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

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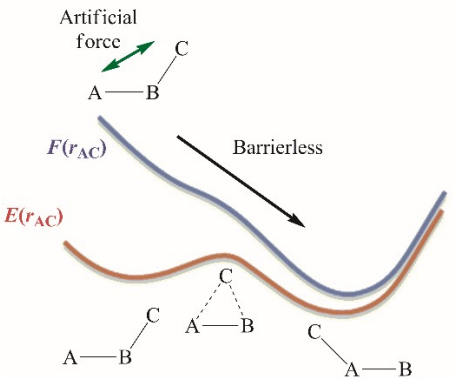

Figure 1. Potential energy surface $E(r_{AC})$ along the r_{AC} (distance between the atoms A and C), and the AFIR function $F(r_{AC})$ along the same coordinate (blue).

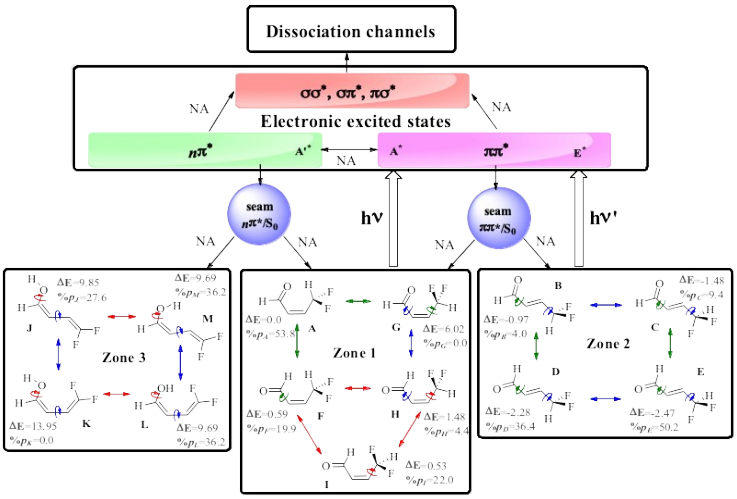

Figure 2. Representation of the lower ground state minima and the non-adiabatic processes studied in in this article (NA=non-adiabatic process). Energies (in kcal·mol^{-1}) calculated at the B3LYP/6-31G(d) level; $\%p_i$ are the Boltzmann population inside each zone expressed in terms of percentage.

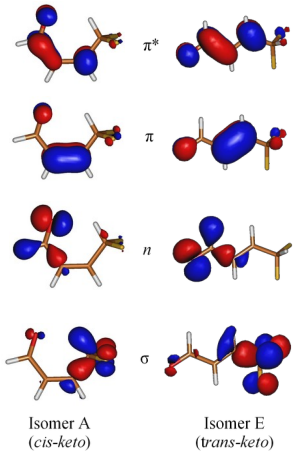

Figure 3. Molecular orbitals implied in the single excitations to describe the lower excited states in the A and E isomers.

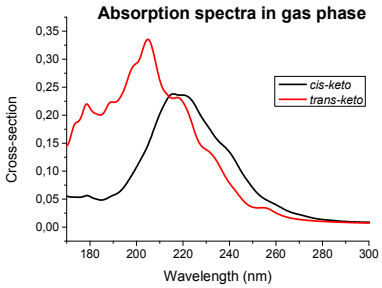

Figure 4. Cross-section σ(*E*) calculated for the *cis* (black line) and *trans-keto* (red line) isomers in the gas phase using a nuclear ensemble composed by 300 geometries and the TD-B3LYP/6-31G(d) level.

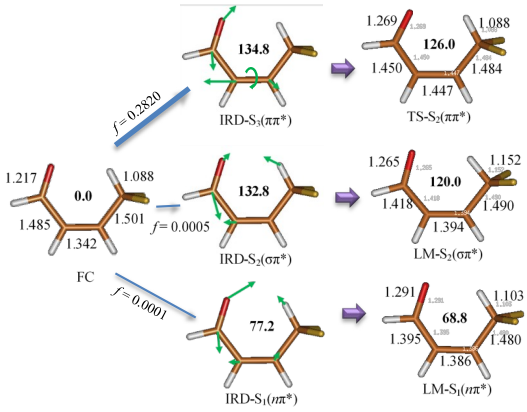

Figure 5. Relative energies (kcal·mol^{-1}) and bond distances (Å) for FC, TS-S_2($\pi\pi^*$), LM-S_2($\sigma\pi^*$) and LM-S_1($n\pi^*$) calculated at the TD-B3LYP/6-31G(d) level. The oscillator strengths and the representation of the initial relaxation directions (the direction of the force on the corresponding electronic state) are shown at the FC geometry.

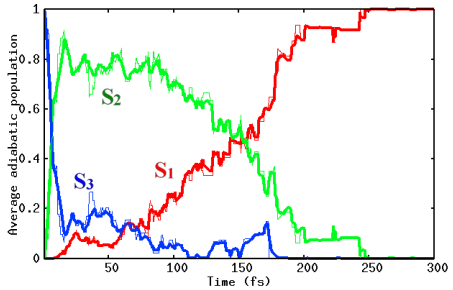

Figure 6. Average fraction of trajectories (thin lines) and average adiabatic population (thick lines) from the A isomer for S_1 (red), S_2 (green) and S_3 (blue) as a function of the time (*fs*).

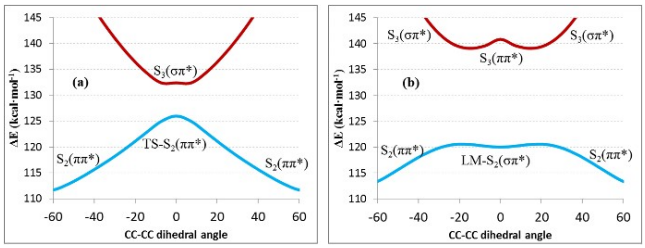

Figure 7. Energy profiles (kcal·mol^{-1}) obtained by the rigid scan along the CC-CC dihedral angle from (a) the TS-$S_2(\pi\pi^*)$ and (b) the LM-$S_2(\sigma\pi^*)$ calculated at the TD-B3LYP/6-31G(d) level.

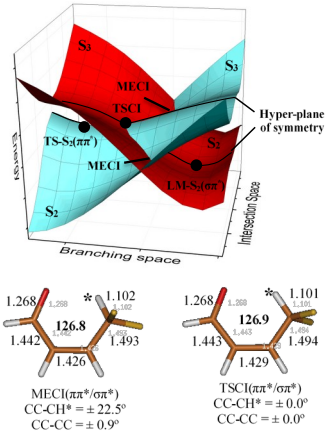

Figure 8. Representation of the *seam*($\pi\pi^*/\sigma\pi^*$) respect with the TS-$S_2(\pi\pi^*)$ and the LM-$S_2(\sigma\pi^*)$; energies in kcal·mol^{-1} (bold) and geometries in angstroms and degrees of the MECI and TSCI calculated at the TD-B3LYP/6-31G(d) level.

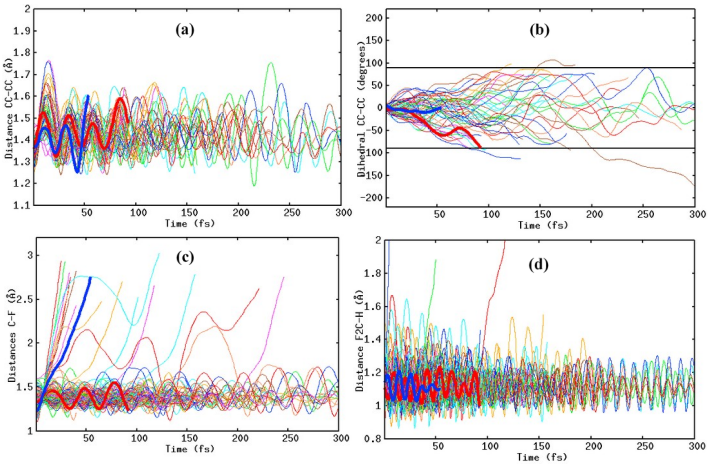

Figure 9. Degrees of freedom as a function of the time (*fs*) starting from the FC zone of the A isomer. The CC-CC distance (a), the CC-CC dihedral angle (b), the C-F distances (c) and the FC-H distance (d). In bold lines are the representative trajectories for the CC-CC *cis-trans* isomerization (red) and the fluorine dissociation (blue).

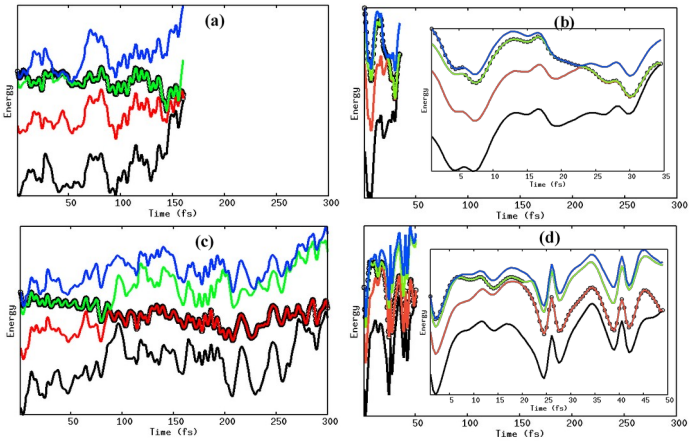

Figure 10. Energy of the system as a function of the time (*fs*) for some typical trajectories along: the CC-CC cis-trans isomerization (a), non-reactive on the $S_1(n\pi^*)$ state (b), fluorine dissociation (c) and γ-hydrogen abstraction (d). The black, red, green and blue lines represent the S_0, S_1, S_2 and S_3, respectively. The black circles highlight the current populated state.

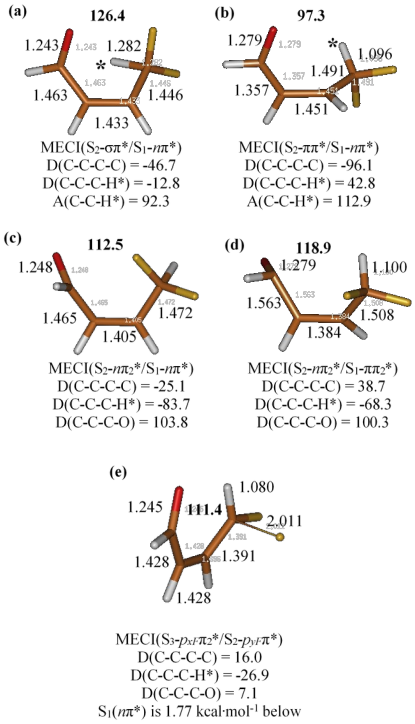

Figure 11. Energies in kcal·mol^{-1} (bold) and geometries in angstroms and degrees of the MECI(S_2/S_1) calculated at the TD-B3LYP/6-31G(d) level.

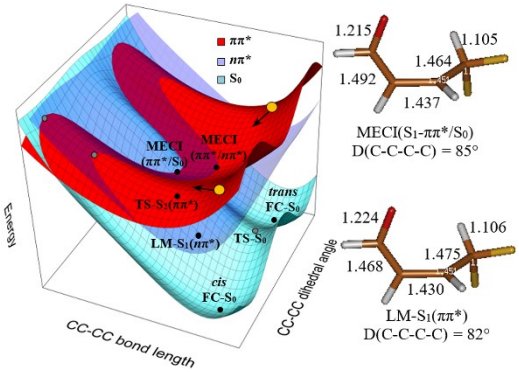

Figure 12. Representations of the potential energy surfaces for the S_0, ππ* and *n*π* states along the CC-CC bond distance and the CC-CC dihedral angle. The σπ* state is omitted for simplicity. The arrows show the main component of the gradient for ππ* states in the FC geometries.

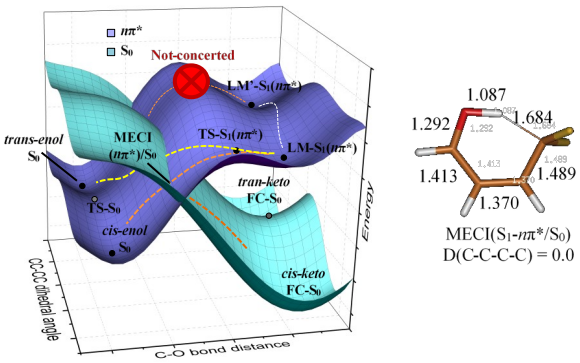

Figure 13. Representations of the potential energy surfaces for S_0 and *n*π* states along the C-O bond distance and the CC-CC dihedral angle.

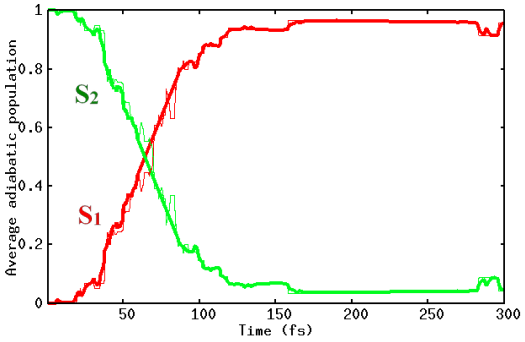

Figure 14. Average fraction of trajectories (thin lines) and average adiabatic population (thick lines) from the E isomer for the S_1 (red) and the S_2 (green) as a function of the time (*fs*).

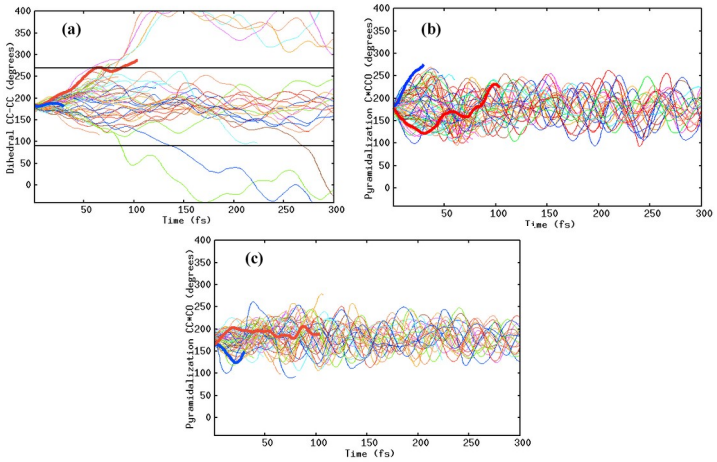

Figure 15. Degrees of freedom as a function of the time (*fs*) starting from the FC zone of the E isomer. The CC-CC dihedral angle (a), the C*CCO pyramidalization (b) and the CC*CO pyramidalization (c). In bold lines the representative trajectories for the CC-CC *cis-trans* isomerization (red) and the photophysical process (blue).

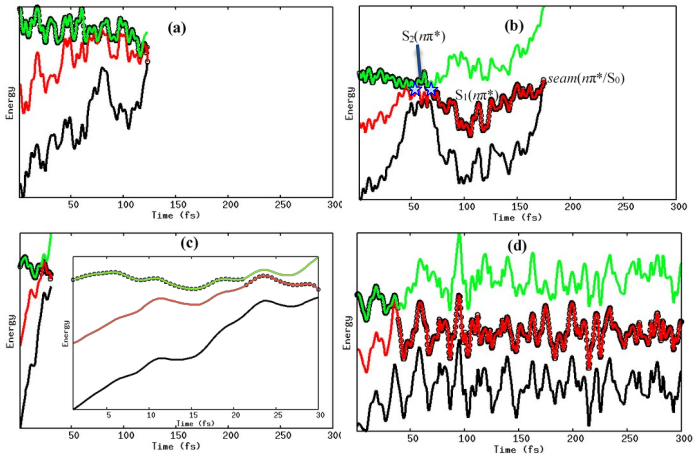

Figure 16. Energy of the system as a function of the time (*fs*) for some typical trajectories along: the CC-CC *trans-cis* isomerization along the ππ* state (a), the *n*π* state (b); a photophysical process (c) and a non-reactive process. The black, red and green lines represent the S_0, S_1, and S_2, respectively. The black circles highlight the current populated state.