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A closed-loop pump-driven wire-guided flow jet for ultrafast spectroscopy of liquid samples

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We describe the design and provide the results of the full characterization of a closed-loop pump-driven wire-guided flow jet system. The jet has excellent optical quality with a wide range of liquids spanning from alcohol to water based solutions, including phosphate buffers used for biological samples. The thickness of the jet film varies depending on the flow rate between 90 μm and 370 μm. The liquid film is very stable, and its thickness varies only by 0.76% under optimal conditions. Measured transmitted signal reveals a long term optical stability (hours) with a RMS of 0.8%, less than the overall noise of the spectroscopy setup used in our experiments. The closed loop nature of the overall jet design has been optimized for the study of precious biological samples, in limited volumes, to remove window contributions from spectroscopic observables. This feature is particularly important for femtosecond studies in the UV range. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4929860]

I. INTRODUCTION

Many ultrafast spectroscopic techniques are rapidly developing to cover the ultraviolet spectral range where the light scattering and stretching of ultrashort pulses in the window material become serious and often create overwhelming problems. For example, an 8-fs laser pulse centered at 275 nm after passing of a 1-mm thick UV-grade fused silica substrate will be stretched up to ~170 fs. In addition, in ultrafast experiments with high-repetitive laser pulses, one has to consider possible photochemical damage of the sample of interest and the need to constantly replenish sample to avoid accumulation of photochemical products and associated artifacts. For this reason, the flow-cuvette systems have been developed and they are commercially available; however, in some circumstances, other problems arise and these systems are not adequate. In particular, light scattering grows nonlinearly with decreasing wavelengths, which in turn dramatically increases the background and decreases signal-to-noise ratio (SNR).

Taking into account that the nonlinear signals in the ultrafast experiments such as transient absorption and two-dimensional photon-echo based spectroscopy performed in the deep UV (200–300 nm) are very small, this becomes the most important limitation in the application of window-containing flow cells (see, e.g., discussion in Ref. 1). All transparent materials are subject to scattering in the UV: any type of glass or crystal windows and the solvents themselves (the Rayleigh scattering grows as $1/\lambda^4$). This scattering affects the signal-to-noise ratio significantly, especially in experiments performed in the UV. Therefore, avoiding windows and reducing the thickness of the path length for decreasing the solvent scattering and its non-linear contribution to signal are attractive solutions.

For all the reasons listed above, it is highly desirable to develop a wire-guided flow jet (WGJ) system which should be stable enough in terms of both short- and long-term stability for performing experiments with femtosecond UV-pulses, and should have a flow speed which is high enough for sample exchange between laser pulses to avoid artifacts from accumulated laser-induced photochemistry.

We developed a closed-loop pump-driven WGJ system that enables the achievements of high SNR values in the deep UV with both high short- and long-term stability. Similar WGJ-systems have been already reported,[2,3] but the present design significantly improves the simplicity, performance, stability, and most important, greatly reduces the needed volume for stable operation. This later feature is particularly important for the study of precious biological samples. Moreover, our WGJ-system is compact (7 × 20 cm foot-print), which can be readily implemented into a typical pump-probe or 2D-setup with focusing optics with focal lengths in the 100–150 mm range.

Besides the design details provided in Sec. II, in this paper, we report the results of the full characterization of our WGJ-system with respect to flow- and optical stabilities which are important for conducting long-term measurements with high SNR (Sec. III).

II. DESIGN OF THE WIRE-GUIDED JET SYSTEM

The WGJ, which allows creation and continuous maintenance of a stable liquid layer between two wires, includes a microfluidic pump, a collector, the sandwich block which holds the wires, a damping syringe, and connecting tubes.

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The active parts of *WGJ* (block with wires and collector) are mounted into an L-shaped bracket attached to a XYZ manual translation stage (Newport, model 9062) which allows positioning of the jet with respect to the laser beam and the beam focal plane with 10-μm precision (see supplementary material[4]).

The sandwich block is home-built, based on an initial design of the H. F. Kauffmann group (University of Vienna, Austria) which was modified to include the above features. For securely holding and to ensure reproducibility of the wire fixation, we milled a channel 0.2 mm in depth in the sandwich block. The internal channel is symmetrically present on both sides of the sandwich block; it has an important role in the creation of high-quality liquid film at the immediate exit on the block and also prevents lateral leaks. The width of that channel defines spacing between wires. In our optimal design, with wires of 0.5 mm in diameter, the channel width is 3.5 mm. The blocks are made from stainless steel AISI 316-L. The flow jet is created through the use of stainless steel wires (same type as the steel of the block) that guide the liquid between them. The wires are manually bent to a *U*-shape and have a length of 90 mm. The internal width between them is 2.5 mm. In general, the length can vary by up to 5% but the width is fixed by the presence of the internal channel that helps make them parallel. These dimensions were found to lead to the best stability of the liquid film for solutions with a wide range of viscosities.

The wires were purchased from Advent Research Materials Ltd (UK). It is important to note that they are provided from the manufacturer straightened with good precision so that no additional straightening is required. The ends of the wires are immersed into a home-built collector. The collector is tilted by 45° with respect to the wires (see Fig. 1 and a photograph Fig. 2), and the tips of the wires are very close, almost touching the internal wall of the collector. This design allows the creation of a smooth curtain flow, and prevents an influence of standing waves (ripples) formed at the end of the jet due to contact with the liquid surface in the collector

FIG. 2. View of the flowing liquid between the wires. Due to the lens in the liquid film, the wires do not appear parallel. The collector is tilted by 45° with respect to the wires.

that might affect the stability of the liquid film (especially its thickness). Any variations of the liquid height in the collector will not affect these standing waves on the jet surface. This secures a smooth, stationary, and continuous flow of liquid in the *WGJ*. The optical quality of the liquid film between the wires can be visually inspected in Fig. 2.

The outlet of the collector is directly connected to the inlet of a microfluidic pump by a plastic tube, whereas the inlet of the sandwich block is connected to the outlet of the pump via a damper (a plastic syringe), and a plastic T-bridge (see in Fig. 1).

This damper has two functions: first, it serves to fill the *WGJ* system with the liquid sample and allows precise control of the amount of sample (and its height) in the collector. Second, it attenuates the pulsations in the flowing liquid caused by the pump. The microfluidic pump implemented in our *WGJ*-system is a gear-type pump from Mikrosysteme GmbH (Germany). The controller mzr-S06 powers the pump motor and controls its rotation speed with good precision and reproducibility (detailed technical characteristics of pump can be found on the company's web site). We employed two different pump models, the only difference being the materials of the internal gears. For compatibility reasons, we are using mzr-2942cp for pumping of biological samples in water-based solutions, and mzr-2921 for organic dyes dissolved in alcohols. In particular, we employed mzr-2921 for characterizations of WGJ-system described in Sections III A–III C, and mzr-2942cp for characterization described in Section III D.

For biological samples, we used tubing made from chemically resistant tygon (B-44-4X and 2075, purchased from Riesbeck GmbH, Germany) with an inner diameter of 1.6 mm, and for the alcohol-based solutions polytetrafluoroethylene (PTFE) tubing with an inner diameter of 1.6 mm (type BOLA-Tubing, purchased from Bohlender GmbH, Germany).
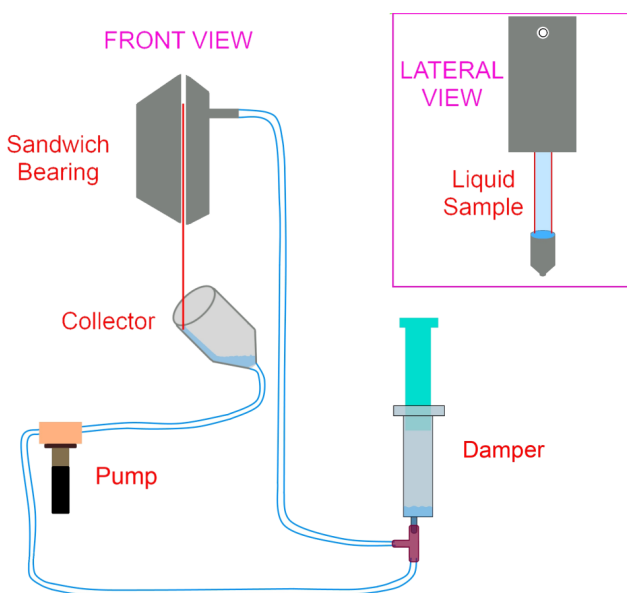

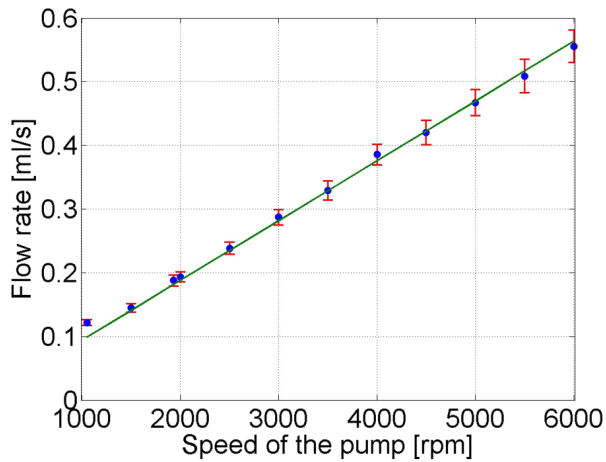FIG. 1. Schematic of the *WGJ* system (description of parts see in text).

FIG. 3. Flow rate of the *WGJ* as a function of the speed of the pump. Dots and error bars — experimental data, line — linear fit.

III. CHARACTERIZATION OF THE SYSTEM

A. Flow rate

The *WGJ*-system is very versatile in the sense that it can be adjusted to specific needs. In particular, the volumetric flow of the jet can be controlled by setting the number of revolutions per minute (RPM) of the pump motor through the controller, and also can be externally set from a computer using a corresponding software provided by the company. The error of the rpm-values is estimated to be ±30 RPM.

The flow rate was measured by using a known volume of liquid passing through an empty system. The time was taken with a stopwatch. This procedure was repeated many times and with different volumes to give enough statistical relevance and performed at different pump speeds. The relationship between rpm and flow was calibrated and shown in Figure 3. From the linear fit (shown as the green line in Figure 3) with the goodness coefficient of 0.98, the flow rate can be linked to RPM with a proportionality coefficient of $9.4 \cdot 10^{(-5)}$ (ml/s)/RPM.

However, for the ultrafast experiments with high repetition rate of laser pulses, it is more important to know the speed of the exchange of sample passing through the excitation spot. This estimation requires, besides of the flow rate and the spacing between wires, the values of the film thickness in the working area.

B. Characterization of the film thickness

Characterization of the thickness and its stability is done by operating the *WGJ*-system filled with the water solution of an organic dye and measuring its transmission using a He-Ne laser and a photodiode (PD) connected to an oscilloscope. A schematic of this measurement is depicted in Figure 4(a). We used Rhodamine 6G (Rh6G, purchased from Radiant Dyes Laser GmbH, Germany) because it has an absorbance peak close to that of the He-Ne laser (543 nm) used in the experiment,[5] and it is a water-soluble dye. At this wavelength, the extinction coefficient of Rh6G is approximately $10.5 \cdot 10^4$ M^{-1}cm^{-1}[6] so that only a small amount of dye is needed to achieve solutions with high OD. Concentrations of
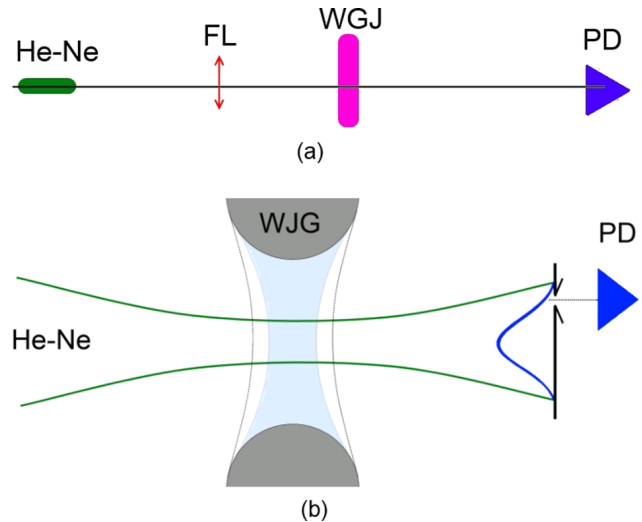

FIG. 4. (a) Schematic of the optical system used for measurement and test of thickness stability in the *WGJ*. He-Ne-laser, FL — focusing lens, PD — photodiode connected to the oscilloscope, and *WGJ* is the jet. (b) Top view of schematic diagram for measurement of the optical stability. The photodiode collects the light at the edge of the beam where instabilities are maximal. The light, depicted as two green convex lines, passes through the jet film (light blue) whose thickness varies up to the gray dotted lines. The dark gray semi-circles represent the stainless steel looped wire sides.

Rh6G and absorption spectra of solutions were tested through a commercial spectrophotometer (Shimadzu UV-2600, Japan) using a quartz cuvette (Hellma GmbH, Germany) with the inner path length of $l = 1$ mm. For correctly measuring the optical density OD_0 (at 543 nm), the prepared solution was 5-times diluted for use in the 1 mm cuvette.

For achieving of a small spot size on the jet, the laser beam was focused with a 150-mm focal length lens; the laser power was measured without liquid and with the jet running, using a photodiode (Newport, USA) with a set of attenuating filters (Thorlabs, USA); the signals were collected using a digital oscilloscope (Tektronix 24658 (USA)). The transmission of sample was calculated as $T = I/I_0$ (without accounting reflections on the jet surfaces). Here, I_0 is the mean value of the PD-signal without sample (jet is stopped), and I — the mean value of PD-signal after sample (jet is running). The thickness d of the sample film can be thus calculated as

$$d = l \frac{10^{-T}}{OD_0}. \tag{1}$$

The neglect of reflections leads to inaccuracy in the thickness estimation up to 2%. Variations in the jet film thickness were estimated by the deviations in the PD-signal measured after the jet (ΔI). The experimental data collected in Table I are a representative set of the results from one of the measurements. This table also gives calculated flow rates at a given RPM (see Subsection III A), the thickness deviation Δd in absolute units and normalized to the values of the layer thickness (RTD).

Figure 5 shows the measured film thickness as a function of flow rate. It can be fitted well to a second-order polynomial with the goodness of fit 0.95 (presented in the figure as a green solid line),

$$d = 645Q^2 + 313Q. \tag{2}$$

TABLE I. Experimental results of the thickness measurements. S.P. is the rotational speed of pump, Q is the flow rate, d and Δd is the thickness and its absolute deviation, and RTD is the relative thickness deviation.

S.P. (rpm)	Q (ml/s)	d (μm)	Δd (μm)	RTD (%)
1200	0.11	99	7	1.06
1300	0.12	95	7	0.94
1400	0.13	113	9	0.94
1500	0.14	123	10	0.80
1600	0.15	146	5	0.89
1700	0.16	169	6	0.88
1800	0.17	184	7	1.23
1900	0.18	227	13	1.40
2000	0.19	214	10	1.18
2500	0.23	284	11	1.94
3000	0.28	368	15	3.68

FIG. 6. Relative thickness instability RTD as a function of the flow rate Q of the jet.

As can be seen from Fig. 5, the thickness is nearly linearly proportional to the flow rate; deviations from the linear dependence are due to non-linear change of the meniscus geometry of the jet. We measured the jet thickness at different vertical positions of the laser beam spot and found that it varies insignificantly within 1–1.5 cm. It can also be seen in the photograph (Fig. 2) that the jet surface has excellent flatness in the vertical direction.

The relative thickness deviation $RTD = \Delta d/d$ vs. flow rate is plotted in Fig. 6. At the highest flow rates, the thickness variation values never exceed 4%. This dependence shows a clear minimum (approximately at 0.15 ml/s flow rate) which corresponds to the maximal stability of the jet thickness (0.8% at 0.76 ml/s flow rate).

The jet becomes unstable at low flow rates due to instability of the pump itself, and at high rates due to strong pulsations of the pumped liquid, also caused by the pump, as expected. It is also important to note that the good stability region has a plateau within of 0.12–0.17 ml/s flow rates. In our ultrafast spectroscopy experiments, we are using this range of flow rates to ensure sample exchange between laser shots. More specifically, it is possible to calculate the flow speed
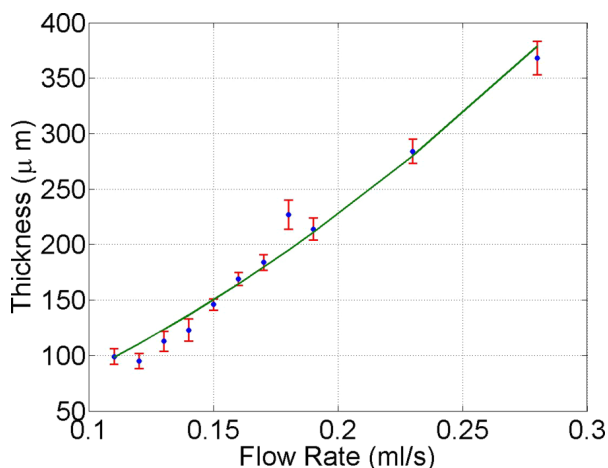
and to estimate the sample exchange rate. In particular, for $Q = 0.28$ ml/s (the highest measured flow rate), the water jet thickness corresponds to 0.37 mm (see in Table I), and taking into account inner spacing between wires (2.5 mm) we obtain a flow speed 300 mm/s, without accounting of the meniscus influence on the geometry of the jet cross section. The stable regime corresponds to the flow rate of $Q = 0.15$ ml/s; however, due to significant lowering of the jet thickness to 0.14 mm (Table I), the actual flow speed becomes higher: ~430 mm/s. For the laser spot of 0.1 mm in diameter, it gives a sample exchange rate of 4.2 kHz. In our experiments, we are using a 1 kHz laser and the spot diameter is approximately 60–70 μm so that this flow speed is well sufficient to ensure adequate sample exchange between laser shots.

C. Optical stability

Due to capillary effect, the profile of flowing liquid between wires corresponds to a negative lens as it is schematically shown in Fig. 4(b). The optical strength (i.e., focal length) of the formed lens and the position of its optical axis depend on the flow speed and its fluctuation.

The flow itself is stable even for long periods if not mechanically perturbed. This condition was tested in our setup for more than 5 h of continuous optical measurement.

To test the optical stability, we performed a series of measurements using a configuration schematically shown in Fig. 4(b). The difference from the previous setup (Fig. 4(a)) is that a small pinhole was placed on the edge of the beam where the beam fluctuations are maximal, and the WGJ-system was filled with pure water. We found that at the worst conditions (high flow rate, $RTD \sim 3\%$), the RMS of measured signal does not exceed 1%, i.e., it is less than the instability of the jet thickness caused by fluctuations of the gear pump. In the center of optical beam, the signal's fluctuations are much lower than at the edge. In case of very thin jet films, especially at low RPM of the pump, the jet itself becomes less stable and the thickness fluctuations affect more the optical stability due to the larger optical strength of the formed lens. Between 0.1 mm and 0.2 mm, the jet is stable, and above these

FIG. 5. Thickness of the water layer in the jet as a function of the flow rate. Dots: experimental points, line: fit from Eq. (2).

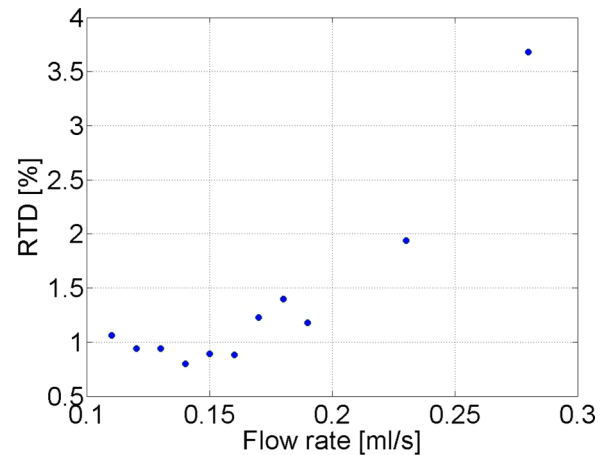values, the fluctuations of the thickness increase non-linearly (see Fig. 6).

D. Evaporation of the liquid

For long-term optical measurements, keeping the concentration of the sample at a constant level is very important, especially in time-resolved transient absorption experiments where uncontrollable changes of concentration can lead to artifacts during data collection. The concentration of the sample can change in the *WGJ* because of the evaporation of solvent from the surfaces of the jet and from the opening of the collector, since this is an "open-space" system. To characterize our system with respect to concentration stability, we conducted an evaporation test. The system was filled with a solution based on a sample used in ultrafast pump probe studies of $(dG)_4$ and left running for an extended period of time at the pump speed of 1500 rpm. $(dG)_4$ is a single strand of DNA formed by four guanosines linked by a phosphate-based backbone. The sample was purchased from Jena Bioscience GmbH (Germany) in the lyophilized form, and used as received, the compound was desalted and purified by the vendor and has an extinction coefficient of $\varepsilon = 47000$ M^{-1}cm^{-1}. It was solvated in a phosphate-based buffer; pH was always between 7.5 and 7.6 for the duration of the experiment. The *WGJ*-system was filled with a known quantity of solution (the "dead" volume of our system is 1 ml). The concentration of the sample was calculated prior the experiment to be 103 μM at 253 nm through the absorption spectrum (quartz cuvette with 1 mm inner path length).

The variation of concentration with time was calculated through the monitored OD of the solution, while the jet was running. The measured OD vs running time and calculated concentrations are plotted in Fig. 7. The linear fit (green line) gives the speed of the concentration change of 4 μM per hour,

$$c = 4*t + 99.8, \tag{3}$$

where c is the concentration in μM and t is the elapsed time in hours. After 3 h, the overall increase of sample concentration was ~10%.
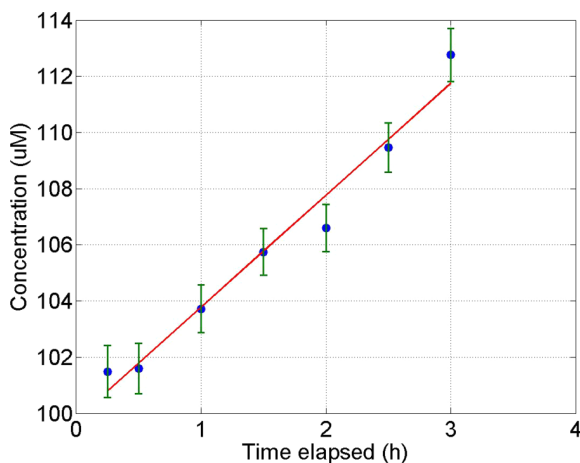

FIG. 7. Variation of the sample concentration during evaporation test. The red line is a linear fit.

We can safely assume that the quantity of $(dG)_4$ accumulated onto different surfaces of the *WGJ*-system (tubes, sandwich block, wires, and interior of gear pump) is negligible since the materials chosen are chemically resistant and non-adsorbing. In addition, we performed series of measurements so that if there is a small adsorption of the sample, it will be saturated after a few runs. There were no visible signs of deposition.

Using the fitting coefficients from Eq. (3) and the final sample concentration, the drop of volume in case of water-based solvents can be estimated to be 100 μl per hour. In case of alcohols as solvents, evaporation rates are much higher. In the particular case of ethanol, the evaporation rate was measured to be 0.5 ml/h.

In our long-term experiments, we are using larger volumes of solutions, typically 5–6 ml for biological samples and up to 10 ml for alcoholic-based solutions. The longest pump-probe scan takes about 30 min (acquiring of one 2D-spectrum takes approximately 5 min); during this period, the overall change of concentration is less than 1%.

IV. CONCLUSION

We developed a close-loop wire-guided jet system capable of conducting ultrafast spectroscopic experiments not only in the VIS but also in the deep UV. The design details are provided along with full characterization of the *WGJ*. The *WGJ*-system is compact, versatile, standalone, and can be fitted in a typical pump-probe or 2D spectrometer. It can run several hours without significant changes in the jet parameters like thickness of liquid layer or flow speed. We also measured the most important parameters of the jet: stability of the liquid film thickness, influence of the thickness fluctuations on the optical stability, and measured the sample evaporation speed.

With this *WGJ*, one can achieve sufficient sample exchange to permit laser repetition rates up to 4 KHz (0.1 mm spot sizes) while maintaining stable pathlengths with less than 0.8% changes in the jet thickness, and the associated optical stability better than 1% (on the edge of outgoing laser beam). Effect of evaporation of the solvents currently limits long-term operation of developed *WGJ* to ~1 h without notable change of the sample concentration. However, this drawback of an open-space system can be easily fixed by automated adding of solvent to the jet (e.g., in collector).

This *WGJ*-system has been tested in ultrafast experiments and is currently used as fully dedicated system for all our time-resolved studies requiring the use of liquid samples and femtosecond laser pulses. For example, in our UV transient absorption experiments with 8 fs pulses, we measure the absorbance changes in the samples on the level of 100 μOD.

ACKNOWLEDGMENTS

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