GAS-PHASE IR SPECTROSCOPY OF PEPTIDES AND PROTEINS

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IR spectroscopy of biologically relevant molecules in the gas phase has become a powerful tool to study their intrinsic structure, free of environmental effects. Particularly IR-UV hole burning techniques have been applied to obtain detailed, conformer-selective, structural information on a wide variety of biomolecules. However, these methods have thus far only been applied to relatively small systems, such as amino acids and di- and tri-peptides.

In this contribution, we present gas-phase IR spectra for much larger biomolecular systems, obtained via IR multiple photon dissociation spectroscopy (IRMPDS) of the ionic molecules stored in a Fourier Transform mass spectrometer[1]. The molecules are brought into the gas phase using an electrospray ionization (ESI) source. A Free Electron Laser provides the widely tunable and high-energy IR radiation required for these experiments.

In contrast to the molecular beam hole burning methods mentioned above, the IRMPDS method is not conformer selective and experiments are carried out at room temperature. On the other hand, the systems studied are (much) larger. Given these major differences, the first question one may ask is if any useful spectroscopic data can be obtained at all.

Two pentapeptides (Bradykinin fragment 1-5 and [Leu]-Enkephalin) have been investigated in the 800-1800 cm^{-1} region and show very distinctive spectra. An interesting question is whether or not these gas-phase peptides assume a zwitterionic state as in solution, and the CO stretching mode of the C-terminus appears to be a good probe. The spectra are further interpreted by comparison with DFT calculations (B. Paisz, Heidelberg) and with experimental IR spectra of two individual amino acids, Tyr and Phe, included in the peptides.

Furthermore, the IR spectrum of a full 104 amino-acid protein (cytochrome C) has been obtained in the region of the Amide bands near 6 μm. Interesting spectral changes are observed as a function of the charge state of the protein. This is likely the largest molecule (MW $\approx$12,500 amu) for which the gas-phase IR spectrum will be presented at the meeting.

1. J.J. Valle, J.R. Eyler, J. Oomens, D.T. Moore, A.F.G. van der Meer, G. von Helden, G. Meijer, C.L. Hendrickson, A.G. Marshall, G.T. Blakney, *Rev. Sci. Instrum.* **76** 023103 (2005).