

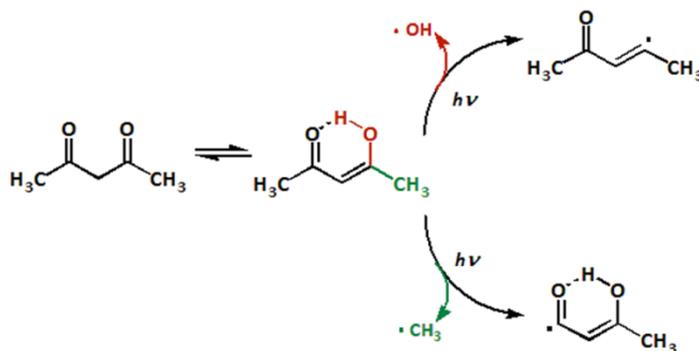
Molecular dynamics on the femtosecond timescale: a closer look at photochemical reactions

The photodynamics of a prototypical system, acetylacetone, have been revealed in unprecedented detail using the FERMI seeded free-electron laser source with a special electron and ion spectrometer, paving the way for deeper investigations of photochemical processes.

The first steps in photochemical processes involve changes in electronic and geometric structure on extremely short timescales. Thanks to an experimental setup unique in the world and the support of advanced molecular dynamics calculations, a team of researchers from the Universities of Uppsala and Gothenburg, Sweden, the Institut Ruđer Bošković, Zagreb, Croatia, the Elettra-FERMI laboratory and the University of Trieste, Italy, the Laboratory of Chemical Physics, Matter and Radiation, Paris, France and the Physical and Theoretical Chemistry Laboratory, University of Oxford, UK has shed light on the very fast dynamics of acetylacetone after photoabsorption.

The combination of intensity, energy resolution and very short pulse duration of the FERMI seeded free-electron laser source recently build at the Elettra laboratory near Trieste, Italy, can now provide exceptionally detailed information on photoexcitation-deexcitation and fragmentation processes of isolated molecules in pump-probe experiments on the 50-femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$) time scale. Photoionization is used to probe the course of reactions, using a magnetic bottle spectrometer for both ions and electrons, used first in the Oxford Chemistry department and developed further in the Physics Department of the University of Gothenburg.

Acetylacetone is a stable molecule used as solvent or as chelating agent with potential environmental and medical applications. The chemical formula and possible fragmentation pathways are shown in Figure 1.



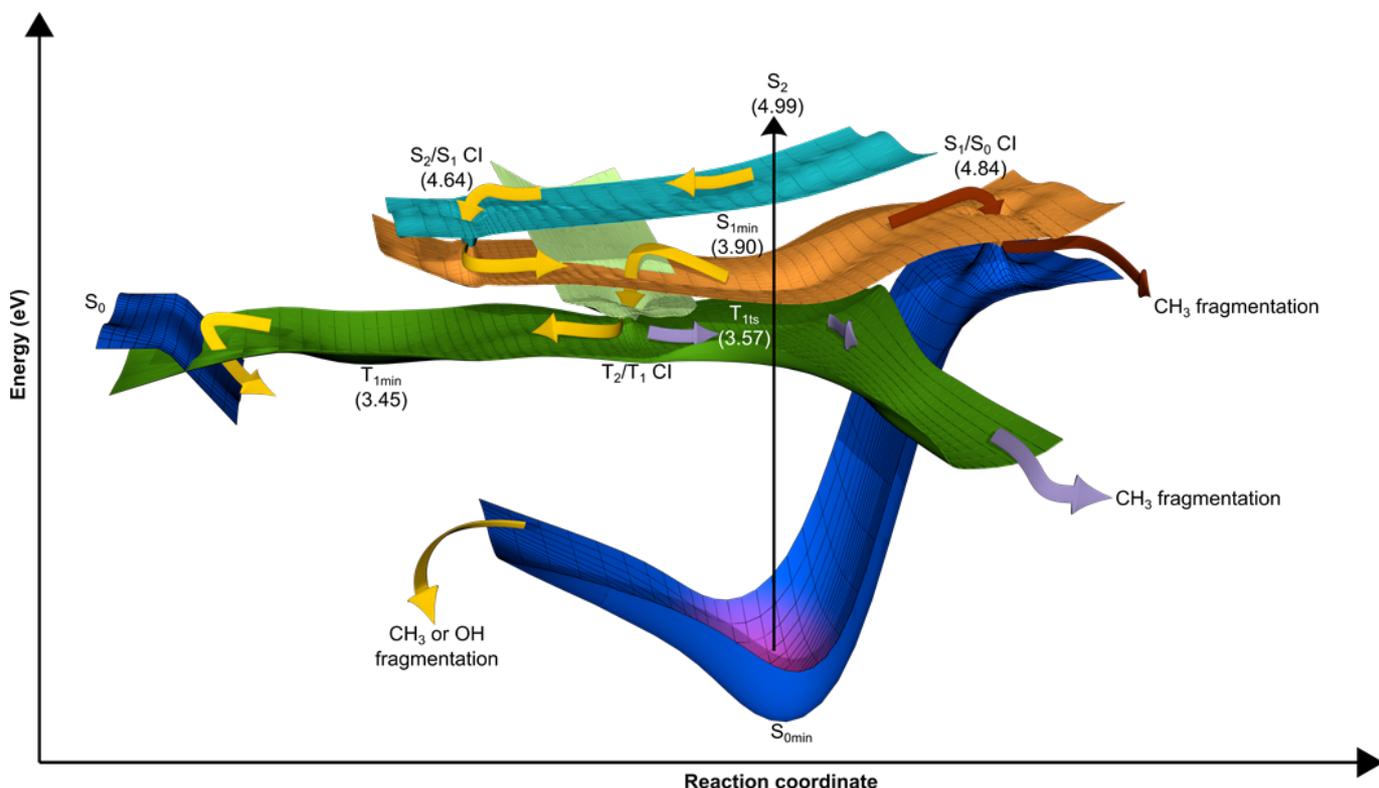
When it absorbs a photon which promotes one valence electron to an empty molecular orbital, this system undergoes a series of fast rearrangements, implying very rapid changes of electronic and geometric structure, on a timescale of tens of femtoseconds.

In the experiment, the molecule has been excited with an optical laser of 261 nm ($1 \text{ nm} = 10^{-9} \text{ m}$) wavelength (the so-called pump), and the evolution of the system has been followed by ionizing the photoexcited species created that way by a 19.23 eV photon beam from the FERMI free-electron laser (the so-called probe) with varying time delays (from zero to 2,000 fs) between the pump and the probe. In this way, several photoexcited species have been characterized by valence photoelectron spectroscopy, ion spectroscopy and molecular dynamics calculations.

In more detail, a clear picture of the evolution of the system is reached, showing that the photoexcitation from the S_0 (ground state) to the S_2 ($\pi\pi^*$) (bright) state is followed by a conical

intersection connecting with the S_1 ($n\pi^*$) (dark) state, and then the T_1 ($\pi\pi^*$) state is reached through ultrafast S_1 ($n\pi^*$)/ T_2 ($n\pi^*$) crossing which is immediately followed by internal conversion to T_1 ($\pi\pi^*$). A minor pathway leading back to the ground state is also identified. Observed fragmentation yielding CH_x species is related to the onset of the T_1 ($\pi\pi^*$) state formation.

A schematic view of the photoexcitation-relaxation mechanism and of the potential surfaces of all ground and excited states is shown in Figure 2.



This approach based on high-resolution valence spectra backed by high-level calculations is the ultimate way to shed light on fundamental, basic photo processes such as photosynthesis, photovoltaic energy production, and vision.

Bibliography

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