Ultrafast spectroscopy of liquid solutions under vacuum

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LAUSANNE CENTRE FOR ULTRAFAST SCIENCE LACUS

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Liquids under vacuum?

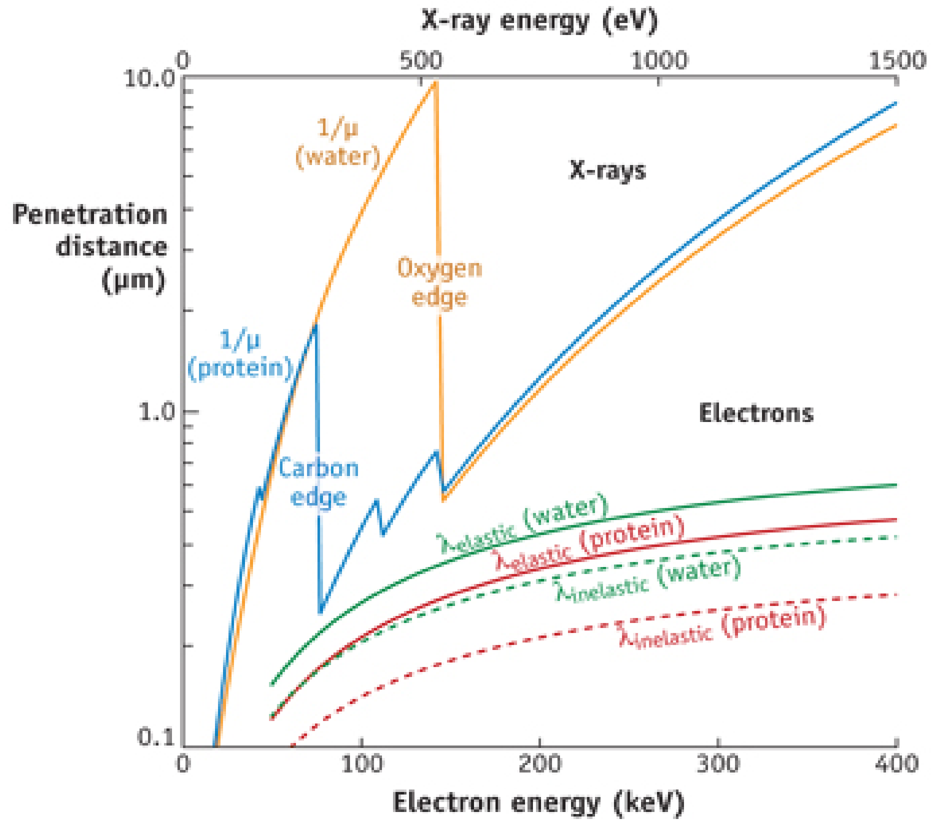
- Photoelectron spectroscopy of liquid solutions (ESCA)
- EUV to soft X-ray absorption of solutions
- Ultrahigh time-resolution spectroscopy (minimize GVD/GVM)

Spectroscopy in the EUV/soft X-ray range (< 1000 eV)

- Water window (282 to 530 eV)
- K-edges of low-Z elements : C, N, O, S, … Interest for molecular solids, catalysis and chemisorption processes, biology, etc.
- $L_{2,3}$-edges of transition metals ($2p_{\frac{1}{2},3/2}$- nd): interest for biology, coordination chemistry, catalsyis, magnetism, etc.
- Sharp spectral features: $\Gamma_L = 0.5\ eV = \hbar / t = 6.58\ 10^{-16}/t$

Challenges:

- Need for vacuum (problem with volatile samples)
- High fluxes: $\alpha_{abs} \sim Z^4$ (Low-Z elements)
- Solvent absorption (need for µm-thick samples)



Contents

I. Ultrafast photoelectron spectroscopy of charge transfer reactions in solutions (cylindrical jets)

II. EUV/soft X-ray absorption studies of molecular systems (Flat jets)

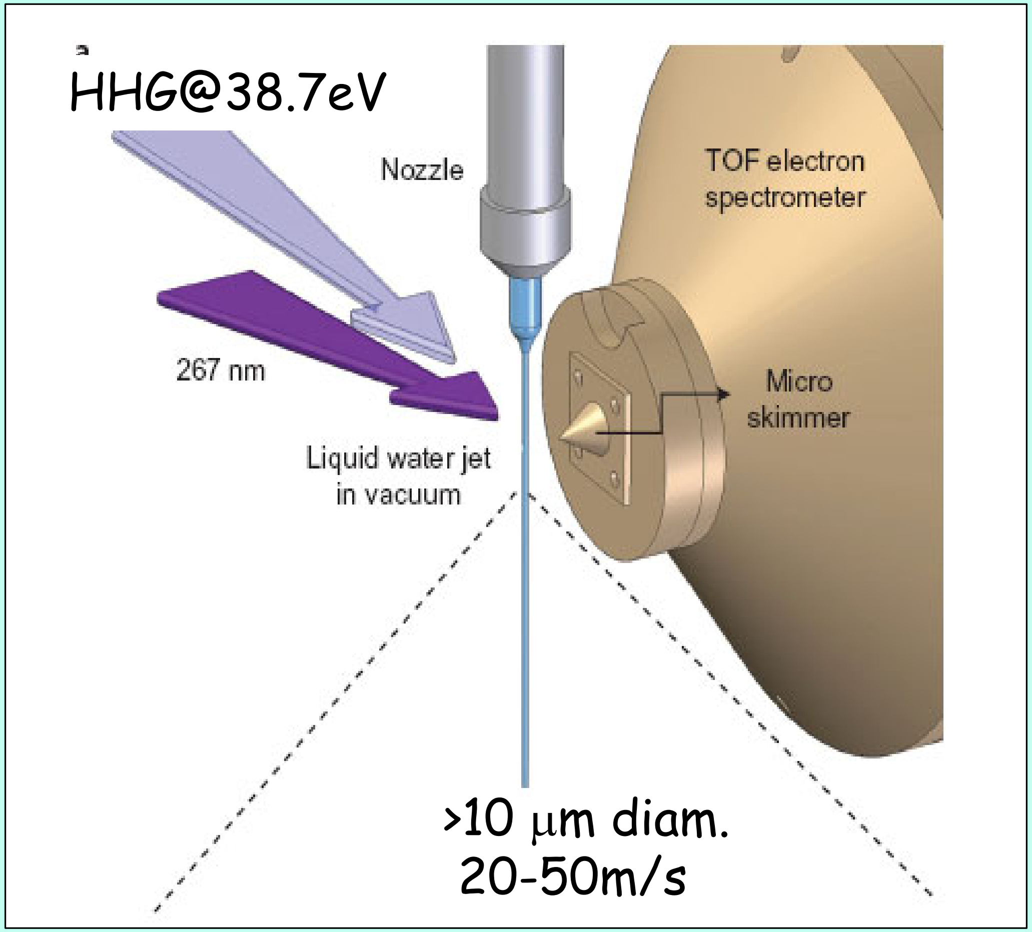
III. ultrahigh time resolution of liquid solutions (Flat jets)

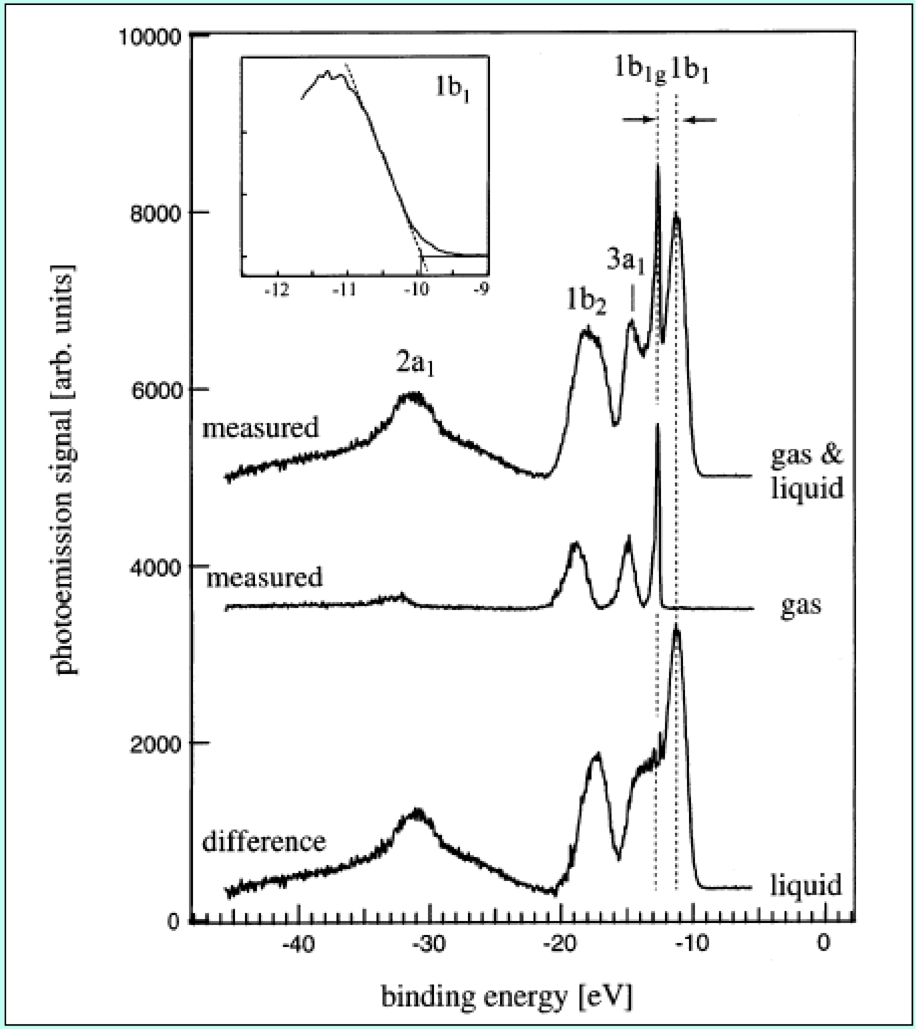
Steady-state UPS/XPS in liquids

Cylindrical jets: typ. 50 μm diameter
Faubel et al. J. Chem. Phys. 1997 & JPCA (2004);
Winter and Fauber, Chem. Rev. (2006)

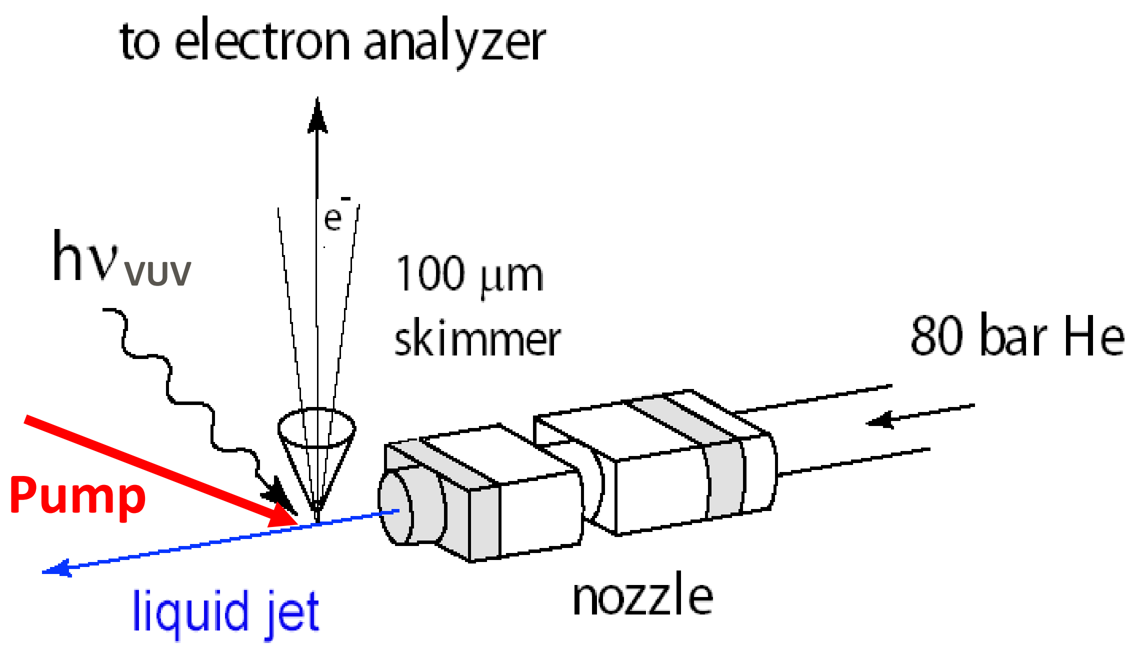
Ultrafast VUV-PES of liquids

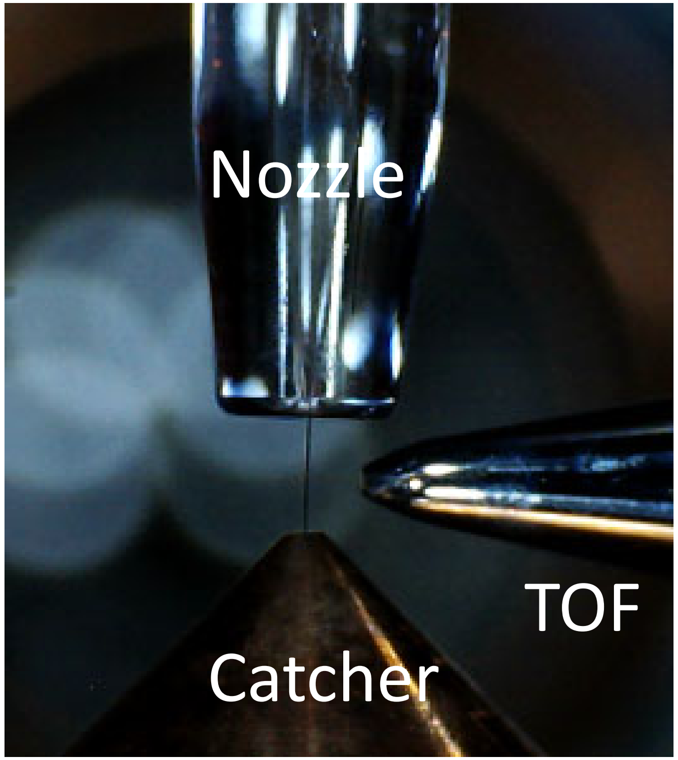
Abel, Faubel et al. Nat. Chem. 2010 &
Appl. Phys. A 2009





Ultrafast (<20 fs) Vacuum ultraviolet photoelectron spectroscopy of solutions



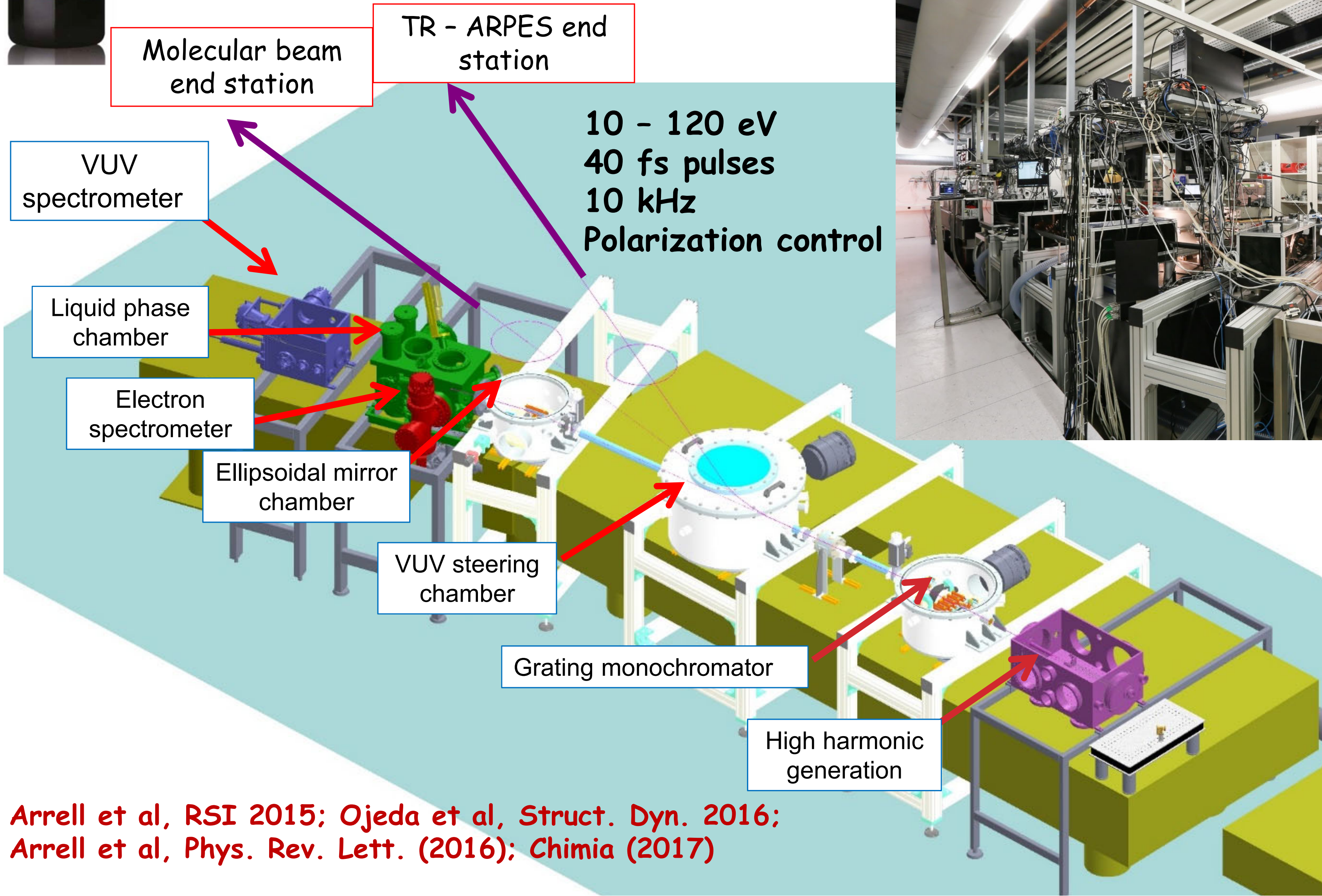


Arrell et al, RSI 2014

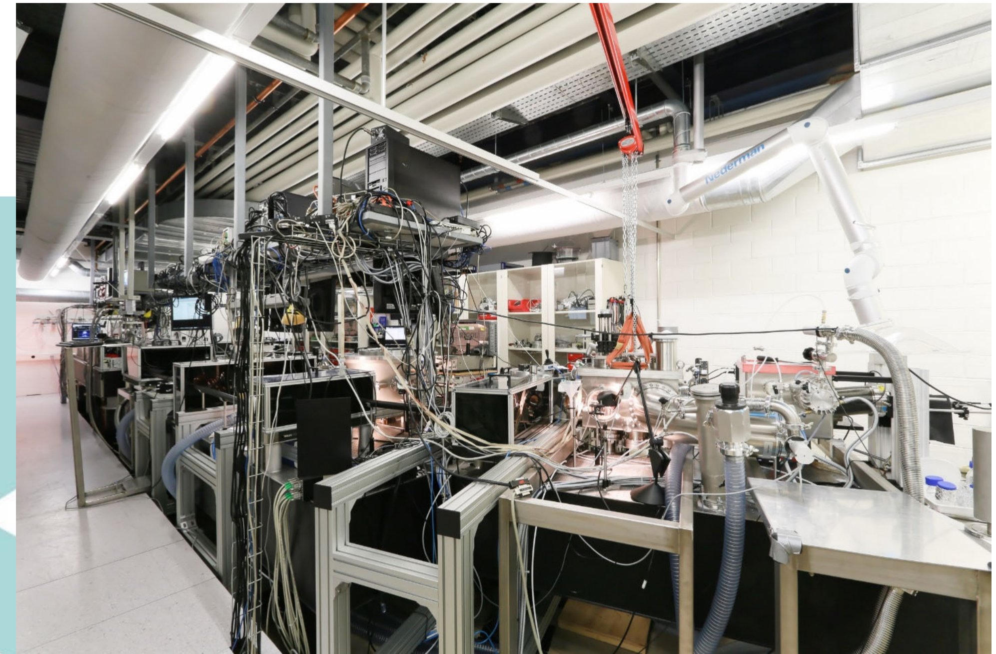
- Rapid ejection of liquid through ~20 µm capillary creates stable region of 1-2 mm laminar flow
- Cryo pumping used to maintain ~10^{-5} mbar conditions
- Probing by EUV pulses from the Harmonium HHG source

Harmonium @ LACUS (Lausanne Centre for Ultrafast Science) EPFL

Extreme-UV femtosecond source:
Facility for photoelectron spectroscopy (ESCA) of liquid, gas and solid phases.
Complementary to X-ray studies at the SLS and XFELs



10 – 120 eV
40 fs pulses
10 kHz
Polarization control



Funding:

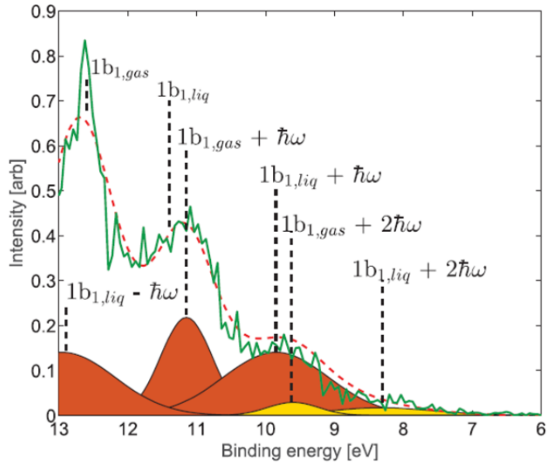
must

erc European Research Council

FNSNF Fonds National Suisse de la Recherche Scientifique

Arrell et al, RSI 2015; Ojeda et al, Struct. Dyn. 2016;
Arrell et al, Phys. Rev. Lett. (2016); Chimia (2017)

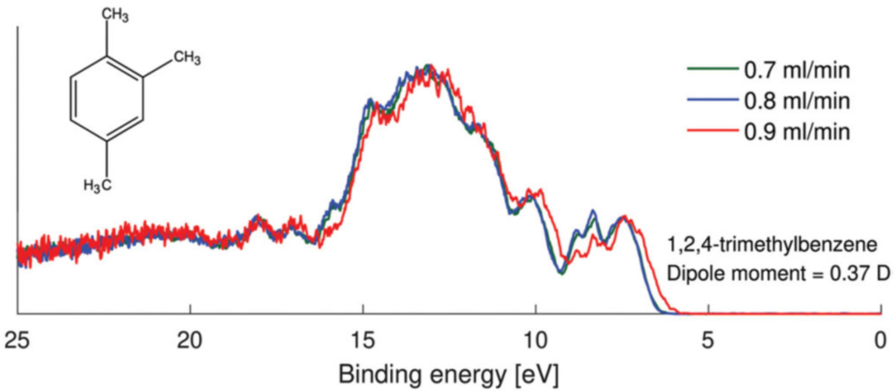
Ultrafast photoelectron spectroscopy



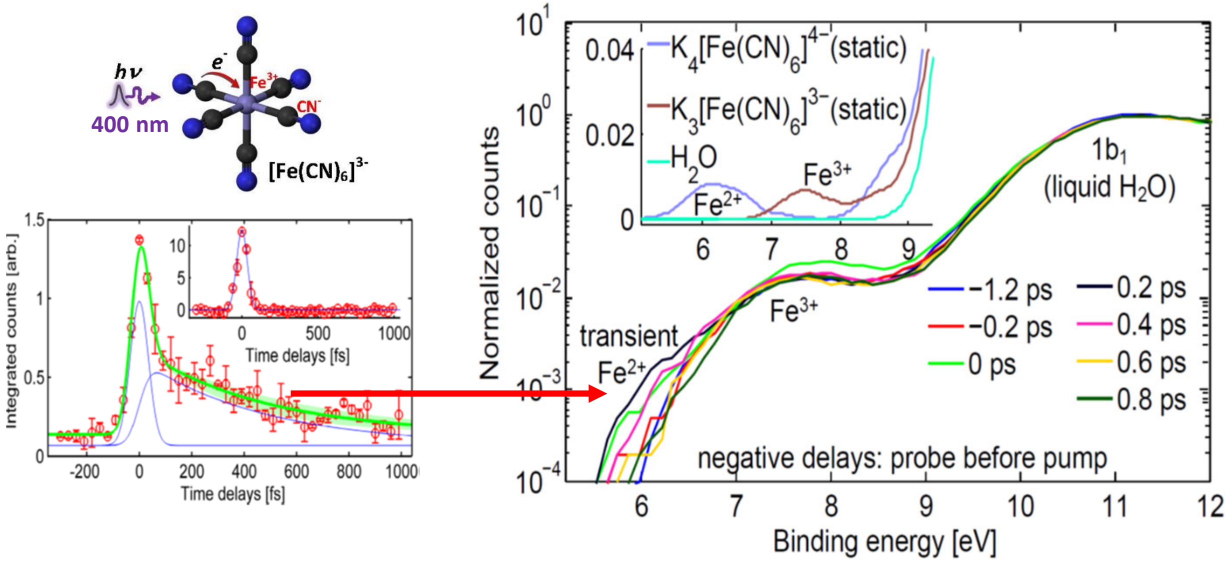
35.6 eV + 1.55 eV

Laser-assisted photoelectric effect (LAPE)
(Arrell et al, Phys. Rev. letters (2016))

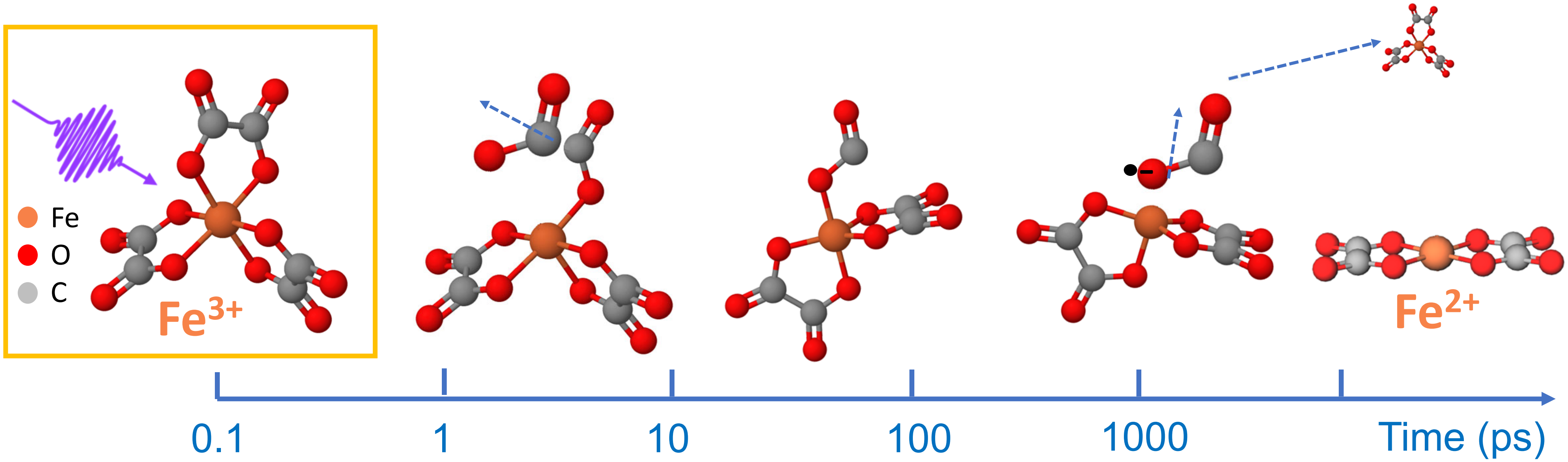
PES of organic solvents:
1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene
(Longetti et al, Phys. Chem. Chem. Phys. (2020))



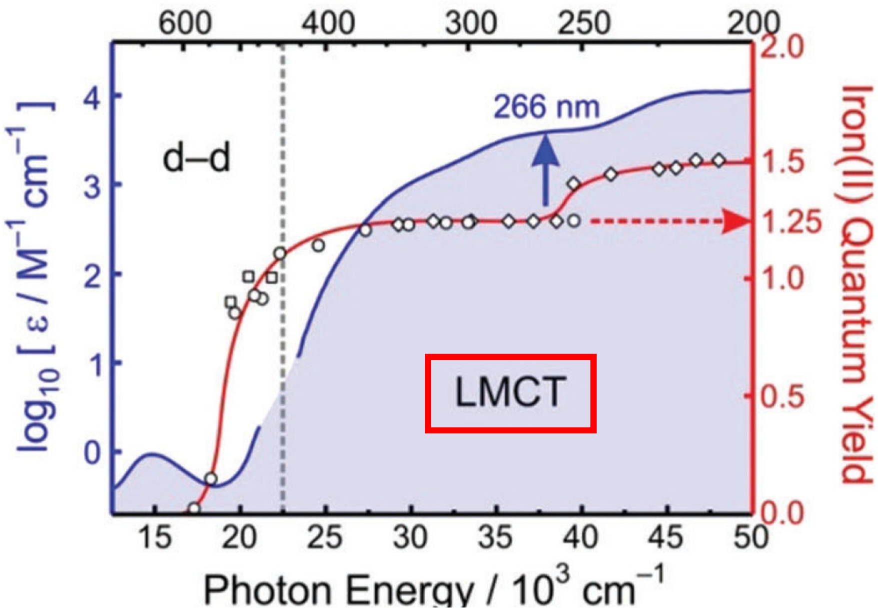
Intramolecular charge transfer and back transfer:
Solvent-dependence (0.5 ps (H_2O), 1.2 ps (EtGly)
(Ojeda et al, Phys. Chem. Chem. Phys. (2017))



Ultrafast PES of a photochemical reaction (Ferrioxalate)



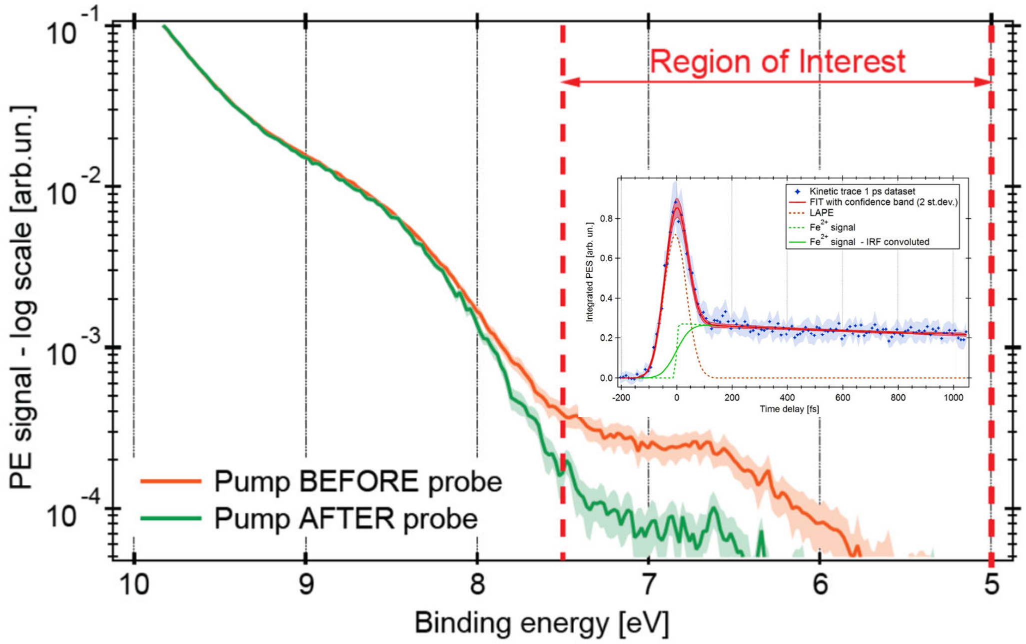
$$[Fe^{III}(C_2O_4)_3]^{3-} + h\nu \rightarrow [(CO_2^{\cdot})Fe^{II}(C_2O_4)_3]^{3-} + CO_2 \rightarrow$$
$$[Fe^{II}(C_2O_4)_2]^{2-} + CO_2 + CO_2^{\cdot -}$$

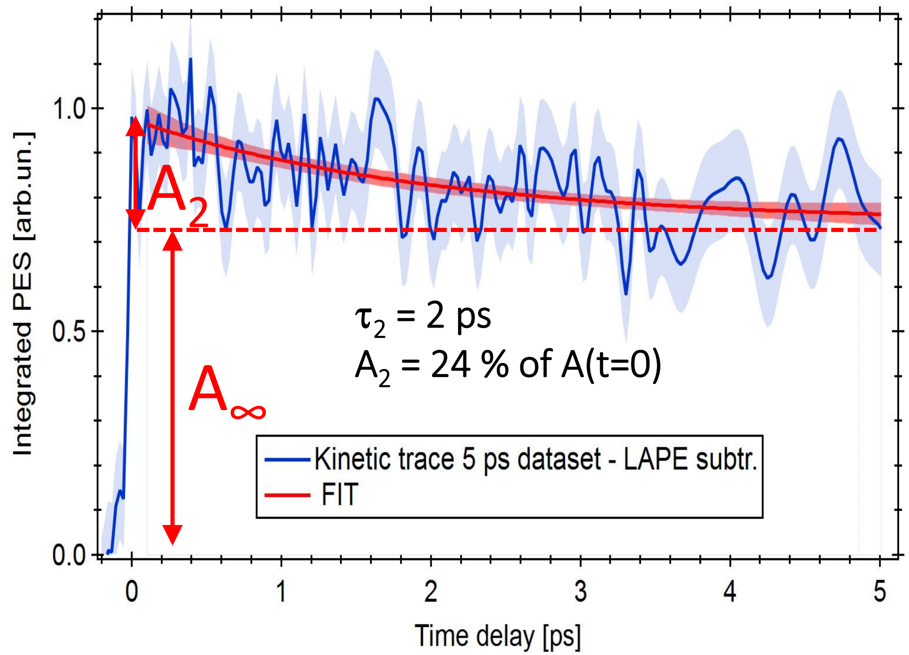


Parker & Hatchard , J. Phys. Chem. 1959; Rentzepis & Co, Inorg. Chem. 2008; Suzuki & Co, Struct. Dyn. 2015; Straub *et al.* PCCP 2018;

- How fast is the photoreduction?
- How fast is the first CO_2 dissociation?
- Does reduction trigger dissociation or vice-versa?
- What is the role of the solvent?

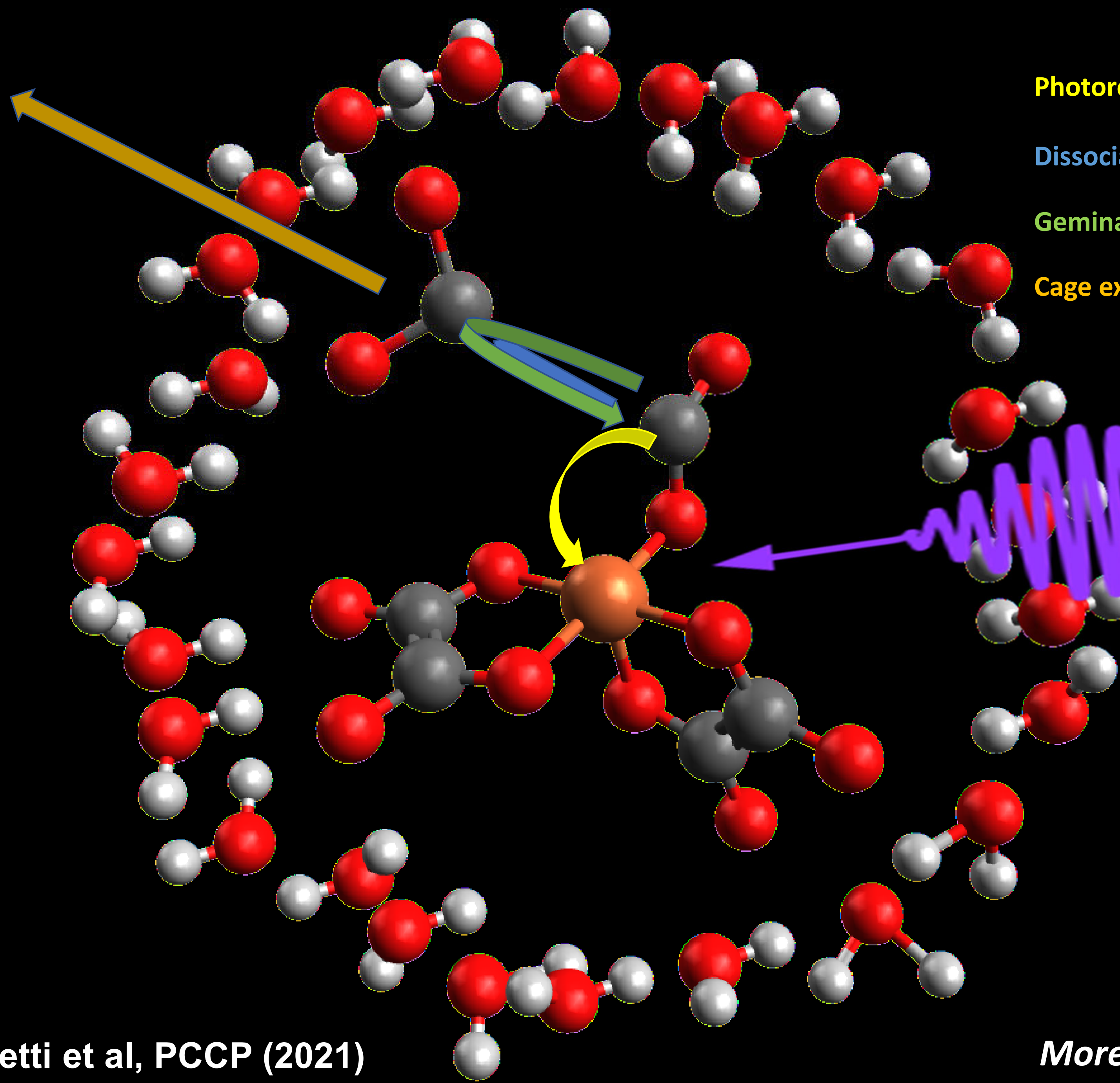
Aqueous Ferrioxalate



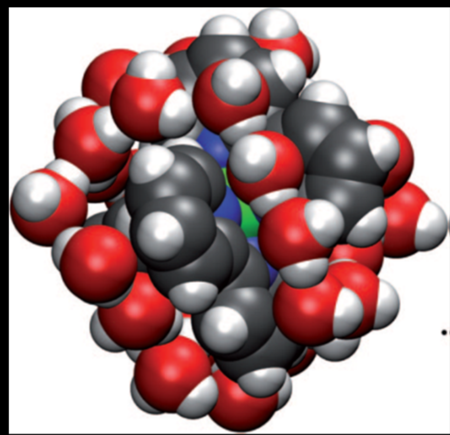


- 25% of ferrous species are lost in 2 ps
- IR TA: partial (25-35 %) recovery of depleted parent molecule population in ca. 2 ps. Attributed to intramolecular relaxation.
- X-ray TA: <140 fs CO_2 dissociation and 2-3 ps relaxation time, attributed to dissociation of the second fragment (the CO_2^- anion)

Aqueous Ferrioxalate

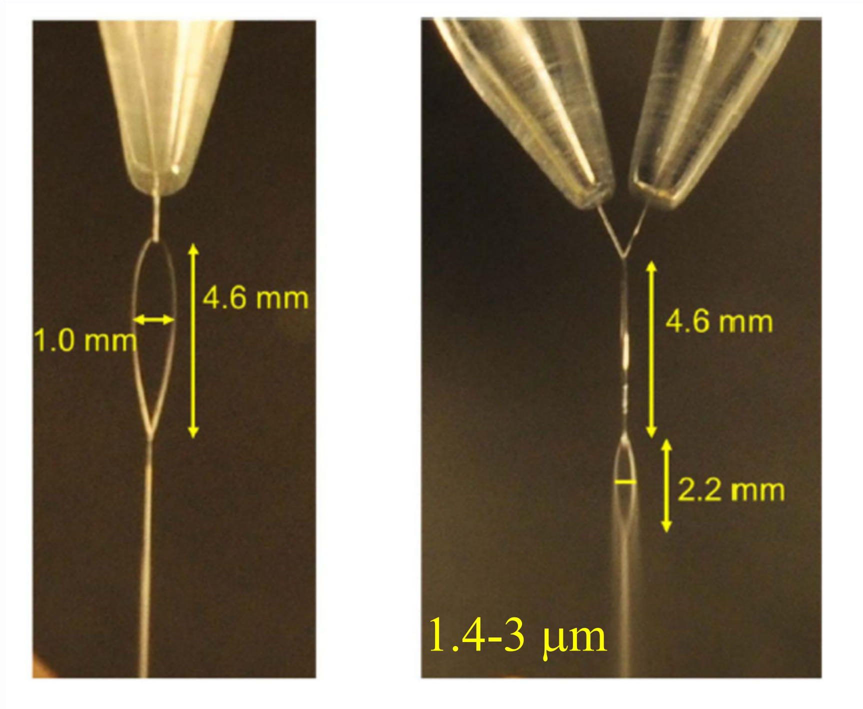


Longetti et al, PCCP (2021)

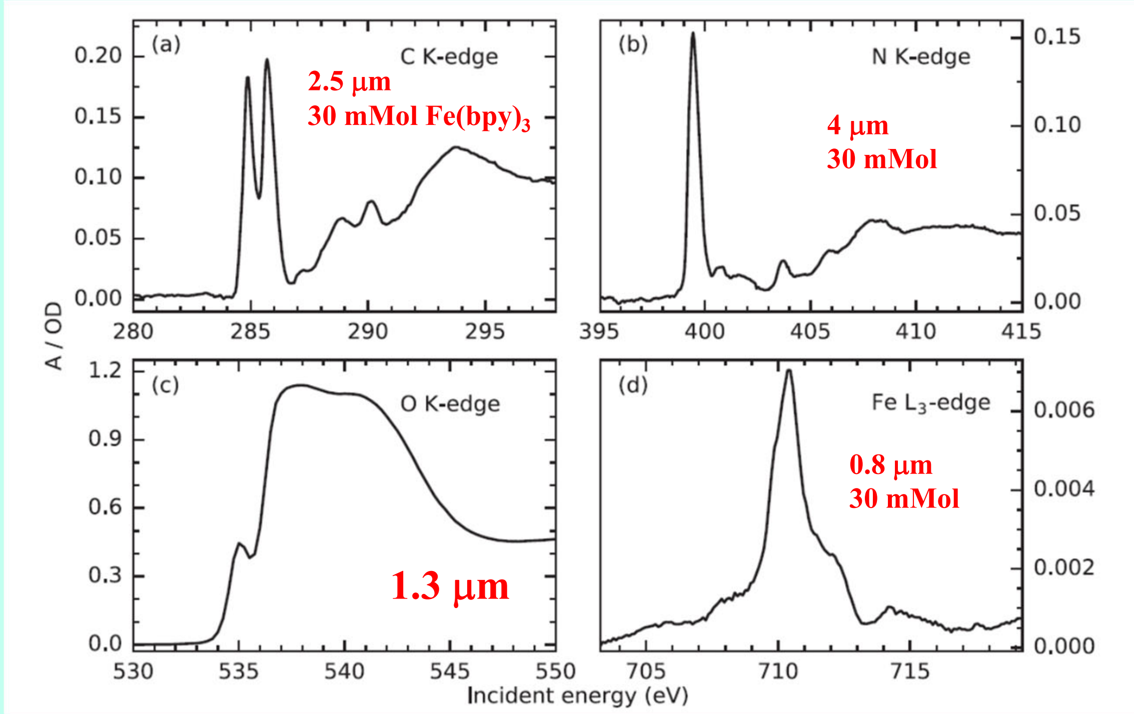


Moret et al, Chem. Eur. J. 2010

Flat liquid jets

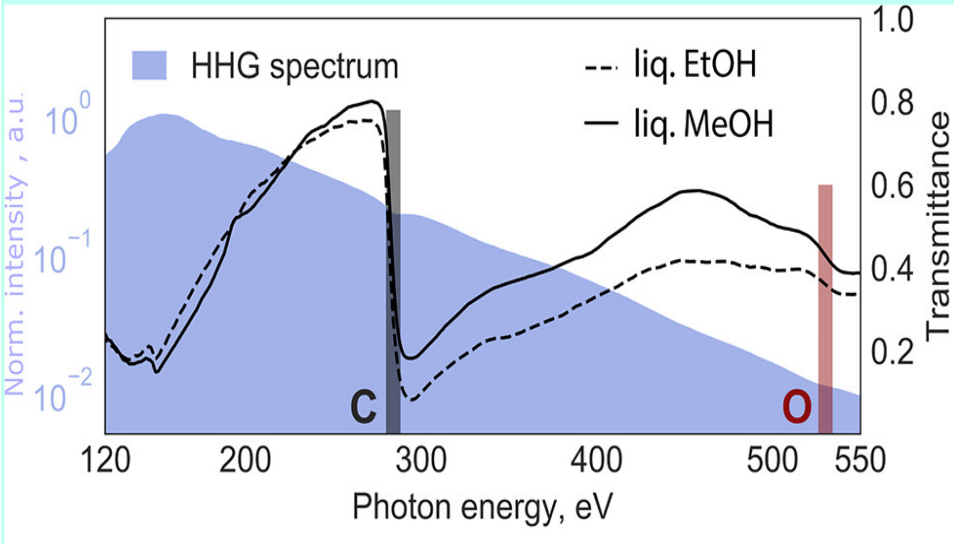


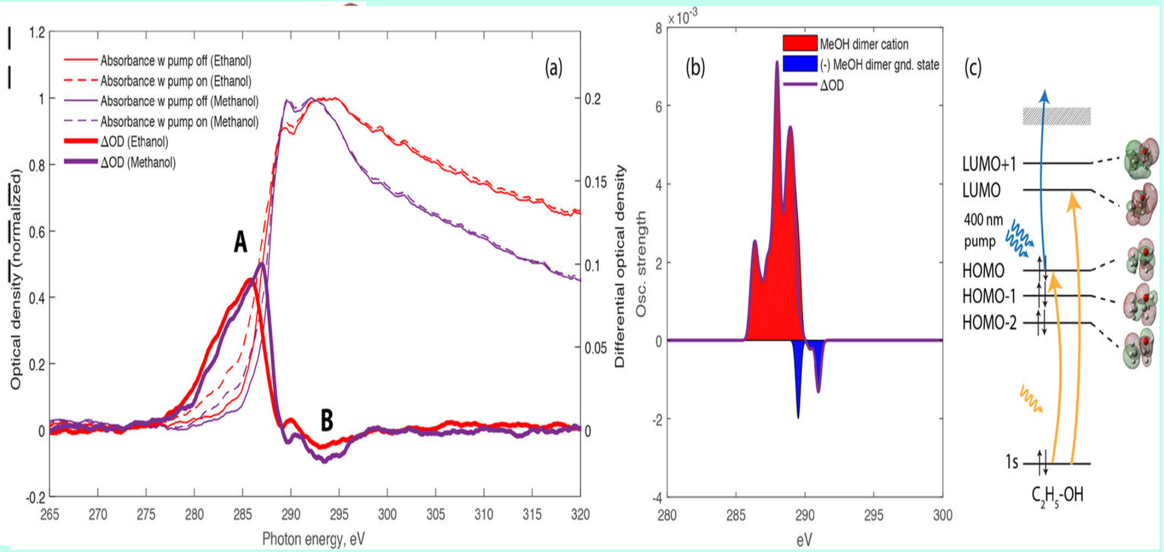
(Ekimova et al, Struct. Dyn. (2015))



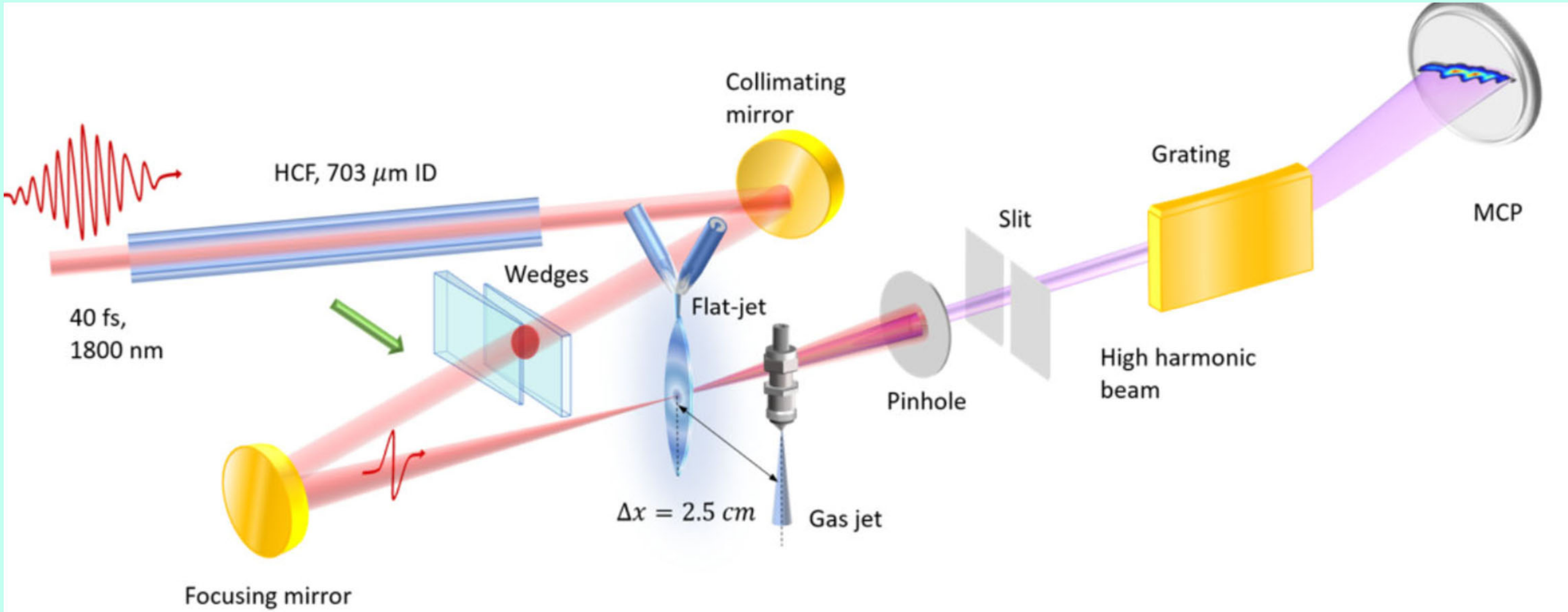
(Synchrotron studies: Fondell et al, Struct. Dyn. (2017))

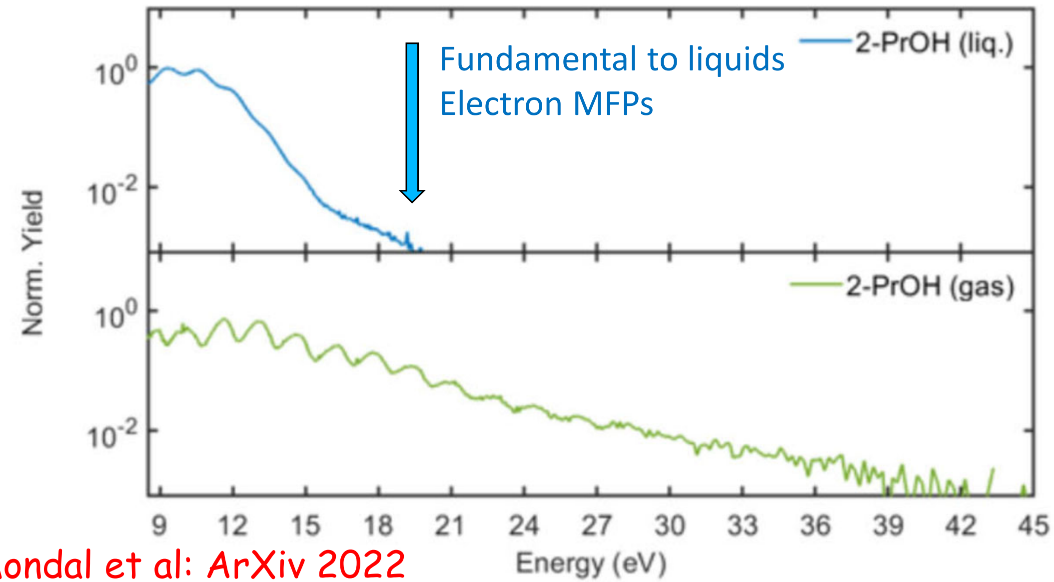
Tabletop HHG sources: Kleine et al: Phys. Chem. Lett. (2019) Smith et al: Phys. Chem. Lett. (2020)

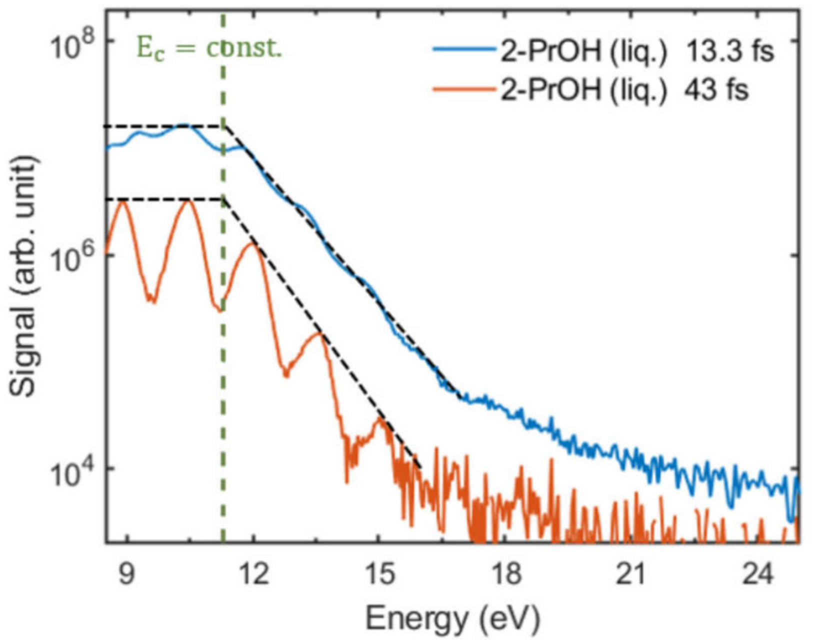




HHG in flat liquid jets

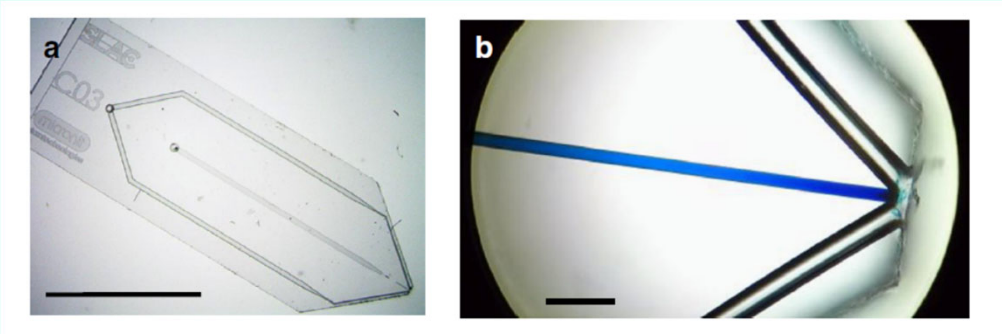


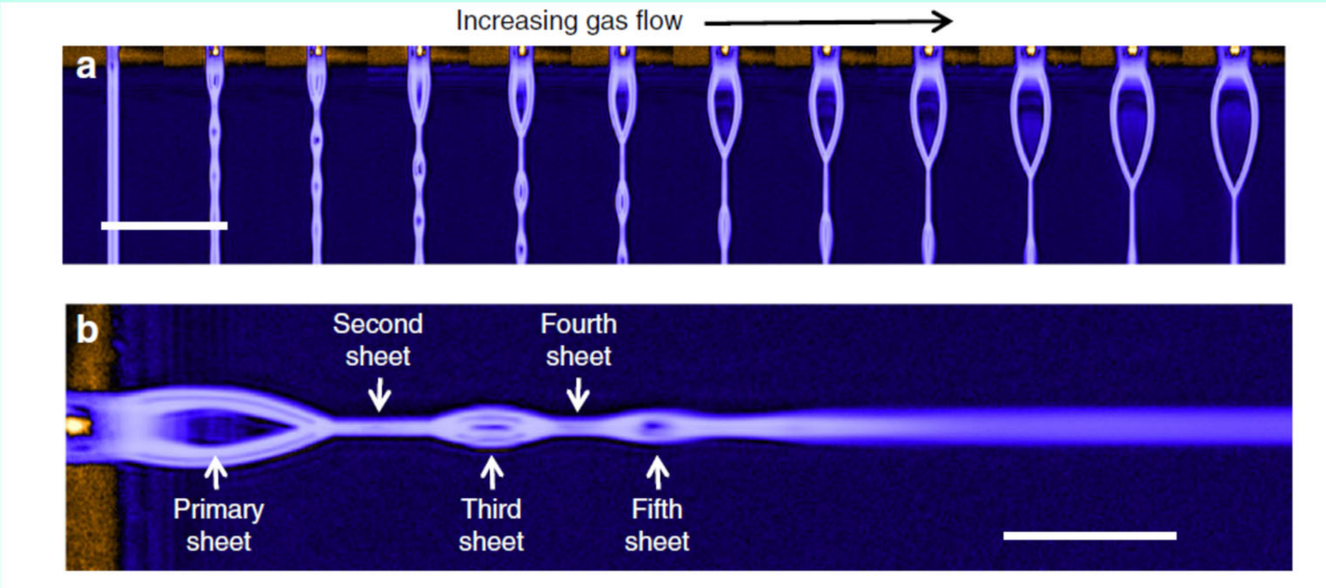


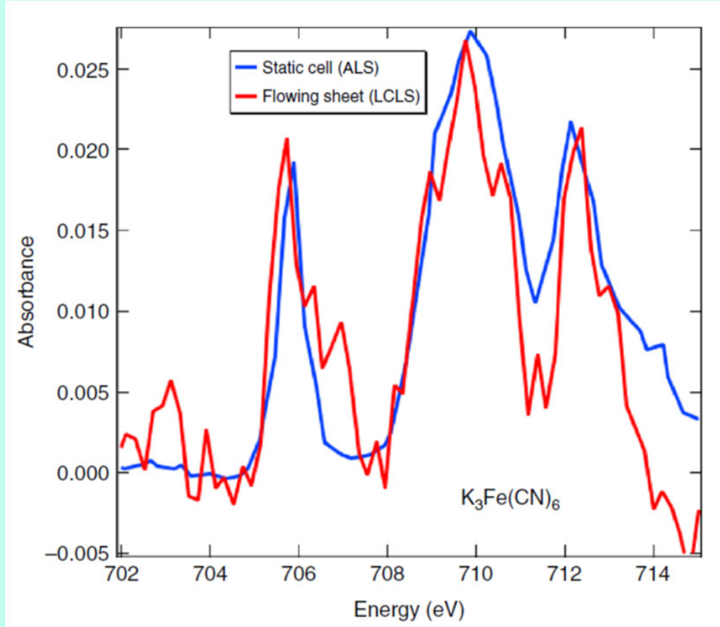


Mondal et al: ArXiv 2022

Gas-compressed Flat liquid jets







De Ponte et al: Nature Comm. 2018

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