

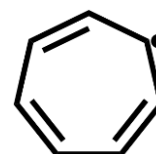
MOLIM STSM report

on the experiments conducted at the CEA Saclay du 20/03 – 28/04/2017

Understanding the excited-state dynamics of reactive intermediates is necessary as to correctly model their role in combustion processes. During the research stay in Saclay the excited-state dynamics of two reactive intermediates, the troyl radical and *para*-xylylene were examined in the gas phase using fs- pump-probe spectroscopy. Produced via pyrolysis from a suitable precursor, both reactive intermediates were excited with 266 nm and ionized with either 800 or 400 nm. The resulting charged particles were detected and time-resolved time-of-flight mass spectra, ion images and photoelectron images were recorded.

Troyl radical:

The troyl radical, C_7H_7 , is a fascinating structure. As a radical it is non-aromatic (7π -electrons=), in contrast to the cation (6π -electrons), hence its very low ionization energy ($IE=6.23$ eV). Its electronic states are also Jahn-Teller distorted, therefore the interpretation of the experimental data is expected to be challenging.



Excited with 266 nm and probed with 800 nm, it shows a short mono-exponential decay. The photoelectron spectrum shows three broad bands, all issued from a $[1+2']$, which all decay within the same time. (see fig. 1)

Probed with 400 nm, the decay of the troyl radical shortens substantially, even though the same amount of energy is deposited in the molecule. This was deduced from the photoelectron spectrum, which shows one broad unstructured band issued from a $[1+1']$ process. The interpretation of this phenomenon is not straightforward. With 800 nm the troyl radical is probably ionized passing via intermediate resonances of Rydberg states, which allows detecting lower-lying electronic states. But the electronic states of the troyl radical are not well-known, making an interpretation difficult.

Therefore collaboration with the theoretical chemistry group of Roland Mitric (Würzburg) is in process, and if the resulting calculations permit a convincing interpretation, a joint paper on the troyl radical will be published.

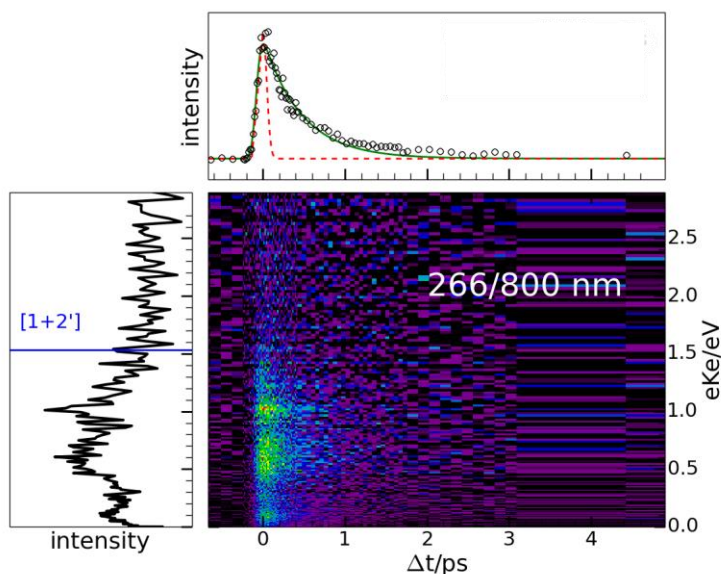
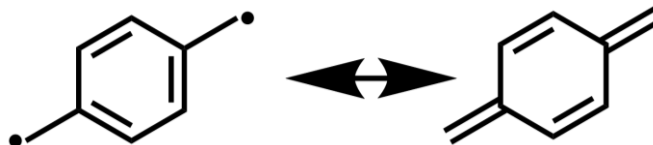


Figure 1: Photoelectron spectrum of the troyl radical with 266 nm pump and 800 nm probe pulse. The left panel corresponds to the summed photoelectron spectrum over all times, the upper panel to the total photoelectron decay.

Para-xylylene:

Para-xylylene can be formulated as a biradical, but its predominant structure is the quinone structure.



Pumped with 266 nm in the S_2 -state and ionized with 800 nm multi-photon probe, the time-resolved mass spectrum of *para*-xylylene is dominated by $m/z=104$ (*para*-xylylene), but two other masses, $m/z=78$ (most likely benzene) and $m/z=103$ (loss of a hydrogen of *para*-xylylene) are still discernible. These two fragments are not pyrolysis byproducts, but are fragments of *para*-xylylene. Whereas *para*-xylylene shows a bi-exponential decay ($S_2 \xrightarrow{\tau_1} S_1 \xrightarrow{\tau_2} GS$), the two fragments reflect the population of state S_1 (see fig. 2). The same mechanism is also visible with 400 nm probe, but less clearly due to an inferior S/N ratio. The time-resolved photoelectron spectra are very similar for both probe wavelengths, showing a broad band with three (four) discernable peaks. Just as for the tropyli radical, a collaboration with the theoretical chemistry group of Roland Mitric is under way to simulate the dynamics of the *para*-xylylene. With the support of these theoretical data an article on the biradical *para*-xylylene will be published, probably end of 2017.

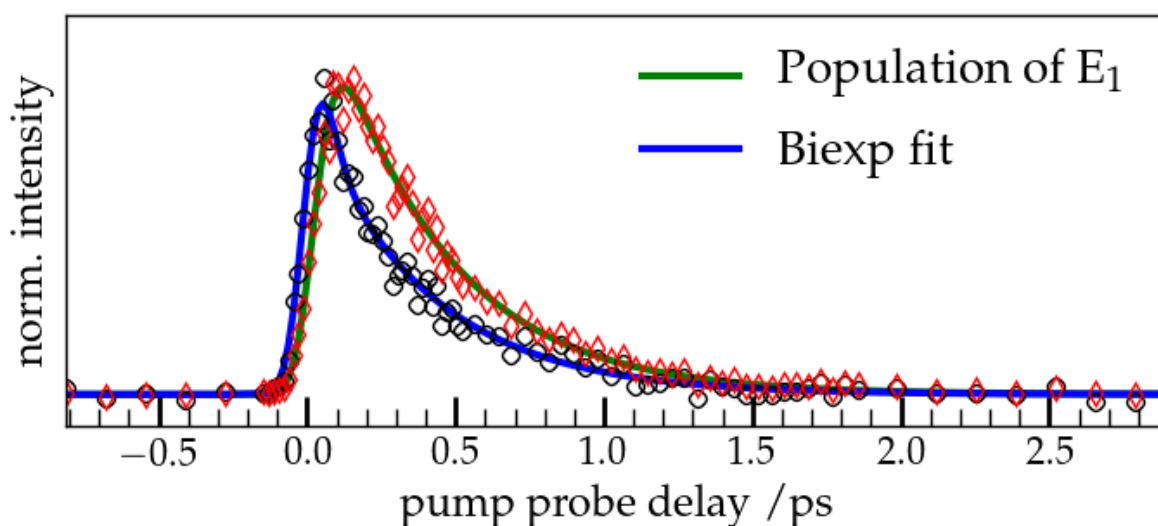


Figure 2: Mass spectra decay of *para*-xylylene (black circles) and $m/z=103$ (red diamonds). The *para*-xylylene signal is well reproduced with a biexponential sequential fit ($S_2 \xrightarrow{\tau_1} S_1 \xrightarrow{\tau_2} GS$), $m/z=103$ reflects perfectly the population of the state S_1 .