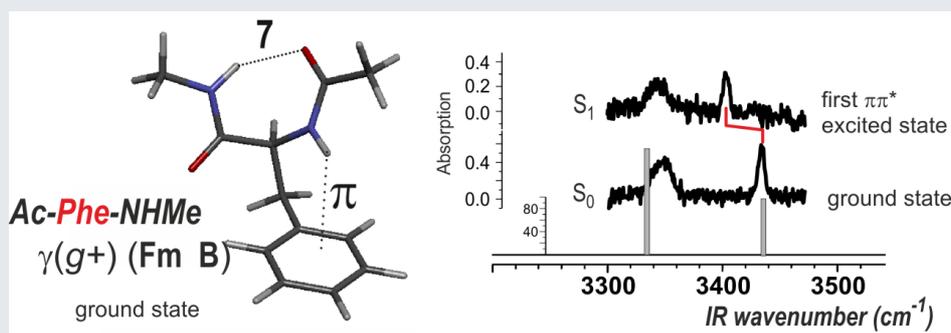


How does a UV excitation modify the structure of a flexible biomolecule?

Valérie Brenner, Eric Gloaguen, Michel Mons, Lionel Poisson, Woon Yong Sohn (LIDYL).

Absorption of UV radiation by flexible biomolecules, such as proteins or peptides, brings them into excited electronic states, which significantly modifies the interactions at play within these molecules and therefore their structure. IR spectroscopy is a tool of choice for characterizing H-bonds within a biomolecule, especially because these bonds control their shape and their structure. The joint use of UV and IR lasers even makes it possible to record conformation-selective IR spectroscopy, providing an elegant access to the structure of each conformation. The IR / UV spectroscopic technique, commonly used to document the structure of jet-cooled molecules in their ground state, has been extended to excited states, whose IR spectrum is obtained by a UV / IR / UV laser excitation scheme coupled with an ion detection by mass spectrometry. The comparison of the IR spectra of the ground state and the electronic state makes it possible to assess the modification of the structure of each conformation upon electronic excitation. The red shift of the frequency of the elongation vibration of an NH bond in a model peptide (Figure) upon excitation will indicate an enhancement of the interaction in the excited state. These precise spectroscopic data are references of choice for evaluating performances of the theoretical methods used to model these systems, notably in the excited state.



Left: structure of the $\gamma(g+)$ conformation of the phenylalanine dipeptide, stabilized by γ and π H-bonds. Right: the IR spectra of the ground (S_0) and first excited (S_1) states obtained by IR/UV and UV/IR/UV photonisation schemes. The highest frequency of the IR spectrum corresponds to the elongation motion of the NH bond involved in a π H-bond with the π electron density of the phenyl ring. Its red shift upon UV excitation (red line) indicates a stronger interaction in the S_1 state.

W. Yong Sohn, V. Brenner, E. Gloaguen, M. Mons, *Local NH- π interactions involving aromatic residues of proteins: influence of backbone conformation and $\pi\pi^*$ excitation on the π H-bond strength, as revealed from studies of isolated model peptides*, Physical Chemistry Chemical Physics 18, 29969 (2016)

Résultats obtenus dans le cadre du projet DIRCOS financé par le thème 3 du LabEx PALM et porté par Lionel Poisson (LIDYL).