Photophysics of fulvene under the non-resonant Stark effect.
Shaping the conical intersection seam

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A new mechanistic strategy to control the excited state lifetime of fulvene is introduced. It's based on shaping the topography of an extended seam of intersection with the non-resonant Stark effect[1]. Fulvene has a very short excited state lifetime due to an energetically accessible seam of intersection which lies along the methylene torsion coordinate, and the initial decay occurs at the seam segment around the planar conical intersection structure[2]. Starting from our previous[3] model for the excited state dynamics, we have followed a three-step approach to simulate the control. First, we have calculated the effect of a non-resonant electric field on the potential energy surface at the *ab initio* level, including the field in a self-consistent way. We find that the relative energy of the planar segment of the seam is increased by the non-resonant field. In the second step we simulate the control with a static field to derive the main control mechanisms. At moderately intense fields ($\varepsilon \leq 0.03$ a.u.) the decay is faster compared to the field free case because the vibrational overlap between the excited and ground state vibrational functions is increased. However, at more intense fields ($\varepsilon = 0.04$ a.u.) the planar conical intersection[4] is energetically inaccessible and the decay occurs at a slower time scale, at the segment of the seam with more twisted geometries. In the third step, the control is exerted with a non-resonant dynamic field. The acceleration of the decay due to the improved vibrational overlap does not occur, but the decay can be made slower with a dynamic field of 0.08 a.u. The results show the viability of our approach to control the photophysics shaping the topology of the conical intersection seam, and they prove that the extended nature of the seam is crucial to simulate and understand the control.
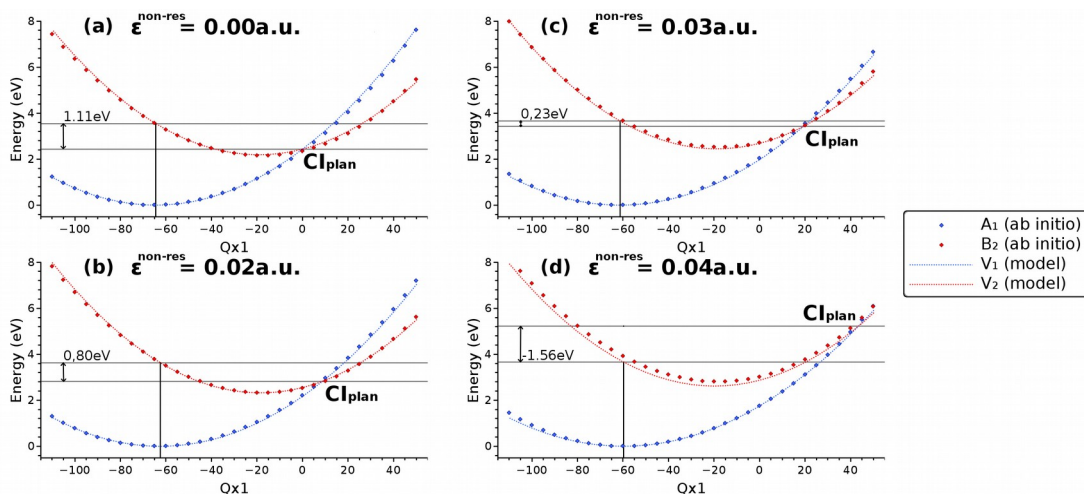
Figure 1: Energy profile along the planar coordinate at different non-resonant field intensities, including energy difference between the vertical excitation and the CI plan . Dots are the *ab initio* energies of the A and B states. Dashed lines are the energies of the model. Energies are in eV.

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