Time-resolved resonance Raman structural investigation of short-lived chemical intermediates in solution

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In the last decades, time-resolved spectroscopy has played a crucial role in the understanding of ultrafast photochemical and photophysical processes in condensed phase. Transient absorption and emission spectroscopies, which are the most widely used techniques, provide real time information on the dynamics of the transient species (excited states, reactive intermediates) involved in photochemical reactions with a very high time-resolution. Unfortunately, the geometrical structure and electronic configuration characterization of these transients is difficult with these techniques due to their lack of spectral resolution in condensed phase. Nevertheless, the transient molecular geometry of chemical intermediates is a key parameter that greatly influences the evolution of the chemical reaction. Therefore, obtaining quantitative information on the transient structure of reactive intermediates is a fundamental aspect of the research on reaction mechanisms which justifies the efforts made to develop complementary techniques able to provide time-resolved structural information in condensed phase. Time-resolved X-ray diffraction techniques which are currently still under development have already proved their large potential to reach this goal with a time resolution that is increasing rapidly. Nevertheless, the geometrical determination of short-lived transient species at low concentration in solution cannot be achieved with these techniques due to a lack of sensitivity. In this context, time-resolved vibrational spectroscopies are alternative methods combining high temporal resolution with rich vibrational specificity that can provide information on the structural modifications of the reactants all along the reaction pathway. In Particular, Time-Resolved Resonance Raman Spectroscopy (TRRRS) that presents high sensitivity and high structural specificity allows one to record vibrational spectra of species with lifetime as short as few picoseconds and with concentration as low as 10^{-4} and 10^{-8}M. From these spectra, detailed information on the electronic configuration and geometrical structure of the transient species can be obtained with the help of quantum chemical calculation.

We will report in this talk some results about the complete structural determination of short-lived excited states and reactive intermediates in solution obtained by TRRRS combined with quantum chemical calculations for different aromatic photochemical systems.