Supplementary Information for **Photo-relaxation Dynamics of Phenolate Anions by Extreme Ultraviolet Time-resolved Photoelectron Spectroscopy in Liquid Jets**

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UV-VIS Absorption Spectra of KI and Phenolate Aqueous Solution

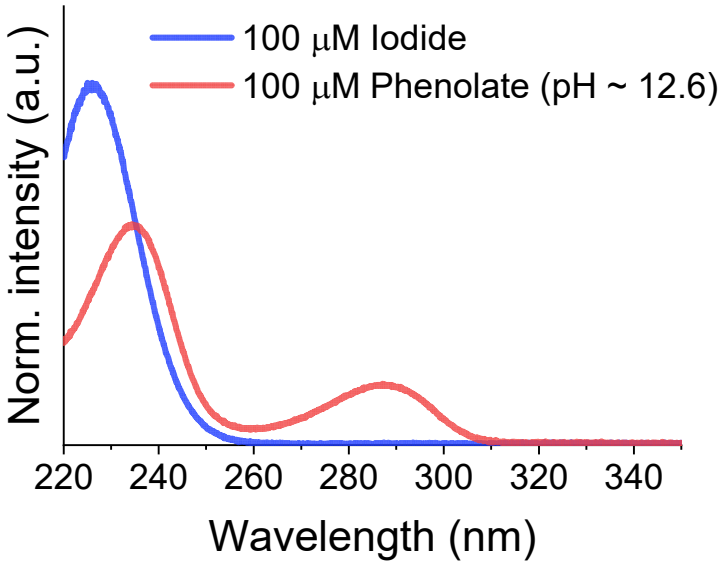

Fig. S1 Normalized ultraviolet-visible (UV-VIS) spectra of 100 μM KI and 100 μM sodium phenolate (PhO^-Na^+) aqueous solutions. The pH of the phenolate solution was 12.6 to ensure that the phenolate anion is the predominant species relative to neutral phenol.

XUV-only Photoelectron Spectrum of 100 mM Sodium Phenolate Aqueous Solution

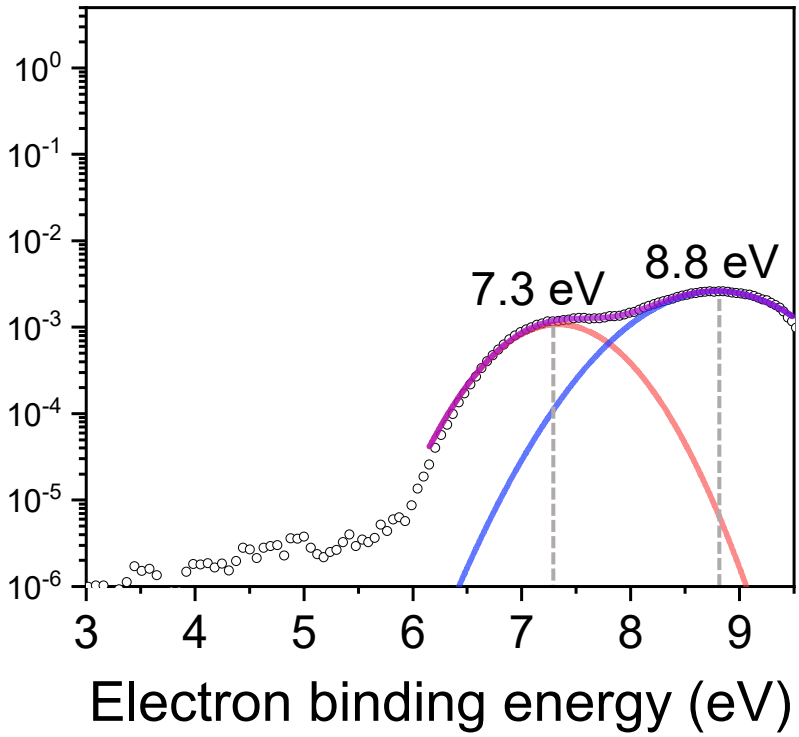

Fig. S2 XUV-only photoelectron spectra of 100 mM phenolate aqueous solution. The phenolate spectrum is obtained from residual plots of water peak fittings shown in Fig.1. The residual spectrum is deconvoluted by two Gaussian functions, which are centered at 7.3 (1) eV and 8.8 (1) eV, respectively. The spectrum is plotted in logarithmic scale.

UV-Induced Space-Charge Correction

The delay-dependent space-charge shift arises from Coulombic interaction between electrons and cations generated by the pump UV pulse and probe XUV pulse, which decelerate the XUV photoelectrons. To correct this shift, the delay-dependent water spectrum is deconvoluted using multiple Gaussian functions to determine the $1b_{1(liq)}$ peak shift at each delay. This procedure follows the approach used in previous studies by Kornilov and by our group.[1-3] However, in the present analysis we employ three Gaussian functions corresponding to the $1b_{1(gas)}$, $1b_{1(liquid)}$, and the cusp associated with $3a_{1(gas+liquid)}$ features. The position of the $1b_{1(gas)}$ peak is fixed at each delay to provide a more accurate determination of the $1b_{1(liquid)}$ peak shift. Representative Gaussian fits for spectra acquired at negative delay (-1.67 ps) and positive delay (200 ps) for phenolate S_1 and S_2 are shown in Figure S3. The resultant space-charge shift profile is presented in Figure S4.

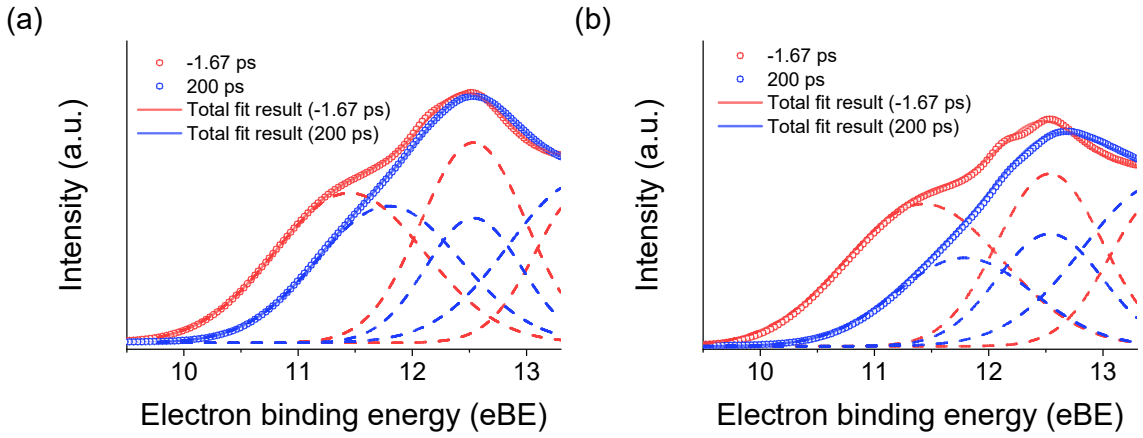

Fig. S3 Gaussian deconvolution of the photoelectron spectra for (a) phenolate S_1 excited at 288.5 nm and (b) phenolate S_2 excited at 240 nm. Red and blue circles represent the spectra acquired at -1.67 ps and 200 ps pump-probe delay, respectively. The corresponding red (-1.67 ps) and blue (200 ps) dotted lines show the Gaussian components assigned to the $1b_{1(gas)}$, $1b_{1(liquid)}$, and $3a_{1(gas+liquid)}$ features, ordered from low to high electron binding energy. Solid lines indicate the total fitted spectra obtained from the Gaussian deconvolution.

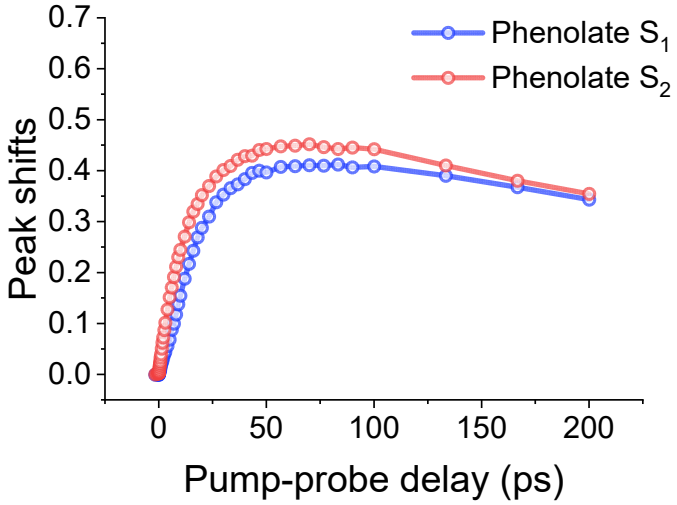

Fig. S4 Time-evolution space-charge shift extracted from the $1b_{1(liq)}$ peak positions in the electron binding energy (eBE) spectra of a 100 mM phenolate aqueous solution following excitation to phenolate (blue) S_1 288.5 nm excitation and (red) S_2 phenolate 240 nm excitation.

Temporal Lineouts of XUV-TRPE Spectra for Phenolate and Iodide

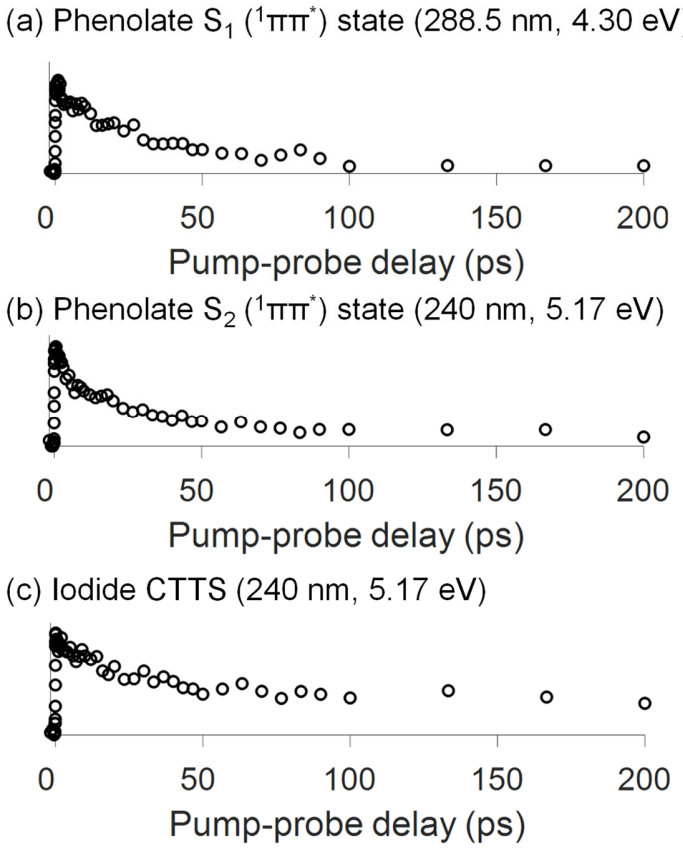

Fig. S5 Temporal lineouts for XUV-TRPE spectra for (a) S_1 (288.5 nm, 4.30 eV) and (b) S_2 (240 nm, 5.17 eV) excitations of 100 mM phenolate anion in liquid flat jets, and (c) iodide CTTS (240 nm, 5.17 eV) excitation in a cylindrical liquid jet.

Laser-Assisted Photoelectric Effect Spectra Obtained from Xe Gas Jets and Liquid Jets

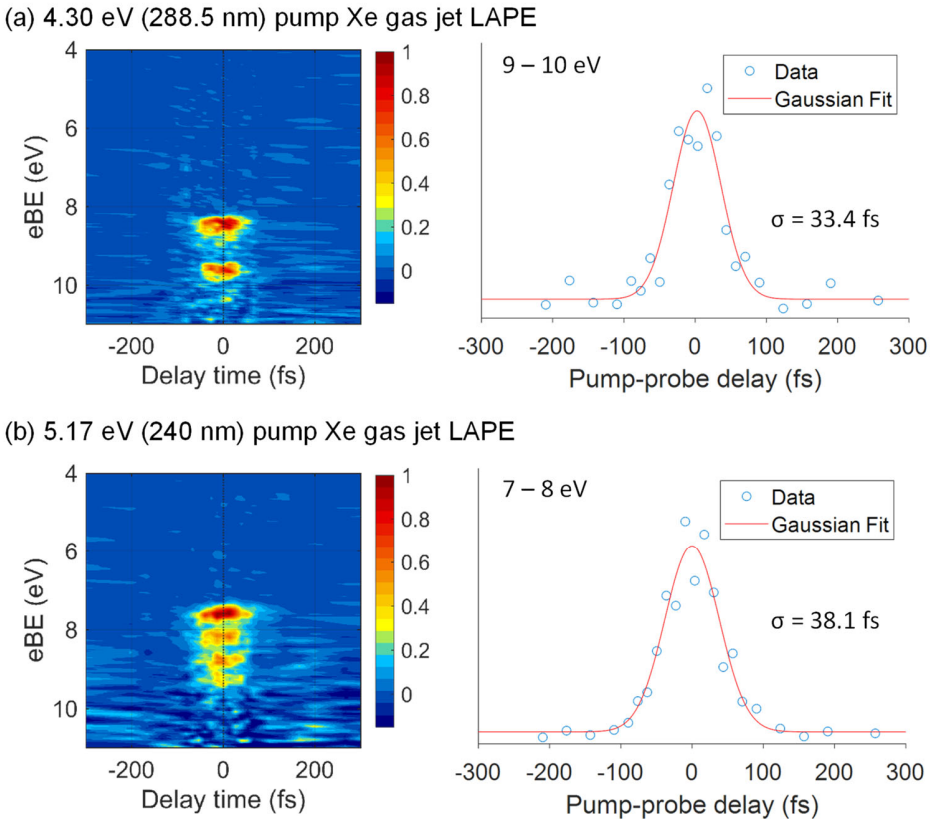

Fig. S6 Laser-assisted photoelectric effect (LAPE) obtained from Xe gas jets at (a) 4.30 eV (288.5 nm) and (b) 5.17 eV (240 nm) pump wavelengths. 2D contour plots of TRPE spectrum are shown in the left panels, while the temporal lineouts integrated over 9 – 10 eV (4.30 eV pump) and 7 – 8 eV (5.17 eV pump) are shown in the right panels. In the temporal lineouts, fit results with a Gaussian function is shown in red line. Extracted Gaussian width (1σ) of each of fits are denoted.

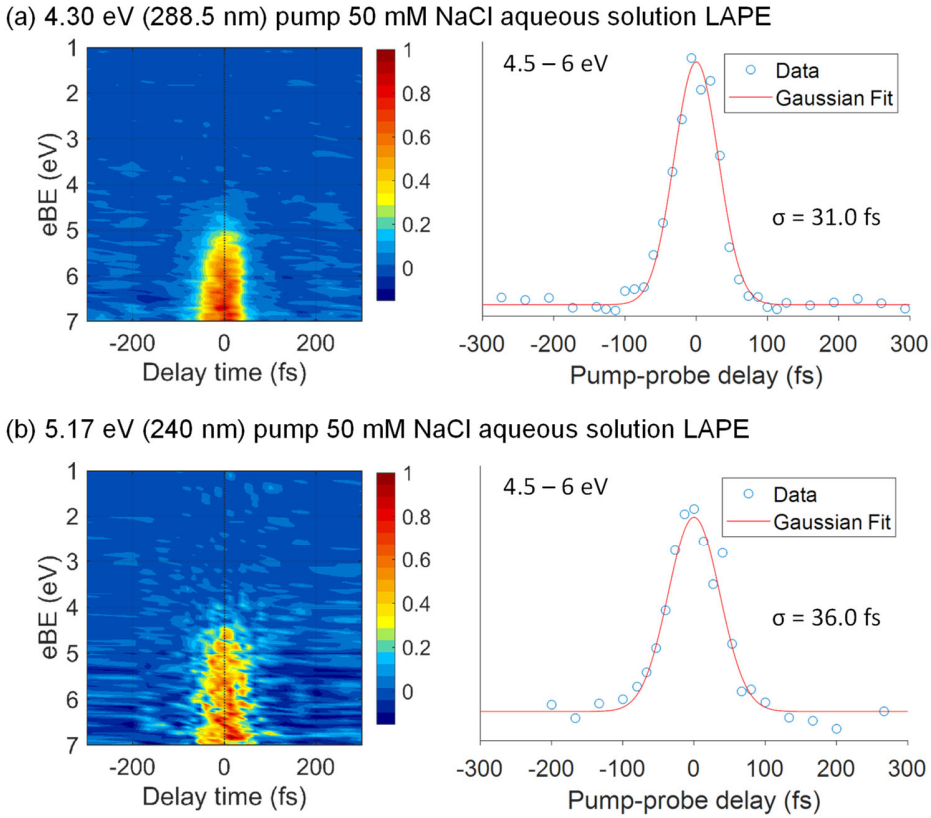

Fig. S7 Laser-assisted photoelectric effect (LAPE) obtained from 50 mM NaCl aqueous solution at (a) 4.30 eV (288.5 nm) and (b) 5.17 eV (240 nm) pump wavelengths. 2D contour plots of TRPE spectrum are shown in the left panels, while the temporal lineouts integrated over 4.5 – 6 eV are shown in the right panels. In the temporal lineouts, fit results with a Gaussian function is shown in red line. Extracted Gaussian width (1σ) of each of fits are denoted.

Kinetic Models for S_1, S_2 Phenolates and Iodide CTTS

The schematic description of the kinetic models used for global lifetime analysis is shown in the Fig 2. For the S_1 phenolate, initial excitation to the phenolate S_1 state ([S_1]) decays into hydrated electron ([HE]) and S_0 ground state. Reaction rates for each component can be expressed as:

$$\frac{\mathrm{d}[S_1]}{dt} = -k_{S1}[S_1]$$

$$\frac{\mathrm{d}[HE]}{dt} = r_{S1\rightarrow HE}k_{S1}[S_1] - k_{HE}[HE] \tag{S1}$$

, where k_{S1} and k_{HE} represents kinetic constants for S_1 state and hydrated electron, and $r_{S1\rightarrow HE}$ corresponds to branching ratio toward electron ejection pathway.

The analytical solution of the Eqs. S1 is described as follows:

$$[S_1] = e^{-k_{S1}t}$$

$$[HE] = \frac{r_{S1\rightarrow \mathrm{HE}}k_{S1}}{k_{S1-HE}}(e^{-k_{HE}t} - e^{-k_{S1}t}) \tag{S2}$$

For S_2 phenolate, initial excitation to the phenolate S_2 state ([S_2]) decays into the vibrationally hot S_1 anions ([$S_{1,\mathrm{hot}}$]), subsequently decays into internally relaxed S_1 anions ([$S_{1,\mathrm{cold}}$]) and hydrated electrons ([HE]). The internally relaxed S_1 anions further decay into the electron ejection pathway to generate hydrated electrons and non-radiative relaxation to yield phenolate S_0 ground state. The reaction rates for each components can be expressed as:

$$\frac{\mathrm{d}[S_2]}{dt} = -k_{S2}[S_2]$$

$$\frac{\mathrm{d}[S_{1,hot}]}{dt} = k_{S2}[S_2] - k_{S1,hot}[S_{1,hot}]$$

$$\frac{\mathrm{d}[S_{1,cold}]}{dt} = (1 - r_{hot\rightarrow HE})k_{S1,hot}[S_{1,hot}] - k_{S1,cold}[S_{1,cold}]$$

$$\frac{\mathrm{d}[HE]}{dt} = r_{hot\rightarrow HE}k_{S1,hot}[S_{1,hot}] + r_{cold\rightarrow HE}k_{S1,hot}[S_{1,cold}] - k_{HE}[HE]$$

(S3)

Here, $r_{hot\rightarrow HE}$ and $r_{cold\rightarrow HE}$ correspond to the branching ratios to the electron ejection channels from internally hot S_1 and cold S_1 anions, respectively. Analytical solutions of the Eqs. S3 are described as follows:

$$[S_2] = e^{-k_{S2}t}$$

$$[S_{1,hot}] = \frac{k_{S2}}{k_{S2-S1,hot}}\left(e^{-k_{S1,hot}t} - e^{-k_{S2}t}\right)$$

$$[S_{1,cold}] = \frac{(1-r_{hot\rightarrow HE})k_{S2}k_{S1,hot}}{k_{S2-S1,hot}k_{S1,hot-S1,cold}k_{S2-S1,cold}}\{k_{S1,hot-S1,cold}e^{-k_{S2}t} - k_{S2-S1,cold}e^{-k_{S1,hot}t} + \left(k_{S2-S1,cold} - k_{S1,hot-S1,cold}\right)e^{-k_{S1,cold}t}\}$$

$$[HE] = A_{S2}e^{-k_{S2}t} + A_{S1,hot}e^{-k_{S1,hot}t} + A_{S1,cold}e^{-k_{S1,cold}t} + A_{HE}e^{-k_{HE}t}$$

$$\text{where, } A_{S2} = \frac{k_{S2}k_{S1,hot}}{k_{S2-S1,hot}}\left[\frac{r_{hot\rightarrow HE}}{k_{S2,HE}} + \frac{(1-r_{hot\rightarrow HE})r_{cold\rightarrow HE}k_{S1,cold}}{k_{S2-S1,cold}k_{S2-HE}}\right]$$

$$A_{S1,hot} = \frac{k_{S2}k_{S1,hot}}{k_{S2-S1,hot}}\left[\frac{r_{hot\rightarrow HE}}{k_{S1,hot-HE}} + \frac{(1-r_{hot\rightarrow HE})r_{cold\rightarrow HE}k_{S1,cold}}{k_{S1,hot-S1,cold}k_{S1,hot-HE}}\right]$$

$$A_{S1,cold} = \frac{(1-r_{hot\rightarrow HE})r_{cold\rightarrow HE}k_{S2}k_{S1,hot}}{k_{S2-S1,cold}k_{S1,hot-S1,cold}k_{S1,cold-HE}}$$

$$A_{HE} = -(\mathrm{A}_{S2} + A_{S1,hot} + A_{S1,cold})$$

(S4)

For iodide CTTS excitation, the initial CTTS state ([CTTS]) decays into a contact pair ([CP]), followed by parallel decays into the iodide ground state or solvent-separated state ([SS]). The solvent-separated state further decays into the hydrated electron ([HE]) or iodide ground state. Overall reaction rates for each component can be written as:

$$\frac{\mathrm{d}[CTTS]}{dt} = -k_{CTTS}[CTTS]$$

$$\frac{\mathrm{d}[CP]}{dt} = k_{CTTS}[CTTS] - k_{CP}[CP]$$

$$\frac{\mathrm{d}[SS]}{dt} = r_{CP\rightarrow SS}k_{CP}[CP] - k_{SS}[SS]$$

$$\frac{\mathrm{d}[HE]}{dt} = \mathrm{r}_{SS\rightarrow HE} k_{SS}[SS] - k_{HE}[HE]$$

(S5)

Here, $r_{CP\rightarrow SS}$ and $r_{SS\rightarrow HE}$ represent branching ratios to the stepwise solvation channels from CP to SS and SS to HE, respectively.

The analytical solutions of Eqs.S5 are described in the following:

$$[CTTS] = e^{-k_{CTTS}t}$$

$$[CP] = \frac{k_{CTTS}}{k_{CTTS-CP}}\left(e^{-k_{CP}t} - e^{-k_{CTTS}t}\right)$$

$$[SS] = \frac{r_{CP\rightarrow SS}k_{CTTS}k_{CP}}{k_{CTTS-CP}k_{CP-SS}k_{CTTS-SS}}\{k_{CP-SS}e^{-k_{CTTS}t} - k_{CTTS-SS}e^{-k_{CP}t} + k_{CTTS-CP}e^{-k_{SS}t}\}$$

$$[\mathrm{HE}] = A_{CTTS}e^{-k_{CTTS}t} + A_{CP}e^{-k_{CP}t} + A_{SS}e^{-k_{SS}t} + A_{HE}e^{-k_{HE}t}$$

where,

$$A_{CTTS} = \frac{r_{SS\rightarrow HE}r_{CP\rightarrow SS}k_{CTTS}k_{CP}k_{SS}}{k_{CTTS-CP}k_{CTTS-SS}k_{CTTS-HE}}$$

$$A_{CP} = -\frac{r_{SS\rightarrow HE}r_{CP\rightarrow SS}k_{CTTS}k_{CP}k_{SS}}{k_{CTTS-CP}k_{CP-SS}k_{CP-HE}}$$

$$A_{CP} = -\frac{r_{SS\rightarrow HE}r_{CP\rightarrow SS}k_{CTTS}k_{CP}}{k_{CTTS-SS}k_{CP-SS}k_{SS-HE}}$$

$$A_{HE} = -(A_{CTTS} + A_{CP} + A_{SS})$$

(S6)

References

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3 Koga, M.; Kang, D. H.; Heim, Z. N.; Haldar, N.; Neumark, D. M., Extreme ultraviolet time-resolved photoelectron spectrometer with an ultrathin liquid flat jet. *Rev. Sci. Instrum.* **2025,** *96*, 073002.