

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

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Isomer A (cis-keto)			
Nature	$\Delta E(\text{B3LYP})/6\text{-}31\text{G(d)}$	$\Delta E(\text{B3LYP})/\text{aug-cc-pVDZ}$	f
$n\pi^*$	$S_1 = 77.2 [S_1 = 79.7]$	$S_1 = 74.3 [S_1 = 77.1]$	0.0004
$\pi\pi^*$	$S_3 = 134.8 [S_2 = 131.7]$	$S_2 = 128.7 [S_2 = 125.0]$	0.2771
$\sigma\pi^*$	$S_2 = 132.8 [S_3 = 162.3]$	$S_3 = 132.9 [S_7 = 156.5]$	0.0001

Isomer E (trans-keto)			
Nature	$\Delta E(\text{B3LYP})/6\text{-}31\text{G(d)}$	$\Delta E(\text{B3LYP})/\text{aug-cc-pVDZ}$	f
$n\pi^*$	$S_1 = 80.4 [S_1 = 84.6]$	$S_1 = 79.3 [S_1 = 84.0]$	0.0000
$\pi\pi^*$	$S_2 = 144.2 [S_2 = 141.8]$	$S_2 = 139.2 [S_2 = 135.3]$	0.3996
$\sigma\pi^*$	$S_3 = 149.0 [S_4 = 171.2]$	$S_4 = 145.8 [S_{10} = 165.9]$	0.0552

Table 1. Excitation energies calculated at the TD-B3LYP level for the A and E isomers and the analogues for the crotonaldehyde (in brackets). The FC geometries were optimized using the same functional and basis set as the one used to calculate the excitation energies. The oscillator strengths were calculated using the aug-cc-pVDZ basis set.

Reaction pathway	Implied state	% of trajectories
<i>cis-trans</i> CC-CC	$\pi\pi^*$	53.2%
<i>cis-trans</i> CC-CO	$\pi\pi^*/n\pi^*$	4.8%
F-Dissociation	$\sigma\pi^*$	25.8%
γ -hydrogen abstraction	$n\pi^*$	4.8%
α -cleavage	$n\pi^*$	4.8%
Non-reactive	$n\pi^*$	6.5%

Table 2. Classification of the reaction pathways, the amount of trajectories following these reaction pathways and the electronic state implied in the dynamic from the A isomer. The assignment of trajectories to products were based on the final geometry (near to the seam S_1/S_0) the nature of electronic states involved and their average adiabatic population.

Reaction pathway	Implied state	% of trajectories
<i>trans-cis</i> CC-CC	$\pi\pi^*$	36.5%
<i>cis-trans</i> CC-CO	$\pi\pi^*/n\pi^*$	3.2%
FCC-H diss	$\sigma\pi^*$	1.6%
FC-H diss	$\sigma\pi^*$	3.2%
Photophysical	$\pi\pi^*/n\pi^*$	31.7%
α -cleavage	$n\pi^*$	3.2%
Non-reactive	$n\pi^*$	19.0%

Table 3. Classification of the reaction pathways, the amount of trajectories following them and the electronic state implied in the dynamic from the E isomer.