Supplementary Information: Picosecond Infrared Laser Driven Sample Delivery for Simultaneous Liquid-phase and Gas-phase Electron Diffraction Studies

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EXPERIMENTAL DETAILS

Delivery of Liquid Glycerol into Vacuum

The sample delivery of liquid glycerol into vacuum is briefly explained in the experimental method section of the main text. A sample reservoir was mounted on a height adjustable frame. One side of a Teflon tube was connected to the reservoir and other side was connected to a stainless-steel needle with an inner diameter of 0.45 mm, which was mounted on a three-axis sample translation stage inside the vacuum chamber. These details were illustrated for convenience in Figure S1. The liquid glycerol was hanging inside the stainless-steel needle, which is shown in upper row of Figures 2 and 3 in the main text. The flow of sample into the chamber was controlled by adjusting the height of the sample reservoir and back pressure to make sure there is liquid glycerol in the stainless-steel needle while avoiding liquid glycerol dropping down to the chamber from the needle tip. The PIRL laser shines on the glycerol in the needle from bottom (with a slight titling angle as can be seen in Figure 1a in the main text).
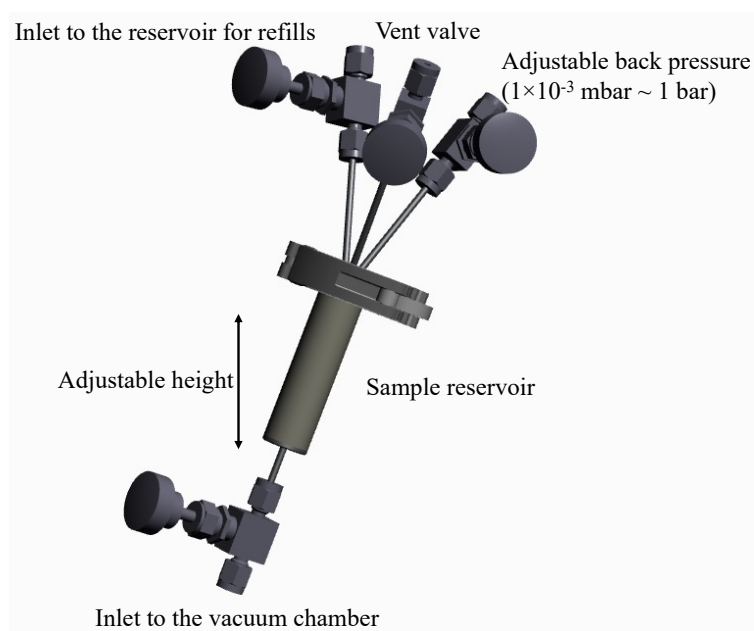

Inlet to the reservoir for refills   Vent valve

Adjustable back pressure
(1×10^{-3} mbar ~ 1 bar)

Adjustable height   Sample reservoir

Inlet to the vacuum chamber

FIG. S1. Schematic drawing of the sample reservoir for delivering liquid glycerol into the vacuum chamber.

Device Synchronization

Different kinds of pulsed sources (i.e. Picosecond Infrared Laser pulse, Ti:Saphire fem-
tosecond laser pulse, flshlamp nanosecond optical illumination source) are involved in the
experiments, so synchronizing these different devices is very important. Figure S2 shows the
diagram of how we synchronize these devices. As mentioned in the main text, the PIRL acts
as the master trigger for other devices. Its repetition rate is 1 KHz, which is the same as the
femtosecond laser. The delay generator (Quantum Composer 9520) was triggered by this
master trigger and synchronized other devices to the PIRL with adjustable delay (in a fine
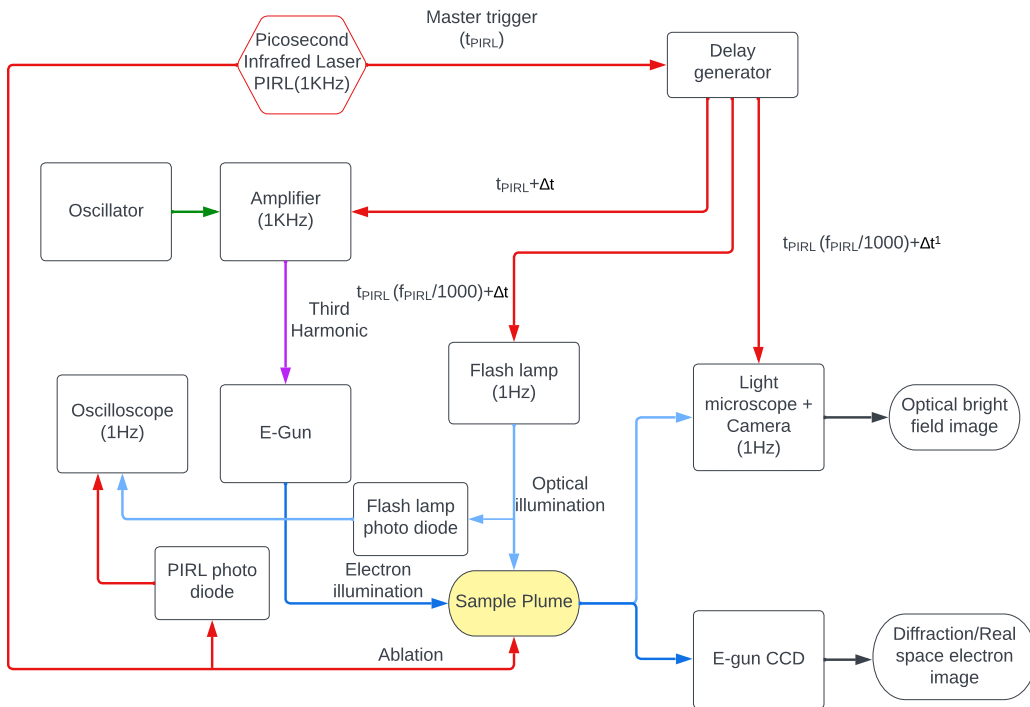step of 1 ns).

FIG. S2. Schematic drawing of the device synchronization diagram.

Sample Consumption Estimation

Based on our previous study,[1] an estimate for the sample ejection is 27 pL per PIRL shot.
The repetition rate of our PIRL laser is 1 KHz, but to avoid cumulative heating effects we
have an ablation window of 50 ms resulting in 50 shots per second. We need 2750 shots for
producing a diffraction image with good signal to noise ratio, giving a sample consumption

of 74.25 nL for a diffraction image. Liquid sheets used in MeV liquid UED experiments have a sample consumption rate of 0.20 ml/min.[2] For a repetition rate of 360 Hz (SLAC MeV UED facility),[2] our method will consume (360 s^{-1}×27 pL×60 s) = 583.2 nL per minute.
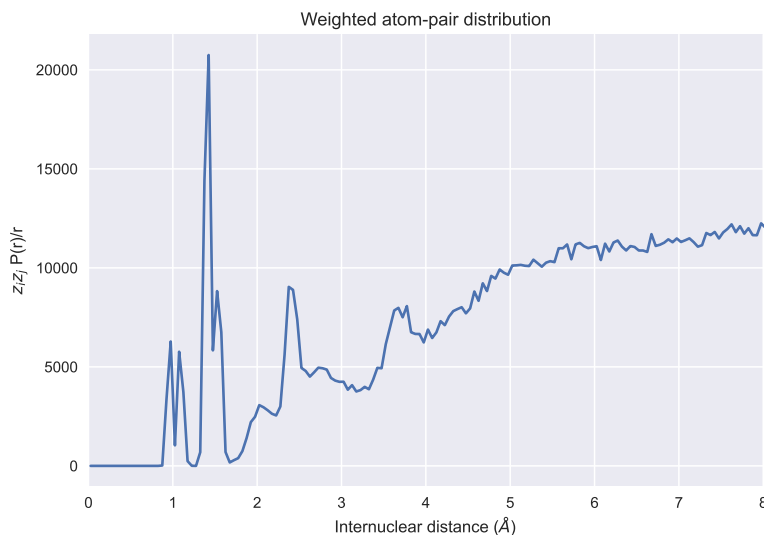
MOLECULAR DYNAMICS SIMULATIONS

FIG. S3. Histogram of the atom-pair distance distribution of liquid glycerol (a box size of 3 nm ×4 nm×5 nm using a Gromacs Molecular Dynamics simulation) of respective atom pairs and multiplied it by the corresponding atomic numbers and divided by the distance along the X-axis.

The molecular mechanics simulation of the structure of liquid glycerol was performed using the program Gromacs.[3] A box size of 3×4×5 nm was chosen and initially filled with 295 molecules with random orientations. After equilibration of the temperature (298K) a large cavity appeared which was filled with additional molecules. This process was repeated once more, resulting in a total of 389 molecules. The temperature and pressure where then equilibrated simultaneously for a total of 250 ps using a step size of 0.8 fs, stopping occasionally to monitor the density to check for convergence. The density increased from just under 1000 kg/m^3, plateauing at 1160∼1170 kg/m^3 after approximately 140 ps, which is slightly lower than the actual value of 1260 kg/m^3. The discrepancy is likely due to the difficulty that force fields have in describing hydrogen bonding accurately, but was sufficiently close for our purposes, since we do not have a precise measurement of either the temperature

or pressure under the experimental conditions. As a comparison, an additional simulation at 400K resulted in a drop in the density to 1060 kg/m^3, but the diffraction simulation result was very similar with just small shift in the 'liquid' peak at about 1.6 Å^{-1}.

We calculated the histogram of the atom-pair distance distribution of liquid glycerol (geometry files from Gromacs Molecular Dynamics simulation result) of respective atom pairs and multiplied it by the corresponding atomic numbers and divided by the distance along the X-axis. The result of the weighted atom-pair distribution is shown in Figure S3. The result is very similar to the Figure 5d in the main article. From this study, the broad distribution at >3 Å is found to be due to the summed contribution of the intermolecular distances.

[1] Y. Lu, C. L. Pieterse, W. D. Robertson, and R. J. D. Miller, "Soft Picosecond Infrared Laser Extraction of Highly Charged Proteins and Peptides from Bulk Liquid Water for Mass Spectrometry," Anal. Chem. **90**, 4422–4428 (2018).

[2] J. Yang, R. Dettori, J. P. F. Nunes, N. H. List, E. Biasin, M. Centurion, Z. Chen, A. A. Cordones, D. P. Deponte, T. F. Heinz, M. E. Kozina, K. Ledbetter, M. F. Lin, A. M. Lindenberg, M. Mo, A. Nilsson, X. Shen, T. J. A. Wolf, D. Donadio, K. J. Gaffney, T. J. Martinez, and X. Wang, "Direct observation of ultrafast hydrogen bond strengthening in liquid water," Nature **596**, 531–535 (2021).

[3] M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess, and E. Lindahl, "Gromacs: High performance molecular simulations through multi-level parallelism from laptops to supercomputers," SoftwareX **1-2**, 19–25 (2015).