GAS PHASE HYDRATION OF MODEL PEPTIDE CHAINS: FAR/MID INFRARED SIGNATURE OF WATER INTER-MOLECULAR MOTIONS IN THE MONOHYDRATE

M. CIRTOG, Y. LOQUAIS, V. BRENNER, B. TARDIVEL, M. MONS, *CEA, IRAMIS, SPAM, Lab. Francis Perrin, URA 2453, F-91191, Gif-sur-Yvette, France*; E. GLOAGUEN, *CNRS, INC & INP, Lab. Francis Perrin, URA 2453, F-91191, Gif-sur-Yvette, France*; A. M. RIJS, *Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 7, 6525 ED Nijmegen, the Netherlands*.

The far/mid infrared region (100 - 800 cm^{-1}) of two hydrated conformations of the model peptide chain N-acetyl-phenylalanine-amide (Ac-Phe-NH_2) have been investigated in a supersonic jet expansion by conformational selective double-resonance IR/UV spectroscopy, using the free electron laser FELIX for the far IR tunability. The two folded conformations (identified in a previous work[a]) share the same H-bonding network, with the water molecule bridging the peptide ends as a donor and acceptor but differ by the orientation of the free hydrogen. By comparison with the isolated peptide, hydration gives rise to new spectroscopic features locate in three different spectral regions namely around 160, 400 and 600 cm^{-1}. The analysis of a series of quantum chemical harmonic frequency calculations using various approaches (DFT and DFT-D) suggests that this spectral region constitutes a real challenge to the theory. As expected, the low frequency modes present a strong anharmonicity[b] and sensitivity to the position of the water molecule. It has nevertheless allowed us to assign the new experimental signatures to a direct excitation of normal modes widely involving intermolecular libration and wagging motions of the water molecule in the complex, and revealed an extended coupling with the peptide backbone deformation motions.

[a] H.S. Biswal, Y. Loquais, B. Tardivel, E. Gloaguen and M. Mons, J. Am. Chem. Soc. 133, 3931 (2011).
[b] S. Jaeqx, M. Schmit, W.J. van der Zande, and A.M. Rijs, manuscript in preparation