

Ab initio approach to UV spectra and photodynamics of small polyenes

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The UV spectra of *s-trans*-butadiene and *cis*- and *trans*-hexatriene in the 5-6 eV energy range are studied theoretically, by an ab initio quantum dynamical approach^[1,2]. They are known to be governed by the nonadiabatically coupled $1B_u$ ($1B_2$) and $2A_g$ ($2A_1$) excited states (symmetry labels in parentheses for the *cis* isomers), featuring a conical intersection^[3] of their potential energy surfaces (PES). These PES and their coupling elements are obtained from MS-CASPT2 computations using state-averaged orbitals and a cc-pVTZ basis set. Up to nine nonseparable nuclear degrees of freedom, represented by curvilinear internal coordinates, are included in the quantum dynamics computations (wave packet propagation). The latter rely on the *Multiconfiguration Time Dependent Hartree* (MCTDH) method as implemented in the Heidelberg MCTDH program package^[4]. As a result, not only the vibronic structure of the UV spectra, but also the electronic population transfer (internal conversion) between the coupled excited states is treated in a microscopic manner.

The vibronic structures of the UV spectra are well reproduced for all three systems^[1,2]. In particular the larger apparent widths of the butadiene spectral peaks as compared to hexatriene come out correctly in the computations, as well as the somewhat stronger vibrational excitation in the *cis*- as compared to the *trans*-hexatriene isomer. In all cases strong excitation of the CH₂ torsional motions is predicted which contributes to the large (apparent) widths, but is not resolved, partly due to finite experimental resolution and also due to lifetime broadening. The conical intersection leads to a $1B_u$ - $2A_g$ ($1B_2$ - $2A_1$) population transfer on a time scale of ~ 30 fs for butadiene^[1] and slightly slower (faster) for *trans*- (*cis*-)hexatriene^[2].

Ongoing calculations on all-*trans*-octatetraene reveal an interesting trend which may explain why this system displays fluorescence whereas the shorter polyenes are (largely or completely) non-emissive species.

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References:

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