

# Excited state electronic structure and ultrafast relaxation dynamics in aqueous pyrazine probed using liquid-jet time-resolved photoelectron spectroscopy

## Content

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Energy and charge transfer processes in aqueous solution play important roles in biochemical processes, material science, and environmental and energy science, where the mechanisms of such phenomena are affected, and even driven, by reactant-water interactions in an aqueous environment. Pyrazine exhibits rich photophysicochemical properties and has been studied extensively in isolated form [1,2]. Due to its high photoabsorption cross-section, vapor pressure, and aqueous solubility, it can be readily studied in the gas and aqueous phases, allowing water-induced electronic structure modifications and its solvent-perturbed photoexcited state dynamics to be studied, through comparison to gas-phase studies.

Here we report liquid-jet-(LJ)-based, fs-time-resolved, UV-EUV photoelectron spectroscopy (TRPES) experiments in aqueous pyrazine. The solute was resonantly-excited to the short-lived S<sub>2</sub> excited state at 267 nm, and the ground and excited states were simultaneously probed with 65-fs time-resolution using 32.1 nm probe pulses, generated via high harmonic generation (HHG). Pump-pulse-intensity studies revealed laser-intensity-dependent system energetics and dynamics. A corresponding mitigation of multi-pump-photon-induced space charge effects, under conditions that still permitted significant photoexcitation, allowed the nascent photoexcited-state dynamics to be interrogated. Global fit analyses to the resulting TRPES data revealed an initial relaxation via internal conversion (IC) in  $50 \pm 8$  fs, with subsequent population transfer to lower-lying states occurring on  $560 \pm 150$  fs,  $9 \pm 3$  ps and  $90 \pm 50$  ps timescales. Comparing our results to those from related gas-phase studies, slower relaxation behaviours are confirmed on  $>100$  fs timescales. These observations will be discussed in the context of the electronic structure of pyrazine and its known dynamic behaviors following photoexcitation in the gas-phase.

## References:

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2. Scutelnic, et.al. "X-ray transient absorption reveals the 1Au ( $n\pi^*$ ) state of pyrazine in electronic relaxation", *Nature Communications*, 12, 5003 (2021).

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