Competition direct vs indirect photochromism dynamics in constrained inverse dithienylethene molecules - Electronic Supplementary Information

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State-of-the-art experimental and theoretical tools were used to investigate the gas-phase relaxation dynamics of various photoexcited photochromic dithienylethene molecules in situations were several relaxation channels are simultaneously at play. Unconstrained and constrained dynamics were addressed by considering unbridged and bidged molecules with a polyether bridge of various size (from 2 to 4 units). Time-resolved ultrafast ionization spectroscopy techniques were used to probe the dynamics. This revealed the existence of several relaxation pathways from the first excited state to the ground-state. Characteristic times were determined for each process. These channels are competing at an early stage of the dynamics only when the initial wavepacket splits in two parts. A striking excited state wavepacket oscillation is observed in bridged molecules. A general reaction mechanism is proposed which rationalizes the carbon-carbon distance rule which is widely used as an empirical tool to predict the photoactivity of photochromic molecules in crystals.

1 Molecular dynamics calculations

Conformational analysis of DTE, $DTE^{-}O_2$ and $DTE^{-}O_3$ has been performed using Molecular Dynamics (MD) simulations at the Molecular Mechanics (MM) level, with the generalized AMBER force field (GAFF)[1] and the AMBER 9 package[2]. For each molecule, the atomic charges were derived following the parametrisation procedure in the generalised AMBER force field, that is to say using HF / 6-31G(d) RESP (Restrained Electrostatic Potential) charges.

The simulations were run in vacuum for both isomers, opened (OF) and closed (CF). To explore the energy landscape, we used a simulated annealing protocol: the system was heated up to 1000 K in 100 ps and the temperature was then gradually cooled down to 150 K during 1 ns. After a subsequent 1 ns equilibration period, a production run was performed within the microcanonical ensemble during 5 ns with a time step of 1 fs. For each isomer, different conformers (parallel (P) and antiparallel (AP)) have been identified by plotting the distance between the two reactive carbon atoms and the different dihedral angles.

For each conformer, we randomly selected a snapshot from MD simulations that was then studied within the DFT framework. We did not performed an extensive exploration of the PES.

2 Molecular Orbitals

HOMO and LUMO Molecular orbitals for the DTE, $DTE^{-}O_2$ and $DTE^{-}O_3$ molecules are displayed on Figure 1.

3 Fitting functions

Here is presented the relaxation mechanism who drives the fitting function used to modelize the experimental data. In the Figure 2 represent the scheme of the relaxation mechanism.

In a first step, we worked on the temporal evolution of PE

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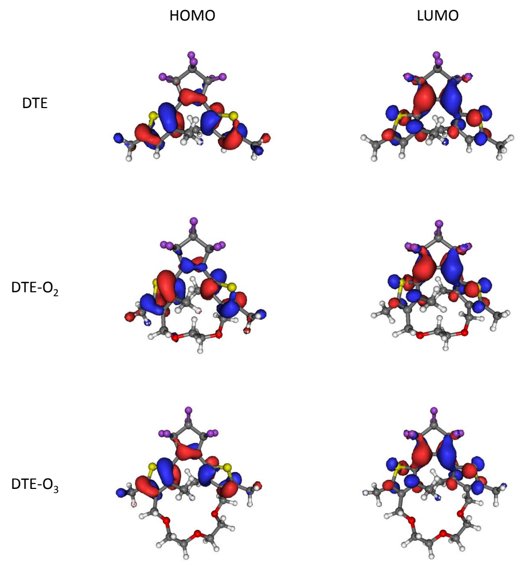

Fig. 1 Molecular orbitals (HOMO, LUMO) of DTE, DTE$^-$O$_2$ and DTE$^-$O$_3$.

spectra using the mechanism presented in the Figure 2. We have used simple multiexponential decays to fit experimental data (Equation 2), with t_1, t_2 are the decay time constants.

$$Gauss(t) = \frac{1}{\sigma.\sqrt{2.\pi}}.\exp\left(-\frac{(t-t_0)^2}{2.\sigma^2}\right) \tag{1}$$

$$evol(t) = \left[a_1.\exp\left(-\frac{t}{t_1}\right) + a_2.\exp\left(-\frac{t}{t_2}\right) + a_3\right] \otimes Gauss(t) \tag{2}$$

In a second time we have worked on the temporal evolution of TOF spectra, we use the decay times obtained with the PE's temporal evolution of each molecule. Then in order to reproduce the oscillation in the TOF's evolution on the bridged molecules, we added a sinusoid modulation on the second component of the evolution's equation (Equation 3).

$$\begin{aligned} evol'(t) \quad = \quad & \left[b_1.\exp\left(-\frac{t}{t_1}\right) + b_2.\exp\left(-\frac{t}{t_2}\right) \times \right. \\ & \left(1 + ampl \times \cos\left(\frac{2\pi t}{per} + \frac{\arctan(phase)+\pi}{2}\right)\right) \\ & \left. + b_3\right] \otimes Gauss(t) \end{aligned} \tag{3}$$

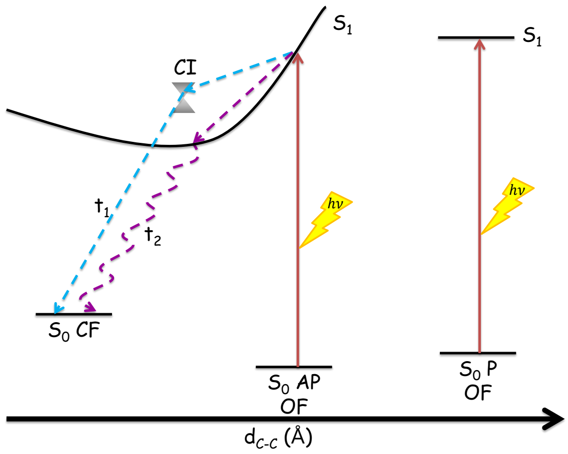

Fig. 2 Schematic representation of the reaction mechanism.

4 Energies

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Molecule	Conformer	State	Excitation energy (eV)	f	State description
DTE	OF-AP	S_1	3.63	0.28	HOMO → LUMO
		S_2	4.23	0.07	HOMO-1 → LUMO
		S_3	4.45	0.06	HOMO-2 → LUMO
	OF-P	S_1	3.50	0.24	HOMO → LUMO
		S_2	4.04	0.09	HOMO-1 → LUMO
		S_3	4.32	0.03	HOMO-2 → LUMO
	CF	S_1	2.88	0.09	HOMO → LUMO
		S_2	3.91	0.03	HOMO-1 → LUMO
		S_3	4.43	0.01	HOMO → LUMO+2
DTE$^-$O$_2$	OF-AP	S_1	3.53	0.15	HOMO → LUMO
		S_2	4.16	0.05	HOMO-1 → LUMO
		S_3	4.31	0.04	HOMO-2 → LUMO
	OF-P	S_1	3.66	0.04	HOMO → LUMO
		S_2	3.94	0.02	HOMO-1 → LUMO
		S_3	4.27	0.01	HOMO-2 → LUMO
	CF	S_1	2.68	0.07	HOMO → LUMO
		S_2	3.87	0.05	HOMO-1 → LUMO
		S_3	4.11	0.03	HOMO → LUMO+1
DTE$^-$O$_3$	OF-AP	S_1	3.67	0.34	HOMO → LUMO
		S_2	4.27	0.07	HOMO-1 → LUMO
		S_3	4.35	0.01	HOMO-2 → LUMO
	OF-P	S_1	3.60	0.17	HOMO → LUMO
		S_2	4.00	0.04	HOMO-1 → LUMO
		S_3	4.33	0.05	HOMO-2 → LUMO
	CF	S_1	2.67	0.07	HOMO → LUMO
		S_2	3.82	0.04	HOMO-1 → LUMO
		S_3	4.14	0.03	HOMO → LUMO+1

Table 1 Vertical excitation energy calculated at the TD-PBE0/6-31+G(d)//ωB97X/6-31+G(d) level, corresponding oscillator strengths f and state description in the $S_{0,opt}$ geometry.

Molecule	Structure	Conformer	d_{C-C} (Å)	ΔE (eV)	ΔG (eV)
DTE	S_0	OF-AP	3.58	0.00	0.00
		OF-P	4.39	0.07	0.07
		CF	1.55	0.72	0.84
	$S_{1,opt}$	OF-AP	2.82	3.41	3.42
		OF-P	4.35	3.43	3.37
		CF	1.74	3.44	-
DTE$^-$O$_2$	S_0	OF-AP	3.48	0.00	0.00
		OF-P	3.74	0.14	0.11
		CF	1.57	1.10	1.21
	$S_{1,opt}$	OF-AP	3.09	3.41	3.38
		OF-P	3.80	3.78	-
DTE$^-$O$_3$	S_0	OF-AP	3.65	0.00	0.00
		OF-P	4.21	-0.005	-0.004
		CF	1.58	1.17	1.30
	$S_{1,opt}$	OF-AP	3.25	3.54	3.48
		OF-P	4.36	3.36	-

Table 2 Energetic and geometrical parameters for both the ground state S_0 and the first excited state $S_{1,opt}$ minima of the different OF conformers and CF isomer computed at the ωB97X/6-31+G(d) level. ΔE is the relative electronic energy difference taking the most stable structure as reference and ΔG the relative Gibbs energy. The d_{C-C} distance between the two reactive carbon atoms is in Å.