

# X-ray absorption study of selected amino acids

O. Fuchs<sup>1</sup>, L. Weinhardt<sup>1</sup>, C. Heske<sup>1</sup>, E. Umbach<sup>1</sup>, Y. Zubavichus<sup>2</sup>, M. Grunze<sup>2</sup>, and J.D. Denlinger<sup>3</sup>

<sup>1</sup>*Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

<sup>2</sup>*Angewandte Physikalische Chemie, Universität Heidelberg, INF 253, 69120 Heidelberg, Germany*

<sup>3</sup>*Advanced Light Source, 1 Cyclotron Rd., Berkeley, CA 94720*

## INTRODUCTION

In order to understand the function of biologically relevant molecules in organisms, the analysis of the electronic properties is of large relevance, since many important biological processes are based on electronic interactions, e.g., with ions. By using bulk sensitive photon-in-photon-out techniques such as NEXAFS (near-edge x-ray absorption fine structure) in the fluorescence yield mode for probing unoccupied states and RIXS (resonant inelastic x-ray scattering) for the occupied states, the sample surface preparation and charging effects do not impact the experimental results, in contrast to surface sensitive techniques using electrons. This allows the investigation of any UHV-compatible material, for example in commercial powder form. In the near future, it will be even possible to perform measurements of liquid solutions in wet cells in order to investigate the interaction of biologically relevant molecules with the solvent (e.g., water).

## EXPERIMENT

We have performed a NEXAFS and RIXS study on selected amino acid powders, including proline (Pro), cysteine (Cys), lysine (Lys), threonine (Thr), glycine (Gly), phenylalanine (Phe), and histidine (His). Here, the NEXAFS data will be discussed. In the past, x-ray absorption spectra on amino acids have been recorded by measuring the transmission of thin films prepared by drying solutions of amino acids [1,2]. As a prerequisite of the above-mentioned wet cell experiments, we have followed a different approach by detecting the fluorescence yield in reflection geometry. Furthermore, we used a simple preparation method, namely to press amino acid powders in indium foil, which is applicable to all amino acid powders and avoids artefacts from the drying process of the liquid solutions. Note that only a limited number of (smaller) amino acids can be sublimated in-vacuo. In these cases, the adsorption on a single crystal substrate allows to gather symmetry-resolved information about the molecular orbitals by choosing appropriate excitation and emission geometries, as shown for the case of glycine on Cu(110) in [3].

The measurements were performed at the undulator Beamline 8.0.1 using the SXF endstation. For the NEXAFS experiments, the entrance and exit slits of the beamline monochromator were fully closed in order to minimize the flux and to slow down radiation damage of the investigated molecules. The fluorescence yield detector consisted of a negatively charged gold grid repelling incoming electrons and a subsequent channeltron acting as a photon detector in a single photon counting mode, providing a very high count rate even at the minimized beam flux.

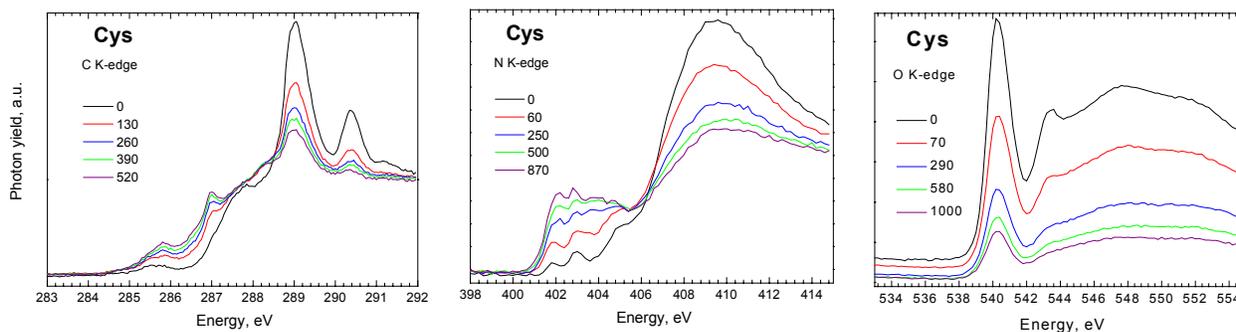


Fig. 1. Time evolution of NEXAFS spectra of cysteine during soft x-ray exposure (numbers denote exposure time in seconds)

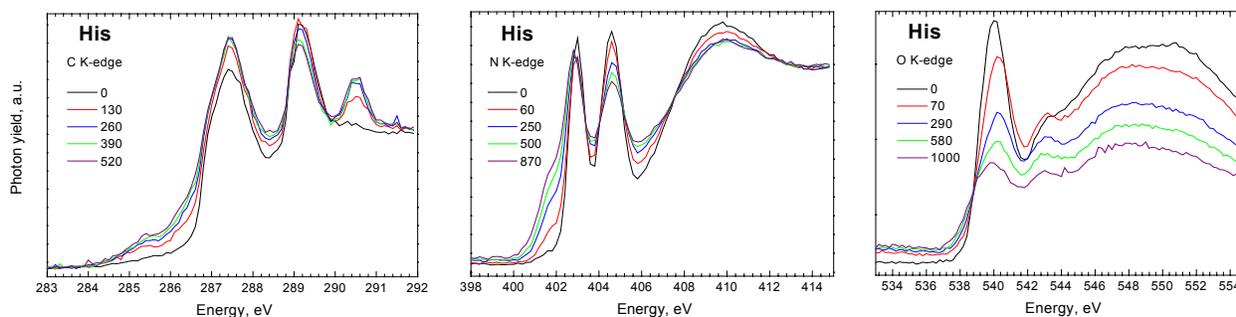


Fig. 2. Time evolution of NEXAFS spectra of histidine during soft x-ray exposure (numbers denote exposure time in seconds)

## RESULTS

Figures 1 and 2 show three series of carbon, nitrogen, and oxygen K-edge NEXAFS spectra of cysteine and histidine, respectively, illustrating the fast change in spectral shape due to irradiation with soft x-rays. Apparently (and as expected), it is very important to monitor irradiation effects when taking spectra of amino acids utilizing brilliant soft x-rays. A technical prerequisite for such measurements is the capability of beamline 8.0 to scan the undulator gap and the monochromator simultaneously in a fast mode with short settling times, leading to scan durations as short as one to two minutes. In the case of carbon and nitrogen, we observe changes of relative peak intensities and appearance of new peaks in the energy range typical for  $\pi^*$  resonances of C-C and C-N multiple bonds, revealing a change of the chemical state of some of the carbon and nitrogen atoms. A prominent decrease in total intensity is seen in the case of oxygen, which indicates a loss of oxygen atoms due to dehydration and decarboxylation of the molecules.

Figure 3 shows C K-edge NEXAFS spectra of 7 amino acids measured on pristine spots (left side) and on damaged spots (right side). The spectra of undamaged molecules reveal distinct features which vary strongly dependent on the studied amino acid, making NEXAFS also useful as a fingerprint technique. The carbon spectra are in general agreement with the results reported by Kaznacheyev et al. [2]. In all cases, the changes due to radiation damage are significant. Currently, theoretical investigations of the spectra are underway, which will not only give more insight into the electronic structure of the investigated amino acids, but also allow a more detailed analysis of the observed degradation processes.

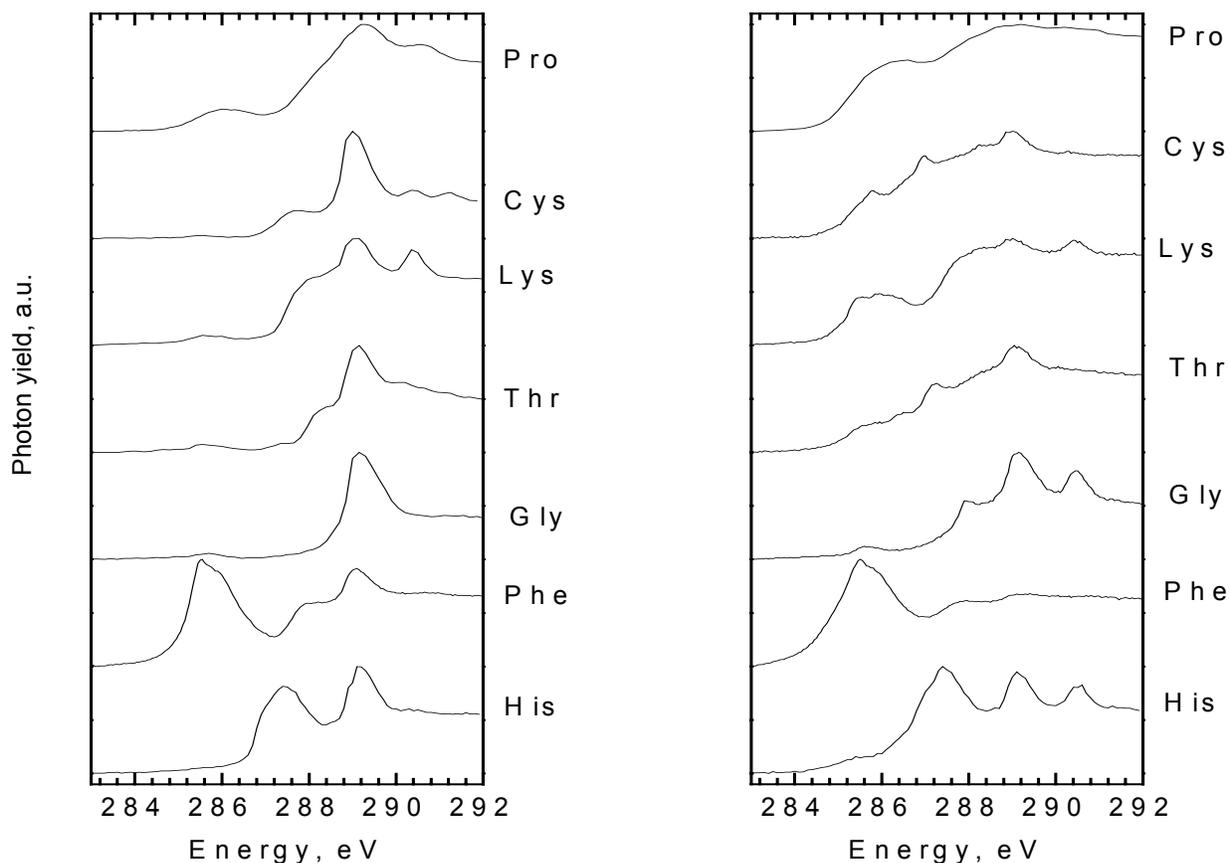


Fig. 3. C K-edge NEXAFS spectra of selected amino acids in the pristine state (left) and after exposure to x-rays for 10-20 min. (right). From top to bottom: proline (Pro), cysteine (Cys), Lysine (Lys), threonine (Thr), glycine (Gly), phenylalanine (Phe), histidine (His).

## OUTLOOK

While NEXAFS measurements of high quality can be achieved with the above-mentioned technique, further efforts have to be undertaken in order to obtain resonant x-ray emission (RIXS) spectra of undamaged molecules, which require much longer exposures. For instance, scanning of the sample with respect to the exciting beam during the measurement could prove helpful. Also, a new high-efficiency soft x-ray fluorescence spectrometer is currently under development in order to minimize measurement time. A major improvement is expected from using liquid cells in a flow-through mode, which will reduce the influence of the probing beam even further. With all these improvements on their way, NEXAFS and RIXS will present an ideal combination to derive a complete picture of the electronic states of amino acids, both for occupied and unoccupied frontier molecular orbitals.

## REFERENCES

- [1] J. Boese, A. Osanna, C. Jacobsen, and J. Kirz, *J. Electr. Spectr. Relat. Phen.* **85** (1997) 9-15.
- [2] K. Kaznatcheyev, A. Osanna, C. Jacobsen, O. Plashkevych, O. Vahtras, H. Ågren, V. Carravetta, and A. P. Hitchcock, *J. Phys. Chem. A* **106** (2002) 3153-3168.
- [3] A. Nilsson, *J. Electr. Spectr. Relat. Phenom.* **126** (2002) 3-42.

This work was funded by the German BMBF (projects 05KS1WW1/6 and 05 KS1VHA/3).  
Principal investigator: C. Heske, E. Umbach, Experimentelle Physik II, University of Würzburg (Germany).  
Email: [heske@physik.uni-wuerzburg.de](mailto:heske@physik.uni-wuerzburg.de). Telephone: ++49-931-888-5127