

# X-ray spectroscopy with variable line spacing based on reflection zone plate optics

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X-ray spectroscopy is a method, ideally suited for investigating the electronic structure of matter, which has been enabled by the rapid developments in light sources and instruments. The X-ray fluorescence lines of life-relevant elements such as carbon, nitrogen, and oxygen are located in the soft X-ray regime and call for suitable spectrometer devices. In this work, we present a high resolution spectrum of liquid water, recorded with a soft X-ray spectrometer based on a reflection zone plate (RZP) design. The RZP-based spectrometer with meridional variation of line space density from 2953 l/mm to 3757 l/mm, offers extremely high detection efficiency and at the same time medium energy resolution. We can reproduce the well-known splitting of liquid water in the lone pair regime with 10 s acquisition time.

**OCIS codes:** 300.6330 Spectroscopy, inelastic scattering including Raman; 300.6560 Spectroscopy, x-ray; 340.7480 X-rays, soft x-rays, extreme ultraviolet (EUV)

The electronic structure of a system governs its bonding characteristics. Therefore, the electronic properties contain information about the nature of chemical bonds [1-3]. A suitable

method to probe the electronic structure of a system is X-ray spectroscopy. It is selectively sensitive to different molecular orbitals, specific elements at various sites and probes truly bulk properties [4]. Limitations are the low radiative decay yield after core-excitation for biologically and chemically relevant systems due to the fact that they contain mostly light elements, as well as the low detection efficiency of typical instruments [5,6]. Consequently, high brilliant X-ray sources are required to perform such kinds of experiments. The rapid development of modern light sources can provide a high flux of photons with small energetic bandwidth. Therefore, X-ray spectroscopy in its entire manifold is well represented at synchrotron and free-electron laser facilities around the world and emerged as a very popular tool to study the electronic properties of matter [7-15].

Efforts have been made to increase the detection efficiency and to optimize the scientific output as well as to study small volumes of precious samples [16-25]. Recent developments include installing collecting mirrors in front of the diffractive optical elements [20,21], modular spectrometers [16], multilayer coating [24, 25] and zone plate optics [17-19]. While most concepts are based on conventional constant density or varied line spacing (VLS) gratings, the latter use zone plates as diffractive optical elements. Collecting mirrors have the advantage of increasing the analyzed

solid angle, but the alignment procedure can be very time-consuming. In Ref. [16], it is proposed to multiply the number of spectrometers in order to increase the signal. Alternatively, reflection zone plates (RZP) offer the advantage of increased solid angle with energy resolution comparable to more conventional X-ray optical elements by compensating for aberrations. Unfortunately, this compensation is only efficient for a limited energy range [17-19]. Recent efforts in overcoming this shortcoming include displacement of the zone plate in an off-axis design or using a holder containing multiple optics [19]. It has been shown that displacement allows for a high energy resolution over an energy range of  $\sim 30$  eV [19].

RZPs offer a wide range of advantages, the essential ones in comparison to conventional gratings are:

- I. The grooves on RZPs have a two-dimensional variation of line density, which corresponds to a two-dimensional aberration correction of the image plane. Such a correction enhances the energy resolution and produces an ideal, linear focus in the focal plane.
- II. The short distance between source and optical element provides extremely large angular acceptance of the RZP (see also Table 1): In this case five times larger distance to the CCD detector means five times higher magnification in the focal plane, which corresponds to the CCD pixel size and, eventually, maximizes the energy resolving power.
- III. The RZP manufacturing technology is based on electron-beam lithography with extremely high positioning accuracy (down to 2 nm accuracy on the area of  $80 \times 10$  mm<sup>2</sup>) and reactive ion etching with 0.5 nm in-depth accuracy. In combination with flexible groove shapes, it leads to a record line density of up to 3800 l/mm and low noise spectral imaging.
- IV. RZPs are produced on planar substrates, which have the most precise polished surface quality, much better than any shaped or curved substrates. This makes RZP less expensive, but it is a much more accurate optical element than the conventional ones using curved substrates.
- V. For conventional gratings, the energy range is continuous from i.e. 300 eV to 600 eV. With the RZP design several different K, L, or M edges can be combined without having a large energy gap in between, which would fit on a standard 2D detector.

Despite the advantages, the lack of energy resolution over a broader range is an obstacle in utilizing RZPs for spectroscopic purposes. The X-ray fluorescence signal contains several spectrally sharp emission lines. So far, it has not been demonstrated that a recorded fluorescence signal utilizing a RZP shows similar energy resolution as conventional X-ray optical elements.

In this work we report, for the first time, the reproduction of the X-ray emission (XE) signal of liquid water at the oxygen K-edge using a zone plate. The XE spectrum of liquid water is a very good example, since the splitting of the lone pair peak has been discovered after soft X-ray spectrometers with sufficient energy resolution at the oxygen K-edge became available [26, 27]. The discovery has triggered a strong interest in the research of chemical and biological systems in the liquid phase with soft X-ray emission spectroscopy [12, 28-34]. Yet, the investigations are

limited to systems, which are procurable on a macroscopic scale. For more precious systems, for example macromolecules like proteins, the conventional approach of using a renewable micro liquid jet would require an unreasonable amount of sample. Therefore, highly efficient soft X-ray spectrometers with sufficient energy resolution are needed.

#### Experimental conditions and optics design

The measurements have been performed at the soft X-ray beamline P04 at PETRA III, DESY, Germany using the ChemRIXS end-station [35]. The exit slit of the beamline was set to 300  $\mu\text{m}$  or 1000  $\mu\text{m}$ , which corresponds to an energy bandwidth of around 200 meV or 700 meV, respectively [36].

The vertical focus of the X-ray beam of the synchrotron depends on the exit slit size with  $\sim 100$   $\mu\text{m}$  for the 300  $\mu\text{m}$  exit slit and  $\sim 300$   $\mu\text{m}$  for the 1000  $\mu\text{m}$  exit slit, while the horizontal focus was around 10  $\mu\text{m}$  [34]. The surface of the zone plate is placed parallel to the liquid jet such that the dispersion plane is coplanar with the incoming X-ray beam. Figure 1(a) illustrates the geometrical configuration of the experiment. The essential geometrical parameters are summarized in Table 1. The incident angle is  $2^\circ$  and the diffraction angle is  $7.5^\circ$ . An Andor iKON M CCD camera has been used for the detection of the diffracted X-ray emission signal and is placed perpendicular to the surface of the RZP.

As sample delivery a cylindrical micro liquid jet was utilized with a radius of  $\sim 25$   $\mu\text{m}$  [37]. Purified water with an electrical resistivity of  $\sim 18.0$  M $\Omega\text{cm}$  was used for the measurements. A detailed description of the end-station can be found in [35].

**Table 1. Essential geometrical parameters of the reflection zone plate for the oxygen K-edge.**

Design energy	526 eV
Line density 2D VLS-grating (Figure 1)	2953 - 3371 - 3757 lines/mm
Lamellar groove profile	15 nm
Incident angle $\alpha$	$2^\circ$
Diffraction angle $\beta$	$7.5^\circ$
Sagittal acceptance	$3^\circ$
Meridional acceptance	$0.95^\circ$
Incident arm length	200 mm
Exit arm length	1000 mm
Micro roughness	$<0.6$ nm

The basic design of RZP optics is described in various publications [36-38]. In this specific case we decided to use the following design: a two-dimensional VLS-grating with an aberration-corrected linear focus, calculated using our RZP Fresnel algorithm. A schematic of this grating is shown in Figure 1(b). This approach has the advantage that the RZP aperture is not limited due to technological limitations defined by the minimum size of the outer zones. The highest possible transmission is achieved by exploring extremely large angular acceptances of the optical element, limited only by the CCD detector size. The energy resolution is defined by the high average line density of the grating in the order of 3371 lines/mm. The RZP has a line density variation in the order of 11.5%, which is not achievable with conventional technology for diffraction gratings. The depth of the optimized lamellar line profile of 15 nm is optimized for the design energy of 526 eV and the average line density. A deeper discussion how groove shapes affect the performance was shown by Braig *et al.* [40]. The grating efficiency is around 3.5%.

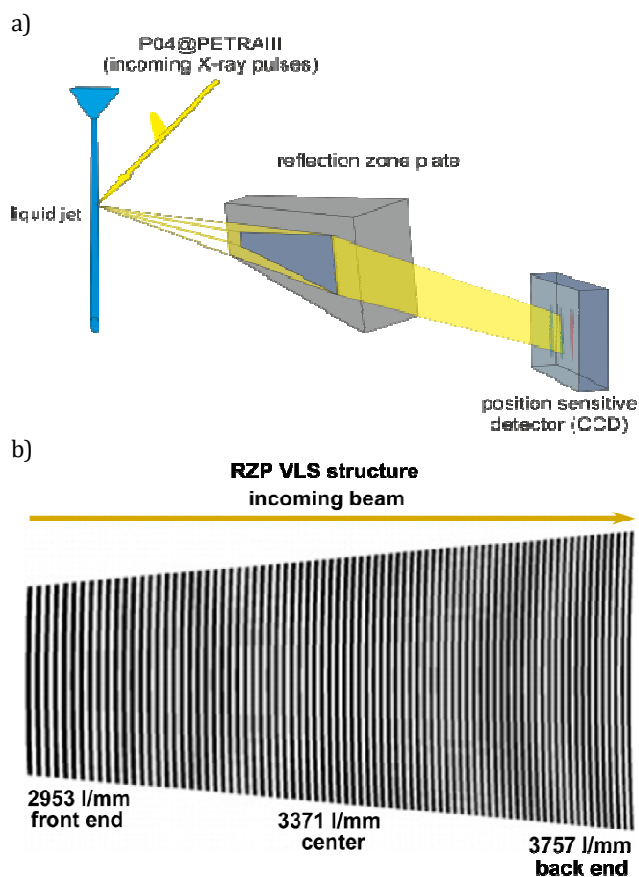


Fig. 1. a) Schematic view of the experimental setup. The incoming soft X-ray beam excites the sample delivered by the liquid jet. The following X-ray fluorescence is recorded with the RZP spectrometer. b) Schematic view of the 2D VLS RZP with slightly curved lines for an aberration-corrected focus. The periods vary between  $0.35 \mu\text{m}$  (front end) and  $0.26 \mu\text{m}$  along the optical axis.

## Results

Figure 2 shows a, so-called, resonant inelastic X-ray scattering (RIXS) map of liquid water. It is a combination of several XE spectra, each recorded at different excitation energies, around the absorption edge of oxygen in liquid water. In this case, the excitation energies range from 532 eV to 540 eV. Above the excitation energy of  $\sim 536$  eV, the  $1b_1$  peak fine structure is observed. The total acquisition time of the entire RIXS map was 90 s. Our results match very well previously reported findings [26, 27].

In the next section, the XE spectrum for non-resonant excitation is compared to the spectra acquired over a longer period of time from previous publications and the energy resolution of the RZP is investigated.

Figure 3 shows the XE spectrum for a 10 s acquisition time with an excitation energy of 540 eV and a  $1000 \mu\text{m}$  beam slit. The peaks corresponding to the outer valence orbitals are well resolved. The peak labelled  $1b_1$  corresponds to the lone pair orbital with the splitting well-resolved;  $1b_2$  and  $3a_1$  denote the bonding orbitals. The latter are broadened due to vibrational excitations during the emission process [26].

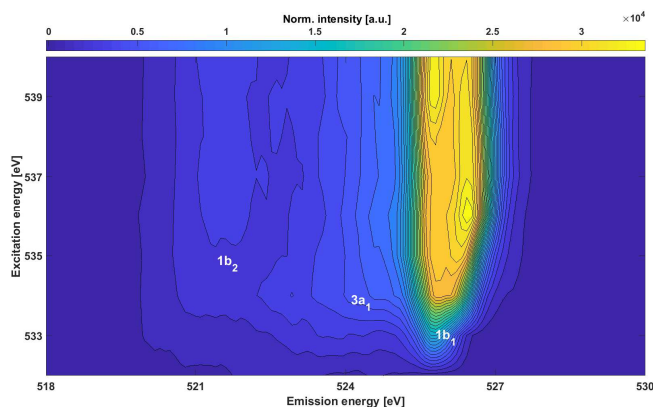


Fig. 2. RIXS map of liquid water at the oxygen K-edge with a total acquisition time of 90 s equally divided between 9 different excitation energies ranging from 532 eV to 540 eV with 10 s recording time each. The beamline exit slit was set to  $1000 \mu\text{m}$ .

The origin of the fine structure of the  $1b_1$  peak is still debated with two prominent, but contradictory models [26, 27]. One model proposes the splitting is due to different structural motifs while the other model sees core-hole dynamics as the origin of the split peak. Both models claim support by temperature-dependent measurements and changes to the spectra due to the solvation of salt ions [12, 26-29, 32]. In either case, there is a strong consensus that the XE signal is sensitive to the hydrogen bond. In the inset of Figure 3 a liquid water spectrum at the oxygen K-edge, recorded with a conventional grating spectrometer is shown for reference. The acquisition time was 55 min.

The 10 s XE spectrum recorded with the RZP already shows the characteristic structure of liquid water and agrees very well with the 55 min spectrum.

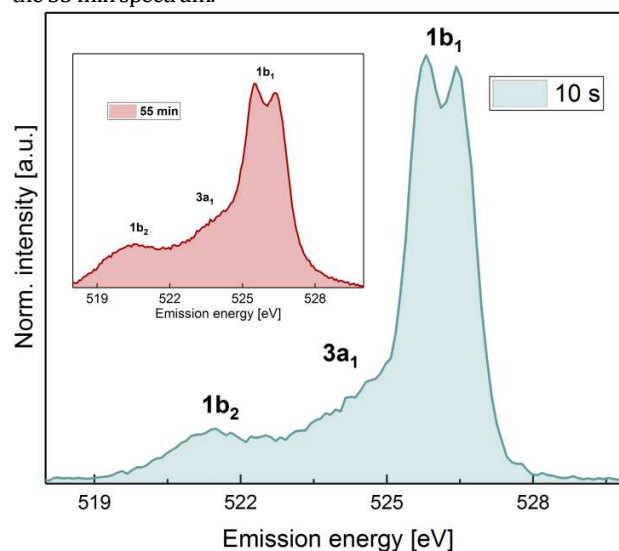


Fig. 3. A recorded XE spectrum of liquid water with an acquisition time of 10 s. For comparison, the inset shows a spectrum recorded with a conventional spectrometer for 55 min from Ref. [28] with the same excitation energy of 540 eV. Both show the characteristic fluorescence signals corresponding to the outer valence orbitals. The splitting in the lone pair regime is well resolved.

In the next step, the energy resolution is investigated. Figure 4 shows a Gaussian fit of the elastic peak at 532 eV. The synchrotron beam and spectrometer resolution are assumed, to be Gaussian in shape. The FWHM of the fit is 0.5 eV, which is a convolution between the two. The exit slit of the beamline was set to 300  $\mu\text{m}$ , which corresponds to an energy bandwidth of  $\sim 0.2$  eV.

This leads to an energy resolution of the spectrometer of  $\sim 0.46$  eV at 532 eV, corresponding to a resolving power of  $E/\Delta E \sim 1200$ . This is comparable with conventional X-ray optical elements [5], though at much higher detection efficiency, when taking into consideration the pure optical element (grating) without efficiency-enhancing treatments or covers. Usually, a good-quality spectrum of liquid water requires tens of minutes [28, 29]. With the RZP the recording time is reduced significantly while maintaining the energy resolution, see Fig. 3.

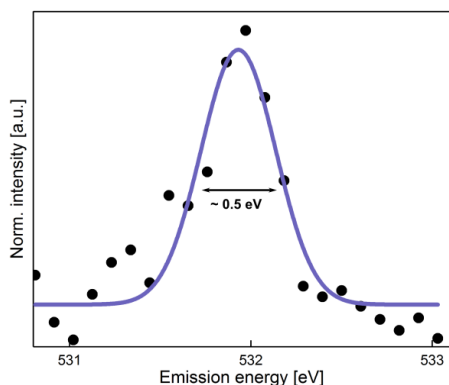


Fig 4. A Gaussian fit of the elastic peak at 532 eV shows a FWHM of  $\sim 0.5$  eV. The total acquisition time was 30 s.

Compared to previous studies using reflection zone plates, this work demonstrates that by recording the inelastic scattering signal one is able to reproduce the fine structure in the XE spectrum of liquid water, which requires a certain minimum energy resolution at the oxygen edge.

As an aside, it is worth mentioning that the zone plate used in these measurements was made out of silicon and was not coated. The first order diffraction efficiency could be even higher with a coating appropriate for this geometry and photon energy range, e.g., with Ni or Au deposition.

## Conclusion

In this work, we demonstrated the first X-ray emission spectroscopy measurements of liquid water using a RZP as a dispersive element. The resolving power is around 1200 at the oxygen K-edge, which is sufficient to resolve the fine structure in the XE spectrum of liquid water. The data acquisition time was only 10 s for a reasonable quality spectrum, already revealing all characteristic spectroscopic features of liquid water. A complete RIXS map can be recorded within 90 s. This is significantly higher in efficiency compared to conventional optics.

This high efficiency of RZP optics enables new possibilities in the investigation of biological and chemical systems while maintaining sufficient energy resolution.

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