

Observing the complete reaction pathway of CS₂ dissociation

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Introduction

Much of our current understanding of chemical dynamics relies on carefully applied assumptions, most famously the Born-Oppenheimer approximation, which allows us to disentangle the motion of electrons and nuclei from each other. Photochemistry, however, occurs on timescales too fast for those assumptions to stand. As a result, even relatively small and structurally simple molecules, when treated with light, undergo a complex cascade of competing processes and pass through a large number of electronic states of near-identical energy. This is a case for CS₂, whose dynamics of dissociation by ultraviolet light have for long baffled the scientists. This reaction produces two spin states of a sulphur atom: spin-allowed singlet and spin-forbidden triplet. Surprisingly, the spin-forbidden product is dominant in the dissociation yield. To provide a satisfactory explanation, it is necessary to monitor the complete reaction pathway – a partial observation may lead to the omission of key steps in the mechanism. In Figure 1, CLF's artist-in-residence suggests an excellent metaphor to this situation: imagine a World Championships race transmission. Three athletes can be seen at the start line, but then the connection snaps and the next picture shown is just one contestant finishing the competition. Without the middle scenes, it is unclear what happened; moreover, would anyone believe that the broadcast was not manipulated?

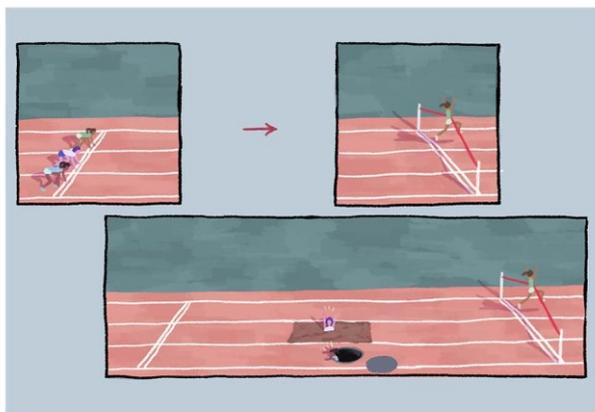


Figure 1. An artist's impression of the reported study's meaning and significance: if one only snapshots the beginning and the end of the reaction (here metaphorically depicted as a race), one is liable to miss the crucial events happening in-between, and misinterpret the entire situation. Courtesy of Helen Towrie, CLF.

For most experimental methods, recording the entire race is difficult - the required time resolution to observe both electronic and nuclear structure motion comes at the cost of the probe

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energy. Consequently, the changes in some of the high-lying excited states remain obscure. Time-resolved photoelectron spectroscopy (TR-PES) is a well-established and widely used technique in the UV spectral region, owing to its sensitivity to coupled electronic and nuclear dynamics, as well as low noise data collection. On top of that, extending the probe energies to extreme UV (XUV) region via the process of high harmonic generation (HHG) gives it a virtually universal ability to access excited states.¹ In the reported experiment, we use a tabletop femtosecond laser source and HHG to perform UV-XUV pump-probe measurements of CS₂ dissociation dynamics. This way, we are able to follow the complete path of this reaction and infer its full mechanism.

Experiment

The layout of the experiment is schematically represented in Figure 2. A femtosecond chirped pulse amplification system (Red Dragon, KMLabs) generates 30 fs pulses centered around 800 nm. At repetition rate of 1 kHz, pulse energy reaches up to 11 mJ. This 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 frequency doubling and two stages of sum frequency generation in BBO. Approximately 1 μJ of pulse energy is available at 200 nm.

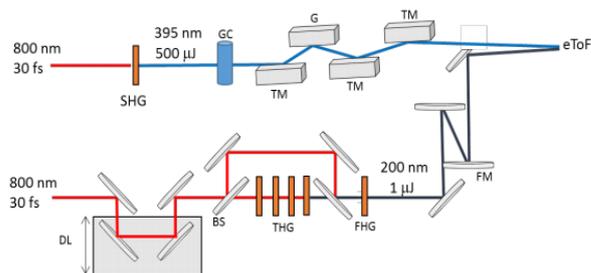


Figure 2. Schematic diagram of the experiment. The output of compressor 2 (top red beam) is frequency doubled in a BBO producing 0.5 mJ at 400 nm (blue beam). The 400 nm light is focused in an argon jet (GJ), generating high harmonics, which are in turn sent through a time preserving monochromator consisting of two torroidal mirrors (TM) and a grating (G). By tuning the grating angle the 7th harmonic is isolated and focused into the electron time-of-flight (eToF) spectrometer using a final torroidal mirror (TM). The probe beam is generated through fourth harmonic generation (FHG) of the output of compressor 1 (bottom red beam). 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 eToF spectrometer, where it overlaps the isolated harmonic at a small angle and intersects the beam of CS₂. Adapted from [2].

The probe is produced from the output of compressor two. The compressed 800 nm output undergoes second harmonic generation in BBO, yielding approximately 0.5 mJ of 400 nm light. The 400 nm light is then separated from the residual fundamental beam at a series of dielectric mirrors before being tightly focused into an argon gas jet generating a series of odd harmonics. The harmonics are passed through a time preserving monochromator, separating the 7th harmonic at 21.6 eV. The isolated harmonic is refocused into the center of the interaction region of an electron time-of-flight spectrometer, where it is crossed at a small angle by the focused 200 nm beam. Using 400 nm driving field allows for a higher harmonic flux (approximately 10^{10} photons per second on target) due to the λ^{-6} efficiency scaling of HHG.³ On the other hand, the maximum energy that can be achieved is controlled by the available ponderomotive potential, which has the opposite scaling of λ^2 . For the purposes of the reported experiment, relatively low energy is sufficient to ionize all relevant ground and excited states, and so the reduction in cut-off does not affect our choice of harmonic. 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 2% CS₂ in He which is expanded through a 1 kHz pulsed nozzle at 1 bar pressure. The central part of the resulting expansion is passed through a skimmer before entering the interaction chamber.

A mechanical translation stage is used to vary the optical path length of the pump beam, which controls the relative pump-probe delay. The stage moves through a series of positions corresponding to the delays between -2 and 10 ps. At each time step within a cycle, a spectrum from 1000 laser pulses is collected. In order to average out any long term power fluctuations, 650 cycles are performed per delay scan, giving approximately 13 hour of data collection.

The assignment of measured spectral features analysis is based on known ionization limits and previous static photoelectron spectroscopy results from He-I radiation sources,^{4,5} aided by *ab initio* calculations.

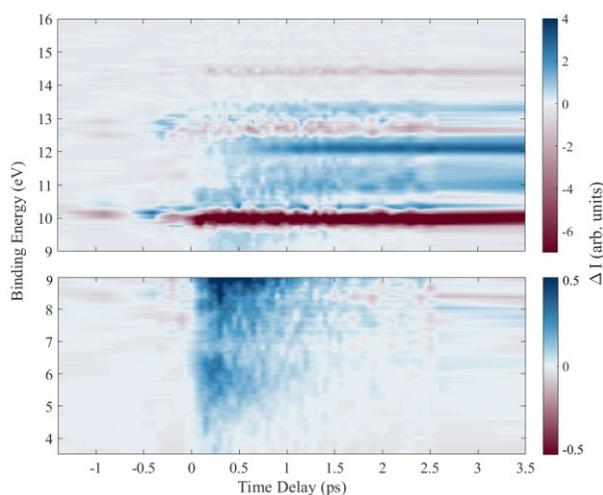
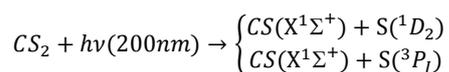


Figure 3. Pump-probe background-subtracted photoelectron spectrum. Dark red regions correspond to ground-state bleaching, whereas blue areas represent the new species produced over the course of the reaction. Adapted from [2].

Results and Discussion

Upon irradiation with 200 nm pump pulse, CS₂ is excited from the ground state of X¹Σ⁺ into the X (²Π) and B (²Σ⁺) ion states. Subsequently, the ion dissociates to form CS molecule and atomic S in either the ¹D excited or ³P ground state:



The dynamics following the UV excitation are shaped by the competition between dissociation through a singlet channel, rapid internal conversion (IC) and intersystem crossing (ISC).⁶

Figure 3 shows the pump-probe photoelectron spectrum for this reaction. At the early stages of the reaction, features due to the excited CS₂ singlet and triplet states can be seen at lower binding energies. These are very broad as their ionization energy strongly depends on the molecular geometry.⁷ The later times, the spectrum is dominated by the ground-state CS(X¹Σ⁺) fragment, ground (³P) and excited (¹D) state sulphur atoms.

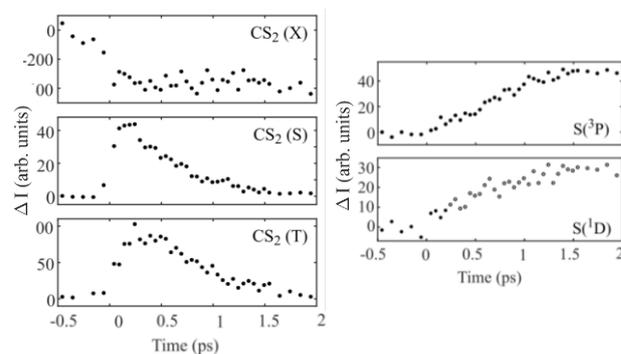


Figure 4. Integrated electron count over energy regions correlating with specific states in the dynamic process. Left-hand-side panels show the decay of ground (X) and excited (S, T) states of CS₂ molecule, while right-hand-side panels illustrate the increase in population of dissociation products. Adapted from [2].

In order to uncover the lifetimes of the aforementioned species, the selected regions of the full time-resolved spectrum are then integrated and plotted against time, as depicted in Figure 4. We then fit the data according to a kinetic model which considers each of the chemical species present in the reaction separately, and includes convolution with the instrument response function. In this way, we are able to track the changing populations of all the states involved throughout the whole course of the reaction. For the details on the mechanism we propose, please consult the recent PRL article.²

Conclusions

The study demonstrates the suitability of tabletop HHG sources for observing the competing processes leading to dissociation of CS₂ molecule, initiated by irradiation by UV light. Femtosecond time resolution combined with high-energy probe allows us to monitor the evolution of all species involved in the reaction simultaneously. These measurements highlight the importance of studying the entire reaction pathways, and thus mark a beginning of a development of a global experimental and theoretical analysis procedure for photochemical reactions, which integrates calculations of complete dynamical traces with the photoionization spectra.

Acknowledgements

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