Wavelength dependent photochemistry via semiclassical dynamics

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Ab initio photodynamical simulations are gradually becoming a mature field, allowing for a routine simulations of light-induced processes in medium sized molecule. Theoretical treatment of photochemical reactions is typically based on semiclassical simulations, non-realistically assuming vertical promotion of initial vibrational wavefunction. Experimentally, molecules are typically excited with a light of a well defined wavelength. In fact, photochemistry is often controlled by the wavelength of light. For instance, molecules of photoswitches are able to change their conformation based on the light's energy, ultimately allowing us to control large molecular structures. Recently, there has been a Nobel price awarded for design of molecular machines, working on similar principle.
In this work, we show various applications of our new ground state nuclear density sampling method corresponding to a constant wavelength excitation. This method enables to generate structures from different regions of absorption spectra and thus to account for the experimental laser setup. We then proceed with subsequent semiclassical simulations, using methods like trajectory surface hopping (TSH) or Landau-Zener's (LZ) approach. Ultimately, we are able to interpret the results in terms of final quantum yields for various products.
So far, we were able to successfully apply this method to Freon-12 molecule[1] and faithfully reconstruct the experimental Cl fragment kinetic energy distributions. Currently, we explore so called photoinitiators - molecules, which create reactive species after interaction with light. Another task is to faithfully describe photochemistry of cyclopropanone. We discuss the difficulty of electronic structure calculations and the heavy influence of electron correlation.

References

1. J. Suchan, D. Hollas, B.F.E. Curchod and P. Slavíček, *Faraday Discuss.* **212** (2018), 307-330.