

Photochemical dynamics on $\sigma\pi$ excited states in ethylene cation $C_2H_4^+$



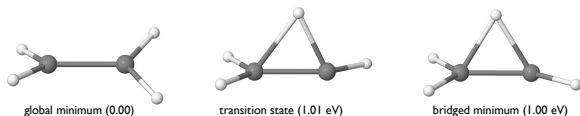
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The ethylene cation $C_2H_4^+$ is, with the isoelectronic neutral vinyl C_2H_3 , the simplest organic π radical system: one electron populates a unique π orbital in the ground state electronic configuration. This system thus offers an opportunity to study in detail the complex electronic and vibronic dynamics in a prototype π radical. We present a combined electronic structure/photochemical dynamics study that investigates the non-adiabatic effects in ethylene cation $C_2H_4^+$ after photoexcitation to its three first excited states. Emphasis is given on the role of the torsional coordinate which is associated to strong vibronic couplings. This study raises questions concerning the dynamics of highly electronically frustrated radicals and the influence of low-lying conical intersections on vibrational energy redistribution.

Electronic structure Photochemical Dynamics with the *Ab Initio* Multiple Spawning Method

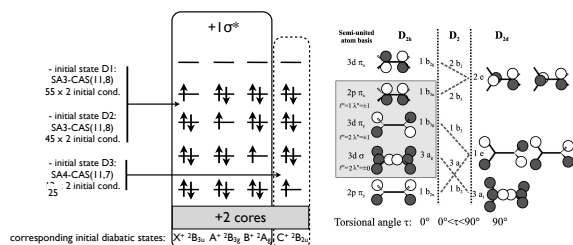
Ground state:
 $C_2H_4^+ \rightarrow C_2H_2^+ + H_2$ 2.62 eV (1)
 $C_2H_4^+ \rightarrow C_2H_3^+ + H$ 2.70 eV (2)



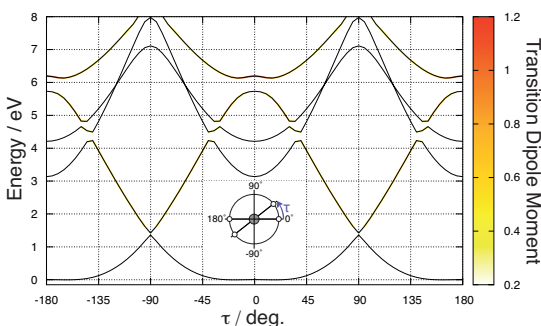
Minima and connecting saddle-point on the ground state PES at the SA4-CASPT2(7,8) level of theory

- ultra-flat double well along torsional coordinate
- torsional barrier < 0.01 eV (MRCI and CAS)
- minima around 20-25 deg at the MRCI level, lower angle at the CASSCF level (lack of dynamical correlation) and comprised between 8 and 30 deg, in the literature
- ZPE tends to strongly decrease the torsional angle at 0K
- => **No ethylenic-like minimum (CH_2CH^+)**

Excited states:



The dominant electronic configurations of the first three electronic states of the ethylene radical cation and the different active spaces used in this study (left); a schematic representation of the most important molecular orbitals in terms of a linear combination of atomic orbitals (right).



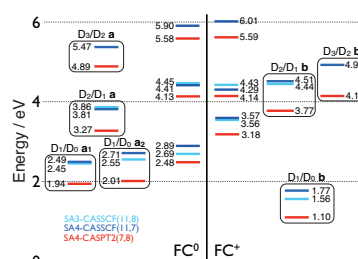
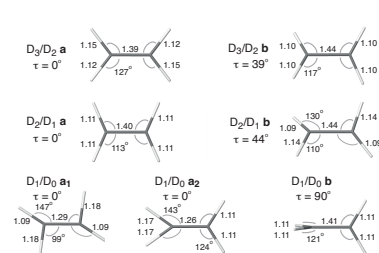
Relaxed PESs of ground state D0, $\sigma\pi$ states D1, D2, D3, and $\pi\pi^*$ state D4 along torsion calculated at the MRCI level of theory.

References:

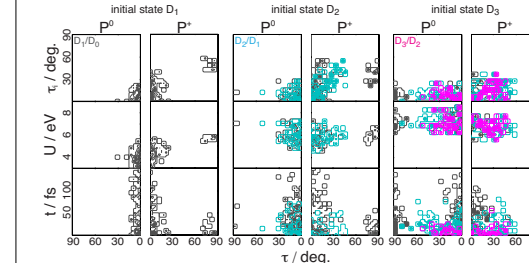
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S. Wittmann, U. Hohenester and F. Merz, *The Journal of Chemical Physics*, 2004, 120, 3762.
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For each initial state: 2 sets of Wigner distributions generated from planar (neutral, P^0) and twisted (cationic, P^+) geometries (optimized at the MP2/6-311** level).

Franck-Condon energies and MECIs



Distributions of spawning geometries

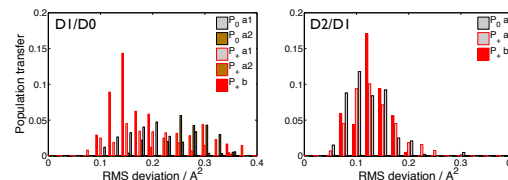


Distribution of the spawning events characterized by their torsional angle τ as functions of time, total energy and initial torsional angle τ_i , with contours interpolated from population transfers.

Initial conditions	< τ_i > deg.	<U> eV	$t_{1/2}$ fs	Population transfers %							
				D1/D0 a1	D1/D0 a2	D2/D1 a	D2/D1 b	D3/D2 a	D3/D2 b		
D1	P^0	9	4.1	78	75	25	0	/	/	/	/
	P^+	20	4.6	43	69	21	10	/	/	/	/
D2	P^0	9	6.0	37	86	13	1	99	1	/	/
	P^+	18	6.0	27	78	11	11	85	15	/	/
D3	P^0	9	7.2	43	51	11	38	52	48	38	62
	P^+	16	6.8	35	47	16	37	48	52	21	79

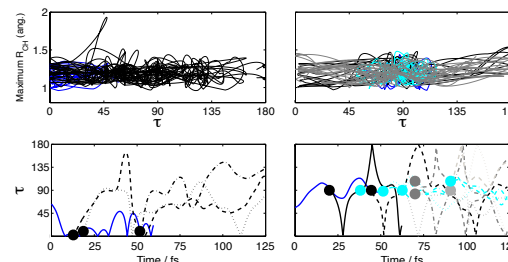
Average values of the initial torsional angle τ_i , the internal energy U, and the excited state lifetime for each initial excited state D1, D2 and D3 and Wigner populations P^0 and P^+ . (Right) Corresponding population transfers associated to each minimum energy conical intersections (MECIs).

Population transfers



Population transfers as a function of the RMSD from MECI geometries.

Typical D1-D0 trajectories involving CIs at $\tau=0$ deg. and at $\tau=90$ deg



- On the left the system spawns to the ground state (black) via the CI at 0 deg (3 times), no more living trajectory on D1 after 60 fs. We notice 1 short H migration event.
- On the right the initial wavepacket spawns twice on the ground state via the CI at 90 deg, and then disappears after 50 fs. Then its 2 D0 children "back-spawn" to D1 (3 times, cyan) via the same CI at 90 deg that it encounters twice each complete CH2 rotation. The D1 back-spawned children rapidly loose the torsional excitation then spawn to D0 (grey) and we can observe other later back-spawn events from this 2nd generation of D0 wavepackets.

What have we learned?

- No dissociation occurs from the excited states, nor any migration event over a thousand of trajectories.
- The main CI involved in the relaxation to the ground state is located near the H migration TS, and leads to prompt H migration events.
- Torsion is involved in the opening of a nonadiabatic relaxation pathway that allows a more rapid transition to the ground state. Besides, the decay through the Jahn-Teller CI at $\tau = 90^\circ$ provokes strong excitation of the torsional mode, and ultimately hindered rotation with a lifetime comparable of the vibration energy redistribution (~ 0.5 ps).
- Revisiting the changes of the H/H₂ ratio measured in the vibrationally-mediated photodissociation experiments (cf. figure), the threshold in favor of H loss observed at an energy of 4.1 eV may be a signature of the opening of the torsional channel on the B state. The excitation of the torsional mode could then either directly favor the H loss channel with a lower C-H dissociation energy at this geometry or indirectly by delaying the energy randomization over the other vibrational modes.

