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Near-Edge X-Ray Absorption Fine Structure Measurements Using a Laser Plasma XUV Source

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Abstract. We present a compact setup for near-edge x-ray absorption spectroscopy at the carbon K-edge based on a laser-driven plasma source. Thin polymer films were investigated, showing good agreement with corresponding synchrotron data. Furthermore we have examined the carbon near-edge structure of phospholipids and fulvic acids, providing detailed information on intermolecular binding states.

1. Introduction

The progress in development of laboratory-scale soft x-ray sources in recent years has enabled experimental techniques that could be performed before almost exclusively at synchrotron sources. Table-top soft x-ray sources of high brilliance are now used for various applications, e.g. x-ray microscopy [1], lensless diffractive imaging [2], photoelectron spectroscopy [3] or absorption spectroscopy [4]. The latter, among other techniques, accomplishes the investigation of the near edge x-ray absorption fine structure (NEXAFS).

NEXAFS is a well established method for elemental and compositional analysis of a sample yielding also surface sensitive information [5]. In particular, NEXAFS is used to study the structure of intermolecular bonds of polymers by probing the electronic transition from the core level to unoccupied states. Since each element has a characteristic core binding energy NEXAFS spectra contain element specific information. The analysis of these unique spectroscopic fingerprints allows the identification and distinction of different polymers [6].

In this paper we present NEXAFS measurements that were obtained by using a flexible laboratory scale setup based on a laser-driven plasma source. The table-top setup can be used for NEXAFS experiments in transmission as well as reflection under grazing incidence conditions. For transmission measurements thin films have to be used due to the low penetration depth of soft x-rays into matter. In contrast, NEXAFS experiments performed in reflection mode (ReflEXAFS) offer the advantage that thin film preparation is not necessary. Moreover, the surface sensitivity is strongly increased.

2. Experimental Setup

The experimental setup for the generation and characterization of soft x-ray radiation emitted from laser plasmas in the "water window" is shown schematically in Figure 1. A Nd:YAG laser beam (Innolas, 1064 nm, 1 Hz, 800 mJ, 7 ns) is focused into a pulsed gas puff target centred in a vacuum chamber, as described in detail elsewhere [7]. The laser focus has a diameter of about 60 µm, yielding power densities of up to 4 x 10^{12} W/cm² that are sufficient to ignite a hot and dense plasma. Krypton is employed as target gas (backing pressure 25 bar), accomplishing broadband radiation (Kr XXV – Kr XXXVI) in the spectral range of the "water window". Due to the small mean free path of the soft x-ray radiation at atmospheric pressure the target vacuum chamber is evacuated to approx. 10^{-4} mbar.

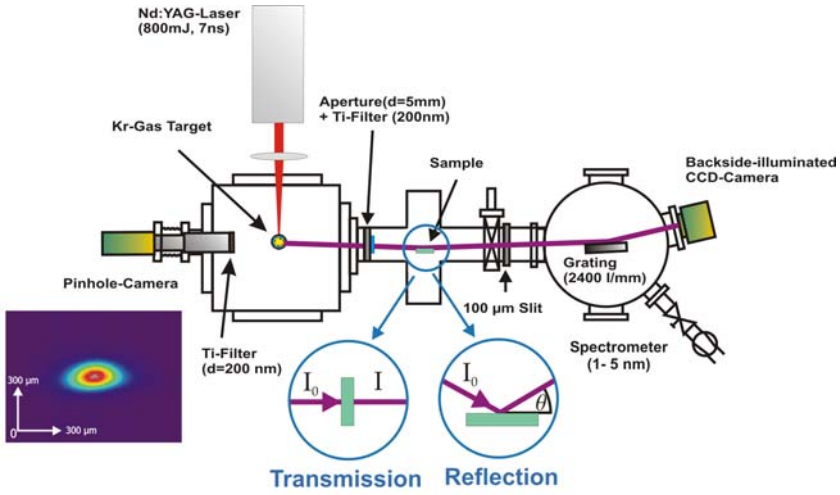

Figure 1. Experimental setup of the laser-plasma XUV source used for NEXAFS experiments. The insert on the left shows a picture of the krypton plasma taken by the pinhole camera.

An XUV spectrometer (1 – 5 nm) was used both for the spectral investigation of the plasma source and the NEXAFS experiments. The spectrometer consists of a 100 µm entrance slit, an aberration corrected flat-field grating (Hitachi, 2400 lines/mm) and a back-side illuminated CCD camera (Roper Scientific, pixel size 13 µm). The resolution of this spectrometer was experimentally determined to be $\lambda/\Delta\lambda \approx 200$ @ 2.87 nm. It was mounted 90° to the laser beam and opposite to the pinhole camera (cf. Fig. 1). To block visible radiation from the plasma and scattered laser light a titanium foil (200 nm thickness) was positioned between plasma source and sample.

To calibrate the spectrometer nitrogen was used as target gas. The spectrum of the nitrogen plasma, ignited under the same experimental conditions as krypton, consists of several lines (e.g. $1s^2$ - 1s2p transition of N VI at 2.8787 nm) that were used for spectral calibration.

3. Results

For thin samples it is possible to determine the x-ray absorption fine structure by measuring the transmitted flux through the sample. The optical density can be evaluated according to Lambert-Beer's law: $\mu(E) \cdot d = -\ln(I/I_0)$. $\mu(E)$ is the linear energy dependent absorption coefficient, d the sample thickness, I the transmitted and I_0 the reference intensity, respectively.

Figure 2 shows NEXAFS spectra that were recorded in transmission for a polyimide film (d=200 nm), a dried phospholipid layer (1,2-Dioleoyl-sn-Glycero-3-Phosphatidilserine (DOPS)) and a fulvic acid from aquatic origin. The lipid multilayers and the fulvic acid were prepared on thin Si_3N_4 membranes (d=100nm). The spectra show several sharp peaks below the carbon K-absorption edge which can be attributed to C 1s – π^* transitions and broader features above the edge that belong to C 1s - σ^* transitions. To evaluate the data multi-Gaussian/Lorentzian fits were performed using the software SpecFit. In Table 1 the identified features are summarized.

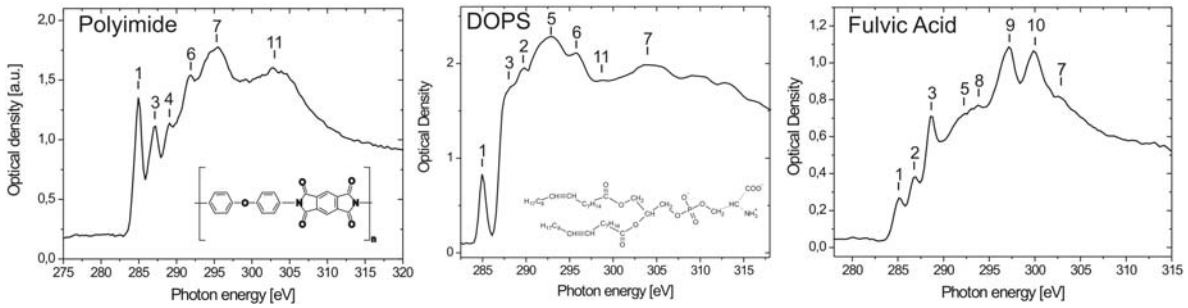

Figure 2. NEXAFS spectra of a polyimide film (d=200 nm), a phospholipid layer (DOPS) and a fulvic acid.

Polyimide films were used as a first test sample and the comparison with corresponding synchrotron data shows a good agreement. The peak positions deviate by less than 0.4 eV from reference data [8]. The lipid spectrum exhibits a sharp peak that can clearly be assigned to C=C bond of the unsaturated fatty acid chains. In the NEXAFS spectrum of the fulvic acid also potassium resonances can be identified.

Table 1. Energies and assignments of features in the NEXAFS spectra of Poyimide (PI), a phospholipid layer (DOPC) and a fulvic acid.

Feature	Energy [eV]			Assignment
	PI	DOPS	Fulvic Acid	
1	285.2	285.0	285.2	1s → π* (C=C)
2			286.3	1s → 3s /Ryd.
3	287.3	288.0	288.6	1s → π* (C=O)
4	289.3			1s → π*
5		292.8	291.8	1s → σ*(C-C)
6	291.6	295.8		1s → σ* (C-O, C-N)
7	295.0	302.9	302.4	1s → σ*(C=C)
8			293.7	1s → 4p (COOH)
9 / 10			296.9 / 299.8	K L_{III} / K L_{II}
11	303.0	298.7		1s → σ*(C=O)

4. Conclusion

The results demonstrate that it is possible to investigate the near edge absorption fine structure by utilizing broad-band radiation from a laboratory-scale laser driven plasma source. In the future the spectral resolution will be improved by using higher resolution gratings.

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