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Near-edge x-ray absorption fine structure spectroscopy at atmospheric pressure with a table-top laser-induced soft x-ray source

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The authors present a table-top soft x-ray absorption spectrometer, accomplishing investigations of the near-edge x-ray absorption fine structure (NEXAFS) in a laboratory environment. The system is based on a low debris plasma ignited by a picosecond laser in a pulsed krypton gas jet, emitting soft x-ray radiation in the range from 1 to 5 nm. For absorption spectroscopy in and around the "water window" (2.3–4.4 nm), a compact helium purged sample compartment for experiments at atmospheric pressure has been constructed and tested. NEXAFS measurements on CaCl₂ and KMnO₄ samples were conducted at the calcium and manganese L-edges, as well as at the oxygen K-edge in air, atmospheric helium, and under vacuum, respectively. The results indicate the importance of atmospheric conditions for an investigation of sample hydration processes. © 2016 American Vacuum Society. [http://dx.doi.org/10.1116/1.4950599]

I. INTRODUCTION

The development of laboratory-scale extreme UV and soft x-ray sources in recent years has resulted in compact systems of considerable brilliance and average power, with emission properties that could before only be provided by synchrotron radiation. These systems, based primarily on laser- or discharge-produced plasmas,^{1–6} high harmonic generation,^{7,8} or x-ray lasers⁹ are now already enabling a variety of short wavelength applications in a laboratory environment. For instance, in the "water window" region ($\lambda = 2.3$ –4.4 nm), high resolution microscopy of both organic and inorganic matter has been demonstrated already by a large number of groups, mainly employing radiation from laser-produced plasmas.^{10–13}

Another highly important application of soft x-rays is absorption spectroscopy. It accomplishes investigations of the fine structure of the x-ray absorption edges [near-edge x-ray absorption fine structure (NEXAFS)], by probing the electronic transitions from core levels to higher lying unoccupied states. Since the energy levels of both initial and final states depend on the involved molecular bonds and their chemical environment, the spectral features of the near-edge fine structure provide a unique "molecular fingerprint." Thus, NEXAFS spectroscopy is a well-established analytical method for compositional surface analysis and one of the most important applications of synchrotron radiation.¹⁴ However, in contrast to soft x-ray microscopy, it has been conducted only a few times with laboratory sources until now, $^{15-17}$ although almost identical results as with radiation from storage rings are achievable. In particular, other than at synchrotrons where absorption spectroscopy is conducted mainly by recording the total electron yield using monochromatic radiation for excitation, the broadband radiation emitted from lab-scale sources allows for a polychromatic spectroscopic approach, being also ideally suited for time-resolved and pump-probe experiments.¹⁸

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One obstacle common to all NEXAFS experiments is related to the fact that the mean free path of soft x-rays in air is only a few millimeters, requiring a high vacuum environment for source, sample and spectrometer. This can lead to problems with outgassing when aqueous solutions or adsorbed gasses are to be analyzed or when dehydration causes structural changes of the sample (proteins, deoxyribonucleic acid, and hydrated transition metal compounds). Likewise, covalent bonds between substrate and adsorbate can be formed in consequence of drying, resulting in a change of the NEXAFS signal. To avoid this, especially designed gas cells for *in situ* measurements¹⁹ and helium purged sample compartments²⁰ have been employed at synchrotrons, since helium is by far less absorbing than air at atmospheric pressure.

Inspired by this concept, we have constructed and tested a highly compact helium chamber for our existing table-top NEXAFS spectrometer. In this paper, we describe the performance of the new sample compartment for NEXAFS measurements at atmospheric pressure. In addition, we present a comparison of spectra of identical samples measured in vacuum, helium and air at the calcium and manganese L-absorption edge, as well as at the oxygen K-edge.

II. EXPERIMENTAL SETUP

The setup for NEXAFS measurements of transmission samples under different atmospheric conditions is depicted in Fig. 1. It consists basically of a laser-induced plasma source, a sample chamber and a spectrometer. Due to the high absorption of soft x-ray radiation in matter, the experiments

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FIG. 1. (Color online) (a) Schematic drawing and (c) photograph of the table-top soft x-ray plasma source used for NEXAFS experiments. The compact helium purged sample chamber (red rectangle) is mounted in between the source and spectrometer. The inset (b) displays a pinhole camera image of the laser-induced krypton plasma. (d) Close-up sketch and (e) photograph of the sample compartment with its helium inlet on top and the sample slide on the bottom.

are performed in a vacuum system with a base pressure of 5×10^{-6} mbar.

The laser-induced plasma source based on a gas target and a Nd:YAG laser system (Ekspla SL312P, wavelength 1064 nm, pulse energy 500 mJ, and pulse duration 170 ps) has been described in detail elsewhere.²¹ The pulsed gas jet is created by a fast valve (Proch-Trickl setup; Ref. 22), consisting of a piezo disk translator (Physik-Instrumente P-286.72) in order to generate short gas pulses ($t_{open} \approx 900 \,\mu$ s) that allow for a working pressure of about 5×10^{-3} mbar during operation (gas backing pressure p = 20 bar and repetition rate 5 Hz). The gas jet is formed by a conically diverging nozzle (300–550 μ m diameter). The laser beam is focused by a lens with a focal length of f = 120 mm onto a krypton gas jet, accomplishing broad-band radiation in the spectral range of the water window (see Fig. 2). In order to block out-of-band radiation, such as visible light or scattered laser radiation, the



FIG. 2. (Color online) Emission spectra of the krypton plasma measured under different conditions in the sample chamber, i.e., in vacuum, 1000 mbar helium and atmospheric air, respectively (average over 10 000 pulses). For comparison, the calculated transmission of 300 nm Si_3N_4 in combination with both 4 mm helium and 4 mm air from tabulated data (Ref. 23) is shown.

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emitted radiation from the krypton plasma is filtered by an aluminum filter (thickness 200 nm).

The spatial distribution of the krypton plasma is monitored by a pinhole camera (pinhole diameter $50 \,\mu\text{m}$) utilizing a CCD chip (Sony ICX285, $6.45 \times 6.45 \,\mu\text{m}^2$ pixel size, and 1280×1024 pixels) sensitized to the soft x-ray spectral range by a phosphor coating. The krypton plasma size is measured to be $0.37 \times 0.24 \,\text{mm}^2$ (FWHM, see Fig. 1 inset) recorded with a Ti filter for blocking of out-of-band radiation.

The spectrometer used for the NEXAFS measurements consists of a 100 μ m entrance slit, an aberration-corrected concave flat-field grating (Hitachi, 2400 grooves per mm, wavelength range 1–5 nm), and a soft x-ray sensitive CCD camera (Roper Scientific, back-thinned, back-illuminated, $13 \times 13 \ \mu$ m² pixel size, and 2048 × 512 pixels). The CCD camera is cooled down to $-30 \ ^{\circ}$ C to reduce its intrinsic thermal noise during acquisition. Additionally, the background signal was subtracted from all spectra to account for systematic nonuniformities of the CCD camera. The energy resolution of the spectrometer was experimentally determined to be E/ $\Delta E \approx 170$ at a photon energy of 430 eV.

The samples are mounted on a linear motion stage for adjustment in the soft x-ray beam. The distance between plasma source and sample is about 240 mm, and the distance between sample and entrance slit of the spectrometer about 180 mm. The setup can be used for NEXAFS experiments with the sample being held under vacuum or atmospheric helium/air conditions, respectively. For this purpose, a compact sample chamber was developed utilizing two silicon nitride (Si₃N₄) membranes (Silson, Ltd.) to isolate the sample from the vacuum chamber [see Fig. 1(d)]. Due to the high pressure difference, the Si_3N_4 membranes separating these two regions have to be strong enough to prevent them from breaking. Two 150 nm thick membranes (window size 1.0×1.0 mm) being 4 mm apart [cf. Fig. 1(c)] provide sufficient stability, still maintaining acceptable transmission of soft x-ray radiation (cf. Fig. 2). Within the new chamber the sample can be held at atmospheric pressure of either air or helium gas (backing pressure 1000 mbar).

III. RESULTS AND DISCUSSION

Before measuring NEXAFS spectra, the performance of the newly incorporated sample chamber was investigated (cf. Fig. 2). Compared to the krypton emission spectrum recorded in vacuum, the spectra measured under helium and air conditions show an overall decrease in intensity, being in good agreement with the calculated transmission taken from tabulated data.²³

Furthermore, the nitrogen K-edge at a photon energy of \sim 410 eV, caused by the Si₃N₄ membranes, is clearly visible in both spectra. Due to the additional absorption of atmospheric nitrogen, the intensity of the emission spectrum measured in air is almost zero above the nitrogen K-edge. From the krypton emission spectra recorded in combination with a carrier substrate, both with and without sample, the optical density can be evaluated according to Lambert-Beer's law [Eq. (1)]

$$OD(E) = \mu(E) \cdot d = -\ln\left(\frac{I(E)}{I_0(E)}\right),\tag{1}$$

where $\mu(E)$ is the linear energy dependent absorption coefficient, *d* the sample thickness, *I*(*E*) the transmitted, and *I*₀(*E*) the reference spectrum, respectively.

In order to increase the signal-to-noise ratio, the NEXAFS spectra measured in air and helium are averaged over twice the number of pulses compared to the spectrum recorded in vacuum. All spectra are baseline corrected and normalized.

As a first example, NEXAFS spectra at the calcium L-edge and oxygen K-edge of crystalline calcium chloride were recorded under different conditions in the sample chamber, i.e., vacuum and atmospheric air and helium, respectively. An aqueous solution of calcium chloride (CaCl₂·H₂O) was dispensed on a Si₃N₄ membrane and the water dissipated in a stream of heated air. Under atmospheric conditions, the highly hygroscopic calcium chloride is known to form a tetra-or hexahydrate, showing an octahedral coordination.²⁴

The data displayed in Fig. 3 indicate the characteristic L_2 (352.5 eV) and L_3 (349.3 eV) absorption edges of calcium, representing electronic transitions from $2p_{1/2}$ and $2p_{3/2}$ to 3d levels. Both peak positions remain constant for the three different environmental conditions and deviate less than 0.4% from synchrotron data.²⁵ Obviously, NEXAFS measurements at atmospheric pressure, both in helium and air, are feasible at the calcium L-edge by employing the new sample chamber.

Due to well known hygroscopic properties of CaCl₂ rehydration takes place after the preparation process. However, as seen in Fig. 4, the oxygen signal is absent both in vacuum and atmospheric air: During measurement in vacuum, the crystalline structure is changing along with the decreasing atmospheric pressure from a tetra- or hexahydrate into a water-free distorted "rutile-structure,"²⁶ therefore no traces of water can be detected. In air, these hydrate structures are still present, but are failed to be measured due to the strong absorption above the nitrogen K-edge (cf. Fig. 2). Therefore, helium purging turns out to be essential for the proper



Fig. 3. (Color online) NEXAFS spectra at the calcium $L_{3,2}$ edge of calcium chloride (CaCl₂) sample measured in vacuum (average over 10 000 pulses), helium and air (1000 mbar, average over 20 000 pulses), respectively.

investigation of all sensitive life-science samples, such as enzymes or proteins, whose chemical structure and function is disturbed by outgassing.

Furthermore, absorption measurements were also performed on a potassium permanganate (KMnO₄) sample under different atmospheric conditions (cf. Fig. 5). Again an aqueous solution of KMnO₄ was dispensed on a Si₃N₄ carrier substrate. In order to achieve a homogenous coverage of KMnO₄ on the substrate, the solution was moderately heated at temperatures below the boiling point.

The splitting of the manganese L-edge into L_3 (644.3 eV) and L_2 (655.1 eV) peaks, indicating electronic transitions from $2p_{3/2}$ and $2p_{1/2}$ to 3d levels is clearly visible in the spectra recorded under vacuum and helium condition. However, as to be expected, the strong attenuation of the plasma emission above 400 eV prevents registration of these peaks in atmospheric air. Again, the obtained energy values of the $L_{3,2}$ -peaks deviate less than 1 eV (0.2%) from corresponding synchrotron data.²⁷



FIG. 4. (Color online) NEXAFS spectra at the oxygen K-edge of a calcium chloride (CaCl₂) sample measured in vacuum (average over 10 000 pulses), helium and air (1000 mbar, average over 20 000 pulses), respectively.



FIG. 5. (Color online) NEXAFS spectra at the manganese $L_{3,2}$ -edge of potassium permanganate (KMnO₄) measured in vacuum (average over 10 000 pulses), helium and air (1000 mbar, average over 20 000 pulses), respectively.

In future, an increased plasma source performance will enable also measurements at higher photon energies [up to kiloelectron volt (keV) range] employing the helium purged sample chamber. Currently, NEXAFS spectra can already be obtained at the important iron L-edge (\approx 710 eV) with the sample held in vacuum, as seen from Fig. 6. Here, we exemplarily investigated goethite, a common Fe(III) oxyhydroxide in rust, soil and sediments,²⁸ which is technically produced as a pigment for paint. Natural goethites often form nanometer-sized crystals with a high degree of lattice defects; thus, they are difficult to identify and quantify by xray diffraction techniques. Moreover, organic matter on Fe oxides can be analyzed by NEXAFS, for example, at the carbon K-edge. This is not possible by NMR due to the magnetic properties of Fe. Under reducing conditions, e.g., in waterlogged soils, goethite and other iron oxides may dissolve and reprecipitate as Fe(II)-containing phases such as magnetite, green rust, vivianite, or FeS.²⁹ As some of these



FIG. 6. NEXAFS spectra at the Iron L-edge of goethite (α -FeO(OH)) measured in vacuum (average over 10 000 pulses).

phases will oxidize within minutes when exposed to air, a helium purged sample compartment will become crucial for investigating the original iron speciation.

IV. CONCLUSION

The results presented in this paper demonstrate the possibility of near-edge absorption fine structure investigations in an atmospheric pressure environment, using a broad-band laboratory-scale laser-driven plasma source and a compact helium purged sample compartment. The obtained NEXAFS spectra covering the measurable energy range of the spectrometer from 250 to 800 eV are in excellent agreement with synchrotron data. In addition, the CaCl₂ fine-structure recorded at the oxygen K-absorption edge indicates that helium purging is crucial for investigations of the hydration level, as important also for denaturized organic samples.

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