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The Sudden-Polarization Effect and its Role in the Ultrafast Photochemistry of Ethene **

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The term *sudden polarization*, describing the charge separation in excited singlet states of twisted polyenes, especially of ethene, has been introduced in the mid 70s by Salem.¹ The ionic character and the high polarization upon a small perturbation of these valence excited states has been pointed out as early as in 1971 by Wulfman and Kumei² for alkenes. Bonačić-Koutecký et al.³ were the first to perform an *ab initio* study of the charge separation in 90°-twisted ethene as a function of an internal perturbation: the one-sided pyramidalization of a CH₂ group. To our knowledge, all following studies of the sudden-polarization effect of ethene have considered only one-sided pyramidalization as internal geometrical distortion to break the D_{2d} symmetry.⁴⁻⁸ We discuss here

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the effects of one-sided scissoring as another internal perturbation and show that the transfer of electronic charge between the CH₂ groups occurs in first order of this perturbation, whereas the effect is of second order in the pyramidalization. Moreover, we show that the one-sided scissors mode plays an essential role in the nonadiabatic photochemistry of ethene.

The sudden-polarization effect can be understood as the direct consequence of a small dissymmetry of the molecule. At the ground-state equilibrium geometry, ethene is planar and belongs to the symmetry group D_{2h} . In this group, the delocalized molecular orbitals, π and π^* , span the b_{3u} and b_{2g} representations, respectively (within Mulliken's axis definition⁹). The three relevant valence states⁹ N (π^2), V ($\pi\pi^*$) and Z (π^{*2}) thus have A_g , B_{1u} and A_g symmetry. Upon torsion of the CH₂ groups around the CC bond, the symmetry is lowered to D_2 . In this symmetry group, the π (π^*) orbital spans the b_3 (b_2) representation. This holds for all torsional angles φ not equal to 0° (planar geometry) and 90° (perpendicular geometry). For $\varphi = 90^\circ$, the symmetry group is D_{2d} . In this group, both π and π^* belong to the e representation. At this particular geometry, any linear combination of the π and π^* orbitals is acceptable, in particular the orbitals ϕ_r and ϕ_l which are localized on the right and left CH₂ groups, respectively. Since the two CH₂ groups are rigorously symmetry equivalent, the molecular orbitals have to reproduce a zero dipole moment. The symmetrized linear combinations $\phi_r^2 - \phi_l^2$ and $\phi_r^2 + \phi_l^2$, which have B_2 and A_1 symmetry, respectively, are acceptable solutions. They correspond to two excited states, V and Z, which do not have to be degenerate by symmetry. They are nevertheless close in energy, with the Z state being approximately 0.1 eV below the V state.⁶ The V and Z potential-energy functions cross at $\varphi \simeq 82^\circ$,^{6, 10} since the Z state is much higher in energy than the V state for planar geometry. If, for some reason, one side of the molecule is distinguished, an asymmetry of the electronic wave

functions results, leading to charge separation.¹¹ Because of the small overlap between the left and right orbitals and the small energy difference between the V and Z states of perpendicular ethene, the localization of the charge is pronounced, even for small perturbations. Both one-sided pyramidalization as well as one-sided scissoring lower the D_{2d} symmetry of perpendicular ethene to C_s and C_{2v} , respectively, breaking the left-right symmetry and thus allowing for a non-zero dipole moment.

Due to the complexity of the electronic structure of the excited-states of ethene (due to pronounced valence-Rydberg mixing and strong multi-reference character of the electronic wave functions^{12–15}), the *ab initio* determination of the energies and dipole moments of the three lowest valence states is not an easy task and has been the subject of many publications.^{3,5–7,11} Figure 1 shows the dipole moment μ_z of the V and Z states obtained at the CASSCF level with a cc-pVTZ basis set¹⁶ as a function of one-sided pyramidalization ϑ (Figure 1a) and one-sided scissoring α (Figure 1b) for perpendicular ethene. Since upward and downward pyramidalizations are symmetry-equivalent, it is obvious that any physical observable is an even function of ϑ . Consequently, for small ϑ , the dipole moments depend not linearly, but quadratically, on ϑ . This can be seen in Figure 1a, where the $\mu_z(\vartheta)$ functions exhibit a typical parabolic shape for small values of ϑ . For the scissors angle, on the other hand, increases and decreases, respectively, from the ground-state equilibrium value are not symmetry-equivalent. Consequently, the dipole moments as a function of the scissors angle (Figure 1b), are linear in α close to the origin. For both curves, the beginning of saturation, visible by the change of curvature, occurs at around $\mu_z = 1$ au, corresponding to $\vartheta \simeq 20^\circ$ and $\alpha - \alpha_0 \simeq 10^\circ$, respectively, where $\alpha_0 = 117.3^\circ$ is the HCH angle in the ground state of ethene.

Because of the linear dependence of μ_z on α , versus a quadratic dependence

of μ_z on ϑ , the polarization induced by one-sided scissoring is more pronounced than the one induced by one-sided pyramidalization for small distortions. The slope of $\mu_z(\alpha)$ is even larger for $\varphi \simeq 82^\circ$, as one expects from the smaller energy difference between the V and Z states at this torsional angle. The magnitude of the dipole moment in the saturation region is very similar for both distortions ($\mu = 1.4$ au for $\vartheta = 60^\circ$, $\mu = 1.2$ au for $\alpha - \alpha_0 = 30^\circ$).

The sudden-polarization effect implies a pronounced modification in the electronic wavefunctions by a small perturbation of the symmetry. This rapid change of the electronic structure in response to small nuclear deformations implies a strong non-adiabatic coupling between the two excited states for near-perpendicular geometries.¹⁷ The effect of this coupling on the nonradiative decay of the V state has been investigated by two-dimensional wave-packet propagations of the photoinduced nuclear motion on the non-adiabatically coupled potential-energy surfaces of the three valence-type singlet states. A diabatic representation of the N, V and Z states, including 6 of the 12 vibrational degrees of freedom, has been developed recently.¹⁸ In this model, based on accurate CASPT2 *ab initio* data, the diabatic states are coupled linearly by the antisymmetric scissors mode and quadratically by the pyramidalization. A more detailed description of the six-dimensional potential-energy surfaces can be found in Ref 18. To illustrate the impact of the sudden-polarization effect on the photochemical dynamics, two calculations have been performed, including either the one sided-scissoring or the one-sided pyramidalization together with the torsion. All other coordinates have been kept frozen at their ground-state equilibrium values. Figure 2 shows the time evolution, on a time scale of 50 fs, of the population probability of the initially ($t = 0$) prepared diabatic $\pi\pi^*$ state, which is, in D_2 symmetry, the (adiabatic) V state. After vertical electronic excitation from the ground state to the V state, the population probability stays

close to unity during the first 7 fs. After this period, the population decreases in both calculations, but the drop of the population is nearly twice as large in the φ, α calculation than in the φ, ϑ calculation. The initial 7 fs correspond to the time which the torsional wave-packet, initially located at the planar geometry, needs to reach the perpendicular geometry and thus the region of strong non-adiabatic coupling between the V and Z states. The coupling in the φ, α case is seen to be more efficient than in the φ, ϑ case, reflecting the fact that the vibronic coupling is linear in the former case, but quadratic in the latter case.

To conclude, we have shown that the sudden polarization in perpendicular ethene occurs in first order in the one-sided scissors deformation, and in second order in the one-sided pyramidalization. Although it has been emphasized in the literature that *any* geometrical distortion breaking the D_{2d} symmetry of perpendicular ethene will produce a charge separation, the distinguished role of the one-sided scissoring has not been recognized. Following the initial work of Bonačić-Koutecký et al.,³ all subsequent researchers have focussed on the pyramidalization. The relevance of the first-order V-Z vibronic coupling by the scissors coordinate for the photoinduced dynamics has been demonstrated by quantum wave-packet calculations. These calculations reveal that the linear V-Z coupling via the scissors mode provides a substantially faster flow of the electronic population probability out of the initially prepared V state than the quadratic coupling via the pyramidalization mode.

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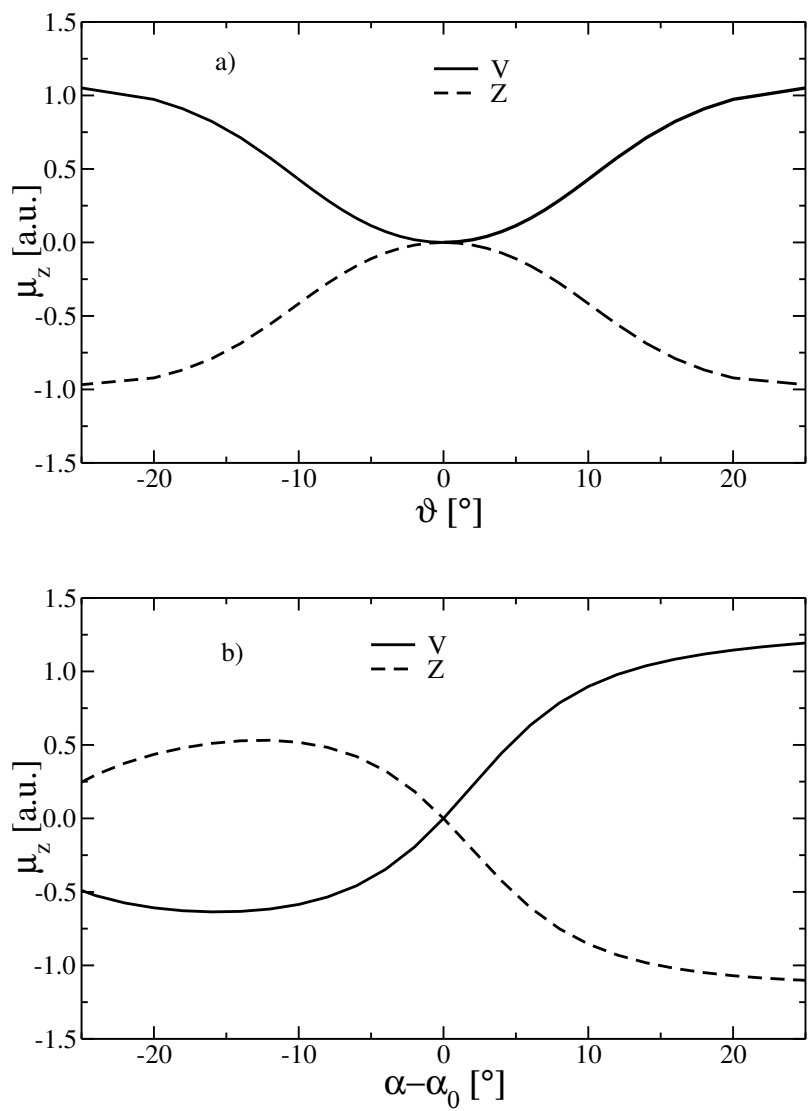


Figure 1: Dipole moment (in atomic units) along the CC bond for the V and Z states of 90° -twisted ethene as a function of a) pyramidalization and b) scissoring.

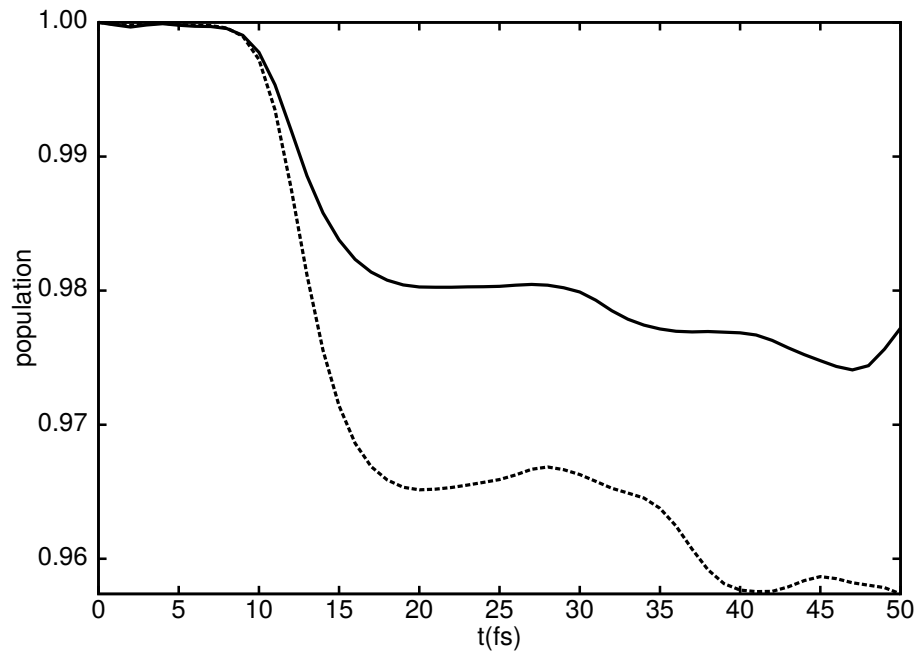


Figure 2: Time evolution of the population probability of the V state for a φ, ν (full line) and a φ, α (dotted line) wave-packet propagation, respectively.