Direct comparison of multi-photon and EUV single photon probing of molecular relaxation processes

T. J. A. Wolf[1,*), M. Koch[1,2,*), E. Sistrunk[1), J. Grilj[1,3), M. Gühr[1)

1) Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA
2) Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria, EU
3) Laboratoire de Spectroscopie Ultrarapide, Ecole Polytechnique Federale de Lausanne EPFL, 1015, Switzerland
*) These authors equally contributed to the current work.
E-mail: thomas.wolf@stanford.edu

Abstract: We present a new setup for time-resolved photoelectron and photoion spectroscopy allowing for single-photon EUV or multi-photon NIR ionization. Comparison of different probe schemes reveals disagreements shedding light on the underlying advantages of different probes.
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1. Introduction

Time-resolved photoelectron and photoion spectroscopy methods have proven to be a unique tool for investigating ultrafast processes in the excited states of organic molecules in the gas phase [1]. The method relies on probe photon energies overcoming the ionization potential of the molecular excited states. However, crystal-based frequency conversion techniques are limited to photon energies below 6 eV, which is often too low for a single-photon ionization process [2]. The problem can be circumvented by multi-photon ionization. In this case, care has to be taken not to cover the molecular response by implications from the probe process, as will be shown in the following.

With our recently completed setup [3], we pursue a different approach. We probe excited state molecular dynamics via single photon ionization by EUV pulses from high harmonic generation (HHG). The latter has been developed in the past years to a reliable and sufficiently intense source of ultrashort EUV light [4]. We are using the 9th harmonic (14 eV), providing sufficient photon energy to ionize most organic molecules even from their ground states. Careful separation of signatures of the dynamical response from static background is, however, necessary.

As a first sample we investigated the fluorescence dye perylene. Its first excited state (S_1) exhibits a lifetime of 5 ns [5] and its fluorescence spectrum shows a negligible Stokes-shift [6]. That makes it an ideal sample to compare results from different ionization mechanisms, since only weak or no intramolecular vibrational redistribution (IVR) are expected within the first picoseconds after photoexcitation.

2. Experimental

We use up to 4.5 mJ of a commercial Ti:Sapph 25 fs laser system for generation of EUV probe pulses. A comparably small pulse energy is available for pumping the sample via the second harmonic (400 nm). EUV probe pulses are produced in a HHG beamline which is described and characterized in Ref. [3]. We use the combination of an Indium filter and an MgF_2 coated aluminum mirror to select the 9th harmonic from the harmonic comb. By removing the indium filter from the beamline, samples can also be probed via multi-photon ionization at 800 nm. The focused pump and probe beams are temporally and spatially overlapped in the interaction region of the time-of-flight spectrometer chamber. The spectrometer can be operated in an ion and an electron mode. For the latter, a magnetic bottle scheme is used consisting of a permanent magnet and a solenoid around the spectrometer flight tube. For the ion mode a high voltage is applied to a repeller plate in front of the magnet. The spectrometer was calibrated in both modes with xenon. Samples can be evaporated into the interaction region by a capillary-oven described in detail elsewhere [7]. The time resolution is extracted from a pump-probe cross-correlation in perylene to be 70±10 fs and observed to be primarily dependent on the second harmonic pulse length.

3. Results and Discussion

Typical photoion spectra of perylene from *multi-photon ionization* at 800 nm with and without 400 nm pre-excitation into its first excited state (S_1) are shown in Fig. 1 a), top. The time dependence of ion counts at the mass peaks of the singly and doubly charged unfragmented perylene parent ions is depicted in Fig. 1 a), bottom. The time-dependent ion count shows an exponential decay by more than 50 % with a time constant of (1.1±0.1) ps to a level, which is stable for the rest of the investigated time-delay window (5 ps). This is in good agreement with earlier measurements of the internal vibrational redistribution (IVR) time scale in S_1 [8].

Figure 1 b), top, shows the *single-photon* photoelectron spectrum from ionization at 14 eV. Additionally, a typical transient difference photoelectron spectrum obtained by subtracting spectra at a positive time delay from those at -660 fs delay is depicted. It resembles a shift of the ground state spectrum by about the pump photon energy (3.1 eV,

400 nm), the zero-order expectation of the excited state photoelectron spectrum. To investigate the time-dependence of the transient spectrum we analyzed the peak integrals and positions at 8 and 10 eV kinetic energy, as marked by bars in Fig. 1 b), top. They do not show a time-dependent intensity change, broadening or peak shift as expected from the transient multi-photon photoionization data (see Fig. 1 b), bottom).
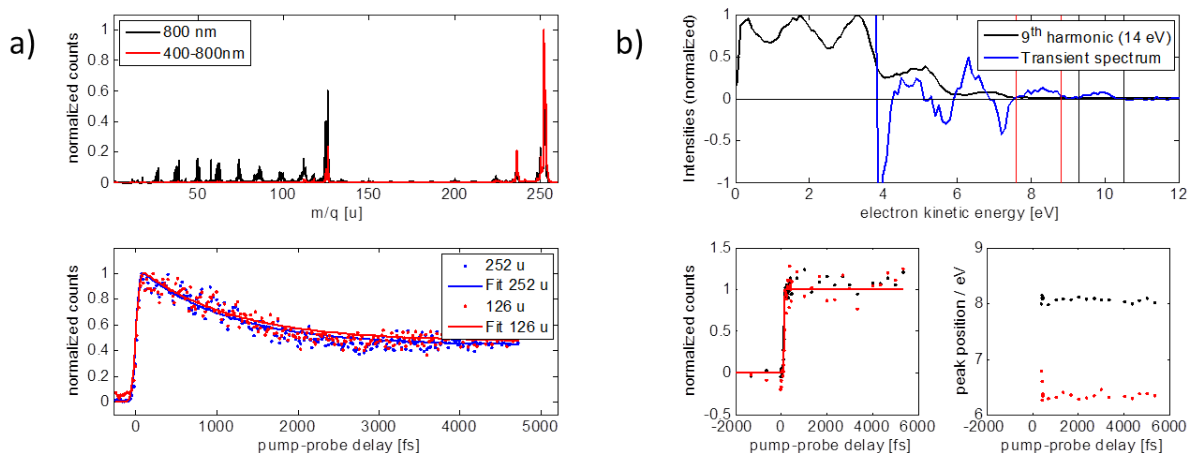

Figure 1: a)) Typical one-color 800 nm and two-color 400/800 nm photoion spectra of perylene (top) and their time-dependence (bottom) together with an errorfunction and exponential fit. b) 14 eV photoelectron spectrum together with the transient spectrum after pre-excitation at 400 nm (top) generated by substracting 400 nm/14 eV spectra with positive and negative delay times. In the latter spectra, slow photoelectrons were filtered out by applying a retardation voltage at the entrance of the flight tube. Additionally, the time dependence of the integrals and positions of the transient peaks around 8 and 10 eV is visualized (bottom left and right).

The disagreement between the two datasets can be assigned to the difference in the single-photon compared to the multi-photon probe processes. Since the S_0 and S_1 minimum geometries differ, the ultrafast excitation induces nuclear dynamics. The absence of dynamics in the 14 eV photoelectron spectra points to a constant ionization potential from S_1 to the cationic states over the geometry range from Franck-Condon region to S_1 minimum. For the multi-photon probes we observed intermediate resonant states, as verified by the intensity trend of the ion signal revealing a very low order of the probe process. A scan of the S_1 potential energy surface by TDDFT methods reveals that in contrast to the lowest cationic state these intermediate states experience a *considerable shift* in energy relative to S_1. This in turn strongly modulates the transition amplitude along the nuclear path in the S_1 state.

Thus, in this case, time-resolved photoion spectroscopy with multi-photon ionization reveals a more modulated information about the excited state processes of the sample than time-resolved single-photon photoelectron spectroscopy. However, one has to keep in mind that the additional observations are due to resonant intermediate states, which are often not very well known. In the case of perylene, the excited state dynamics is sufficiently simple. Multi-photon probe results from more complex molecules showing intersystem crossing or internal conversion need to be thoroughly checked for intermediate resonances modulating the multi-photon ionization.

4. References

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