Generation and simple characterization of flat, liquid jets

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ABSTRACT

We present an approach to determine the absolute thickness profile of flat liquid jets, which takes advantage of the information of thin film interference combined with light absorption, both captured in a single microscopic image. The feasibility of the proposed method is demonstrated on our compact experimental setup used to generate micrometer thin, free-flowing liquid jet sheets upon collision of two identical laminar cylindrical jets. Stable operation was achieved over several hours of the flat jet in vacuum ($10^{-4}$ mbar), making the system ideally suitable for soft x-ray photon spectroscopy of liquid solutions. We characterize the flat jet size and thickness generated with two solvents, water and ethanol, employing different flow rates and nozzles of variable sizes. Our results show that a gradient of thickness ranging from a minimal thickness of 2 $\mu$m to over 10 $\mu$m can be found within the jet surface area. This enables the tunability of the sample thickness in situ, allowing the optimization of the transmitted photon flux for the chosen photon energy and sample. We demonstrate the feasibility of x-ray absorption spectroscopy experiments in transmission mode by measuring at the oxygen K-edge of ethanol. Our characterization method and the description of the experimental setup and its reported performance are expected to expand the range of applications and facilitate the use of flat liquid jets for spectroscopy experiments.

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I. INTRODUCTION

Most chemical and almost all bio-chemical reactions occur in aqueous solutions. The investigation of dynamics and the structure of reacting species in their natural environment is indispensable and essential for understanding the functionality, the interrelation, and the importance of specific subsystems in reaction pathways.

In recent years, x-ray spectroscopy evolved to a valuable tool for the studies of (bio-) chemical static and dynamic processes in aqueous solutions. In particular, methods based on extreme ultraviolet and soft x-ray absorption spectroscopy (XAS) became pivotal to understand the fundamental physics and chemistry of the underlying electronic processes for multiple reasons: (1) an experimentally higher energy resolution in the soft x-ray regime compared to hard x-ray spectroscopy for both instrumental reasons and due to the intrinsically smaller lifetime broadening of energetically more stable core-holes; (2) enhanced sensitivity to the valence electrons involved in the reactions while still having elemental sensitivity; and (3) K-edges of key-elements in (bio-) organic systems, such as C, O, and N, lie in the soft x-ray regime.

However, spectroscopic methods in this photon energy range are extremely challenging due to the large absorption of light by matter. The most direct spectroscopic application, XAS measured in transmission, requires thin samples with thicknesses on the order of the photon penetration depth to allow significant transmission through the sample.

For soft x rays, the penetration depths are of a few $\mu$m. More specifically, in the case of ethanol, the penetration depth is 1.7 $\mu$m at...
200 eV, 1 μm around the O-edge at 540 eV, and 15 μm at 1500 eV, as estimated from atomic scattering factors of the individual elements.\textsuperscript{7}

To avoid unnecessary losses due to the sample environment, the experiments are typically performed under vacuum conditions. Under these experimental conditions, methods based on total or partial electron yield detection are generally favorable. However, they are difficult to be applied for liquid samples due to the requirement of measuring the sample electric drain current or their demand of high vacuum conditions.

Alternative methods, such as total or partial fluorescence yield XAS (TFY-XAS or PFY-XAS), that provide similar information are hindered due to low fluorescence yield at soft x-ray energies. In addition, the relation between the absorption cross section and the integrated fluorescence yield can be ambiguous because state-dependent fluorescence can result in relative peak intensities differing from the true absorption peaks. Furthermore, such indirect absorption measurements are affected by self-absorption of the emitted radiation (i.e., fluorescence radiation re-absorbed in the sample).

Recently, great efforts have been put into realizing compact experimental setups capable of delivering liquid samples as stable sheets with thicknesses on the order of a few μm, which corresponds to the attenuation length in water (and most other relevant solvents) for photons in the soft x-ray energy range. While this paper focuses on the application for x-ray absorption spectroscopy, the use of thin, flat liquid jets are also advantageous in combination with other techniques such as angle-resolved photoemission spectroscopy or UV/Vis spectroscopy with highly absorbing samples.

Various methods of generating thin liquid samples have been demonstrated.

A convenient approach is to use sample cells consisting of transparent windows, typically made of Si₃N₄,\textsuperscript{11–13} spaced micrometers apart. While these cells require very little sample volumes and provided soft x-ray absorption data in transmission mode of excellent quality,\textsuperscript{14} to date, no report has been published using a flow rate high enough to replenish the sample between subsequent light shots,\textsuperscript{10} hindering time-resolved measurements. This is problematic for samples subjected to photo-induced degradation, very common when using high brilliance x-ray sources. Another complication of high brilliance x-ray sources is that the beam may burn a hole into the cell window, making the cells incompatible with the high photon flux of modern x-ray sources. In addition, for pump–probe experiments where the sample is photo-excited by an optical pump pulse, the sample may interact with the (laser heated) cell windows. Hence, the choice of the most suited window is often a compromise between x rays and laser transmission and its material compatibility with the sample under irradiation.

Window-less sample delivery is a key method to overcome the aforementioned problems. The very first results showing interaction of x rays with free-flowing liquid jets have been published about two decades ago.\textsuperscript{15} In this pioneering work, x-ray absorption spectra of liquid water were measured around the oxygen K-edge, allowing the identification of features attributed to the bulk liquid phase, demonstrating for the first time the feasibility of liquid phase x-ray spectroscopy experiments.

In the following years, further developments have been driven by the scientific interest in high pressure x-ray photoelectron spectroscopy.\textsuperscript{17} Here round about 20 μm–50 μm thick jets have been used. However, these systems are too thick for use in transmission spectroscopy, which requires a sample thickness in the micrometer or even sub-micrometer range. While circular jets, in principle, can be made thinner, their thickness gradient over a typical x-ray focal spot diameter of 10–50 μm is large, potentially leading to significant changes in the spectral features measured in transmission.\textsuperscript{19}

The signal contribution from the measurement area of too low transmission T, typically if T < 0.05, may lead to saturation effects in the spectrum.

Window-less sample delivery techniques for in-vacuum applications with sufficiently thin liquid samples suitable for transmission XAS may be categorized into gas-squeezed liquid jets,\textsuperscript{7} flat nozzles,\textsuperscript{20,21} and impinging liquid jets (as used here).\textsuperscript{22}

Gas-squeezed liquid jets (a gas-dynamic nozzle consisting of one liquid- and two gas-channels in a borosilicate chip) are reported to allow tunable thicknesses down to 20 nm,\textsuperscript{23} which makes it the most promising method for the generation of nm-thin liquid sheets. A drawback of this method is that gas is actively pumped into the experimental chamber, which counteracts the requirement of low atmospheric pressure in the chamber.

Single, slit-type nozzles with diameters of typically >100 μm are used to generate liquid sheets that have a thickness down to a few micrometers.\textsuperscript{21} While this is the simplest technique to generate free-flowing liquid sheets, the large nozzle dimensions come together with the requirement of huge flow rates, typically on the order of 40 ml/min–80 ml/min. This makes such slit-type nozzles not ideally suited when dealing with limited quantity of samples or applications in vacuum chambers. The development of this method to smaller slits diameters of a few micrometers might overcome this problem but has not been demonstrated yet, possibly due to the ease of clogging of such thin nozzles.

Impinging liquid jets are able to generate flat sheets over a wide thickness range. Examples of water jets found in the literature employ 30 μm nozzles to generate thicknesses down to 0.8 μm\textsuperscript{1} at a flow rate of 3 ml/min or 50 μm nozzles to generate a thickness profile from 1.4 μm to 3 μm at a flow rate of 6 ml/min.\textsuperscript{15} Also 3D printed, single nozzle type injectors, at which the liquid streamlines collide within the nozzle, have been demonstrated to produce sheet thicknesses in the range of 1.0 μm–4.6 μm. Hereby, a flow rate of 9.4 ml/min and isopropanol as the test sample have been used.\textsuperscript{24} However, the small thickness has been achieved on the cost of probe sample consumption due to high liquid flow rates. It is worth pointing out that isopropanol has a very low surface tension, which allows us to get thinner sheets compared to water.

The generation of a flat liquid sheet by crossing two cylindrical liquid jets has the advantage of (1) no artificial gas–liquid or solid–liquid interface to chemicals different to those in the probed liquid, (2) allowing sample renewal up to MHz repetition rate experiments,\textsuperscript{7} and (3) a relatively large and flat sheet surface area. Typically, these advantages come with the drawback of relatively high sample consumption. While the reported limits of the flow rate used to generate a first liquid sheet including the point of first contraction are 3.9 ml/min–7.2 ml/min,\textsuperscript{25} we could demonstrate the presence of a chain of sheets already at much lower flow rates (see, e.g., Fig. 6 for 1.5 ml/min). We speculate that this is due to the different shape of nozzle employed here, although the orifice diameter is 50 μm for both experimental setups.
The sample needs to be collected after introducing it into the vacuum chamber, and there are different sample catching strategies proposed. The catching of the sample in a differentially pumped volume with an orifice of a few hundred $\mu$m allows us to recycle the sample but is very challenging experimentally. As soon as some liquid touches the surface of the catcher, it freezes, inducing ice growing toward the nozzle and eventually its clogging. We have chosen the approach of freezing the sample in a cryocooled catcher, which is simple and reliable.

We refined the impinging liquid technique to nozzle diameters of only 25 $\mu$m, resulting in sample flow rates approximately four times lower as compared to standard nozzle diameters of 50 $\mu$m. The lower flow rate matches well with the sample-catching strategy of accumulating ice.

In order to obtain quantitative absorption information, such as molecular absorption coefficients, it is crucial to know the thickness of the probed liquid sheet. Furthermore, the possibility of measuring thickness fluctuations with time gives a measure to optimize both the tunable parameters influencing the sheet geometry as well as to select a best sample point on the sheet surface.

In this manuscript, we present a thorough characterization of our liquid flat jet. The properties of the flat jet are determined by a novel approach based on the thin-film interference of monochromatic laser light, combined with the absorption information of a solvated dye in the liquid. The jet stability is given in terms of sheet stability on the short (thickness fluctuations) and long (events terminating the sheet generation) timescale.

We estimate the thickness profiles of the liquid sheets for different experimental conditions achieved by varying the nozzle diameter (25 $\mu$m and 50 $\mu$m) and flow rate and employing different solvents (water and ethanol).

Finally, we present an example of an x-ray absorption spectrum measured at the oxygen K-edge of ethanol in transmission mode and compare it to the one obtained in PFY, confirming the good quality of XAS data that can be achieved with flat liquid jet setups.

II. EXPERIMENTAL METHODS

A. Experimental setup

Deionized water (18.2 MΩ cm at 25 °C) and ethanol, 99%, were used as solvents, and methylene blue (MB), 99% from Sigma-Aldrich, was dissolved in order to achieve significant absorption of monochromatic laser light, emitting monochromatic light at 632.8 nm. The absorption coefficients of the used MB solutions (see Figs. S5 and S7 in the supplementary material) were measured with a UV/Vis spectrometer using a thin cuvette with a path length of 12.65 $\mu$m, as shown in Fig. S4 in the supplementary material.

The liquids were pumped through PEEK capillaries using a HPLC double piston pump (Deltachrom P102 from Watrex). The liquid flow was split into two similar parts with a T-piece and directed into two custom-made 25 $\mu$m or 50 $\mu$m inner diameter nozzles. The nozzles were fabricated from fused-silica capillaries, as widely used for gas chromatography, by grinding one end into a cone shape with an apex angle of $30^\circ$–$40^\circ$. The pressure difference $\Delta P$ between the two ends of each nozzle is estimated using the Hagen–Poiseuille equation,

$$\Delta P = \frac{8\mu LQ}{\pi R^4},$$

where $\mu$ is the dynamic viscosity, $L$ is the pipe length, $Q$ is the volumetric flow rate, and $R$ is the pipe radius. A standard HPLC pump system provided pressures up to $\sim$500 bars, allowing for a huge range in liquid flow rates using capillary lengths of 1 cm–3 cm. However, in our experiment, the circular liquid jets start to spray significantly once the applied pressures exceed 100 bars. As a consequence, we used nozzle dimensions, which allow us to work below this threshold.

The nozzles were oriented such that the two identical circular liquid jets collide at a distance of about 1 mm from the nozzle exits at an angle of typically $60^\circ$. Larger distances resulted in less stability and finally into the breakup of the generated liquid sheet. The two nozzles were originally located on a four-axis translational stage setup. Three stages allowed the combined motion of the two nozzles in x, y, and z, while the fourth stage moved only one nozzle in order to find the overlap of the circular liquid jets. For the synchrotron measurement, as shown in Fig. 10, the nozzles were mounted on a plate that constrained the relative nozzle positions such that during the experiment, one parameter less had to be optimized.

If operated under vacuum, the liquid jet freezes during the flight time, which is about 10 ms–70 ms for typical jet velocities of 10 m/s and distances between nozzles and the catcher bottom of 10 cm–70 cm. The freezing of the sample constrains the design of the catcher because the frozen sample has to be collected to prevent disruption of the sample injection.

For a nozzle–catcher distance of only $\sim$10 cm–20 cm, the entire assembly made by the injector and catcher is very compact. However, during operation at pressures $<10^{-3}$ mbar, the formed ice particles bounce back from the bottom of the catcher, potentially perturbing the flat jet and increasing the pressure in the chamber due to evaporation of the bouncing particles. If the jet is operated at a pressure around 20 mbar, the ice particles are mostly sticking to the catcher bottom plate, forming a pile of frozen water at the position of impact. However, the growing of the pile of ice up to the nozzle disables the jet operation within minutes. A rotating ice-cutting blade did prolong the stable jet duration to $\sim$20 min before an ice block became too massive to be cut.

For the flat jet system presented here, the best performances have been reached by sacrificing the compactness of the system and increasing the nozzle–catcher distance to $\sim$60 cm. With this geometry, the catcher base plate was relatively uniformly covered with ice particles due to the cone-like spray of the jet after the point of destabilization of the liquid chain.

This new arrangement allowed us to perform experiments for more than 12 h with a nearly constant surface area of the liquid sheet varying only with the pump pressure oscillation as visualized in the supplementary material, S9 (Multimedia view). As detailed in Secs. III and IV, these oscillations induce only small changes to the thickness of the liquid sheet.

B. Jet characterization

We used the combination of thin-film interference and absorption of monochromatic laser light in order to characterize the thickness and stability of the flat jet.

The thin film interference was generated by illuminating the flat jet with a He–Ne laser, emitting monochromatic light at 632.8 nm. The laser intensity was adjusted by using a neutral density filter.
A polarizer cube was inserted to generate s-polarized light. After reflection on the liquid sheet, the light is imaged with an infinity-corrected long-range microscope objective (Mitutoyo MY10X-803) and a 10 cm or 20 cm focal distance lens with a CMOS color sensor (Basler acA 1920-48gc). The magnification factor of the optical setup was 2. For a cleaner image, the reflected light passes through a second polarizer cube for filtering out p-polarized components of the scattered light. The interference images are typically collected within the 10 ms exposure time.

### C. Thickness model

The Hasson–Peck model describes the thickness $d$ distribution of a flat sheet generated by two impinging circular jets.

$$d = \frac{R^2}{r} \frac{\sin^3 \alpha}{(1 - \cos \beta \cos \alpha)^2}, \quad (2)$$

with $R$ being the radius of the two cylindrical jets, $r$ being the distance from the impinging point, $\beta$ being the angular position on the liquid sheet with respect to the plane spanned by the two cylindrical jets, and $2\alpha$ being the impinging angle or approximately the angle between the two nozzles. In essence, the thickness scales with $1/r$.

The geometrical parameters are visualized in Fig. 1.

While this model is too simplistic to describe the liquid jet profile accurately, it provides a good basis for the prediction of trends in thickness. Indeed, an experimental study testing this prediction found qualitative agreement. More specifically, a thinner sheet was found by using larger impinging angle $\alpha$, a smaller orifice diameter, and higher angular position $\phi$.

### D. Thin film interference

Figure 2 shows a microscopic image of the liquid sheets generated using water. Conservation of mass and momentum results in a liquid sheet formation in the plane perpendicular to the plane containing the two cylindrical liquid jets, and the surface tension of the liquid causes the sheet to re-converge, generating a subsequent liquid sheet in the plane perpendicular to the former. This generates a series of alternating perpendicular sheets decreasing in surface area with increasing sheet number. The first largest sheet is the most stable as the flow rate is increased and provides the thinnest areas. In the following discussion, we will concentrate exclusively on the first sheet.

Measuring thin film interference, it is possible to extract the relative thickness gradient of the liquid sheet. In combination with an absorption measurement, the spatially resolved thickness over the full area can be determined quantitatively. Figure 3 shows a sketch of the thin film geometry and the definition of the coordinate system. We will consider only s-polarized electromagnetic waves ($E$ perpendicular to the plane of incidence) in this discussion. The electric field intensity measured on the pixel detector is the superposition of the electric fields from the waves $E_1$ and $E_2$, the first being reflected from the first interface and the second from the second interface (see Fig. 3 and Eq. (3)). Since $E_2$ travels through the liquid with path length $\frac{n_2d_2}{\cos(\beta_2)}$, it is damped by a Lambert–Beer term $e^{-\frac{nc}{e'}}$, where $e'$ is the concentration of the absorbing species and $c$ its extinction coefficient.

The Fresnel coefficients are written as $r_{ij}$ and $t_{ij}$, describing the reflection and transmission coefficients for light interacting with an interface between medium $i$ and $j$. The contribution of a third wave $E_3$ traveling four times between the two interfaces $[l_{(12)} f_{(23)} f_{(23)} f_{(23)} f_{(23)} = l_{(12)} f_{(23)}]^3$ can be neglected due to $r_{23} \ll 1$ to good approximation. The following abbreviations are chosen for better readability:

![FIG. 1. Schematics of the liquid jet setup (a) and the definition of the angles $\beta$ in the flat jet plane (b) and $2\alpha$ between the two nozzles (c). The nozzles (in orange) and the liquid jets are drawn much bigger relative to the other components.](image)

![FIG. 2. Two cylindrical liquid jets are entering the photograph on the left and form a cascade of liquid sheets after the impinging point. Sheets 2 and 4 lie in the plane formed by the axes of the two impinging cylindrical jets, while sheets 1, 3, and 5 are in the plane perpendicular to that.](image)

![FIG. 3. Schematic diagram of the thin film interference geometry.](image)
\[ E_0 = h \cdot e^{-\frac{(\omega-u)^2}{2\sigma^2}}, \]
\[ E_1 = r_{(12)} E_0, \]
\[ E_2 = r_{(23)} E_1, \]
\[ L = \frac{2}{\cos(\theta_2)} c', \]
\[ B = 2\sqrt{2} \cos(\theta_2) \cdot \frac{\omega}{c}. \]

The laser profile \( E_0 \) mapped on the pixel axis \( u \) is expressed as a Gaussian distribution of standard deviation \( \sigma \), amplitude \( h \), and the center position on the pixel axis \( \mu \). With the notations of Eq. (3), the optical path difference in the radiant and the Lambert–Beer term can then be expressed as
\[ \Delta \]
\[ \Delta \]

Given a finite resolution of the detector of \( \phi \) during the propagation: while the phase shift of the phase shift accumulated upon reflection on interface 2 and the reflection on the first interface, the phase shift of \( C \) speed of light, and integration constant \( \mu \) being the magnetic permeability of free space, \( c \) being the speed of light, and integration constant \( C_1 \) being set to 0. The phases \( \phi_1 \) and \( \phi_2 \) can be estimated considering the phase shifts accumulated during the propagation: while the phase shift of \( E_1 \) is entirely due to the reflection on the first interface, the phase shift of \( E_2 \) is the sum of the phase shift accumulated upon reflection on interface 2 and the phase shift due to the optical path length difference \( Bd \).

\[ \phi_1 = \phi_{(12)}, \]
\[ \phi_2 = \phi_{(23)} + Bd. \]

Given a finite resolution of the detector of \( \Delta d_{\text{pixel}} = d_2 - d_1 \). (Note that \( \Delta d_{\text{pixel}} \) is the range in film thickness observed by a single pixel), the intensity contribution of Eq. (4) on a single pixel is calculated as

The intensity data are a function of pixel-number. The relative thickness distribution is directly readable in these data since the maximal constructive interference (peaks in the intensity curve) happens only if the interference condition is fulfilled (see Eq. (4)) or, in short, if \( \phi_1 - \phi_2 = m \cdot 2\pi \), for \( m \) being an integer.

This condition returns a direct mapping between the jet thickness and the position of the maxima of the interference fringes. However, this relation provides only the relative change of thickness along the flat jet \( \Delta d \); in order to estimate the absolute value \( d \), we can attribute an unknown variable \( d_0 \) to the interference maximum corresponding to the thinnest thickness [the outermost right maximum in Fig. 4(c)]. The other values of the jet thickness along the jet result to be equal to \( d = d_0 + \Delta d \). In Sec. III and Sec. IV, we will show how to retrieve the thickness parameter \( d_0 \).

Equation (6) is the fit function that depends on five fit parameters: the amplitude, position and width of the Gaussian laser profile, an averaged background intensity restricted to an upper limit of 10 counts/pixel, and the thickness \( d_0 \). As previously stated in the discussion of the interference condition, \( d_0 \) may only take values corresponding to an integer value \( m \). This constraint is used to our advantage, and the fit procedure is repeated for a range of \( m \) values, thus effectively decreasing the number of simultaneous fit parameters by one. This procedure yields a fitted model for every used \( m \) value and the corresponding least squares error.

\[ \frac{I_{\text{pixel}}}{t} = \frac{1}{d_2 - d_1} \int_{d_1}^{d_2} I(d) dl. \]
Figure 5 shows the fit of the exemplary data from Fig. 4. While the fit in the central panel (b) shows an excellent agreement with the data, the fits on panels (a) and (c) are included to show the systematic disagreement between the fit and data when the value of $m$ is underestimated (a) or overestimated (b).

The $m$ value leading to the lowest least squares error is the final fit result, which also gives the lowest systematic deviation from the experimental data. The $m - 1$ and $m + 1$ values give satisfactory agreement as well within the quality of our experimental data, although with a slightly larger least squares error, while $m - 2$ and $m + 2$ lead to significantly worse agreement. The uncertainty of the fit results is thus defined as ±1 m, corresponding to ±0.25 μm.

III. RESULTS

The microscopic images of the liquid sheets generated using water and ethanol are shown in Fig. 6. While the two liquids form sheets of similar shapes, ethanol produces sheet lengths and widths two times bigger for a comparable flow rate. This difference is attributed to the difference in surface tension, which is 21.8 mN m$^{-1}$ for ethanol and 72.0 mN m$^{-1}$ for water at 25°C, respectively. The liquid sheet starts to disintegrate at 3 ml/min for water at the used nozzle geometry.

A. Thickness characterization

In order to increase the number of absorbed photons, methylene blue (MB) is dissolved into the liquid. Figure 7 shows the liquid sheet obtained with pure water [panels (a) and (c)] and a MB solution of 46.3 mmol/l [panels (b) and (d)]. It is interesting to note that in Fig. 7(b), the thickness gradient is directly apparent as a gradient in blue color. The comparison between the pictures without [panel (c)] and with MB [panel (d)] demonstrate the influence of absorbance on the interference pattern.

The most striking difference is that for destructive interference, the laser intensity annihilates without absorption, while a residual intensity is observed adding an absorptive medium. In fact, the effect is quite sensitive and leads to damping of the oscillating amplitude in the interference pattern.
The thickness was determined, as described in Sec. II D, and the resulting thickness values are shown in Fig. 8 for 50 μm, panels (a) and (b) for different flow rates, and 25 μm nozzles, panel (c) using water as the solvent.

It is worth noting that although the value of the jet thickness was fitted only at one point, the interference picture allows propagating the thickness values to all points on the sheet, which are connected by thin film interference fringes. In case of irregularities such as the black spots in Fig. 7, the accessible thickness determination is limited to the regions where the interference fringes are detected.

Using the previously defined notation, two subsequent interference maxima have to satisfy the condition $Bd_1 - Bd_2 = 2\pi$. This leads to a change in thickness between two subsequent interference fringes.
The thickness profiles using ethanol as a liquid sample (see Fig. 9) show that ethanol generates sheets with thicknesses significantly lower than water. Intuitively, the lower surface tension of ethanol results in sheets with a higher surface area, favoring lower thickness. In order to compare the influence of the tunable parameters and the solvent on the jet thickness, we compare the thickness values at a given distance away from the impinging point. The white crosses in Figs. 8 and 9 mark the position of $r = 500 \mu m$, and the corresponding thickness values at these positions, $d_{500}$, are summarized in Table I for the case of ethanol.

The thickness of the flat jet at this position varies with different flow rates. For the ethanol sheets, $d_{500}$ tends to increase with increasing flow rate toward a constant value. For the water sheets, the behavior is the opposite with a decrease in thickness for a higher flow rate. However, we would like to stress that a direct comparison of the $d_{500}$ values of different sheets is not trivial and has to be taken with caution. Several other parameters change when increasing the liquid flow rate for different trials, including the setup geometry used to determine the thickness.

For instance, in the case of water sheets, the patterns for the two flow rates listed in Table I are shown in Figs. 8(a) and 8(b) and clearly present different dark patterns in between the interference fringes. These black areas are probably due to curvatures in the liquid sheets, which result in the reflection of the laser light toward a different direction outside the collection angle of the microscope objective. As will be discussed later, the reason for the inhomogeneous sheet profiles is assumed to be a slightly different impinging geometry (circular jets not lying in a plane), as may be expected for two independent nozzles.

In addition, in the movies in the supplementary material S9 (Multimedia view), the pump pressure oscillations (equal to liquid flow rate oscillations) are visible as oscillations in thickness. Based on this observation, we conclude that there is a causal relation between the liquid flow rate and the thickness of the jet at position $r$.

The liquid sheet thickness oscillates in time due to oscillations in the HPLC pump pressure, which is characteristic for piston pumps. A double-piston pump was used for all experiments, which delivers pump pressure oscillations of much smaller magnitude. A further decrease in pressure oscillations can be achieved by implementing a pressure pulsation damping element.

The resulting maximum thickness changes of the liquid-sheet thickness are estimated to be at most 130 nm for the jet generated by 25 μm nozzles and at most 60 nm if generated by 50 μm nozzles, respectively, as the movies in the supplementary material S9 (Multimedia view) indicate. The oscillation period depends on the period of the piston pump, which is a function of sample flow rate and is 2 s for the flow rate of 0.5 ml/min.

We can conclude that thickness profiles measured at different settings proved to be hard to compare in detail as there are features in the interference pictures originating from uncontrolled parameters. We estimate that one potential important parameter is the actual angle of incidence between the two cylindrical jets.

While the nozzles are aligned satisfactorily by the eye, the actual direction of the generated cylindrical liquid jets can sometimes deviate from the defined direction of the nozzle. Two impinging jets not lying in the same plane will produce asymmetrical features if looked at in the plane of the detector and have thickness profiles depending on the degree of misalignment. While the results presented here are good fits to the experimental needs in the soft x-ray regime, it is highly advisable to have a method for thickness characterization of the jet during the experiment in case absolute cross sections are targeted.

### B. Soft x-ray absorption spectrum

The liquid jet system was installed and successfully tested at the soft x-ray branch of the PHOENIX beamline at Swiss Light Source (SLS). The detection scheme consisted of a silicon photodiode for measuring transmitted intensity and a Ketek silicon drift diode on the side for measuring the fluorescence. The flat jet thickness at the point of measurement was 3.3 μm as approximated using atomic scattering factors for the photon energy 510 eV and the x-ray beam...
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was focused to 20 × 20 μm². In order to get an It spectrum, the flat jet was moved 500 μm away from the x-ray beam such that the x rays did not pass the liquid sheet anymore. This It spectrum contains both the relatively small absorption of the gas phase in the vacuum chamber as well as the oxygen contamination of the Si3N4 window. The latter separates the experimental chamber from the focusing optics of the x rays and its signal is the reason for the small spectral feature at 530 eV.

Figure 10 shows the absorption spectrum measured in transmission and in PFY for pure ethanol at the oxygen K-edge. These spectra were collected in about 2.5 min, with an integration time of only 1 s/energy point.

It is interesting to note that the spectrum measured in transmission (blue line) has a significantly higher signal-to-noise ratio with respect to the one measured in fluorescence (red line), demonstrating the excellent quality of spectroscopic data achievable in liquid systems with our setup in the challenging soft x-ray region.

The ethanol XAS agrees well with the TEY spectrum obtained by a 30 μm circular jet and a 100 × 35 μm² x-ray spot size. Remarkably, these authors managed to get satisfactory signals with a positively biased (2.1 keV) copper electrode placed 1 cm away from the jet. Their TEY spectrum shows a lower signal-to-noise ratio than the absorption spectrum measured in transmission reported here. The reason for this could be that the TEY method makes use only of a fraction of the impinging photons since several factors, among which are geometrical constraints or vacuum conditions next to the liquid jet sample, hinder the detection efficiency of the emitted photoelectrons.

IV. CONCLUSION AND OUTLOOK

We presented a simple method to determine the absolute thickness of flat liquid jets, based on thin film interference and absorption of monochromatic light, achieving 250 nm precision. The flat sheets have been generated by a compact experimental setup that is able to produce liquid sample volumes with thicknesses in the range of a few micrometers and is stable at a pressure of 10⁻⁴ mbar over several hours, thus making it ideally suitable for measurements of XAS spectra in transmission in the soft x-ray energy range. Although not directly demonstrated here, we believe that fluorescence yield measurements would profit as well, due to the relatively low and tunable self-absorption (by varying the jet thickness). We demonstrated that through changing the solvent and flow rate, it is possible to tune the jet surface area and the thickness over a sufficiently large range. In particular, the jet thickness can be tuned between 2.2 μm and 10 μm. This feature is particularly useful because it allows the optimization of the sample delivery for different experimental conditions, such as sample concentrations or the x-ray spot size, among others. The setup has been used for experiments at a synchrotron facility providing good quality x-ray absorption data. Therefore, we envision that the results presented here can be helpful in planning and performing experiments with flat liquid jets with both large-scale facilities and table-top light sources.

SUPPLEMENTARY MATERIAL

See the supplementary material for the additional description of data acquisition, more interference data, determination of absorption coefficients, and movies visualizing jet stability.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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FIG. 10. X-ray absorption spectrum at the oxygen K-edge measured in transmission (higher blue line) and partial fluorescence yield (lower orange line) of pure ethanol acquired using 50 μm nozzles and a flow rate of 1.7 ml/min. The angle of incidence of the nozzles is ~ 60°.
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