Ab initio simulation of time-resolved photoelectron spectra : a case study of $B_{2u}(\pi\pi^*)$-excited pyrazine

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Time-resolved photoelectron spectroscopy (TRPES) has proven to be one of the most convenient pump-probe techniques for monitoring the coupled nuclear and electronic molecular dynamics. [1] However, in order to take full advantage of it, the theoretical simulation and assignment of the TRPES spectra are needed.

In this work we present an efficient procedure for the calculation of TRPES signal within the classical doorway-window (DW) [2] formalism and apply it on the case of pyrazine molecule excited to $^1B_{2u}(\pi\pi^*)$ state by the pump pulse, for which the experimental TRPES has been recorded. [3] We have used already published ADC(2)-based surface hopping trajectories [4] to account for the post-pump nonadiabatic dynamics, but recalculated the ionization quantities (ionization energies and the Dyson orbitals) on the multireference XMS-CASPT2 level. Also, to obtain the photoionization cross sections and asymmetry parameters, we employed the static-exchange DFT to calculate the continuum orbitals in the radial B-spline basis. [5] The method yielded excellent agreement with the experiment, owing such efficacy to the combination of an accurate description of the photoionization continuum and multireference treatment of electronic bound states. Finally, to assign the spectrum in the terms of electronic characters being responsible for the appearance of observed spectral bands, we apply a simple spectral decomposition scheme based on the diabatization procedure.

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