

## ELECTRONIC RELAXATION OF THE PHENYLALANINE RESIDUE IN GAS PHASE PEPTIDES: ROLE OF THE NEIGHBOURING AMIDE GROUPS IN THE PHOTOPHYSICS

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Protein absorption in the near UV is mainly due to the presence of aromatic systems on the side chain of three residues: phenylalanine, tryptophan and tyrosine. It is generally expected that the photophysics of these UV chromophores depends on their immediate environment within the molecule and thus on the conformation of these flexible molecules. This property may in particular be used as an optical diagnostic of the conformational state of the peptide chain.

The structure of peptide chains isolated in the gas phase can be characterized by UV and IR laser spectroscopy<sup>a</sup>. These measurements allow us to distinguish the spectral contributions of the different conformers and thus provide us with an elegant way to address the issue of the conformational dependence on the photophysics. For this purpose, the dynamics of relaxation of the  $\pi\pi^*$  excited state of several peptides containing a phenylalanine residue have been studied using two-colour resonant two-photon ionization (2C-R2PI) in the ns time scale at CEA and ps at CLUPS and laser-induced fluorescence as well. The lifetime of the  $\pi\pi^*$  excited state is found to strongly depend on the conformation adopted by the molecule and on the excess energy in the excited state, with measured lifetimes ranging from 1 ns to 80 ns.

The nature of the end caps of the phenylalanine residue (Ac-Phe-NH<sub>2</sub> vs. Ac-Phe-NHMe) or the deuteration of the amide groups induce different behaviours. The substitution of some atoms of the molecule provide additional information on their role in the relaxation dynamics and can be used to tell which relaxation pathways found by quantum chemistry calculations are compatible with the experiments. The first results suggest the occurrence of a conical intersection between the excited  $\pi\pi^*$  state and backbone local excitation states.

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<sup>a</sup>W. Chin; F. Piuze; I. Dimicoli and M. Mons, *Phys. Chem. Chem. Phys.*, 8, pp 1033-1048 (2006)