where the initial vibrational energy is deposited during the first 10−20 fs, a short simulation is adequate.

The results of a simulation started on S_1 and presented in Figure 2C show the population of S_1 and S_2 as a function of time. Even starting on a pure adiabatic state one can see some population of S_2 after a few femtoseconds pointing to non-negligible nonadiabatic coupling between the two states. After a few femtoseconds, one can begin to observe the single−double bond inversion (Figure 2D) typical of a BLA mode that completes a full oscillation in about ca. 15 fs. Remarkably, such a result is consistent with the BLA progression obtained from quantum−classical trajectory calculation (Figure 2B) performed using a full QM/MM model of bR, a result found to be consistent with the spectroscopic observations.[2,3]

In Figure 2E we show the effect of mixing S_1 and S_2 in equal amounts. One can observe that the S_2 population rapidly increases and then persists on an S_1/S_2 mixture with a dominant S_2 component. In Figure 2F we can see that the bond-order inversion increases, similar to what is seen in Figure 2D, but then persists for the entire simulation time featuring elongated, and thus geometrically unlocked, double bonds. These bond lengths do not appear to be related to either pure S_2 or S_1 states but indicate a different regime and, more specifically, a reduction of the S_1 restraining force causing the oscillatory motion seen in Figure 2D and a far from harmonic behavior. Of course, because of the time constraint of such calculations, here we are looking at only the initial stage of the reaction.

We hypothesize that the behavior described above is connected with a time-dependent progression of the electronic structure. It is apparent from the comparison of of panels D and F of Figure 2 that the coherent superposition of S_1 and S_2 creates, similar to the evolution starting on S_1, nuclear motion corresponding to bond-order inversion within 4 fs. However, such a superposition is then conserved during the rest of the simulation, causing a deviation from the S_1 motion.

In Figure S2 of the Supporting Information we display the S_2/S_1 derivative coupling vector $\langle\psi_{\mathrm{I}}|\partial/\partial Q_i\hat{H}_e|\psi_{\mathrm{II}}\rangle$ computed at the FC point and compare it with the gradient of the 50:50 S_1/S_2 superposition. Both vectors are dominated by a type of bond-order inversion coordinate. Therefore, the coherent superposition of S_1 and S_2 at the FC geometry stimulates a nuclear motion in a direction different from the BLA direction seen when only S_1 is dominating the molecule electronic structure. This is expected because theory suggests that one component of the initial gradient should contain the derivative coupling. Thus, the nuclear dynamics that results from a coherent superposition of S_1 and S_2 has some similarities to the dynamics that occurs at an S_2/S_1 CoIn (see Figure S1 for the main geometrical parameters of such intersection), even though the two states are nondegenerate.

It is concluded that attochemistry[16] generated by laser science (which has been mainly applied to charged species) might provide a method in the future for controlling PSB isomerization. The nuclear dynamics that occurs when the initial excited state is a superposition of the S_1 and S_2 electronic excited states of a PSB model is similar to that which occurs at a conical intersection. Thus, it is evident that the electronic state mixing creates conical intersection (CI-like) conditions have a large impact on the bond-length-alternation coordinate motion, but the exact mechanism would need to be clarified by further investigations. Furthermore, while our short simulations cannot tell us how long the electronic coherence would last, the electronic coherence creates a vibrational coherence that can control the reactivity. Finally, we should mention that recent theoretical work[28] has shown that state mixing, similar to that used in this study, but near a conical intersection can be achieved with control options that rely on the carrier envelope phase of a few-cycle IR pulse.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c01379.

> Computed bond lengths (Figure S1), the initial gradient for S_1/S_2 mixing compared with the derivative coupling vector at the FC point (Figure S2), and as for Figure 2 but for 75:25 S_1/S_2 mixing (Figure S3) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Massimo Olivucci − *Chemistry Deparment, University of Siena, 53100 Siena, Italy; Chemistry Department, Bowling Green State University, Bowling Green, Ohio 43403, United States;* orcid.org/0000-0002-8247-209X; Email: massimo.olivucci@unisi.it

Thierry Tran − *Department of Chemistry, University College London, WC1H 0AJ London, United Kingdom; Department of Chemistry, Molecular Sciences Research Hub, Imperial College, London SW7 2AZ, United Kingdom;* orcid.org/0000-0002-0722-0159; Email: thierry.tran.18@ucl.ac.u

Graham A. Worth − *Department of Chemistry, University College London, WC1H 0AJ London, United Kingdom;* orcid.org/0000-0002-2044-4499; Email: g.a.worth@ucl.ac.uk

Michael A. Robb − *Department of Chemistry, Molecular Sciences Research Hub, Imperial College, London SW7 2AZ, United Kingdom;* orcid.org/0000-0003-0478-8301; Email: mike.robb@imperial.ac.uk

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.1c01379

Notes

The authors declare no competing financial interest.

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