

Time resolved photoelectron imaging with a XUV high harmonic generation source

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Introduction

New light sources, such as those based on free-electron laser (FEL) technology and high harmonic generation (HHG), provide access to femtosecond duration light pulses of high energy. A primary focus of the FEL community has been on the development of X-ray diffraction measurements that provide molecular movies of the dynamic molecular structure as a photochemical reaction proceeds. These measurements of the molecular structure only provide half of the picture required to truly understand the chemical process occurring, as they are insensitive to changes in the electronic structure which drive the dynamics and define the chemical bonding and stable structures. These new light sources also provide opportunities for new spectroscopic probes of chemical dynamics, with the XUV range particularly useful for the study of valence electronic structure through time resolved photoelectron spectroscopy (TRPES) measurements.

TRPES is a well-established technique in the UV and has become a major workhorse for the chemical dynamics community. The wide use of TRPES can be attributed to its sensitivity to both electronic and nuclear structure and also to its universal detection ability as all states can be ionized.¹ The universal detection is however often not achieved due to the limited energy range over which femtosecond laser sources can operate. If femtosecond XUV sources can be utilized in a TRPES experiment then it opens a new window into chemical dynamics and potentially provides a complete measure of the dynamic nuclear and electronic structure. Despite the obvious advantages of using an XUV probe for TRPES very few examples exist in the literature. Most XFEL sources work at higher energy than are required for TRPES studies of valence electrons and the relatively low flux attainable from HHG sources has limited what can be achieved. Here we report the first results of a series of experiments aimed at performing UV pump-XUV probe TRPES experiments on the photodissociation dynamics of CS₂.

Experiment

The experiment is schematically represented in Figure 1. An amplified femtosecond laser system (Red Dragon, KM labs) generates 800 nm light with a pulse energy of up to 11 mJ. The energy is split before compression to allow for independent tuning of the pump and probe pulse characteristics. The output of compressor one is used to generate the pump at 200 nm. This is achieved through sequential second harmonic and frequency mixing in BBO and generates approximately 1 μ J pulses at 200 nm. The probe is generated from the output of compressor two. The compressed 800 nm output is frequency doubled in BBO to generate approximately 0.5 mJ of 400 nm light. The 400 nm light is separated at a series of dielectric

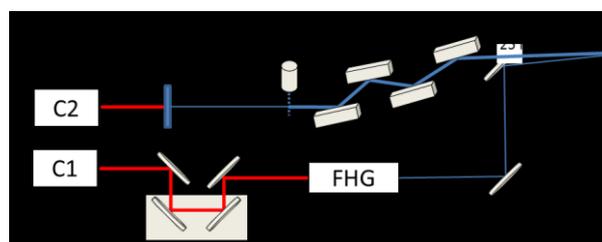


Figure 1. Schematic diagram of the experiment. The output of compressor 2 (C2) is frequency doubled in a BBO producing 0.5 mJ at 400 nm. The 400 nm light is focused in an argon jet produced by a pulsed nozzle (PN), generating high harmonics. The high harmonics are monochromated at a time preserving monochromator consisting of two toroidal mirrors (TM) and a grating (G). By tuning the grating angle the 7th harmonic is isolated and focused into the velocity-map imaging (VMI) spectrometer using a final toroidal mirror (TM). The probe beam is generated through fourth harmonic generation (FHG) of the output of compressor 1 (C1). The relative timing of the pump and probe is controlled by a mechanical translation stage delay line (DL) and is focused into the center of the VMI spectrometer, where it overlaps the isolated harmonic at a small angle and intersects the beam of CS₂.

mirrors before being tightly focused into an argon gas jet generating a series of odd harmonics. The harmonics are separated at a time preserving monochromator allowing for the isolation of the 5th harmonic at 15.5 eV. The isolated harmonic is refocused into the center of the interaction region of a velocity-map imaging spectrometer, where it is crossed at a small angle by the focused 200 nm beam. The choice of 400 nm as the driving field is due to the λ^{-6} efficiency scaling of HHG.² The shorter wavelength therefore provides a much higher intensity harmonic beam but at the expense of the maximum energy that can be achieved. This is controlled by the available ponderomotive potential, which has the opposite scaling with the maximum cut-off energy scaling as λ^2 . As we are interested in relatively low-energy harmonics the reduction in cut-off does not affect our choice of harmonic, as we still have sufficient energy to ionize all relevant ground and excited states. Spatial overlap of the VUV and UV beams is checked with a LuAG:Ce phosphorescent crystal placed at the interaction region and imaged with a CCD camera. The CS₂ molecular beam consists of 5% CS₂ in He which is expanded through a 1 kHz pulsed nozzle at 1 bar pressure. The central part of the resulting expansion passes through a 1 mm skimmer before entering the VMI spectrometer through a hole in the repeller.

The potentials relevant to the dissociation process are shown in Figure 2. Full details on the calculation of the potentials can be found in reference 3. The 200 nm pump pulse excites a vibrational wavepacket in the S₂ electronic state, which is then probed using a time delayed XUV pulse at 15.5 eV that ionizes the molecule. Dissociation products are subsequently detected in the VMI spectrometer. The resulting images are inverted

using the polar onion-peeling algorithm to obtain the photoelectron spectrum and associated angular distributions.

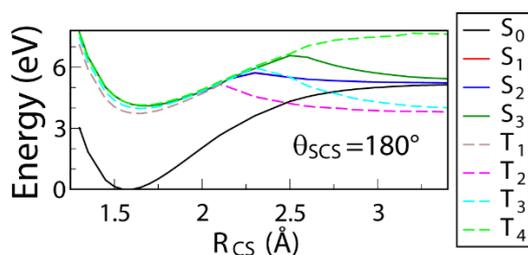


Figure 2. Ab-initio potentials for the CS₂ molecule at fixed SCS bond angle of 180°. Adapted from [3].

Results and Discussion

An example pump probe image is shown in figure 3 along with the resulting photoelectron spectrum. The spectrum shows three distinct peaks at 5.5 eV, 2.5 eV and 1 eV. The peaks at 5.5 eV and 1 eV are from the direct ionization of the CS₂ ground state into the X (²Π) and B (²Σ⁺) ion states, respectively. The peak at 2.5 eV contains contributions from the direct ionization into the A (²Π) ion state and from the two-photon ionization of CS₂ by the 200 nm pump into the X (²Π) ground ion state.

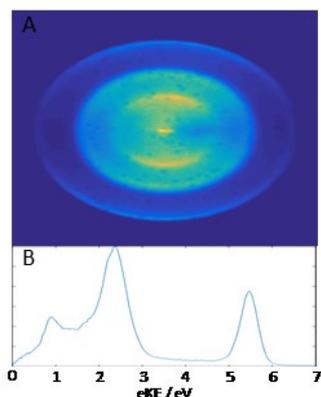


Figure 3. Photoelectron image (A) and spectrum (B) of CS₂ following excitation with UV (6.2 eV) and probing with XUV (15.5 eV) light.

The crossing angle and large acceptance volume of the VMI spectrometer mean that the pump-probe signal is very small compared with the overall signal from the XUV probe alone. This limited our analysis of the time resolved changes to the photoelectron spectrum as the low flux meant that reliable photoelectron angular distributions for the pump probe signal were not obtained.

Following UV excitation CS₂ dissociates to form CS molecule and atomic S in either the ¹D excited or ³P ground state. Despite being the spin forbidden process, at the excitation energy used in this experiment the dominant decay pathway leads to the ³P ground state product. None of the expected products are free from the ground state CS₂ background. The first peak overlaps with the low energy side of the peak at 5.5 eV. We therefore plot the integrated photoelectron intensity for the high and low energy side of this peak in figure 4. The traces show a depletion at time zero (pump and probe pulses overlap), corresponding to excitation from the ground state into the S₂ excited state and a delayed recovery. This is more pronounced on the side where the signal associated with the S ³P dissociation product should be observed. We fit this trace to a kinetic model that includes the ground state depletion and S production. Based on the width of the peaks we believe that the recovery seen on both sides of the peak correspond to the S production, but as we are unable to resolve this it could also be due to some ground state recovery. We feel the second explanation is less likely due to previous measurements not observing such a process with any

appreciable quantum yield.⁴⁻⁸ We fit the data using a simplified kinetic model that takes into account the ground state depletion and assumes the formation of the S fragment is the result of a single process resulting from the decay of the initially excited state. This gives an effective dissociation lifetime, which will be a combination of the decay constants for the initially excited and any subsequently populated (triplet) states involved in the dissociation. The resulting fits can be seen as solid lines in figure 4 and provide a dissociation lifetime of 800 fs. This is in good agreement with previous experiments and the measured lifetime of the singlet excited state.^{4,5,8}

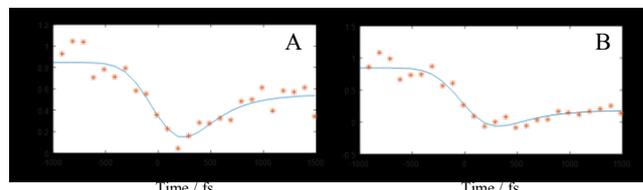


Figure 4. Integrated signal between 5-5.5 eV(A) and between 5.5-6 eV (B) photoelectron kinetic energy. The solid lines are fits to the data with a simplified kinetic model (see text for details).

Conclusions

These results highlight the potential of HHG sources for mapping chemical dynamics, but also the potential problems with such measurements and the need for a highly optimized experimental configuration. Through the continued development of the XUV source and molecular beam source high quality photoelectron images can now be obtained from molecular systems. The high collection efficiency and large acceptance area of the VMI spectrometer significantly helps in this regard. However, it also represents a major limitation. Recombination of the XUV and UV pulses requires a small angle between them, which limits the region over which they overlap. When combined with the low levels of population transfer that are common in UV excitation steps, typically <10 %, this means that the pump probe signal is within a large XUV-only background. The pump-probe signal is therefore often on the order of 1% and requires a highly stable laser source and low noise detection to obtain appreciable signal levels. Improvements in the experimental geometry to reduce the crossing angle further would improve this significantly. Restriction of the acceptance volume would also aid in this regard. Despite this limitation we have demonstrated the potential to obtain pump probe photoelectron images with a HHG XUV source. From the experiments we have obtained a dissociation lifetime of 800 fs for the dominant dissociation pathway into the CS and S ground state.

Acknowledgements

All authors thank the STFC for access to the Artemis facility (app. number 13220015). RSM thanks the Royal Society for a University Research Fellowship (UF100047). AK and RSM thank the Leverhulme trust for research support and for ADS's studentship (RPG-2013-365). HMW thanks the Central Laser Facility and Chemistry at the University of Southampton for a studentship. EJ thanks Chemistry at the University of Southampton for a studentship. We also acknowledge funding from the EC's Seventh Framework Programme (LASERLAB-EUROPE, grant agreement no 228334). We thank Phil Rice for technical assistance. This work has been supported by the excellence cluster "The Hamburg Center for Ultrafast Imaging - Structure, Dynamics and Control of Matter at the Atomic Scale" of the Deutsche Forschungsgemeinschaft (CUI, DFG-EXC1074). D.A.H. was supported by the European Research Council through the Consolidator Grant Küpper-614507-COMOTION. AK acknowledges funding from the European Union (FP7-PEOPLE-2013-CIG-NEWLIGHT). DB acknowledges a PhD studentship from the University of Edinburgh. The computational work reported used the

ARCHER UK National Supercomputing Service (<http://www.archer.ac.uk>) and the Edinburgh Compute and Data Facility (ECDF) (<http://www.ecdf.ed.ac.uk>). DB thanks Sebastian Mai (Wien) for helpful discussions.

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