

Non-adiabatic dynamic of atmospheric unimolecular photochemical reactions of 4,4-difluoro-crotonaldehyde using TD-DFT and TSH approaches

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Photochemical reactions of small molecules occur upon irradiation by ultraviolet or visible light, and they are a very important and controversial chemical process in the Earth's atmosphere because they impact our quality of life and health. Small-unsaturated carbonyl compounds play an important role in the chemistry of the polluted troposphere. The fluorinated aldehydes are very reactive under the sunlight driving to species that trigger more atmospheric reactions. This paper is focused on a theoretical study of the photochemistry of difluoro-crotonaldehyde using static and dynamic calculations by combination of Global Reaction Route mapping (GRRM) and Trajectory Surface Hopping (TSH) approach. The static analysis of the electronic and geometrical structures at the critical points allowed to rationalize the possible pathways that interconnect the stationary and crossing points in order to get a map of the unimolecular photochemical reactions which take place. The time evolution of the electronic states and the degrees of freedom enabled the identification of the requirements to follow the most probable deactivation pathways. This article reports the unimolecular deactivation pathways after the electronic excitation of the *trans* and *cis* isomers. In both cases, the excitation energies were calculated and compared with the analogous in the crotonaldehyde in order to elucidate the effect of fluorine atoms on the electronic structure and stabilities. After the initial excitations to the $\pi\pi^*$ excited states, the main deactivation channels follow non-adiabatic pathways via S_1/S_0 conical intersections. Ultrafast processes leading to the early activation of the S_1 govern the decay of the difluoro-crotonaldehyde. Depending on the nature of the S_1 state before the crossing with the S_0 , the system can follow several reaction pathways. The main photochemical processes observed were the *cis-trans* isomerization, the Norrish type I reaction (α -cleavage), Norrish type II reaction (γ -hydrogen abstraction) and fluorine photodissociation. The time scale, the molecular deformations and the electronic states implied for the different photochemical processes, as well as how these compete with the photophysical deactivation are discussed.

INTRODUCTION

Photochemical reactions of small molecules are initiated upon irradiation by ultraviolet or visible light and are considered as one of the most important chemical processes of the Earth's and other planets' atmosphere. Photochemical reactions involve the evolution of a molecule along its ground and excited-state potential energy surfaces (PESs). Small-unsaturated carbonyl compounds play an important role in the chemistry of the polluted troposphere. The most relevant unsaturated compounds of atmospheric interest are the $\alpha\beta$ -unsaturated carbonyl species such as acrolein (prop-2-en-1-al) and crotonaldehyde (but-2-en-1-al). Both of these compounds are released into the atmosphere through different sources such as combustion processes and chemical industries.¹ The hydrofluorocarbons (HFCs) are being highly used in industry as an alternative to the chlorofluorocarbon (CFCs), which are harmful to the ozone layer because of the generation of Chlorine atoms that act as catalyzer to degrade the O_3 .² The HFCs compounds can lead to fluorinated aldehydes³ that are very reactive under the sunlight and subsequently generate species that trigger more atmospheric reactions. The photochemistry of simple aldehydes in the gas phase has been widely studied at different excitation energies.^{4,5} Recently, photochemistry of fluorinated aldehydes has gained a lot of attention.⁶⁻⁹ It is well-established that the main degradation processes of carbonyl compounds in the gas phase are controlled by photolysis or reaction with OH or NO_3 radicals

and eventually with O_3 in the case of unsaturated compounds. Despite the fact that the photochemistry of crotonaldehyde has been previously studied,^{10,5} there are no reports about the unimolecular reactions of its fluorinated derivatives. Therefore, this work is focused on the theoretical understanding of the unimolecular elementary photochemical reactions of the *4,4-difluorobut-2-enal* (difluoro-crotonaldehyde).

One molecular system can evolve along a pathway on a single PES, a phenomenon known as adiabatic process, and can take place along well-defined ground or excited states PESs under the Born-Oppenheimer approximation. Typically, the adiabatic processes lead to chemical reactions via transition states (TSs). In many situations, however, the molecular system owns enough energy (usually by electronic excitation) to reach some regions of the nuclear configuration space where the energies of two electronic states are nearby to the degeneracy. The geometries where two electronic states with the same multiplicity are degenerated are known as Conical Intersections (CIs). At one CI, the set of molecular deformations that maintain the degeneracy form a $3N-8$ hyper-surface called intersection space (IS). The set of all the CIs between two electronic states from a *seam* whose minimum energy points are known as Minimum Energy Conical Intersections (MECIs). The branching space is the orthogonal complement of the IS and contains the remaining internal degrees of freedom (IDOF). It is composed by two coordinates that conduce to leave the degeneracy and form a plane called

the Branching Plane (BP). The coordinates forming the BP are the Gradient Difference Vector (GDV) and the Derivative Coupling Vector (DCV). Along the intersection space and surroundings, the Born-Oppenheimer approximation may often fail. As a consequence, it is possible that the adiabatic PES driving the time evolution of the system branches and the nuclear wavepacket is allowed to split among the manifold of states, leading to population transfer between different electronic states. This phenomenon is known as non-adiabatic process, and allows the radiationless decay of electronically excited molecular systems. Taking into account that the quantum wavepacket propagation is very time consuming, we treated the non-adiabatic dynamics at the semiclassical level via the Trajectory Surface Hopping (TSH) approach.^{11,12} The accurate modeling of the unimolecular processes is of great significance and requires kinetic data of all possible elementary reactions. Some quantum-chemical calculations,¹³⁻¹⁵ in combination with kinetic theories,¹⁶⁻¹⁷ have become a powerful tool for the prediction of atmospheric reaction rate constants that occur on the ground state PES.¹⁸ Nevertheless, making similar predictions for the photochemical reactions involving excited electronic state PESs is not simple for two main reasons. The first one being the accuracy and efficiency of quantum-chemical calculations on excited electronic states. The second reason is the difficulty to find all of the feasible reaction pathways for high-energy molecules that involve excited electronic states, as well as the ground state, using a conventional geometry optimization approach. In order to gain a complete theoretical understanding of the photochemical mechanisms it is necessary to determine all of the important non-adiabatic and adiabatic pathways available after the photo-excitation. Considering that this is not an easy task, we used the global reaction route mapping (GRRM) strategy, which is an efficient program that possesses a set of innovative computational methods that allow a theoretical exploration of ground and excited state PESs and their crossing *seams* in a systematic way.

COMPUTATIONAL DETAILS

We have studied the lower singlet states on the *cis* and *trans* isomers of *4,4-difluorobut-2-enal*, which is a derivative of crotonaldehyde where two hydrogen atoms on the sp^3 carbon have been replaced by fluorine atoms. All computational strategies used in this work are based on the Density Functional Theory energies using the d-polarized split-valence 6-31G(d)^{19,20} basis set for optimizations and the dunning type aug-cc-pVDZ²¹⁻²⁴ basis set for the excitation energies. To explore the PES of the singlet ground state (S_0), we used a fully automated strategy in GRRM (coupled to Gaussian 09²⁵) based on the Single Component (SC) version of the Artificial Force Induced Reaction (AFIR) approach.²⁶⁻²⁷ In SC-AFIR, an artificial potential is applied between all the pairs of atoms aimed to modify the shape of the PES in order to induce barrierless chemical reactions as shown in Figure 1. This

method generates AFIR paths along all induced reaction coordinates giving rise to approximated local minima and transition states. Then, the real stationary points were fully optimized automatically.

The strength of the artificial potential depends on one parameter γ , which can be seen as an approximate upper limit of the reaction barrier, and all of the reaction pathways that had barriers less than $\sim\gamma$ were explored. Thus, the reaction pathways explored in this study were depended on the parameter γ and the number of pairs of atoms that were artificially induced to trigger chemical reactions. In our calculations for the electronic ground state, we allowed that all possible combinations of pairs of atoms experienced an attractive and repulsive artificial force, obtained by using a $\gamma = 95.6 \text{ kcal}\cdot\text{mol}^{-1}$ ($400 \text{ kJ}\cdot\text{mol}^{-1}$). The energies for the minima located on the S_0 were calculated using the hybrid functional B3LYP. Once all the equilibrium geometries were automatically located on S_0 , they were classified in groups of conformers separated by twisting along single bonds. Then, the Boltzmann populations (p_i) of the conformers were calculated based on their relative energy E_i , according the Eq. 1. Where M is the number of conformers, R is the molar ideal gas constant approximately equal to $0.001987 \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and T is the room temperature (298 K).

$$p_i = \frac{e^{\frac{-\Delta E_i}{RT}}}{\sum_{j=1}^M e^{\frac{-\Delta E_j}{RT}}} \quad \text{Eq. 1}$$

All minima on the excited states PESs were calculated using the Time-Dependent (TD)-DFT method in combination with the same functional used to explore S_0 . All stationary points located on the excited states PESs were confirmed by frequency calculations.

As a first approximation, we combined the Seam Model Function (SMF) and SC-AFIR approaches to explore the S_3/S_2 and S_2/S_1 *seams*. The SMF approach consists in minimizing the function in Eq.2. The minima on this function are approximated Minimum Energy Crossing Points (MECP) of the adiabatic target states.

$$F^{\text{SMF}}(Q) = \frac{[E_1(Q) + E_2(Q)]}{2} + \frac{[E_1(Q) - E_2(Q)]^2}{\alpha} \quad \text{Eq. 2}$$

This function is composed by two terms that depend on the nuclear coordinates Q . The first term is the average of the energies $E_1(Q)$ and $E_2(Q)$ for the two target PESs and the second one is a penalty function for their energy gap. Tests have shown that the results are not very sensitive to the value of α , and it is usually set to a standard value of $\alpha = 7.17 \text{ kcal}\cdot\text{mol}^{-1}$ ($30 \text{ kJ}\cdot\text{mol}^{-1}$).²⁸ The minima found on $F^{\text{SMF}}(Q)$ were re-optimized to MECIs by the Gradient Projection (GP) method combined with the Branching Plane Updating (BPU)

approach.²⁹ In the GP method, a composed gradient is used in MECI optimization, where the composed gradient is generated by adding the GDV of the two target states multiplied by a certain factor to the mean energy gradient from which the projections of the branching plane (BP) are eliminated. The BP is a plane in which geometrical displacements lifts the degeneracy at conical intersections, and is formed by the GDV and DCV. In the BPU approach, the BP in the course of MECI optimization is obtained by systematically improving the initial crude BP using the GDVs computed in previous optimization steps; MECI optimization can be done without any DCV calculation.

The S_1/S_0 -MECIs were also optimized via the BPU approach. In this case, however, the energies were calculated using the Spin-Flip (SF)-TDDFT method,³⁰⁻³⁷ which expresses the excited states as linear combinations of all possible Slater determinants obtained by one-electron excitations accompanied with the α to β spin flip, using as reference state the triplet (T_1) calculated at the Kohn-Sham (KS)-DFT level. Unlike conventional TDDFT, in the SF-TDDFT approach, the configuration space contains the $H(\alpha)H(\beta)$, $L(\alpha)L(\beta)$, $H(\alpha)L(\beta)$ and $H(\beta)L(\alpha)$ Slater determinants, which are the same determinants in the space spanned by a CAS(2,2) where the HOMO (H) and LUMO (L) form the active space. It is considered to be the minimum active space to model a well-behaved S_1/S_0 -MECI. As consequence, by using T_1 as reference, the S_0 can be described in a multiconfigurational way. Therefore, SF-TDFT becomes a cheap way to get an approximated S_1/S_0 -MECIs. However, the description of the excited states characterized by excitations from the molecular orbitals (MO) lower than the HOMO, gives solutions with unphysical $\langle S^2 \rangle$ spin expectation values since some counterparts of their configuration state functions (CSF) are missing. In the practice, the calculations of low-lying states lead to spin contaminated states, so three types of spin states appear: singlet states with $\langle S^2 \rangle \approx 0.0$, triplet states with $\langle S^2 \rangle \approx 2.0$, and singlet/triplet mixed states with $\langle S^2 \rangle \approx 1.0$.

The nuclear ensemble approach³⁸ was used to simulate the absorption spectra of the *cis* and *trans* isomers. An ensemble of geometries around each Frank-Condon (FC) point was generated via a Wigner distribution³⁹ of non-coupled harmonic oscillators in Newton-X package.⁴⁰⁻⁴¹ The absorption spectra were simulated by calculating the cross-section $\sigma(E)$ as shown in Eq.3.

$$\sigma(E) = \frac{\pi e^2 \hbar}{2mc \epsilon_0 E} \sum_n \frac{1}{N_p} \sum_l^{N_p} \Delta E_{0,n}(R_l) f_{0n}(R_l) \times g[E - \Delta E_{0,n}(R_l)] \quad \text{Eq. 3}$$

- N_p is the number of geometries in the ensemble
- N_{fs} is the number of excited states calculated
- $\Delta E_{0,n}(R_l)$ is the vertical excitation for the S_n calculated at R_l geometry
- $f_{0n}(R_l)$ is the oscillator strength calculated for the S_n at R_l geometry
- g is a Lorentzian function centered at $\Delta E_{0,n}(R_l)$ with $\delta=0.05\text{eV}$
- E is the photon energy (consecutive E are separated 0.005eV)

Once all the critical points were located, non-adiabatic quantum dynamics based on the Trajectory Surface Hopping approach were performed. In this approximation, the wavepacket propagation along the time is approximated by a swarm of semiclassical trajectories evolving on the Born-Oppenheimer PESs of multiple electronic states. The statistical analysis over the ensemble of trajectories (in terms of fraction of trajectories in each electronic state in each time step) is expected to be an approximated representation of the wavepacket density distribution among the excited states as a function of time.⁴² The time-dependent wavepacket for each trajectory is expressed as Eq.4, where the $\Psi_J(r; R(t))$ are the electronic wavefunctions obtained in Gaussian 09, the expansion coefficients $c_J(t)$ depend on the coupling terms σ_{LM} for two given L and M electronic states; at the same time, σ_{LM} depends on the first order non-adiabatic coupling vector d_{LM} . Since the energies are based on DFT, there is no explicit d_{LM} . Therefore, at the time t , the σ_{LM} was approximated by using the wavefunction overlap at different time-steps⁴² as shown in Eq.5, whereas the $\Psi_L^{-i\dot{t}}$ and $\Psi_M^{-i\dot{t}}$ are the electronic wavefunctions at the time $t_{-i\dot{t}} = \left(t - \frac{\Delta t}{2}\right)\dot{t}$ for the states L and M , respectively. Besides, the $\Psi_L^{+i\dot{t}}$ and $\Psi_M^{+i\dot{t}}$ are the electronic wavefunctions at the time $t_{+i\dot{t}} = \left(t + \frac{\Delta t}{2}\right)\dot{t}$ for the same electronic states.

$$\phi(r, R, t) = \sum_J^{fs} c_J(t) \Psi_J(r; R(t)) \quad \text{Eq. 4}$$

$$\sigma_{LM} \approx \frac{1}{2\Delta t} \dot{t} \quad \text{Eq. 5}$$

The fewest switches approach allows each trajectory to jump to other states during the propagation in order to simulate the non-adiabatic processes (wavepacket density transfer between states)⁴³⁻⁴⁴.

The quantum non-adiabatic dynamics were simulated in Newton-X package, using the electronic energies obtained from Gaussian 09 at the TDDFT(B3LYP)/6-31G(d) level. We simulated 62 trajectories for each isomer (*trans* and *cis*). The maximum time (t_{max}) and the time steps (Δt) used were 300 and 0.5 fs, respectively. The trajectories where the $\Delta E(S_1-S_0)$ was less than 0.2 eV were considered as reaching the *seam* (S_1/S_0). The couplings terms related with the S_0 were not computed because they are not reliable near to the S_1/S_0 conical intersections at the TD-DFT level; a consequence of the multiconfigurational nature of the ground state near to the crossing *seam* and the inability to describe it at the TDDFT level.

RESULTS AND DISCUSSION

Exploring the ground state PES and the relationships with the excited states

The ground state PES was explored automatically at the B3LYP/6-31G(d) level, using the SC-AFIR ($\gamma = 400 \text{ kJ mol}^{-1}$) in GRRM code coupled to Gaussian 09. There were automatically located 105 ground state minima and 125 transition states. The relevant structures for the pathways studied in this article are schematized in Figure 2.

The lower energy species on the ground states are the *keto* and *enol* forms, where each form has the *cis* and *trans* isomers with respect to the CC-CC dihedral angle. The lowest energy *keto-cis* isomer was used as a reference because of its richer reactivity and this isomer was labeled as **A**. This isomer is characterized by a molecular geometry belonging to the C_s symmetry point group, and an intramolecular hydrogen bond which makes **A** more stable than the surrounding *keto-cis* isomers labeled as **F**, **G**, **H** and **I**, which are connected adiabatically to **A** by following the twisting coordinates along the CC-CO and CC-CF dihedral angles. This set of *keto-cis* isomers form the **Zone 1** of the nuclear configuration space (Figure 2). The Boltzmann population of the isomers **A**, **F** and **I**, in terms of percentage ($\%p_i$), are equal to 53, 22 y 19%, respectively. According these results, **A** is the predominant isomer in this region at room temperature due to its thermodynamic stability. As expected, similar situation characterizes **Zone 2**, which contains the equilibrium geometries for the *keto-trans* isomers labeled as **B**, **C**, **D** and **E**, which have similar stabilities. The most populated isomers are the labeled as **E** and **D**, whose Boltzmann populations are equal to 0.502 ($\%p_E=50.2$) and 0.364 ($\%p_D=36.4$), respectively.

The reaction coordinate to transform one specie from **Zone 1** into **Zone 2** is the *cis-trans* isomerization, which entails twisting around the CC=CC double bond in the ground state. This pathway is unlikely to occurs on the S_0 , thus, we only studied this reaction along the excited states where the weakening of this double bond takes place. On the other hand, *keto-enolization* reaction conducting from **Zone 1** to **Zone 3** could take place from the isomer **A** since it has a suitable intramolecular hydrogen bond. This chemical reaction can only be triggered by **A**, which is the only one with the proper nuclear arrangement to allow the γ -hydrogen abstraction responsible for the *keto-enolization*. The **Zone 3** contains the **J**, **K**, **L** and **M** equilibrium geometries, which are the *enol-cis* and *enol-trans* isomers with the same conformation as the isomer **A** with respect to the CC-CO dihedral angle. The Boltzmann population of these isomers indicates that **L** and **M** are equally populated with a $\%p_i$ of 36.2, while the isomer **J** is 27.6, and **K** has a negligible population.

This work was focused in the non-adiabatic connections between the different zones of the nuclear configuration space. As such, only the photochemical mechanisms from the *keto-cis* and *keto-trans* isomers were examined. If the system

is irradiated when the molecular geometry is in the **Zone 1**, the excited *keto-cis* isomers **A***, **F*** or **I*** could be generated. Since **A** is the dominant isomer in **Zone 1**, in this paper, we report the mechanistic implications when **A** is irradiated to **A***. The largest oscillator strength is expected to belong to a $\pi\pi^*$ excited state while a significantly smaller value is expected for the $n\pi^*$ states. However, non-adiabatic processes along the *seam*($\pi\pi^*/n\pi^*$) could take place, leading to the population of the $n\pi^*$ states, or even other species which follow different deactivation pathways. If the $\pi\pi^*$ excited state of a $\alpha\beta$ -unsaturated carbonyl compound is populated for relatively long time, it typically follows a *cis-trans* isomerization as a deactivation pathway. The **E** isomer belong to the **Zone 2**, and it is the most stable minimum on the S_0 among those shown in Figure 2, thus, we chose the excited states of **E** (**E***) as starting point to study the photochemistry from **Zone 2**. The *cis-trans* isomerization reaction, photochemically connect **Zone 1** and **Zone 2** through an extended *seam*($\pi\pi^*/S_0$), and it usually does not imply rupture or formation of sigma bonds. In contrast, the $n\pi^*$ states are usually more likely to form or break sigma bonds, so they might lead to γ -hydrogen abstraction via the *seam*($n\pi^*/S_0$) or by α -cleavage the decay following dissociation channels. Both cases can be involved in the evolution of the excited states from **Zone 1**, but only α -cleavage from **Zone 2** because of the unsuitability of the γ -hydrogen atom for the migration. This denotes that **Zone 1** is connected to **Zone 2** and **3**, but **Zone 2** is only connected to **Zone 1**. Nevertheless, it is necessary to remark that all of them could be also connected with dissociation pathways triggered by different excited states such as the one described by excitations implying σ and σ^* molecular orbitals.

Exploring the ground state PES and the relationships with the excited states

The lower excited states on the **A** and **E** isomers are described mainly by single-excitations implying the MO shown in Figure 3. The excited singlet states with the largest oscillator strength have a $\pi\pi^*$ nature and they are responsible for the maximum absorption peak (205 and 220 nm for the **A** and **E**, respectively) in the simulated spectra in the gas phase (Figure 4). The excitation energies for the **A** and **E** were calculated and compared with the analogous in the crotonaldehyde (Table 1). It was observed that the fluorine atoms have a strong stabilization effect on the $\sigma\pi^*$ state. Consequently, the energy gap between the $\pi\pi^*$ and $\sigma\pi^*$ states, denoted as $\Delta E(\pi\pi^*-\sigma\pi^*)$, becomes smaller for the fluorinated compounds. This effect in the *cis-keto* is stronger than in the *trans-keto* isomer. While in the crotonaldehyde the $\Delta E(\pi\pi^*-\sigma\pi^*)$ is nearby 31 kcal·mol⁻¹ in both isomers, in the fluorinated analogous it becomes 4.2 kcal·mol⁻¹ and 6.6 kcal·mol⁻¹ for the *cis* and *keto* isomers, respectively. The lower $\Delta E(\pi\pi^*-\sigma\pi^*)$ in the fluorinated compound allows the population of the $\sigma\pi^*$ via internal conversion, which could increase the quantum yields of the photoproduct obtained by following the $\sigma\pi^*$ -mediated reaction pathways, leading to a different photochemistry than

the one for the crotonaldehyde. However, this phenomenon must be more important in the *cis-keto* isomer where the $\Delta E(\pi\pi^*-\sigma\pi^*)$ is smaller. In the next sections, the photochemistry of the *cis-keto* and *trans-keto* isomers using the TD-B3LYP/6-31G(d), the same level used to calculate the electronic energies during the dynamical calculations, will be studied.

Dynamics Calculations

All the TSH dynamic calculations were performed using a TD-DFT(B3LYP) electronic wavefunction. In principle, this methodology can adequately describe most of the processes of interest. The relaxation through the manifold of excited state depends on the intrinsic capabilities of the B3LYP functional and on the electronic nature of the excited states. If they are dominated by single excitations from a well-behaved ground state, no significant problems exist. Once reached the excited states minima, the oscillation around them can be well described because all minima were not on the top of a multiconfigurational ground state. Following these conditions, the relaxation until near to a *seam*(S_1/S_0) can be described. However, when the system evolves until reaching geometries very close to a *seam*(S_1/S_0) with energy gaps around 2.0 kcal·mol⁻¹, the Kohn-Sham equations usually fail, or in case they achieve convergence, negative excitation energies may be obtained. This problem can mainly arise when the $\pi\pi^*$ state goes to twisted geometries until reaching the *seam*($\pi\pi^*/S_0$). In order to avoid this kind of problem, we have adopted the strategy proposed by Barbatti and Crespo-Otero⁴⁵ that involves stopping the dynamic simulations as soon as a certain S_1/S_0 energy gap threshold is obtained. In this study, the S_1/S_0 energy gap threshold was set to 4.6 kcal·mol⁻¹ (0.2 eV).

In order to get information from the dynamic simulations, we have analyzed the evolution along the time of the degrees of freedom (DOF), the potential energies and the average adiabatic populations (χ). One indication about the quality of the TSH dynamics is obtained by comparison of the χ and the fraction of trajectories for each state; if they match very well is evidence of quality.⁴⁰

Photochemistry from the isomer A (*cis-keto*)

The initial relaxation direction (IRD), i.e., the direction of the force at the FC geometry, on the $\pi\pi^*$ state is shown in the top of Figure 5. The in-plane component leads to a saddle point on the S_2 , labeled as TS- $S_2(\pi\pi^*)$, belonging to C_s symmetry point group, whose imaginary frequency leads to twisted species where a local minima LM- $S_1(\pi\pi^*)$ is located. On the other hand, at the FC geometry, the $\sigma\pi^*$ and $n\pi^*$ states have IRDs following only in-plane coordinates towards planar local minima (LM) on the S_1 and S_2 , respectively (see the middle and bottom, respectively, of Figure 5). According our calculations, just after the initial excitation to the $S_3(\pi\pi^*)$ state, the *seam*(S_3/S_2) is reached. Consequently, the population of the S_3 drops to ~50% in just 7 fs at the same time that the population of the S_2 increases from 0 to ~50%. This ultrafast phenomenon takes place either by internal conversion from the $S_3(\pi\pi^*)$ to

other states on the S_2 , or by relaxation of the $\pi\pi^*$ state to the S_2 without population transfer to the other states. The fraction of trajectories and the average adiabatic populations (χ) for the S_1 , S_2 and S_3 are shown in Figure 6. The S_2 state (either $\pi\pi^*$ or $\sigma\pi^*$, or even another state) reaches its maximum population (83%) around 16 fs. The population of the S_2 is stable until ~85 fs, and then its population begins monotonously to decrease after being populated for a relatively long time. The S_2 is predominating until 155 fs where its population becomes equal to the one for the S_1 (47%). Given that the population to S_0 is not possible because the coupling terms including S_0 were not computed (they are not reliable at the TDDFT level), the S_1 predominates until t_{max} . Once the S_2 is populated, the pathway that the system will follow is defined. The dynamic study from the isomer A showed five different reaction pathways (Table 2), and the *cis-trans* isomerization has the largest yield.

Firsts events upon photoexcitation to $S_3(\pi\pi^*)$

The initial relaxation of the $S_3(\pi\pi^*)$ state implies a very large gradient along the CC-CC distance increasing and, the other main component is the torsion along the CC-CC dihedral angle. Given that the time scale for the bond stretching vibration is shorter than the one for the torsion (Figure 9), the weakening of the double bond takes place just before the system follows the torsion coordinate. The larger CC-CC distance allows that the $\pi\pi^*$ state becomes S_2 in non-twisted geometries. The increased amplitude of the CC-CC stretching vibration is compatible with the IRD for the $S_2(\sigma\pi^*)$, which has a minimum labeled as LM- $S_2(\sigma\pi^*)$. This is a very shallow stationary point, which can barrierlessly twist along the CC-CC dihedral angle (barrier of 0.5 kcal·mol⁻¹) forming an avoided crossing that connects adiabatically the $\sigma\pi^*$ and $\pi\pi^*$ states on S_2 . In Figure 7, the plots along the twisting coordinate from the TS- $S_2(\pi\pi^*)$ and the LM- $S_2(\sigma\pi^*)$ stationary points are shown. The adiabatic connections of the $\sigma\pi^*$ and $\pi\pi^*$ states (Figure 7b) is an avoided crossing on the S_2 generated by the *seam*($\pi\pi^*/\sigma\pi^*$) which was automatically explored in GRRM by using a combination of the SMF and SC-AFIR ($\gamma = 47.8$ kcal·mol⁻¹), followed by the tight optimization by the GP/BPU optimizer in GRRM. Three stationary points in the 25-dimensional intersection space of the $\pi\pi^*$ and $\sigma\pi^*$ states were located. There are two equivalent MECI($S_3-\pi\pi^*/S_2-\sigma\pi^*$) separated by that may be one transition state conical intersection (TSCI) as shown in Figure 8. These three conical intersections are very similar in energy and geometry. They form a very flat *seam*($\pi\pi^*/\sigma\pi^*$) along the CC-CH dihedral angle which is the main component of the coordinate connecting these three conical intersections. In Figure 8, the energies and geometries for the stationary points located along the *seam*($\pi\pi^*/\sigma\pi^*$) and one representation of the relationship of this *seam* with respect to the TS- $S_2(\pi\pi^*)$ and LM- $S_2(\sigma\pi^*)$ stationary points are shown. These findings show that $S_2(\sigma\pi^*)$ could be considerably populated in the firsts femtoseconds, before CC-CC torsion could take place. It would partially explain the ultrafast drop of population of S_3 just 7 fs after the initial excitation of $\pi\pi^*$ (blue line in Figure 6). This ultrafast internal conversion to the $\sigma\pi^*$

state is possible via extended $seam(\pi\pi^*/\sigma\pi^*)$. Nevertheless, taking into consideration the inertia acquired by the nuclei during the relaxation on the PES of the $\pi\pi^*$ state and the different electronic nature of the states, the fraction of the population remained on $\pi\pi^*$ state should be larger than the one transferred to the $\sigma\pi^*$ state. According our calculations, most of the population stay in the $\pi\pi^*$ and reach twisted geometries in around 100 fs (red bold line in Figure 9b), while smaller fraction of population on the $\sigma\pi^*$ follows a completely different reaction pathway where the torsion is not important (blue bold line in Figure 9b). A transient equilibrium between the $\pi\pi^*$ and $\sigma\pi^*$ states takes place in most of the trajectories that follow the *cis-trans* isomerization pathway. From 16 to 85 fs, forward and backward internal conversions ($\pi\pi^* \leftrightarrow \sigma\pi^*$) take place. This explains the stabilization of the population of the S_2 during this period of time. However, the exchange of population between the $\pi\pi^*$ and $\sigma\pi^*$ states is not only limited to the S_2 , but the $S_2 \leftrightarrow S_3$ population transfer is possible as well (around 50 fs in Figure 10a). According the Figure 6 and Figure 10a, the transient equilibrium between the $S_2(\pi\pi^*)$ and $S_2(\sigma\pi^*)$ eventually decay to S_1 . Depending on the nature of S_2 involved in that decay, the system can evolve to different deactivation pathways to S_1 by different S_2/S_1 seams. All the MECI(S_2/S_1) were explored with the same methodology used for the MECI(S_3/S_2) in order to obtain information about the decay from the S_2 (either the $\pi\pi^*$ or $\sigma\pi^*$). Four MECI(S_2/S_1) belonging to different crossing seams were optimized (Figure 11). Since the relative energies of all of the located MECIs(S_2/S_1) are lower than the excitation energy, all of them are accessible during the non-adiabatic decay of the system towards the S_1 . However, the molecular deformations required to reach most of the MECIs(S_2/S_1) are very different with respect to the twisting coordinate that is the main relaxation motion (kinetic energy rich) from the initially populated $\pi\pi^*$ excited state. The MECIs(S_2/S_1) belonging to the ($\sigma\pi^*/n\pi^*$) and ($\pi\pi^*/n\pi^*$) seams (Figure 11a and 11b, respectively) are more relevant than the ($n\pi_2^*/n\pi^*$) and ($n\pi_2^*/\pi\pi_2^*$) (Figure 11c and 11d, respectively) regardless the relative energies, since only few trajectories followed a deactivation pathway through the ($n\pi_2^*/n\pi^*$) and ($n\pi_2^*/\pi\pi_2^*$) seams, since the MECI($S_2-n\pi_2^*/S_1-\pi\pi_2^*$) participates in the deactivation through *cis-trans* isomerization along the CC-CO dihedral angle. However, the most of trajectories did not pass through the ($n\pi_2^*/n\pi^*$) and ($n\pi_2^*/\pi\pi_2^*$) crossings, but, they could be involved in new deactivation channels which could be activated beyond the t_{max} (300 fs).

Deactivation of $\pi\pi^*$ state

The lowest energy MECI(S_2/S_1) is 97.3 kcal·mol⁻¹ and connects the $\pi\pi^*$ and $n\pi^*$ states via a twisted geometry where S_0 is only 15.3 kcal·mol⁻¹ below. After reaching one S_3/S_2 crossing point in the $seam(\pi\pi^*/\sigma\pi^*)$, the fractional population remaining in the $\pi\pi^*$ state follows a twisting coordinate until reaching one point of the $seam(\pi\pi^*/n\pi^*)$ whose MECI owns a CC-CC

dihedral angle equal to 96° (Figure 11b). The $seam(\pi\pi^*/n\pi^*)$ makes possible the population transfer to the $S_1(n\pi^*)$ since the $\pi\pi^*$ state owns a negative curvature along the CC-CC coordinate with a local minimum LM- $S_1(\pi\pi^*)$ around 82° (at SF-TDDFT(B3LYP-V1R)/6-31G(d) level) while the $n\pi^*$ state has a maximum along the same degree of freedom. The topography of the $\pi\pi^*$ potential energy surface suggests that as long as the fractional population remains on this state, it will evolve to the direction of twisted geometries where $n\pi^*$ and S_0 possesses a relatively small energy gap with respect to this state. As such, depending primarily on the amplitude of the motions of the remaining degrees of freedom, the LM- $S_1(\pi\pi^*)$ could be populated before reaching one point of the extended $seam(\pi\pi^*/S_0)$ as shown in Figure 12. According the dynamic calculations, once the system adopts twisted geometries, the $seam(S_1/S_0)$ is reached and the trajectories are ended after few femtoseconds (Figure 9b). The MECI($S_1-\pi\pi^*/S_0$) was located at 86.4 kcal·mol⁻¹ higher than the FC- S_0 (isomer A) at SF-TDDFT(B3LYP)/6-31G(d) level, and its CC-CC dihedral angle is 85°, only 3° more than LM- $S_1(\pi\pi^*)$. The geometry of the MECI($S_1-\pi\pi^*/S_0$) is very close to LM- $S_1(\pi\pi^*)$, and it is only 0.9 kcal·mol⁻¹ higher. Once any twisted point of the $seam(\pi\pi^*/S_0)$ is reached, the non-adiabatic decay to the ground state can be towards the *cis* (Zone 1 in Figure 2) or the *trans-keto* isomers (Zone 2 in Figure 2), but, due to the inertia of the nuclei along the twisting coordinate a larger quantum yield for the *trans* isomer is expected. The $seam(\pi\pi^*/S_0)$ can be accessed along several CC-CC dihedral angle values, however, the non-twisted conical intersection or TSCI($S_1-\pi\pi^*/S_0$) could not be located by GRRM, which implies that in the case that TSCI($S_1-\pi\pi^*/S_0$) exists, it is very energetic, much more than the excitation energy.

Deactivation of $\sigma\pi^*$ state

As shown in Table 2, the highest yield of deactivation, 53.2%, is for the *cis-trans* reaction pathway along the CC-CC dihedral angle. It is consistent with the evolution of the nuclei along the CC-CC twisting coordinate upon initial excitation. However, as explained above, the $S_2(\sigma\pi^*)$ can be populated before the torsion of the CC-CC dihedral angle take place during a transient equilibrium between the $\pi\pi^*$ and $\sigma\pi^*$ states. In the trajectories where the $S_2(\sigma\pi^*)$ stay populated for relatively long time, untwisted molecular geometries remain until reaching mainly the $seam(\sigma\pi^*/n\pi^*)$ or a dissociation channel of C-F bonds, which involve $p_\sigma\sigma^*$ states. The $seam(\sigma\pi^*/n\pi^*)$ has a MECI(S_2/S_1) which is a partially twisted structure (CC-CC dihedral is 47°) that is located 126.4 kcal·mol⁻¹ higher than the FC- S_0 (Figure 11a). The $seam(\sigma\pi^*/n\pi^*)$ unwraps one mechanism of population of the $S_1(n\pi^*)$ via the $\sigma\pi^*$ dark state at untwisted geometries, which could increase the Norrish Reactions yield in comparison with the crotonaldehyde where this dark state is very high in energy. However, according the dynamic calculations, the main role of the $\sigma\pi^*$ state is not even leading to the FC-H homolytic dissociation, but it is adiabatically connecting a $p_\sigma\pi^*$ state, which induces the

fluorine dissociation by turning part of the excitation energy into kinetic energy of the C-F stretching vibrational mode. During this process, the rotation of the molecular orbitals allows the π^* to increase the contribution of the σ^* of the weakened C-F bond as the C-F distance increases, and the σ orbital to rotate enough to become a p orbital that belong to the leaving fluorine atom and represented now and on as p_F . During the exploration of the *seam*(S_3/S_2), the geometry shown in the Figure 11e was located. At this partially dissociated geometry the S_2 and S_3 are degenerated and their electronic nature are $p_{x_F}\pi^*$ and $p_{y_F}\pi^*$, where p_{x_F} and p_{y_F} are molecular orbitals mainly described by the p_x and p_y atomic orbital belonging to the leaving fluorine atom; and the π^* molecular orbital is mostly like the one shown in Figure 2, but with some contribution of the σ^* orbital of the carbon-fluorine bond that is suffering the rupture. At this partially dissociated geometry, the $p_{x_F}\pi^*$ and $p_{y_F}\pi^*$ states are almost degenerated with $S_1(n\pi^*)$, which is only 1.77 kcal·mol⁻¹ below. In a typical trajectory along this reaction coordinate, the $S_3(\pi\pi^*)$ state transfer population to the $S_2(\sigma\pi^*)$ in ~5 fs, then the $\sigma\pi^*$ state overcomes a barrier along the C-F stretching between 10 and 16 fs (Figure 10b). This process is much faster than the torsion, so most of the trajectories following this reaction pathway reach the dissociation in the first 50 fs (blue bold line in Figure 9c). The C-F dissociation has a relatively high probability because of the very accessible $\sigma\pi^*$ state observed in the fluorinated derivative, but having two C-F bonds in the molecule increases this probability significantly. It makes the C-F dissociation reaction pathway the second most important, with a yield of 25.8%, just behind the *cis-trans* isomerization along the CC-CC dihedral angle.

Deactivation of $n\pi^*$ state

Despite the fact that the $n\pi^*$ state is the lowest excited singlet in the Franck-Condon zone, this electronic state was not found to be involved in many trajectories. The $S_1(n\pi^*)$ state can be primarily populated either by internal conversion from the bright $\pi\pi^*$ state or through the dark $\sigma\pi^*$ state when this one behaves like a bridge connecting the $\pi\pi^*$ and the $n\pi^*$. The internal conversion from the $\pi\pi^*$ state takes place along twisted geometries, while the internal conversion from the $\sigma\pi^*$ state takes place in some zones of the nuclear configuration space of untwisted geometries. The $S_1(n\pi^*)$ state usually evolves along the reaction coordinates leading to dissociation and isomerization reactions such as α -cleavage (Norrish type I) and γ -hydrogen abstraction (Norrish type II). In the case of the *cis-keto* isomer there is a hydrogen-oxygen electrostatic interaction stronger than the usual C-H--O because of the polarization of the C-H bond induced by the effect of the fluorine atoms. Due to this interaction, the molecular geometry of **A** has very favorable O and H spatial position to trigger the γ -hydrogen abstraction in the case of the $S_1(n\pi^*)$ state is directly populated. However, the amount of trajectories following the γ -hydrogen abstraction is relatively small (4.8%). The main reason for this kind of behavior is that the FC- $S_1(n\pi^*)$ has a low oscillator strength, so this state is mainly populated by internal conversion from

$S_2(\pi\pi^*)$ at twisted or partially twisted geometries where the γ -hydrogen is not spatially suitable to interact with the oxygen atom to trigger the γ -hydrogen abstraction. Nevertheless, one trajectory showed the possibility of γ -hydrogen abstraction in partially twisted geometries. In this case, one partially twisted (62° of CC-CC torsion) conical intersection ($n\pi^*/S_0$) was reached, which lead to the γ -hydrogen abstraction. This kind of process is unlikely, but the few trajectories following it may populate the isomer **M** (*trans-enol*) directly (yellow arrow in Figure 13). The C-H dissociations can take place in any time as long as the spatial arrangement of the H and O atoms are favorable. However, in the most of the trajectories the set of dihedral angles of the molecule make the γ -hydrogen abstraction a difficult process. Consequently, the $n\pi^*$ state increases its population monotonously until that the system suffers a spatial rearrangement to make possible reaching the *seam*($n\pi^*/S_0$). However, in the majority of the cases that the $n\pi^*$ state is populated, the spatial rearrangement takes so long, so the system stays far away from the *seam*($n\pi^*/S_0$) until the t_{max} (300 fs), becoming a non-reactive trajectory (6.5% of the trajectories), as the shown in Figure 10c. In some cases, the $S_1(n\pi^*)$ state is populated with an energy rich twisting vibrational motion that in combination with the flat shape of the potential energy surface along the CC-CC twisting coordinate, make possible that the system suffers *cis-trans* isomerization on the $S_1(n\pi^*)$ state (white arrow in Figure 13). The *cis* and *trans* minima energy points on $S_1(n\pi^*)$ have almost the same energy, whose energy difference is $\Delta E = 0.1$ kcal·mol⁻¹. Only the *cis* isomer, labeled as LM- $S_1(n\pi^*)$, is a geometry belonging to the C_s symmetry point group, which is very close to one transition state only 0.2 kcal·mol⁻¹ higher than the LM- $S_1(n\pi^*)$ along the γ -hydrogen abstraction coordinate that connects the excited states of **Zone 1** with the ground state of **Zone 3** through the *seam*($S_1-n\pi^*/S_0$). In the trajectories where the $\sigma\pi^*$ state behaves like a bridge linking the $\pi\pi^*$ and the $n\pi^*$ state around non-twisted geometries, the $n\pi^*$ state is populated in suitable geometries around the *cis* LM- $S_1(n\pi^*)$, so the system can follow the γ -hydrogen abstraction with no difficulties (Figures 9d and 10d). The energy barrier for this reaction on $S_1(n\pi^*)$ indicates an almost barrierless process before reaching the *seam*($S_1-n\pi^*/S_0$). A planar MECI($S_1-n\pi^*/S_0$) was located 7.7 kcal·mol⁻¹ lower than the *cis* LM- $S_1(n\pi^*)$ at the SF-TDDFT(BHLYP)/6-31G(d) level. In Figure 13, a projection of the $n\pi^*$ and S_0 potential energy surfaces along the CC-CC dihedral angle and the C-O bond length is illustrated. The non-adiabatic decay via the *seam*($n\pi^*/S_0$) connects **Zone 1** and **Zone 3** (Figure 2). There is not direct connection between **Zone 2** and **3** because it is a multi-step reaction that involves *cis-trans* isomerization plus γ -hydrogen abstraction. In **Zone 3**, the *cis* and *trans-enol* have the same energy and they are connected along the torsion around the CC-CC single bond that imposes a very small barrier. The isomer **L** (*cis-enol*) is expected to be primarily populated just after the non-adiabatic process and a subsequent adiabatic equilibration with the *trans-enol* specie (**M**) could then take place. In the remaining trajectories where the $n\pi^*$ state is populated, the kinetic energy of the OC-H stretching vibration increases, leading to

the *seam*($\pi\pi^*/S_0$) along the α -cleavage reaction pathway (4.8% of the trajectories).

Photochemistry from the isomer E (trans-keto)

Unlike the isomer **A**, where the bright $\pi\pi^*$ state is located on the S_3 , just 2.0 kcal·mol⁻¹ above the $S_2(\sigma\pi^*)$ state, in the isomer **E** the $\pi\pi^*$ state is located on the S_2 at 4.8 kcal·mol⁻¹ below the $S_3(\sigma\pi^*)$ state. During the relaxation of the $S_2(\pi\pi^*)$ state, it is unlikely to reach the *seam*($\pi\pi^*/\sigma\pi^*$), therefore the absent of the $\pi\pi^* \leftrightarrow \sigma\pi^*$ transient equilibrium. Therefore, no considerable population of the $\sigma\pi^*$ state is expected in the first femtoseconds after the absorption of the photon. The energy order of the excited states in the isomer **E** implies that the relaxation of the $S_2(\pi\pi^*)$ state would go immediately towards twisted geometries where the $\pi\pi^*/S_0$ energy gap becomes small and the multiconfigurational nature of the S_0 becomes important. Consequently, a decrease of the S_2 population to ~50% in just ~65 fs takes place, which is much shorter than the ~155 fs observed in the **A** isomer. The twisting coordinate notably simplifies the photochemistry from the **E** isomer, given that it increases the energy of the $\sigma\pi^*$ state. As a consequence, the population of this dark state is unlikely and therefore the system should evolve directly to the *seam*($\pi\pi^*/n\pi^*$) and *seam*($\pi\pi^*/S_0$) for a faster deactivation in comparison to the photochemistry from the **A** isomer. Depending on the nature of the S_1 after ~65 fs, the system can evolve to five different reaction pathways (Table 3). The most probable reactive decay is the *trans-cis* isomerization that was reached in the 36.5% of the trajectories. The photophysical deactivation is the second most important decay process, which was observed in the 31.7% of the trajectories. The relatively large amount of trajectories following a photophysical deactivation is an evidence of a very accessible *seam*(S_1/S_0). In addition, the amount of non-reactive trajectories became 19.0%, which is also significant.

The initial relaxation of the $S_2(\pi\pi^*)$ state implies mainly the torsion coordinate which lead primarily to the *trans-cis* isomerization. However, there are essentially two DOF to reach the *seam*($\pi\pi^*/S_0$): The torsion along the CC-CC dihedral angle and the pyramidalization of the α and β carbons. To estimate the β -carbon pyramidalization we used the dihedral angle formed by the α and γ carbons respect to the H-C(β) bond, and the same approach was applied to the α -carbon. The CC-CC torsion is a slower process than the pyramidalization and it can take place in all the trajectories, but depending on the amount of kinetic energy associated with the faster vibrational modes that lead to the pyramidalization, it is possible to reach the *seam*($\pi\pi^*/S_0$) in a time scale smaller than the one necessary for the torsion movement. In this case, there is not enough time for the torsion takes place (blue bold line in Figure 15 and Figure 16c). Although, this phenomenon should lead to a photophysical process, when the kinetic energy in the pyramidalization modes is not enough, the system will have time enough to twist and consequently lead to the

photochemical process of *trans-cis* isomerization (red bold line in Figure 15 and Figure 16a). Looking at the panel b and c in Figure 15, it can be observed that the β -pyramidalization takes place with larger amplitude of the vibrations, so the photophysical process is mainly dominated by the β -pyramidalization. In Figure 16a the potential energy profile along the time of a typical *trans-cis* isomerization that finishes in the *seam*($\pi\pi^*/S_0$) can be observed. When the $\pi\pi^*$ state transfers population to the $n\pi^*$ in twisted geometries instead of reaching the *seam*($\pi\pi^*/S_0$), the system can follow the *trans-cis* isomerization along $S_1(n\pi^*)$ state. This phenomenon was observed in 11.3% of the trajectories, and the potential energy for one typical trajectory for this kind of process is plotted in Figure 16b. It can additionally be observed that the $S_2(\pi\pi^*)$ state crosses with $S_1(n\pi^*)$ in 54 fs (left star) and internal conversion takes place transferring population to the $S_2(n\pi^*)$. Then, the populated $S_2(n\pi^*)$ state becomes again the S_1 after 66.5 fs (by the crossing represented as the right star) and it is relaxed to the *cis* $S_1(n\pi^*)$ minimum of the **I** isomer, which finally decays to the ground state by reaching the *seam*($\pi\pi^*/S_0$) via a sloped conical intersection. It shows that $n\pi^*$ state can be also involved in the *trans-cis* isomerization along the CC-CC dihedral angle.

In the case of the isomer **A**, 6.5% of the total amount of trajectories became non-reactive in 300 fs because the internal conversion to the $S_1(n\pi^*)$ state was not at suitable set of dihedral angles, so the system needed longer time for reaching a suitable molecular arrangement to follow the γ -hydrogen abstraction pathway. In contrast, this possibility does not exist in the photochemistry from the **E** isomer because of the large separation of the γ -hydrogen and oxygen atom imposed by the initial *trans* conformation. Therefore, the only possible deactivation pathways through the $S_1(n\pi^*)$ state are the *trans-cis* isomerization along CC-CC on the $S_1(n\pi^*)$ state, the α -cleavage and the photophysical decay. However, these kind of processes may require some time while the kinetic energy of the nuclei is redistributed to be concentrated in the normal mode that facilitate these phenomena. Consequently, a considerable amount of trajectories (19.0%) that reached the t_{\max} , became classified as non-reactive (Figure 16d). Only 3.2% of the trajectories followed the α -cleavage by the OC-H dissociation and no trajectories showed a photophysical process via the $S_1(n\pi^*)$ state.

Conclusions

The photochemical reactions of small-unsaturated carbonyl compounds are a very important and controversial chemical process in Earth's atmosphere because they affect our quality of life and health. The theoretical understanding of the unimolecular elementary photochemical reactions of the *4,4-difluorobut-2-enal* (difluoro-crotonaldehyde) was studied. We report the deactivation pathways after the electronic excitation of the *trans* and *cis* isomers by using static and

dynamic calculations. The results obtained by combining the Global Reaction Route mapping (GRRM) package and the Trajectory Surface Hopping (TSH) approach gave sufficient information to rationalize the photochemical behavior of the molecule under investigation.

The fluorine atoms have a strong stabilization effect on the $\sigma\pi^*$ state with respect to the crotonaldehyde. This fact increases the probability of activating dissociative reaction pathway that leads to free radicals and fluorine atoms. This effect becomes only important in the *cis* isomer given that the $\pi\pi^*-\sigma\pi^*$ energy gap becomes smaller. The ultrafast decay to the ground state is slower in the *cis* isomer given the possibility of a transient equilibration of the $\pi\pi^*\leftrightarrow\sigma\pi^*$ internal conversions that delay the molecule deformations necessary to reach the *seam*(S_1/S_0). In contrast, the deactivation of the *trans* isomer goes directly to the *seam*(S_1/S_0) given that the $\sigma\pi^*$ states are high enough to remain unpopulated during the relaxation of the $\pi\pi^*$ toward twisted geometries. Despite the **A** isomer has the right spatial distribution for a γ -hydrogen abstraction, this process is unlikely because the conformation is changed during the first femtoseconds after the electronic excitation to $\pi\pi^*$. Therefore, when the $\pi\pi^*$ state is populated there is not suitable set of dihedral angles for the hydrogen migration. The main deactivations pathways from the **A** isomer are the *cis-trans* isomerization (53.2%) and the fluorine dissociation (25.8%). The probability of these process to take place strongly depends on the nature of the excited state populated at the moment that the system scape from the transient $\pi\pi^*\leftrightarrow\sigma\pi^*$ equilibrium. If the $\pi\pi^*$ is populated, the probability of the *cis-trans* isomerization increases. In contrast, when the $\sigma\pi^*$ state is populated the system can evolve to the fluorine dissociation pathway. This kind of phenomenon was not observed in the photochemistry from the *trans* isomer. So, as long as the *cis* isomer becomes generated the amount of free fluorine atoms will significantly increase. This can affect the amount of hydrogen fluoride (HF) in the atmosphere after the reaction of free fluorine atoms with water molecules to generate hydroxyl radicals and HF. On the other hand, the deactivation from the *trans* isomer mainly leads to *trans-cis* isomerization (36.5%) and photophysical decay to S_0 (31.7%). The competition between these two processes depends on the kinetic energy redistribution on the normal modes associated with the pyramidalization of the α and β carbons. When this kinetic energy is high, the system can reach a slope crossing point belonging to the *seam*($\pi\pi^*/S_0$), and consequently decay to the initial *trans* isomer.

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