Ab Initio Photoisomerization Dynamics of a Simple Retinal Chromophore Model

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The photoisomerization of the 11-*cis*-retinal-protonated Schiff base PSB11 (the chromophore of rhodopsin) to its *all-trans* isomer (PSBT) is the primary event of vision.[1] Recent experimental investigation of the dynamics of native[2,3] and 11-*cis*-locked[3] PSB11 in rhodopsin suggests that relaxation from the Franck−Condon (FC) region leads to a transient "fluorescent state" with a lifetime of 50−60 fs followed by the cis → trans motion leading to the formation of ground-state PSBT within 200 fs.[4] Similar behavior has been observed for bacteriorhodopsin[5] and for PSB11, PSB9, and PSBT in solution.[6,7]
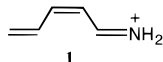
A recent theoretical study has elucidated the detailed topology of the S_1 excited-state potential energy surface of a simple retinal PSB11 model **1** (2-*cis*-$C_5H_6NH_2^+$)[7] in isolated conditions and in the absence of a counterion. While computations on **1** cannot yield a realistic description for the dynamics of retinal PSB11 in the protein or in solution, they do suggest a *model* that may be used to interpret the observed *initial* PSB11 dynamics. The potential energy surface of **1** is illustrated schematically (Figure 1a) in the space of C−C, C=C, and C=N skeletal deformations as well the torsion. A minimum energy path (MEP) computation (dashed line) follows the skeletal deformation coordinate to a flat region where an untwisted transient species may exist for a non-negligible time. Formation of the ground-state trans photoproduct occurs via decay at a crossing (conical intersection) along an orthogonal twisting coordinate.
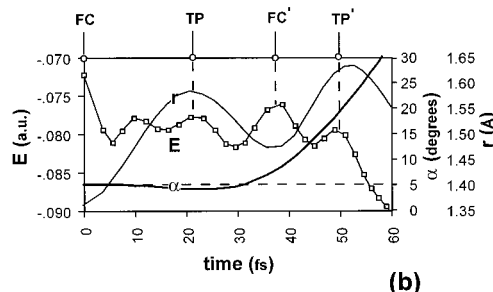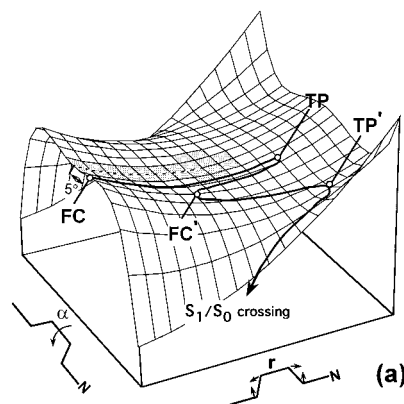

Figure 1. (a) Schematic structure of the S_1 energy surface of compound **1**. The dashed line represents the relaxation path from the **FC** point. The full line represents the semiclassical trajectory documented in Fig. 1b. (b) Potential energy (**E**, with −248 au offset), central C=C twist (α) and central C=C length (**r**) along the initial part of the photoisomerization trajectory discussed in the text.

In this paper, we report *ab initio* "on the fly"[8] semiclassical[9] trajectory calculations, *in the full space of coordinates*, with surface hopping[10,11] (using CASSCF[12] gradients and nonadiabatic coupling matrix elements in a π active space of 6 electrons in 6 orbitals and the 6-31G* basis set) on **1**. These simulations show that for this PSB, S_1 skeletal oscillations can last for a few oscillations (several tens of femtoseconds) before torsional motion is initiated (see Figure 1). While "on the fly" dynamics with coupled surfaces have been reported previously[13] for triatomics, our work provides the first ab initio semiclassical trajectories driven by a CASSCF 3N−6 dimensional force field for a PSB.

Because of the cost of running CASSCF trajectories, it is possible to sample only a very limited region of phase space;

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thus, we have computed (1) a *reference* S_1 *trajectory* (from the planar FC structure) in the space of in-plane skeletal vibrations and (2) a few trajectories with different initial amplitudes in the torsional coordinate. The *reference* trajectory corresponds to idealized initial conditions where all of the ZPE is removed and where the initial acceleration out of the FC region is determined by the initial gradient. The S_1/S_0 crossing can only be reached by redistribution of the energy to nontotally symmetric coordinates (i.e., torsion). Thus, to simulate intramolecular vibrational energy redistribution (IVR) into the torsional mode, three trajectories were run with a realistic initial amplitude[14] in the torsional coordinate of 5, 10, and 20°. The results for an initial twist of 5° are shown in Figure 1. (See Figures 3 and 4 in the Supporting Information for the remaining data). The system relaxes from FC along a "totally symmetric" valley and performs one complete oscillation (from FC to FC′) before significant twisting motion begins (see Figure 1b). During the oscillatory motion, the system samples regions of the S_1 surface where the length of the central double bond is large and the curvature along the torsional coordinate is negative (near point TP). Near this point, the system gains momentum along the cis $\rightarrow$ trans torsional coordinate. By the time the second turning point (TP′) is reached (ca. 50 fs after "excitation") the system has fully abandoned the skeletal vibration region and started to relax toward the S_1/S_0 crossing. In Figure 2, we show a full trajectory (with in initial 10° twist). The crossing is reached after ca. 60 fs (the surface hop itself is essentially diabatic), and the trans photoproduct well is entered on a 90 fs time scale. Trajectories with initial twists of 5, 10, and 20° (Figure 3 in Supporting Information) all show the same qualitative behavior but live for increasingly shorter times in the skeletal vibration region. In particular with an initial twist of 20°, only half an oscillation (i.e., from FC to TP) is accomplished before the cis $\rightarrow$ trans torsional motion takes over. The S_1/S_0 transitions take place (Table 1 in the Supporting Information) over an energy range of ca. 6 kcal mol^{-1} on the conical intersection hyperline (some 15 kcal mol^{-1} above the minimum), but the gap is always less than 4 kcal mol^{-1}. In addition, the effect of substituting the α-hydrogen by an α-methyl group (3-*cis*-$C_5H_5(CH_3)NH_2^+$) has been investigated. Although the slope of the surface has changed, due to the increased inertia of the system, the overall effect is small (see Figure 4 in the Supporting Information).

In conclusion, we have established that the S_1 dynamics of **1** involves (i) large amplitude skeletal oscillations (including the

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(14) The twist increases the S_0 energy of the FC structure by 0.2, 0.8, and 3.4 kcal mol^{-1}, respectively.
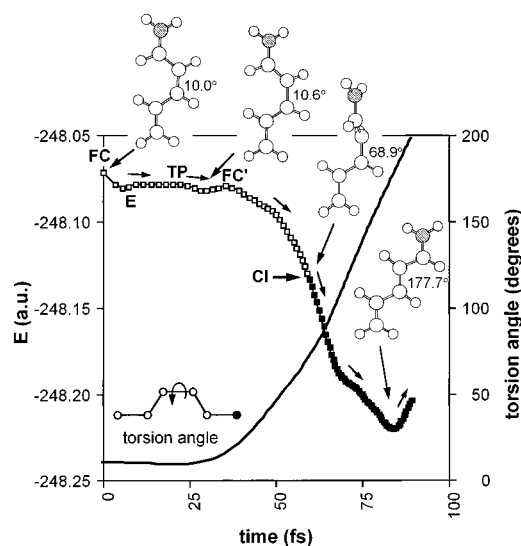

Figure 2. Full potential energy profile (**E**) along the photoisomerization trajectory discussed in the text (10 degree initial twist). Open squares for the S_1 and filled squares for the S_0 state. The structures (geometrical parameters in Å and degrees) document the geometrical progression along the trajectory as a function of time.

expansion of the central double bond) and (ii) efficient IVR to a torsional mode in the region near the oscillation turning point. Our results provide an estimate for the time scale for IVR from the initially populated stretching mode to the reactive torsional mode. Transient fluorescence is observed on a ultrafast 50 fs time scale, we estimate a similar time scale for IVR in **1**. Thus, our results suggest a model for the general structure of the energy surface in the FC region of PSB in general and the nature of the observed transient "fluorescent state". These results are consistent with the more realistic simulations carried out using a semiempirical surface by Warshel,[9b] who first suggested the existence of the surface crossing and skeletal vibrations (which were coupled to a frictional motion).

Supporting Information Available: Figures 3 and 4 and Table 1 (4 pages). See any current masthead page for ordering and Internet access instructions.

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