

Sub-20-fs UV–XUV Beamline for Ultrafast Molecular Pump-Probe Spectroscopy

Stefano Severino^{1,*}, Lorenzo Mai¹, Aurora Crego^{2,3}, Fabio Medeghini¹, Federico Vismarra^{1,2}, Fabio Frassetto⁴, Luca Poletto⁴, Matteo Lucchini^{1,2}, Maurizio Reduzzi¹, Mauro Nisoli^{1,2} and Rocío Borrego-Varillas²

¹ Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

² Istituto di Fotonica e Nanotecnologie – CNR, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

³ Grupo de Investigación en Aplicaciones del Láser y Fotónica, Departamento de Física Aplicada, Universidad de Salamanca, 37008 Salamanca, Spain

⁴ Istituto di Fotonica e Nanotecnologie – CNR, via Trasea 7, 35131 Padova, Italy

Abstract. The experimental investigation of chemically and biologically relevant dynamics induced by visible or ultraviolet (UV) light requires high temporal resolution and spectroscopic techniques capable of resolving the complexity of these processes. Time-resolved photoelectron spectroscopy has proven to be a key tool for the study of these dynamics, but most studies have been conducted with a limited temporal resolution of about 100 fs. Furthermore, typical schemes employ a deep-UV probe, which limits the observations window and leads to spectrally congested traces. In this work, we present a UV pump – extreme-UV probe beamline with sub-20 fs temporal resolution, unambiguously characterized by an in-situ photoelectron cross-correlation measurement. As an example of the capability of the setup, we show a time-resolved investigation of the non-adiabatic dynamics of acetylacetone. The extreme temporal resolution allows us to resolve the passage through the first conical intersection and to identify the coherently excited vibrational modes.

1 Introduction

Photo-induced chemical reactions are at the basis of many biologically and chemically fundamental functions. The strong interplay between the vibrational and electronic degrees of freedom on ultrafast time scales (10-100 fs) that characterize the non-adiabatic dynamics involved poses great challenges to the experimental capability of resolving the wave-packet dynamics. Time-resolved photoelectron spectroscopy (TRPES) is a key tool for the investigation of these processes. In a typical TRPES experiment a pulse in the visible or ultraviolet (UV) range is used to resonantly excite the sample, while a probe pulse, typically lying in the deep-UV range, ionizes the photo-excited system. This scheme is typically limited by insufficient temporal resolution due to the challenges related to the generation of ultrashort UV pulses. Furthermore, employing UV probes reduces the observation window to the low binding energy electrons and leads to the generation of low-kinetic photoelectrons, which are subject to the influence of inelastic scattering. For these reasons, the combination of ultrashort UV and extreme-ultraviolet (XUV) pulses for TRPES attracts great interest in the scientific community.

In this work, we present a tuneable UV pump - XUV probe beamline with sub-20 fs temporal resolution. An in-situ photoelectron cross-correlation measurement allows to unambiguously characterize the instrument response

function (IRF) and to retrieve the temporal profiles of the pump and probe pulses. Finally, we present a time-resolved investigation of the prototypical non-adiabatic relaxation of acetylacetone (AcAc) to demonstrate the capabilities of the beamline to resolve ultrafast molecular dynamics.

2 Experimental Setup

UV pump pulses with energy up to 7 μ J were generated by frequency up-conversion [1] between sub-10 fs visible/IR pulses and narrowband pulses at 400 nm in a 25- μ m Type-I BBO crystal. This scheme allows to generate pulses spectrally tunable between 255 nm and 285 nm (Fig. 1(a)) The temporal durations are characterized through cross-correlation frequency-resolved optical gating measurements and result to be between 15 and 20 fs, depending on the central wavelength. The XUV line (probe pulses) consists of a time-delay compensated monochromator (TDCM) that enables the spectral selection of few-femtosecond XUV pulses between 20 eV and 45 eV, produced through high-harmonic generation, while preserving a sub-10-fs temporal duration [2, 3]. The UV pump and the XUV probe pulses are combined in the interaction region, where gas-phase samples are delivered. The photoelectrons generated from the UV-XUV interaction are collected by a time-of-flight (TOF) spectrometer,

* Corresponding author: stefano.severino@polimi.it

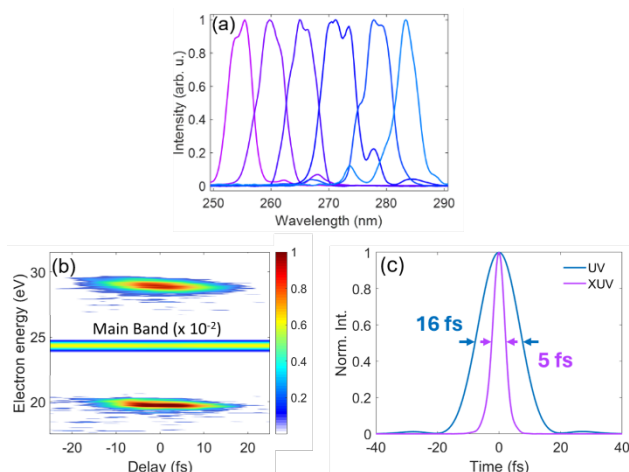


Fig. 1. (a) Spectral tunability of the UV pump pulses. (b) Experimental photoelectron trace reporting the sideband signals which originate from a two-colour, two-photon process in Ar. The amplitude of the main band originated from the XUV ionization is reduced for visualization purposes. (c) Temporal profiles of the pulses retrieved from the trace in (b).

allowing the acquisition of their spectrum as a function of the delay between the two beams.

3 Discussion

In order to obtain a reliable measurement of the temporal resolution of our beamline, an *in-situ* characterization of the IRF was performed by a two-colour photoelectron cross-correlation measurement in argon (Ar). Figure 1(b) shows the delay-dependent photoelectron trace obtained by ionizing Ar with a 40 eV probe, when the atomic states are dressed by a delayed UV pulse centred around 275 nm. The signal arising from XUV-UV photoionization, encompasses details about the spectral phases of both pulses. By means of the Simplified Trace Reconstruction In the Perturbative regime (STRIPe) [4], we fully characterize the temporal properties of both pulses and retrieve a duration of 16 fs for the UV pulses and 5 fs for the XUV pulses (see Fig. 1(c)) with a resulting IRF of ~20 fs.

We demonstrate the application of the beamline for the investigation of the non-adiabatic dynamics of AcAc [5]. The resulting spectrogram is shown in Fig. 2(a): the UV pump pulse induces an electronic excitation to the S₂ state (green), which decays on an ultrafast time scale and is followed by the rise of the S₁ state (red). Once excited, the molecule is driven to the S₂/S₁ passage by an ultrafast structural rearrangement which takes place in the first tens of femtoseconds. The extreme temporal resolution allows us to resolve for the first time ultrashort lifetime of 15 fs of the S₂ state (see Fig. 1(b)). Moreover, the signal of the S₁ state is characterized by periodic chemical shifts which can be interpreted as a signature of vibrational coherence (see inset Fig. 1(b)).

4 Conclusions

We have demonstrated a novel TRPES beamline that integrates UV and XUV pulses, offering spectral tunability for both pump and probe pulses, and exhibiting an IRF superior to 20 fs. Thanks to the temporal resolution of the beamline, it has been possible to resolve the ultrafast electronic and vibrational relaxation dynamics of AcAc with unprecedented detail compared to earlier studies of the same molecule [5, 6].

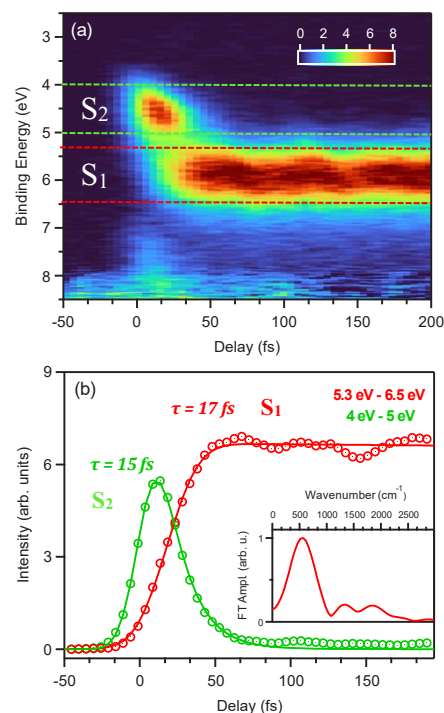


Fig. 2. (a): Experimental TRPES of acetylacetone excited by a UV pulse (4.5 eV photon energy) and probed via XUV pulse (39 eV photon energy). (b) Integrated signal between 4 eV and 5 eV (green, S₂ state) and between 5.3 eV and 6.5 eV (red, S₁ state); experimental data with dots and fit results with solid line. In the inset the Fourier Transform (FT) of the residual oscillations of the S₁ signal showing the presence of vibrational coherence.

References

1. R. Borrego-Varillas, et al., *Opt. Lett.* **39**, 3849-3852 (2014)
2. L. Poletto, et al., *Rev. Sci. Instrum.* **80**, 123109 (2009)
3. M. Lucchini, et al., *Opt. Express* **26**, 6771-6784 (2018)
4. G. L. Dolso, et al., *APL Photonics* **8**, 076101 (2023)
5. R. J. Squibb et al., *Nat. Commun.* **9**, 63 (2018)
6. A. Bhattacharjee et al., *J. Am. Chem. Soc.* **139**, 16576-16583 (2017).