

Unravelling the ultrafast non-adiabatic dynamics of acetylacetone with sub-20 fs UV-XUV photoelectron spectroscopy

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Photo-induced chemical reactions underpin numerous biologically and chemically fundamental processes [1]. Their investigation poses significant challenges in resolving experimentally the non-adiabatic wave-packet dynamics, which originate from the intricate interplay between vibrational and electronic degrees of freedom on ultrafast timescales. In this work we demonstrate how UV pump - XUV probe Time-Resolved Photoelectron Spectroscopy (TRPES) with sub-20 fs temporal resolution, in combination with high-level simulations, allows to track with unprecedented detail the non-adiabatic relaxation of a prototypical molecule, acetylacetone [2]. The photochemical reaction is initiated by sub-20 fs UV pump pulses (4.5 eV) and probed with few-femtosecond XUV pulses (39 eV photon energy), generated through high-order harmonic generation and spectrally selected using a time-delay compensated monochromator [3]. Photoelectron spectra are acquired as function of the UV-XUV delay with a Time-of-Flight spectrometer, yielding the spectrogram shown in Fig. 1(a).

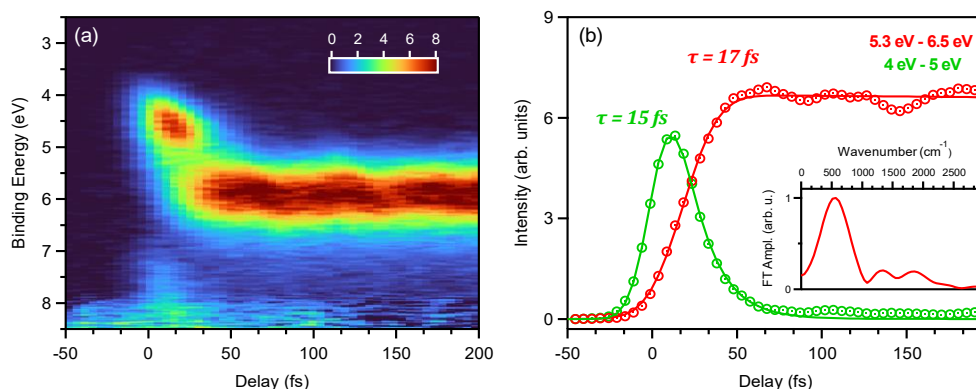


Fig. 1 (a): Experimental TRPES of acetylacetone excited by a sub-20 fs UV pulse and probed via an 8.5 fs XUV pulse. (b) Integrated signal between 4 eV and 5 eV (green) and between 5.3 eV and 6.5 eV (red); experimental data is shown as dots and fit results as solid lines. In the inset the Fourier Transform (FT) of the residual oscillations in the 5.3-6.5 eV dynamics showing the presence of vibrational coherence.

Upon UV-induced electronic excitation to the S2 state, the system undergoes a structural rearrangement within the first tens of femtoseconds, ultimately reaching the S2/S1 conical intersection. The extreme temporal resolution allows us to resolve for the first time the ultrashort lifetime of the S2 state (Fig. 1(b)) and to detect the coherent modulation of the signal during the first hundreds of femtoseconds of the dynamics (see inset Fig. 1(b)). The comparison of our results with molecular dynamics simulations provides insight on the electronic nature of the time and energy resolved signal and allows us to identify the coherently excited vibrational modes.

[1] W. Domcke and D. R. Yarkony, *Annu. Rev. Phys. Chem.* 63:325–52 (2012)

[2] R. J. Squibb et al., *Nat. Commun.* 9, 63 (2018).

[3] M. Lucchini et al., *Opt. Express* 26, 6771-6784 (2018).