TRPES as probe in pump-probe experiments

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Pump-Probe experiments are a very active research area in the femtosecond regime, and recently down to attosecond. Beside investigating photochemical processes of great chemical and biophysical relevance (e.g. the prototype mechanism of human vision), they offer unique insight into the nature of excited states, potential energy surfaces, and the coupled electron-nuclear dynamics which is at the forefront of current theoretical research.

Despite intensive research, one difficult point in such experiments is the probing of the time evolution of the wavepacket generated by the initial excitation. As long as one visualizes the evolution as semiclassical, i.e. a statistical mixture of electronic states at well defined nuclear geometries, ideally one should be able to identify at each time step the electronic state and the molecular geometry, as in a "molecular movie". Actually this goal is often more or less elusive, as current probes may afford ambiguous or inconclusive evidence, and refining the picture may require the merging of information coming from several techniques.

Here I want to concentrate on probing by time resolved photoelectron spectroscopy, TRPES. Photoelectron spectroscopy is an ultrafast technique, so of use in all time domains of interest, and it is an always open channel, if the probing photons have enough energy. It actually encompasses several observables, the ionization energies (the simplest), the intensities (cross sections), and the angular distributions, at various possible levels of detail.

We shall discuss the photoionization process and the relevant observables, and the theoretical approaches for their evaluation for fixed nuclear geometries and initial electronic state (generally excited) [1], and present a few examples.

[1] Aurora Ponzi, Marin Sapunar, Celestino Angeli, Renzo Cimiraglia, Nađa Došlić, and Piero Decleva "Photoionization of furan from the ground and excited electronic states", J. Chem. Phys., **144**, 084307 (2016)