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Multiple pathways in the photodynamics of a polar π-bond: A case study of silaethylene

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Abstract

Surface-hopping dynamics carried out on-the-fly was performed by means of quantum chemical multireference configuration interaction methods in order to investigate the photodynamics of silaethylene ($SiCH_4$). The evolution of the S_0 and S_1 states were investigated during the first 100 fs after photoexcitation. In contrast to expectations based on previous static calculations, two mechanisms were found, corresponding to two minimum energy paths, which show characteristically different lifetimes. The bipyramidalization vs. torsion and stretching modes were identified to be responsible for this behavior driving the molecule into one of the two pathways.

1. Introduction

The dynamics of photoexcited π-bonds is a very interesting and important phenomenon. In this context ethylene has been studied extensively including detailed investigations of the characteristics of its energy surfaces and conical intersections [1–6] and of the dynamics on these surfaces [7–9]. As these investigations show, a complex combination of torsion, pyramidalization and hydrogen-transfer is required in order to reach the region of the intersection seam where rapid transfer to the electronic ground state can occur. The major reason for this complexity comes from the fact that on torsion alone (one of the primary motions in the initial stages of the dynamics) an intersection between the S_1 and S_0 states cannot be achieved. For instance, an energy difference of ~2.5 eV between these two states is found for the orthogonal structure. The width of this gap depends crucially on the electronegativity difference of the two π centers. This situation has been analyzed in detail in the 3 × 3 CI analytical model for biradicaloids developed by Bonačić-Koutecký et al. [1] and Bonačić-Koutecký and Michl [2]. Subsequent ab initio calculations carried out on the formiminium cation (CNH_4^+) [10–12], fluoroethylene [13] and silaethylene [14] confirmed this picture.

In contrast to ethylene, the photodynamics of the polar π systems has been treated to our knowledge so far only for the formiminium (CNH_4^+) [12] and for the pentadieniminium ($C_5NH_8^+$) [15] cations. After ππ* photoexcitation, the potential energy gradient for this kind of system points towards the torsional and stretching coordinates involving the bonding atoms. For this reason, the initial photophysical process is expected to be a coupled torsional and stretching motion occurring within the time-scale of a few tens of femtoseconds. Depending on the electronegativity difference along the π-bond (see above), the straightforward torsional motion towards 90° can drive the system to a region of crossing seam between the S_1 and S_0 states [1], through which it can perform radiationless decay to the ground state.

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Although the basic scenery of ultrafast torsional decay has been described by a single minimum energy path approach [16], the particular aspects of each system might lead to sometimes quite significant deviations from it. For ethylene [5], for example, the afore-mentioned rather large S_1/S_0 gap at 90° of ~2.5 eV involves additionally pyramidalization and hydrogen-migration motions [7,17]. The formiminium cation (CNH_4^+), if excited into the $\pi\pi^*$ (S_2) state, reaches the crossing seam in a completely different region, despite the presence of an energetically low-lying S_1/S_0 crossing at 90°, due to the large momentum along the CN stretch acquired in the S_2/S_1 transition [12].

Both examples show that ethylene and substituted ethylenes form a particularly good class of systems to investigate the photodynamics of an active π-bond. They are small enough to allow the use of a variety of high-level quantum chemical methods [12,17] and ab initio quantum [7,8,18] and semi-classical dynamics [12]. At the same time, it is possible to control their basic features of asymmetry and electronegativity difference along the π bond.

Silaethylene ($SiCH_4$), the subject of the present work, is a prime example for a polar π-bond. Under rigid torsion around the silicon–carbon bond, the potential energy curve of the $\pi\pi^*$ (S_1) state crosses the one for the ground state at 90° [14]. Moreover, there are no complicating factors, such as the additional $\sigma\pi^*$ state found in case of $CH_2NH_2^+$. Therefore, it could be expected that silaethylene acts as a simple model for the ultrafast torsional-decay scenery. However, as we shall see below, two factors make silaethylene deviate substantially from this model. The first factor is the very early activation of the wagging modes in the excited state. The second one is the in-phase coupling between the SiC stretching and torsional modes.

The aim of the present work is to investigate the photodynamics of a polar π-bond by using silaethylene as a specific example and to show the complexity of its motion by means of surface-hopping dynamics using multireference configuration interaction (MRCI) methods. We would like to stress that the availability of analytical gradients and nonadiabatic coupling vectors at the MRCI level within the Columbus program system has made this new approach feasible. In this way it is possible to apply the appropriate quantum chemical multireference method directly without any intervening fitting of energy surfaces for systems large enough to be of chemical relevance.

2. Computational details

State-averaged multiconfiguration self-consistent field (SA-MCSCF) and multireference configuration interaction with single and double excitation (MR-CISD) calculations were carried out for the ground and the S_1 state of silaethylene ($SiCH_4$). A CAS(2,2) complete active space was chosen and the three states calculated at the MCSCF level had equal weights. This active space was then used as a reference space for the MR-CISD calculations. The 1s core orbitals of silicon and carbon were kept frozen in the MR-CISD calculations. All virtual orbitals were included in the CI expansion. The 6-31G* basis set was used [19]. Energies, gradients and nonadiabatic coupling vectors [20–22] were calculated with the Columbus package [23–26]. The AO integrals and AO gradient integrals were taken from Dalton [27].

On-the-fly dynamics calculations were carried out using the just-described MR-CISD energies, gradients and nonadiabatic coupling vectors. We used the fewest-switch surface-hopping algorithm developed by Tully [28]. Details about the present implementation are given in [29,30]. For the integration of the Newtonian equations of motion the velocity-form of the Verlet algorithm was applied [31]. In order to reduce the computational costs, nonadiabatic coupling vectors were computed only when the energy gap between S_0 and S_1 dropped below 4 eV. This threshold was adopted after verifying in test calculations that there is no relevant variation in the state populations for larger energy gaps.

Initial conditions were sampled in order to reproduce the normal-mode quantum harmonic oscillator in its vibrational ground state [32]. At the SA-CASSCF level simulations with 75 trajectories and at the MR-CISD level with 100 trajectories were carried out. A period of 100 fs was chosen for each trajectory with a time step of 0.5 fs. The accuracy of the time integration has been checked by total energy conservation, which was achieved with an error smaller than 0.1 eV in all trajectories.

3. Results

3.1. Types of motion

In contrast to ethylene, the $\pi\pi^*$ state is the lowest vertically excited singlet state [14] in silaethylene. The lowest excited Rydberg state (π-3s) is located about 0.6 eV above the $\pi\pi^*$ state [14]. Geometric distortions are expected to destabilize the Rydberg states further in analogy to ethylene [17]. The potential energy scans, involving the torsional and pyramidalization coordinates in [14] as well as our present calculations, show that the S_2 state is much higher in energy and, therefore, was neglected in our calculations. Thus, only the ground and $\pi\pi^*$-states were considered in the dynamics.

It has been reported previously that rigid 90° torsion around the silicon carbon bond leads directly to a conical intersection between the S_0 and the S_1 states [14]. However, in the dynamics simulations it turned out that mainly two additional modes besides the torsion are of importance. These are the symmetric bipyramidalization and the C–Si stretch.

Within the first 20 fs of the dynamics, two major types of motion were observed: a strong symmetric bipyramidalization with relatively little torsion, which we henceforth denote as type B, and a strong torsion around the Si–C bond with just a small amount of pyramidalization which we denote as type T. These two types of initial motion have