

Electronic and nuclear fluxes during pericyclic reactions: Quantum simulations for the Cope rearrangement of Semibullvalene

T. Bredtmann^a, F. Marquardt^b, D. Andrae^a, I. Barth^a, H.-Ch. Hege^b, A. Kenfack^a,
J. Manz^a, and B. Paulus^a

^aInstitut für Chemie und Biochemie, Freie Universität Berlin, 14195 Berlin

^bVisualization and Data Analysis, Zuse Institut Berlin, 14195, Berlin

Chemical reactions and molecular vibrations involve simultaneous fluxes of the coupled nuclei (F_{nuc}) and electrons (F_{el}) in molecules. Here, we use a general quantum method, recently developed in [1], in order to calculate F_{nuc} and F_{el} during the degenerate Cope rearrangement of Semibullvalene (SBV) (Fig. 1a). We present high level ab-initio data (CCSD(T)/cc-pVTZ) for the calculation of the potential energy curve and compare to less expensive DFT methods (Fig. 1a). We also present visualizations of the coupled time dependent nuclear- and electronic densities during the Cope rearrangement, providing new means for analysis and comprehension of the detailed mechanism underlying the coupled electronic- and nuclear fluxes (Fig. 1b, c).

Our new approach combines the fields of quantum chemistry for stationary molecular properties and quantum reaction dynamics for electronic and nuclear fluxes, hence allowing us to answer questions like: How many electrons are flowing during the Cope rearrangement of SBV? Are they traveling unidirectionally? On which time scale? Do accurate quantum simulations support traditional rules which are used ubiquitously, e.g. in organic chemistry?

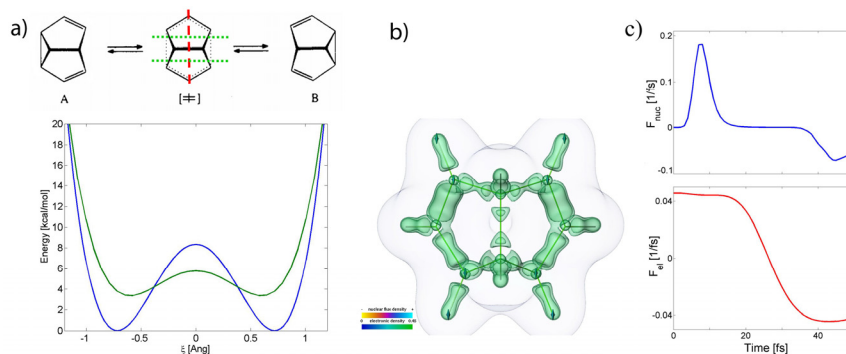


Figure 1 a) Top: Degenerate Cope rearrangement of Semibullvalene (SBV) "with planes of observers" for the electronic (red) and nuclear (green) fluxes. Bottom: Two one dimensional cuts through the potential energy surface calculated at the B3PW91/cc-pVTZ level. One cut goes from Minimum A to B along the coordinate ξ (blue), the other one (green) goes parallel to ξ but passing through the transition state. b) Snapshot of electronic- and nuclear densities. c) Nuclear (top) and electronic (bottom) fluxes.

[1] Barth, I.; Hege, H.-Ch.; Ikeda, H.; Kenfack, A.; Koppitz, M.; Manz, J. Marquardt, F.; Paramanov, G.; *Chem. Phys. Lett.* **2009**, 481, 118