High-level multireference ab initio theory applied to on-the-fly dynamics: the photochemistry of the C=C bond.

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The photochemical properties of π-systems are of fundamental chemical importance. A comprehensive, theoretical description encompasses several computational steps starting from the calculation of electronically excited states up to dynamics calculations. The computation of excited-state surfaces is particularly difficult since the required wave functions have a complicated (multireference) structure and conical intersection will occur, at which the fundament of the Born-Oppenheimer is breaking down. Quantum dynamics calculations are limited to the a few degrees of freedom and usually require the pre-computation of the energy surface. Alternatively, classical on-the-fly surface-hopping dynamics calculations can be performed.

In the present contribution the progress in terms of analytic multireference configuration interaction (MR-CI) gradients and nonadiabatic couplings based on the COLUMBUS program system will be shortly discussed. The results will be used to present the characteristics of the energy surfaces of ethylene and of a selected set of molecules containing polar C=C bonds (silaethylene, fluorethylene and formiminium cation). The latter is of interest since it is the smallest member of protonated Schiff bases. Nonadiabatic surface-hopping dynamics calculations based on the semiempirical AM1 method (including parameter fitting), CASSCF and MR-CI will be presented. The scope of extension to larger molecular systems will be discussed.