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Nonlinear photoswitching in diarylethene systems: exciting opportunities and profound insights from nonadiabatic molecular dynamics

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Among established and experimentally tested photoswitching systems, diarylethene molecules (DAE) are well known for efficient photo-driven cyclization and cycloreversion transformations. Exceptional photostability of DAE compounds and their good photochromic properties made them switching units of choice in many application-oriented investigations on single- and supra-molecular photo-controllable systems. At the same time, despite wide consensus over strongly nonlinear character of their switching, that is – large difference in transformation quantum yield in the two opposite directions – the exact reason for such effect remains unknown. By itself, nonlinear switching characteristics brings exciting possibilities for applications. For instance, nonlinear photoswitches show sensitivity for light intensity and may exhibit different response of switching forms in time. This puts them in fundamental position in numerous emerging photo-technologies, such as molecular photostabilizers or high-fidelity molecular memory with non-destructive readout. In our study, by means of static quantum-chemical calculations and multi-reference non-adiabatic photo-dynamics (MR-NAMD) simulations we investigate the source of DAEs switching nonlinearity at the electronic structure level. Through examination of photo-reaction profiles in multiple electronic states with tracking of their character in different regions along the reaction path, we identify crucial stages in the system evolution following its excitation with the UV irradiation. By means of MR-NAMD methodology we model the full switching process, with special attention paid to the quantitative formation of photoproducts upon switching in both directions. On this ground, we propose exact, step-by-step mechanism of this transformation and discuss possible factors responsible for the nonlinear switching in the model DAE system under study.

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