Communication

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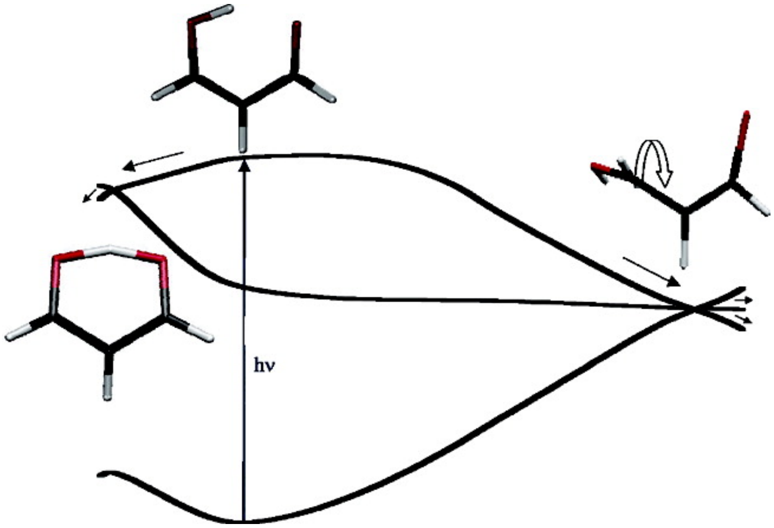

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Competitive Decay at Two- and Three-State Conical Intersections in Excited-State Intramolecular Proton Transfer

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Once thought highly anomalous, conical intersections (geometries where multiple electronic states are exactly degenerate) have come to assume a position of prominence in modern pictures of photochemistry.[1] Not surprisingly, the focus has been on intersections involving a simultaneous degeneracy of two electronic states. The same arguments which originally led workers to believe two-state intersections would be rare are all the more compelling in the case of three-state intersections (3SI). Nevertheless, a (symmetry-required) example[2] of a 3SI was described more than 20 years ago for CH_4^+. More recently, Yarkony and co-workers have found 3SIs at nonsymmetric geometries in ethyl,[3] allyl,[4] and pyrazolyl[5] radicals. For ethyl and allyl radicals, the triple degeneracy involves Rydberg excited states and can be understood chemically as arising from the zeroth-order three-fold degeneracy of the p-type Rydberg state. The pyrazolyl case is more surprising since the 3SI which was found involves the ground electronic state. In most cases, the 3SIs which have been located are in molecules with open-shell ground states. Furthermore, dynamics calculations have not been carried out, and the importance of these 3SIs in the photochemistry is uncertain. In this communication, we report on a 3SI involving S_0 in a molecule with a closed-shell ground state (malonaldehyde, denoted as MA in the following). This 3SI is the lowest-energy conical intersection on S_2 and thus could play a prominent role in the photochemistry. To investigate this, we carried out photodynamics calculations using the ab initio multiple spawning (AIMS) method,[6] as recently[7] combined with the MolPro electronic structure program.[8] These calculations reveal a competition between an S_2/S_1 minimal energy conical intersection (MECI) and the (energetically more favored) $S_2/S_1/S_0$ 3SI. This is the first report of photodynamics simulations involving a 3SI.

Molecules exhibiting excited-state intramolecular proton transfer (ESIPT) provide a framework for understanding the fundamental phenomenon of photoacidity. MA is the simplest molecule which undergoes ESIPT.[9] Femtosecond experiments on related ESIPT molecules such as methyl salicylate[10] (MS) and *o*-hydroxybenzaldehyde[11] (OHBA) have found that proton transfer takes place in less than 100 fs after photon absorption to the $\pi\pi^*$ state (S_2 in MA). We have carried out AIMS simulations of the photochemistry of MA after $\pi\pi^*$ excitation. In the AIMS method, the ground and excited potential energy surfaces (PESs) and nonadiabatic coupling matrix elements (NACMs) which promote electronic transitions are computed simultaneously with nuclear wave packet dynamics. The method is implemented in the full dimensionality of the molecule and describes bond rearrangement without special treatment. The nuclear wave function is described using Gaussian basis functions which evolve along classical trajectories. The number of nuclear basis functions increases with time (new basis functions are "spawned") and the basis functions are all coupled to each other through the nuclear Schrödinger equation. Thus, AIMS can describe intrinsically quantum mechanical effects such as the electronic state changes associated with the breakdown of the Born−Oppenheimer approximation near conical intersections. The electronic structure problem is solved using the complete active-space self-consistent field (CASSCF) method with four electrons in four state-averaged orbitals. The simulations shown involve more than 75 nuclear Gaussian basis functions over the course of 300 fs. Further simulation details can be found in Supporting Information.

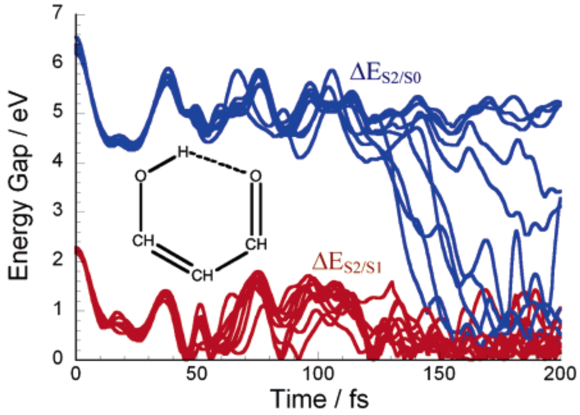

Figure 1. Time evolution of the S_2/S_0 (blue) and S_2/S_1 (red) potential energy gaps (evaluated at the centers of the trajectory basis functions) in MA after photoexcitation to S_2. An S_2/S_1 intersection is accessed after approximately 50 fs, and molecules begin to encounter an $S_0/S_1/S_2$ 3SI after approximately 150 fs. More than half of the population quenches to S_1 at the S_2/S_1 intersection even though this is higher in energy than the 3SI. MA is shown in the inset, with a dashed line indicating the H-bond.

In Figure 1 we show the traces of the S_2/S_1 and S_2/S_0 energy gaps along the centers of the initially populated nuclear basis functions. Two distinct regions of degeneracy are observed. At approximately 50 fs, an S_2/S_1 intersection is reached, and after 150 fs an $S_0/S_1/S_2$ 3SI is accessed. We characterized the two observed intersections using MolPro. The validity of the 3SI was confirmed by carrying out a search for an S_2/S_0 MECI with both larger active spaces and multireference single- and double-excitation configuration interaction (MRSDCI), as shown in Table S14. The S_2/S_1 2SI involves migration of the H atom from C−O to C═O (Table S9), while the $S_0/S_1/S_2$ 3SI is characterized by torsion about the C═C bond (Table S1).

The possibility of a 3SI in MA could be anticipated from well-known behavior of $n\pi^*$ and $\pi\pi^*$ states in α,β-unsaturated enones. The $n\pi^*$ state is insensitive to C═C torsion since it is primarily localized on the C═O bond, while the $\pi\pi^*$ state is strongly stabilized by this torsion and S_0 is of course destabilized. Thus, when the $n\pi^*$ state lies sufficiently below the $\pi\pi^*$ state in the Franck−Condon region, two of the five conditions for a 3SI will often be satisfied at a twisted geometry (Figure S12). This reasoning does not *guarantee* a 3SI since there are also three coupling matrix elements which must vanish, but it does argue that one should not

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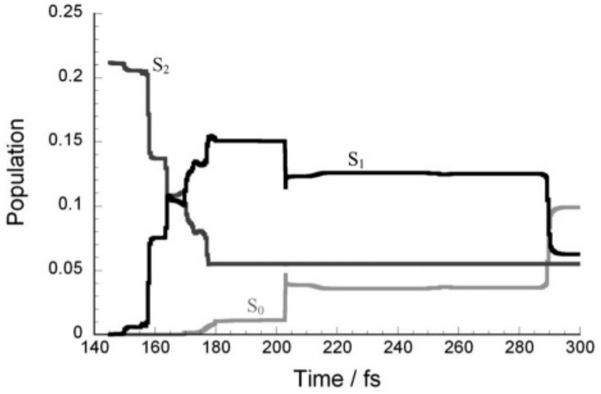

Figure 2. Population decay around the 3SI after $\pi \rightarrow \pi^*$ excitation in MA. Although this decay occurs in the neighborhood of a 3SI, there is a clear lag between population of S_1 and subsequent decay to S_0. Furthermore, a substantial fraction of the population which reaches the 3SI remains on S_1 during the time shown.

be too surprised to find 3SIs in molecules with conjugated C═O and C═C bonds. Recent work has found a 3SI in the DNA base cytosine, where similar considerations apply.[12]

In accord with experiments on closely related molecules such as OHBA and MS, significant proton transfer is observed within 100 fs. In MA, this is accompanied by decay from S_2 mediated by the H-migration 2SI (Figure S11). The nπ^* state in OHBA and MS lies very near or above the $\pi\pi^*$ state in the Franck−Condon region, and thus excited-state decay accompanying the proton transfer is neither expected nor observed in those molecules. In MA, more than 20% of the S_2 population survives to encounter the 3SI.

It is interesting to see an example of decay around a 3SI. In Figure 2, we show the evolution of the electronic population for the part of the wave packet which was not quenched at the 2SI. One might expect efficient quenching from S_2 to S_0 directly at the 3SI. While there may be some direct quenching at the earliest times, most of the population decay is *sequential*, with a clear lag between S_2/S_1 quenching and subsequent S_1/S_0 quenching. What is more, almost half of the population which is quenched to S_1 survives for almost 100 fs, suggesting that quenching at a 3SI is less efficient than previously believed. While the details of the PES around the 3SI are certainly important here, at least one general statement can be made. The increased dimensionality of the branching space at a 3SI—five-dimensional compared to two-dimensional for a 2SI—implies that molecules directed to the 3SI are much more likely to experience nonadiabatic transitions en route to the 3SI. Thus, there is a high likelihood of S_2/S_1 quenching while the S_2/S_0 energy gap is still large. Unless the population which appears on S_1 is also directed to the 3SI, it is likely to get trapped on the intermediate state. We present a cut of the branching space around the 3SI in Figure 3, which shows that population quenched to S_1 near the 3SI is indeed expected to be directed away from the 3SI. With respect to the coordinates shown, the "funnel" character of the 3SI applies *only* to S_2.

In the H-bonded cis isomer of MA, the 2SI is encountered before the 3SI. Excitation of out-of-plane bends that break the H-bond or direct excitation of the trans isomer should lead to increased decay through the 3SI, bypassing the 2SI. Femtosecond pump−probe experiments can verify this prediction.

In conclusion, we have found two MECIs involving S_2 in MA that are accessible after optical excitation. One involves proton transfer and two electronic states, while the other involves twisting about a C═C bond and simultaneous degeneracy of S_2, S_1, and S_0. These MECIs compete, and the one closest to the Franck−Condon region dominates the S_2 photodynamics. However, both are important. Quenching mediated by the 3SI is incomplete, i.e., only from S_2 to S_1, which may be a general phenomenon related to the large dimensionality of the branching space at a 3SI. Further studies concentrating on possible geometric phase effects specific to 3SIs, as discussed by Yarkony,[13] are planned.

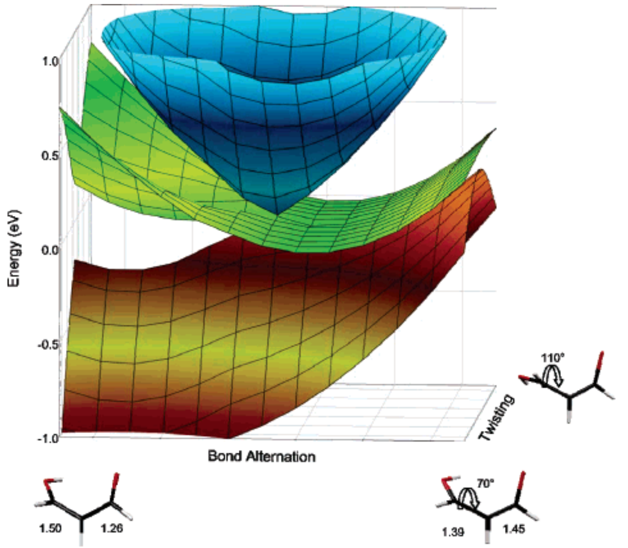

Figure 3. Potential energy surface topography in the neighborhood of the three-state conical intersection. The branching plane displacements correspond to bond alternation along the backbone and twisting about the C═C bond. Note that the full branching plane is five-dimensional, i.e., there are three other independent displacement directions which lift the triple degeneracy. Furthermore, there are directions which only partially lift the triple degeneracy, leaving a double degeneracy, as shown in Figure S10.

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Supporting Information Available: Simulation details; orbitals, geometries, CI vectors, and branching space for intersections discussed; and MRSDCI results. This material is available free of charge via the Internet at http://pubs.acs.org.

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