What is the band gap

…of liquid water?

Fabio Novelli

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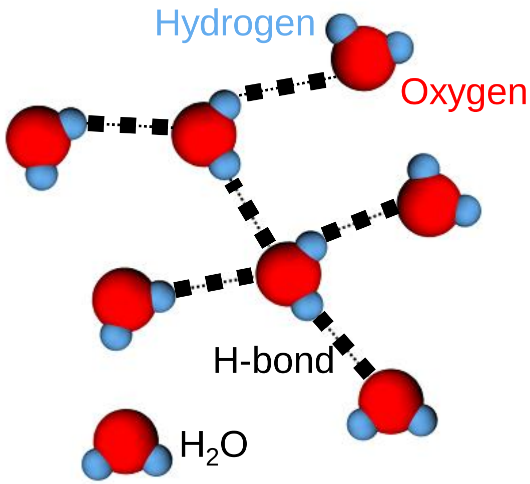
Fabio.Novelli@rub.de

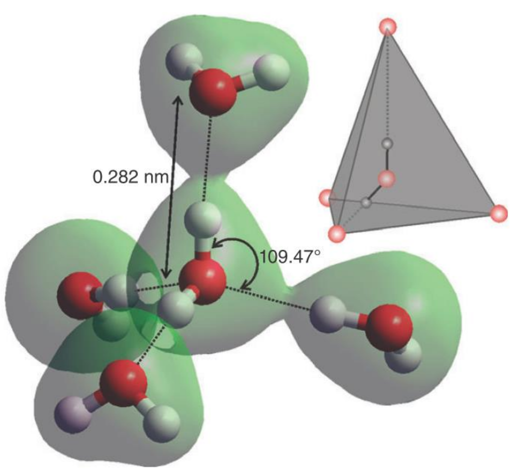
EuPRAXIA facility at LNF, 6 Dec. 24

https://www.pexels.com/photo/glass-window-with-blue-sea-and-sky-view-9226534/

WATER

Picosecond lifetime





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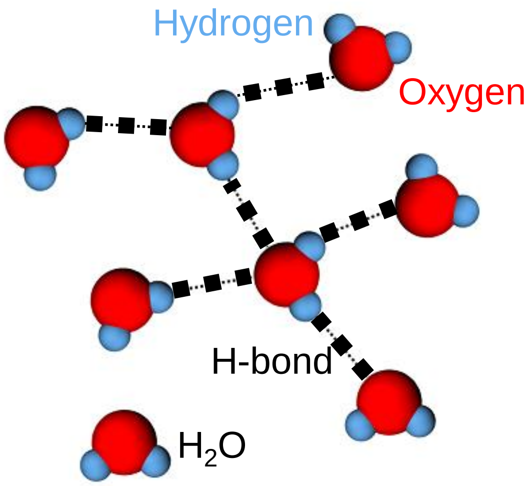
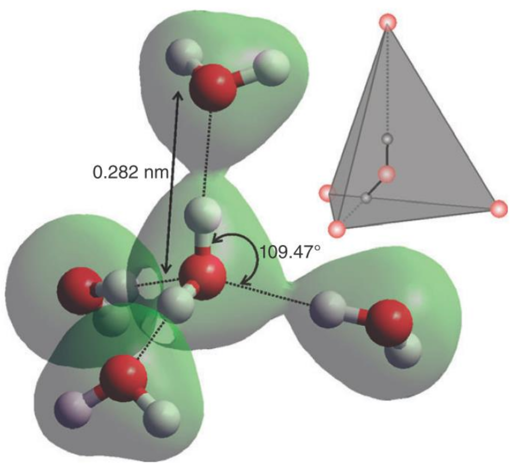
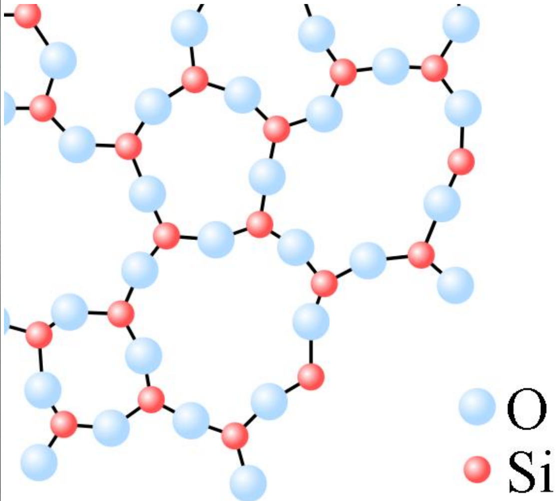


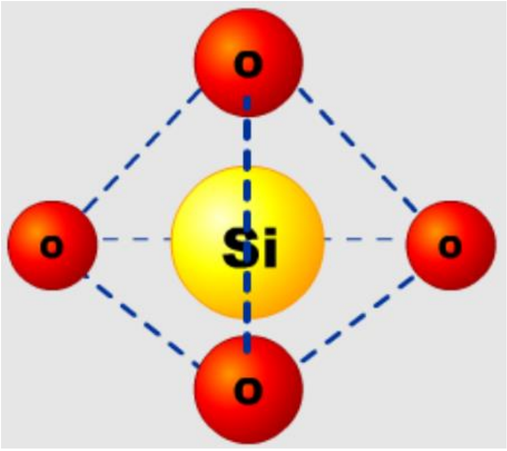


<u>GLASS</u>

" billions of years for viscous flow "

10.1111/jace.15092





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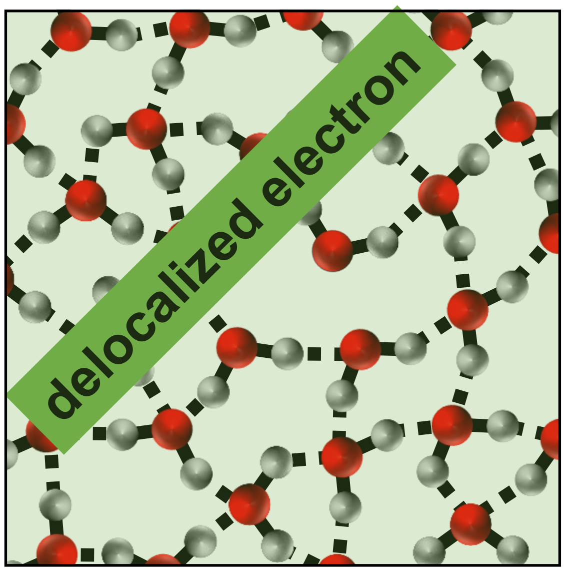
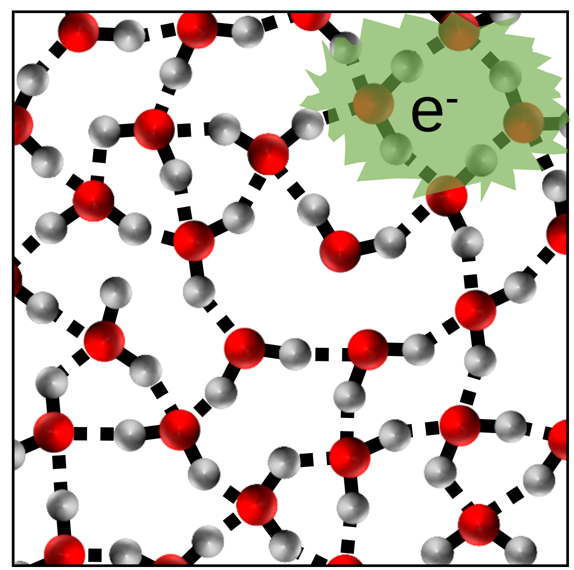


time delay

Electron localization (>0.3 ps)



e^- **delocalized** (r~4 nm) for ~0.2ps

“fill void” (r~2.5 Å), lifetime~100μs

Can THz probe H_2O photo-ionization?

Optical pump (400 nm, 50 fs, 1 TW/cm^2)

Terahertz probe (2 color plasma, 0.1mm GaP)

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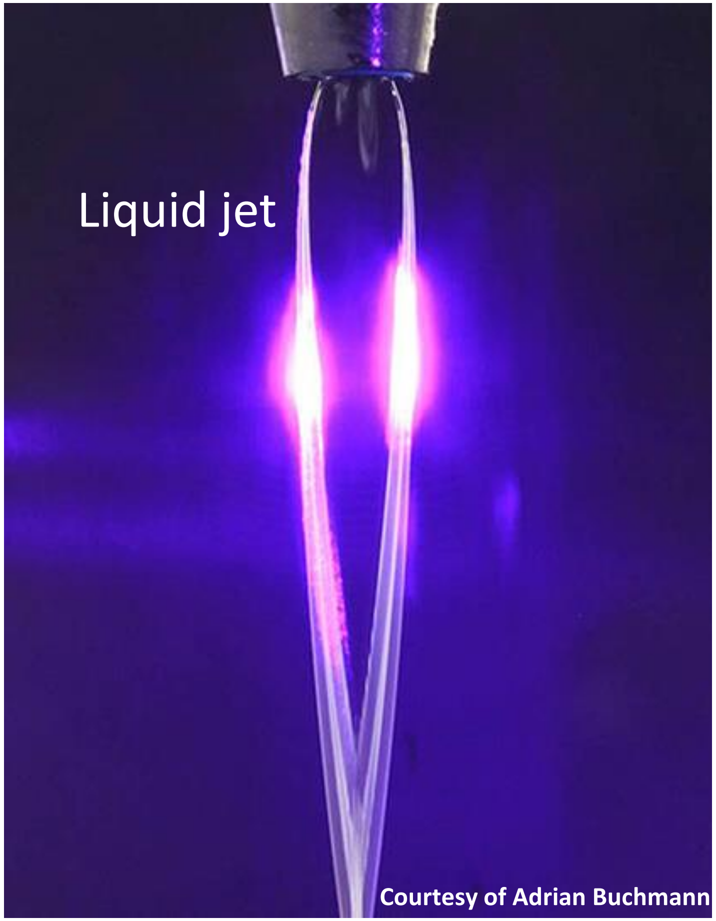

Optics & Photonics News 2023 Photo Contest 3rd place

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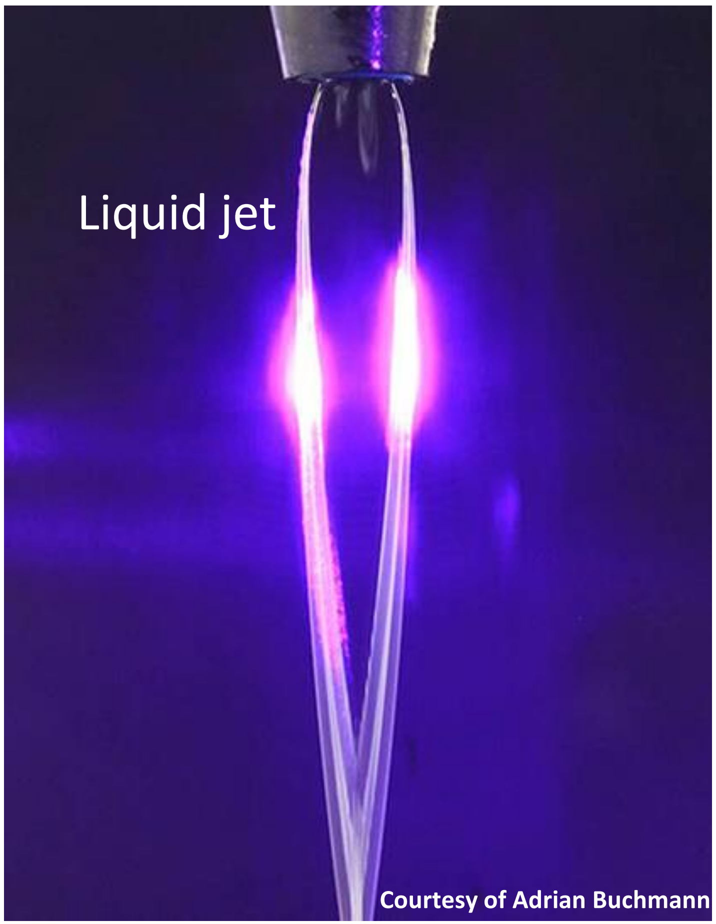

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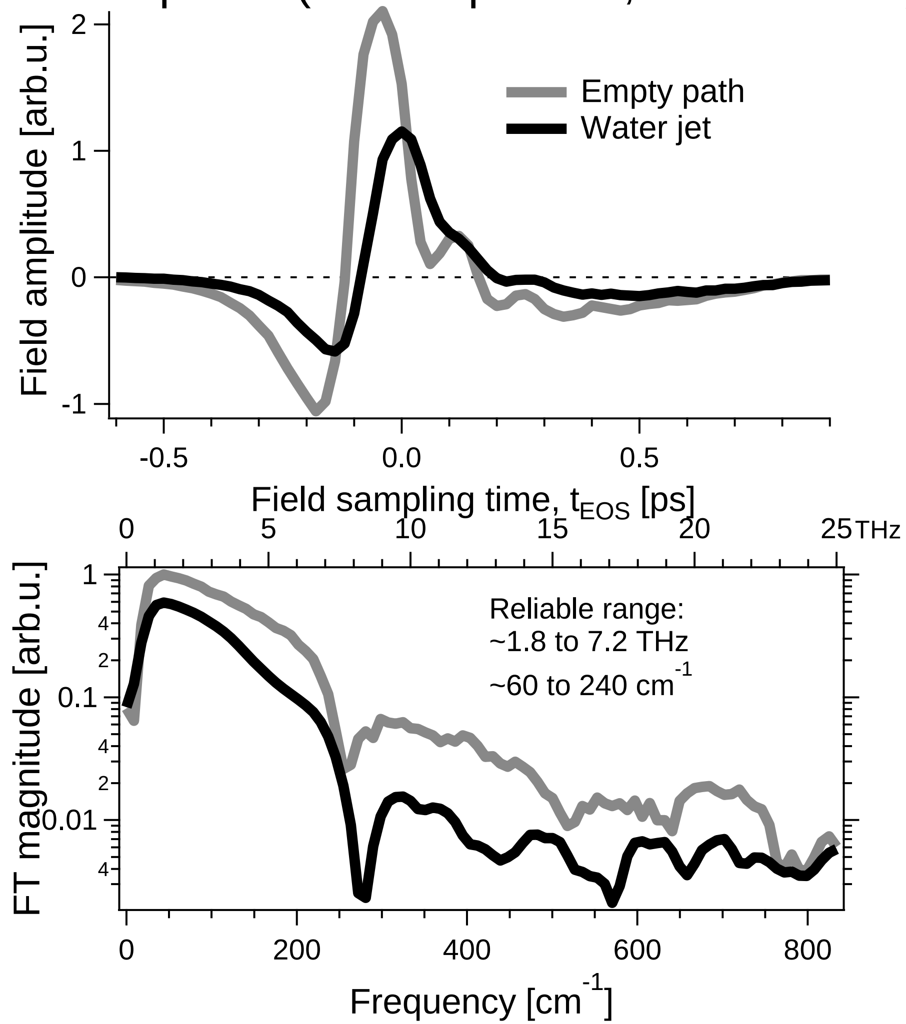
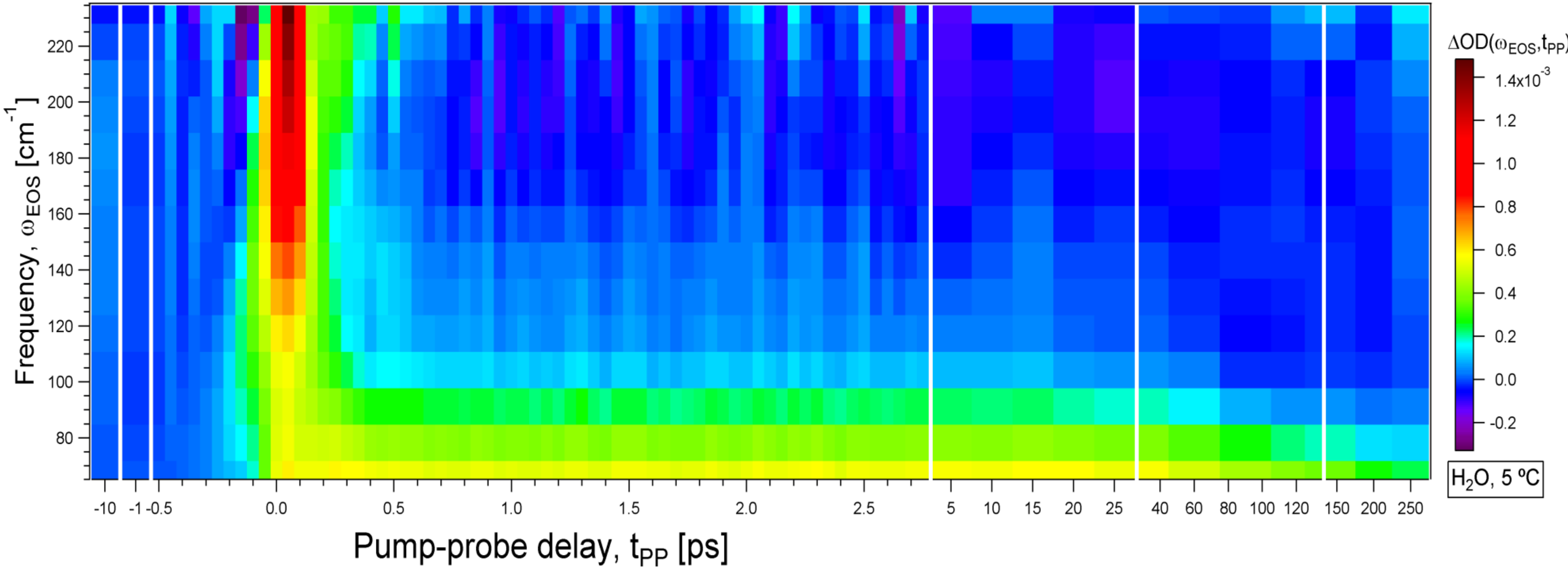


Photo-ionizing pump and THz probe on *pure* liquid water



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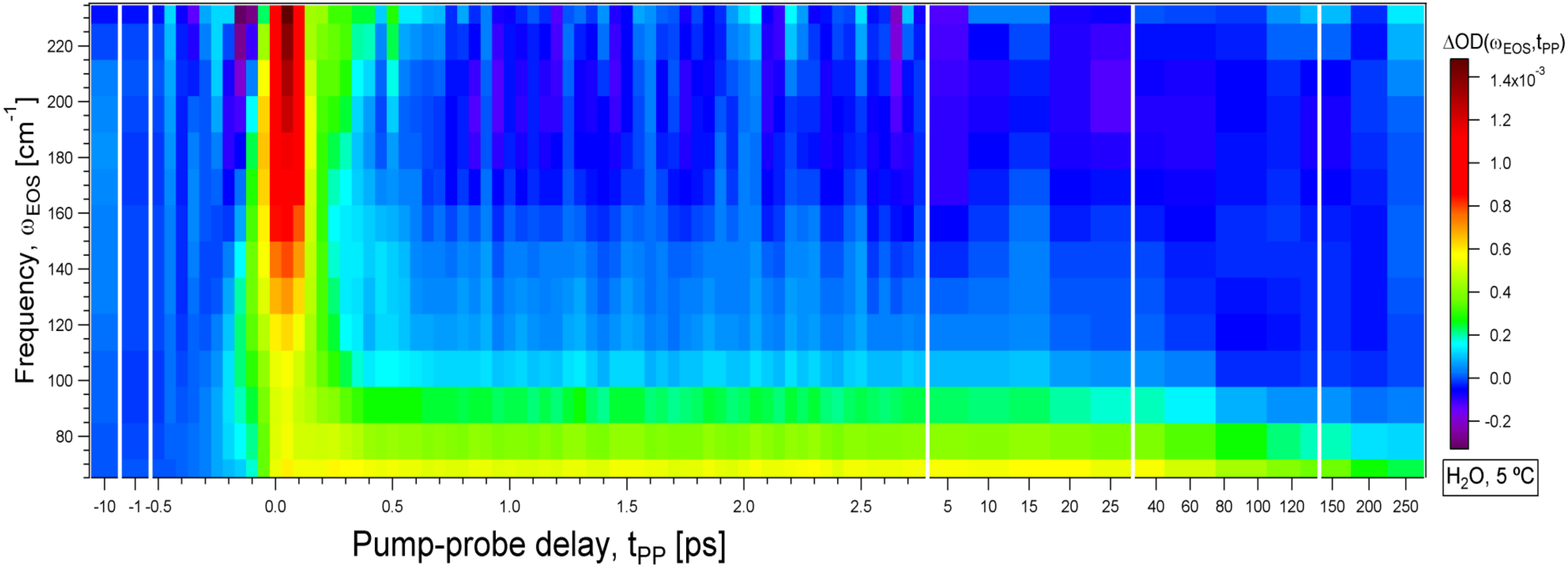

1. Short pump-probe delay: high-frequency, short-lived response

2. Long pump-probe delays: low-frequency, long-lived response

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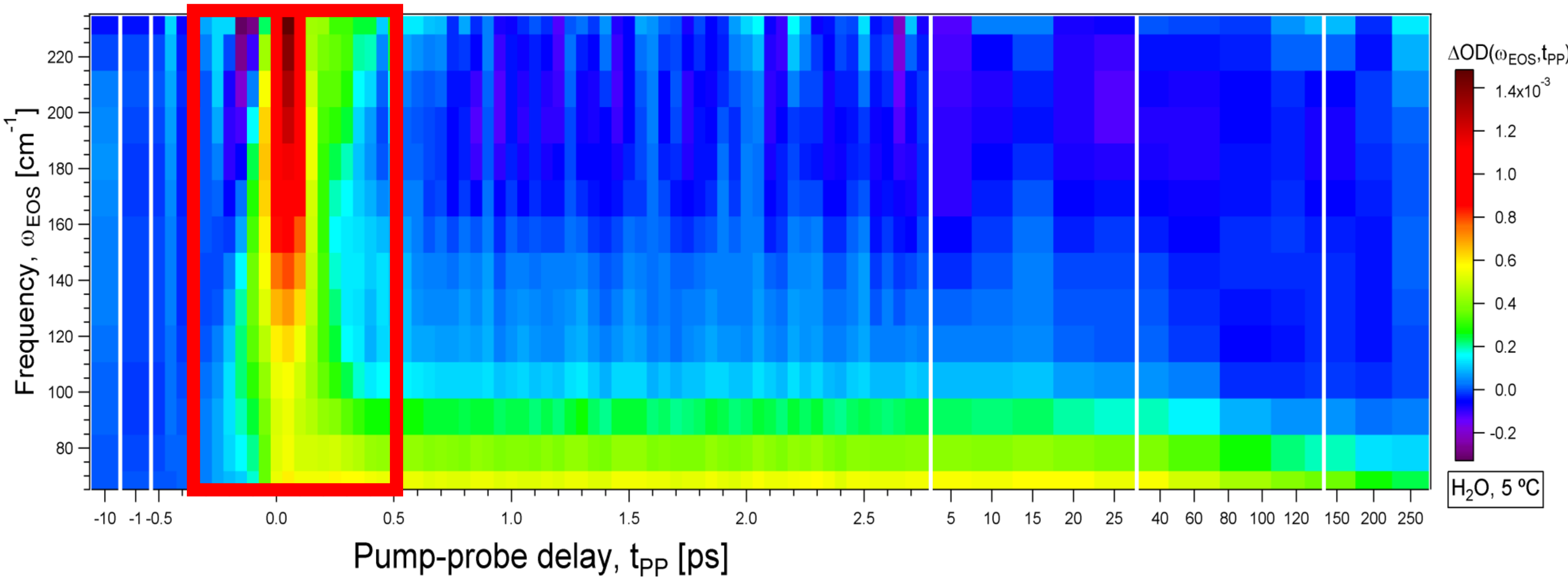

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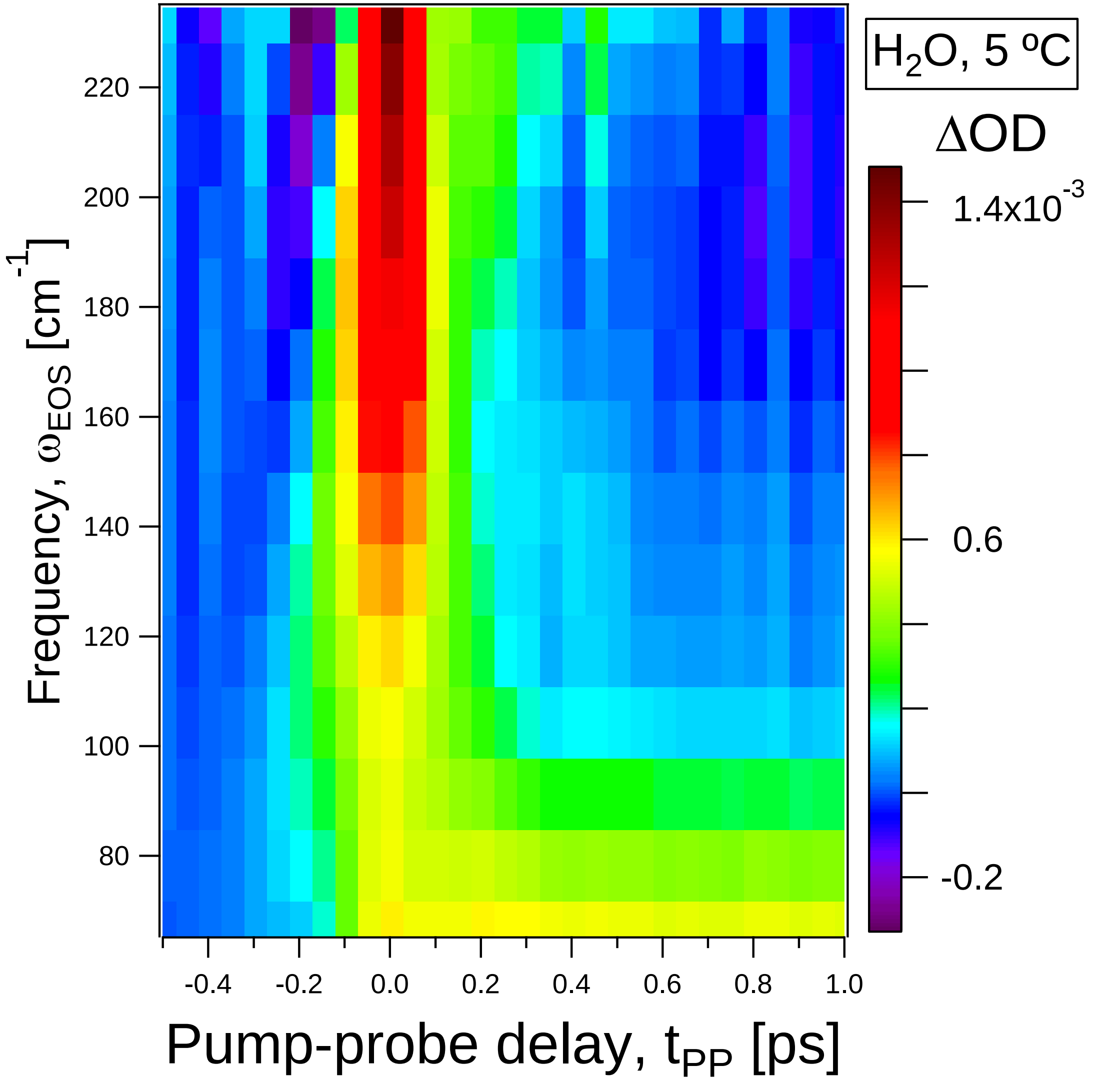

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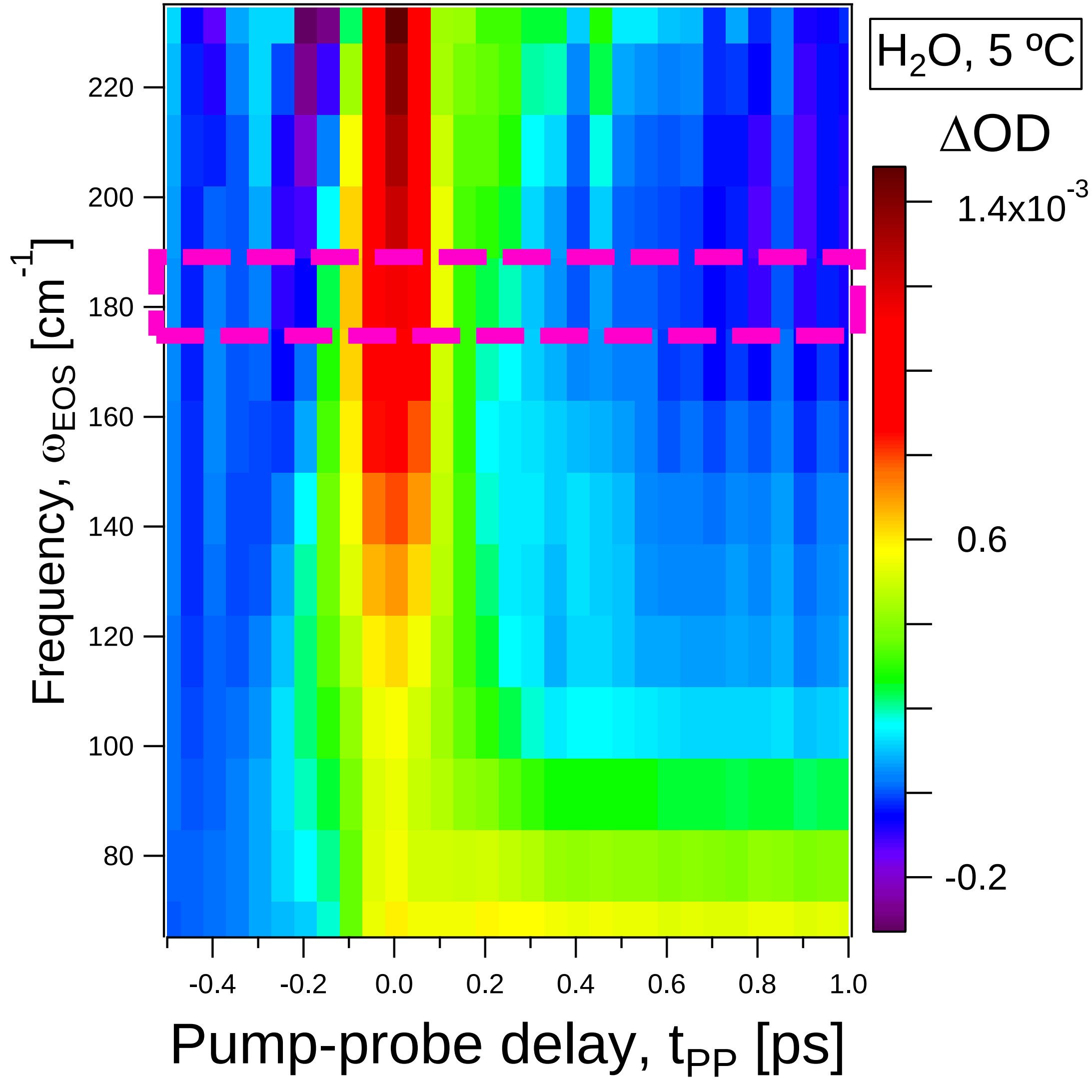


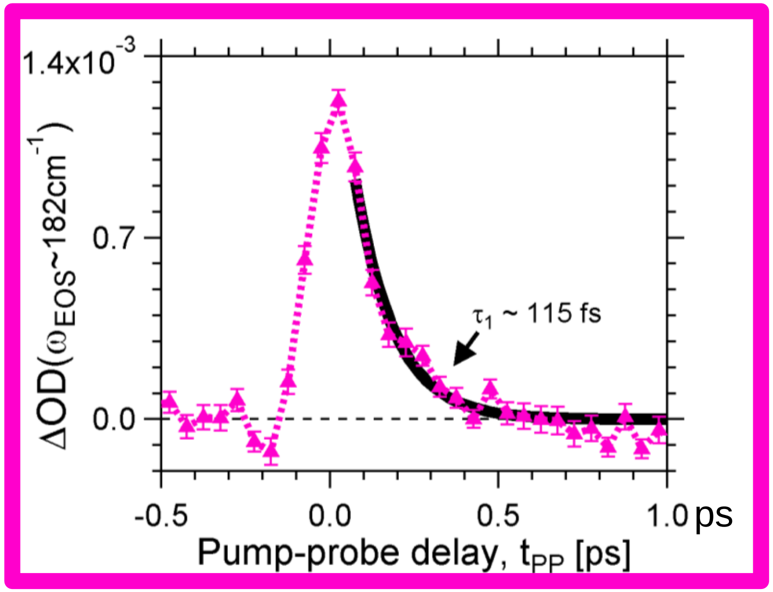
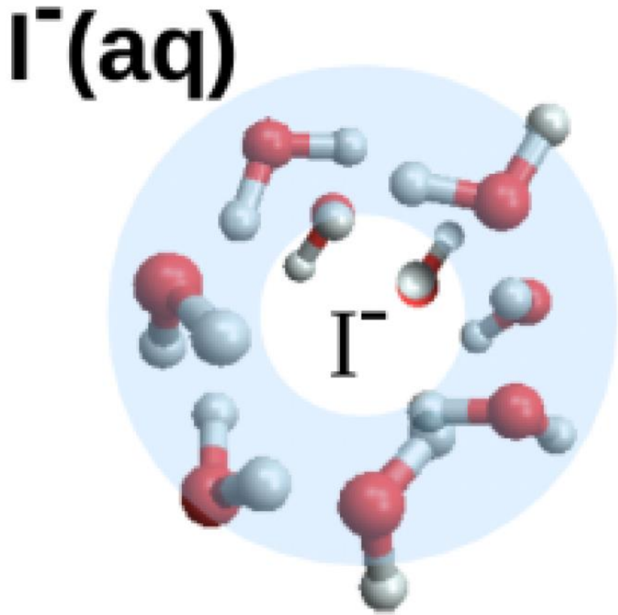


Photo-ionizing pump and THz probe on aqueous *solutions*

e^- donor = larger signal

$I^- + h\nu \rightarrow I + e^-$



Adapted from J. Chem. Phys. 145, 074502, 2016

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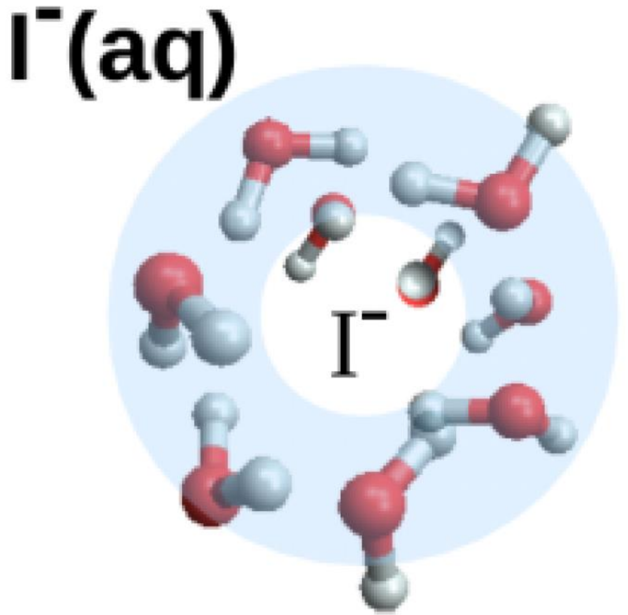

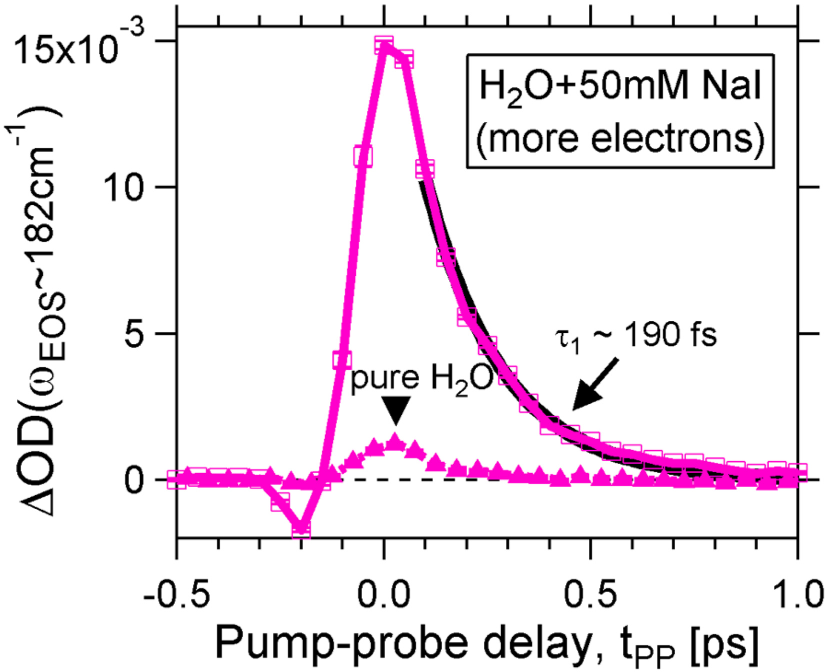

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- ➢ Depends on the number of photo-generated electrons

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PNAS 120, e2216480120, 2023

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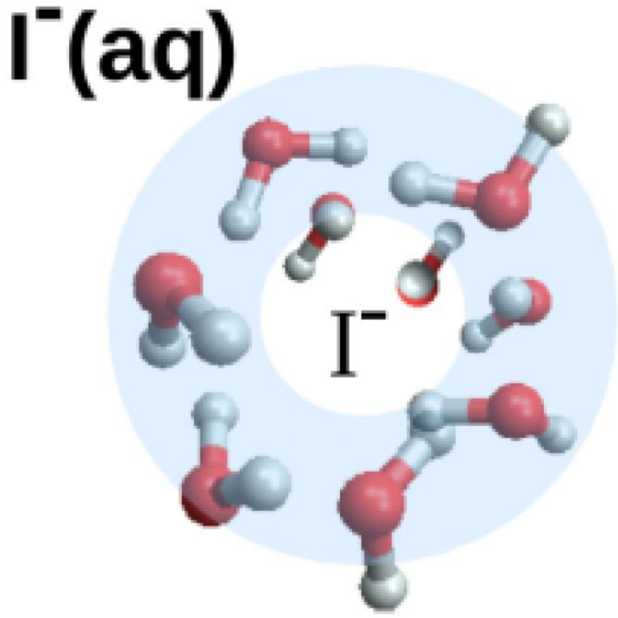

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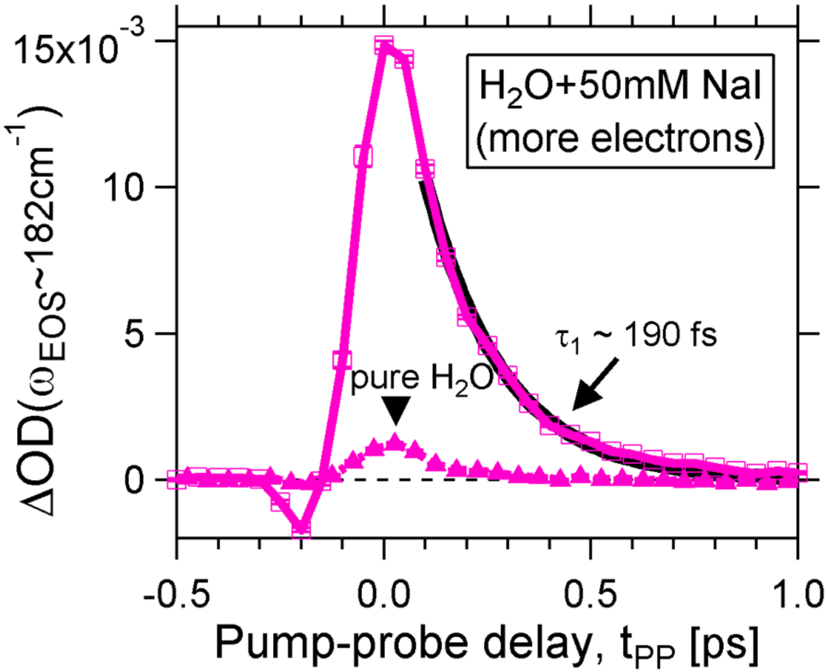

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e^- donor = larger signal

$I^- + h\nu \rightarrow I + e^-$

+50 mM NaI
(1x I^- every 1000x H_2O)
→ ~10x larger THz signal

NaI is highly soluble in water, up to ~11 M at 20 °C
(~1x I^- every 4x H_2O)

→ How much bigger can the THz signal be?

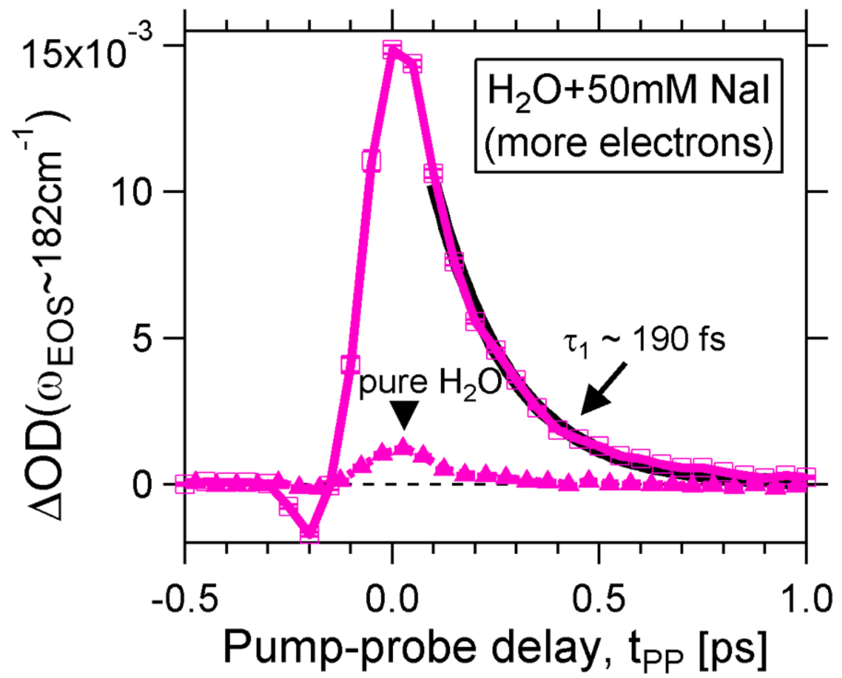
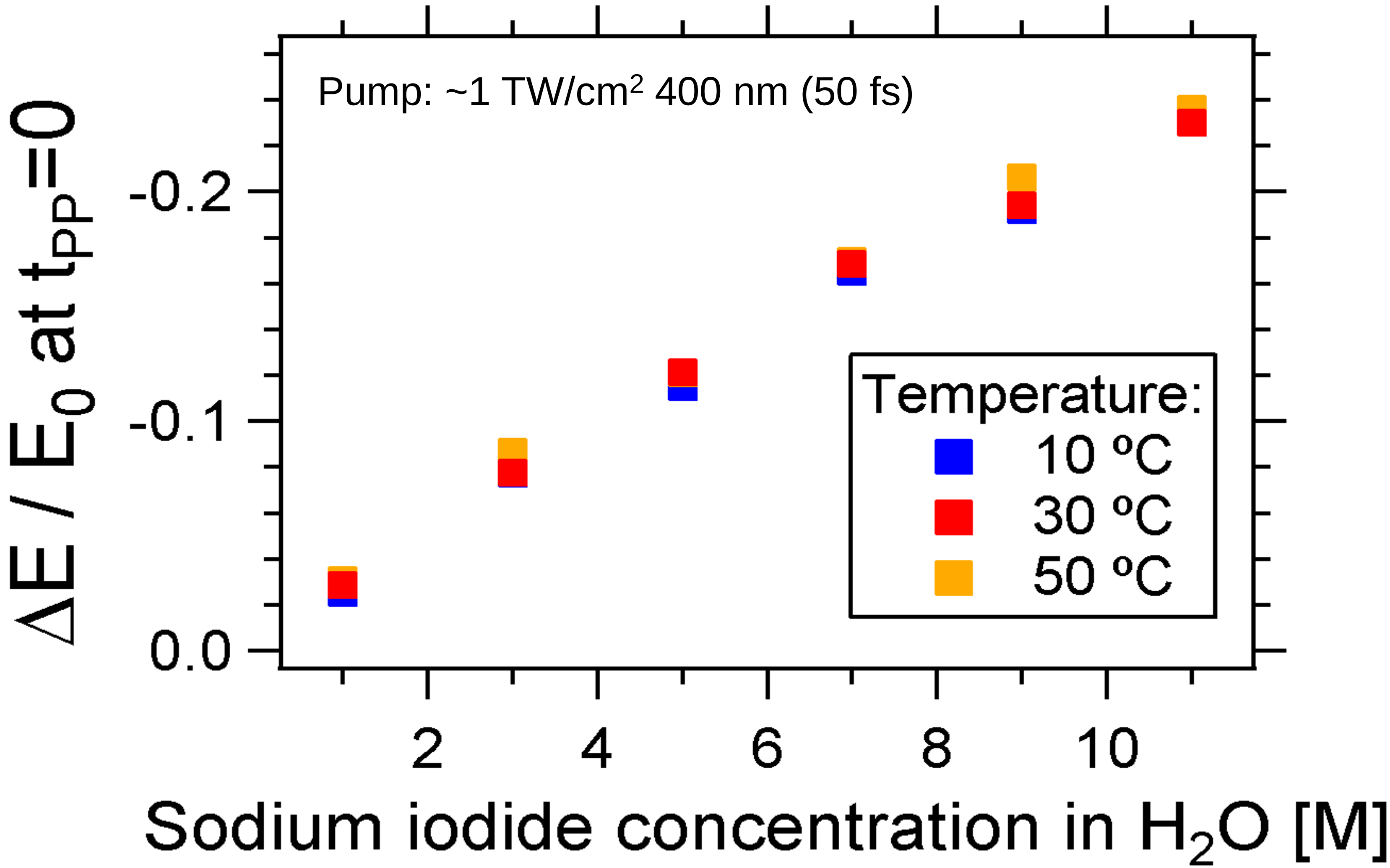


Photo-ionization of *very salty water*



APL Photonics 7, 121302, 2022

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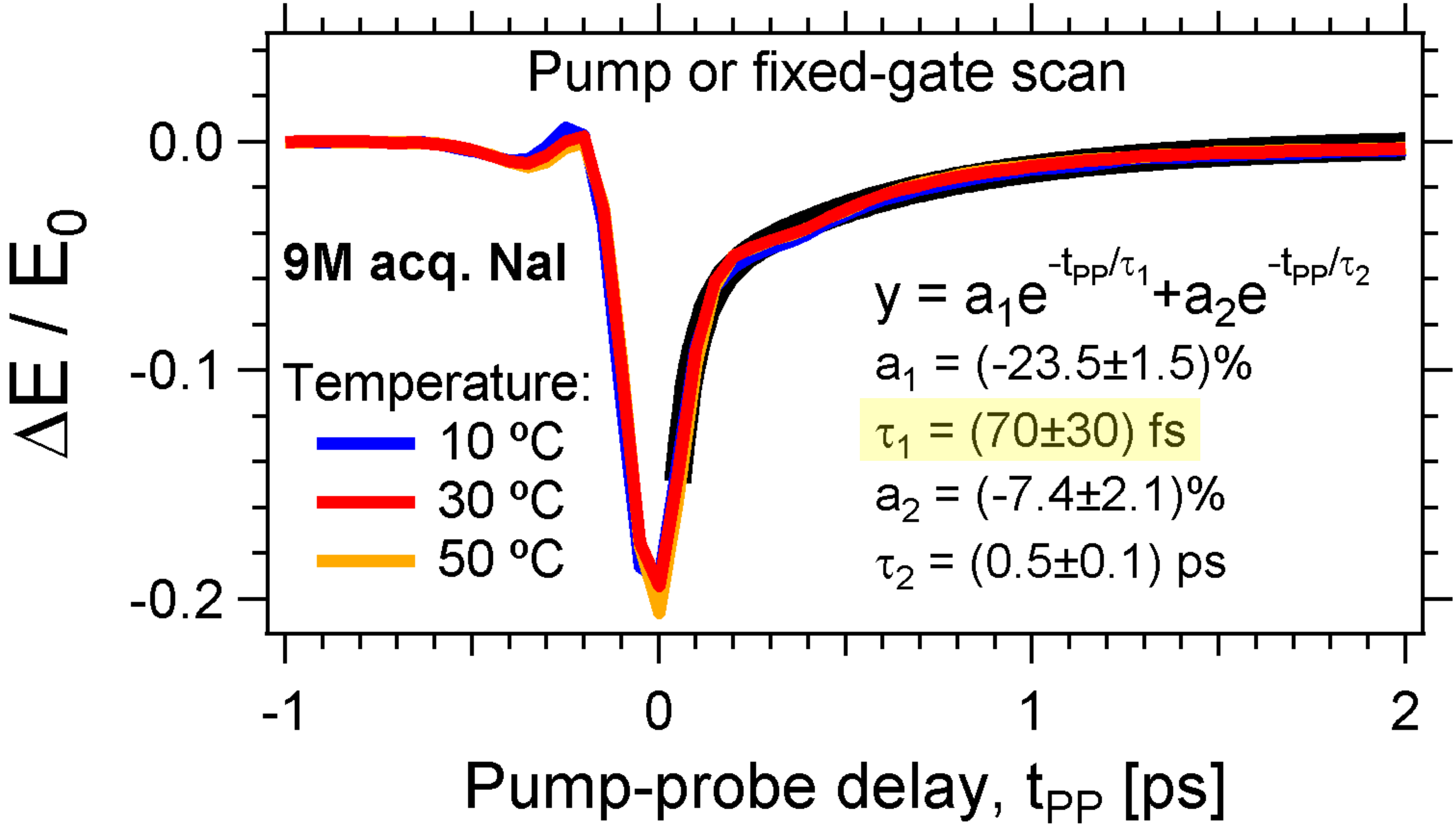

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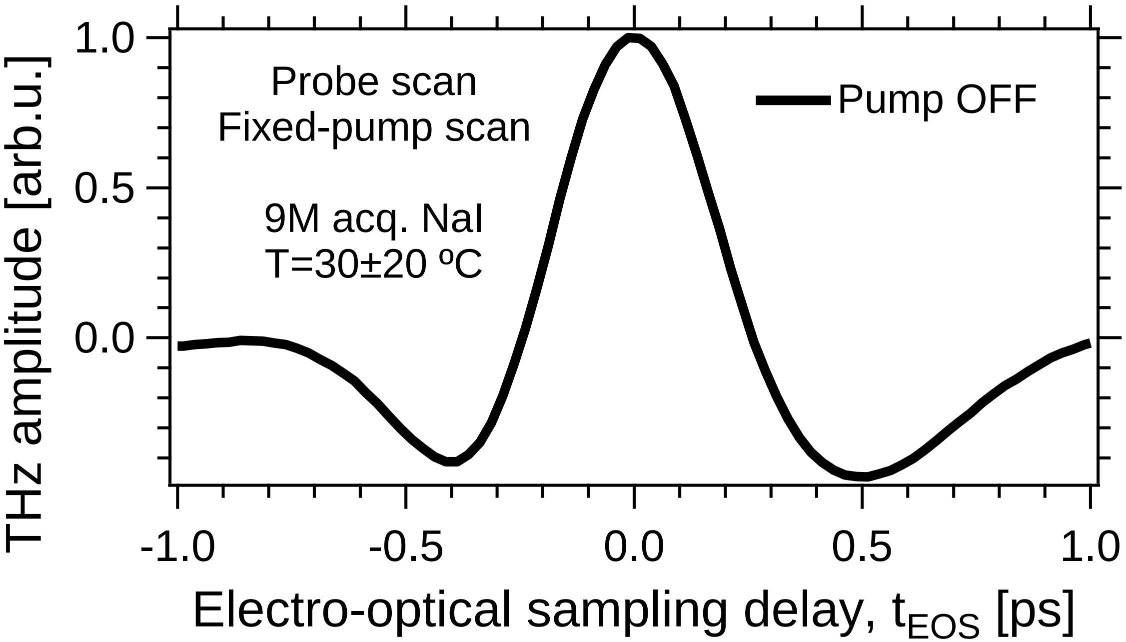

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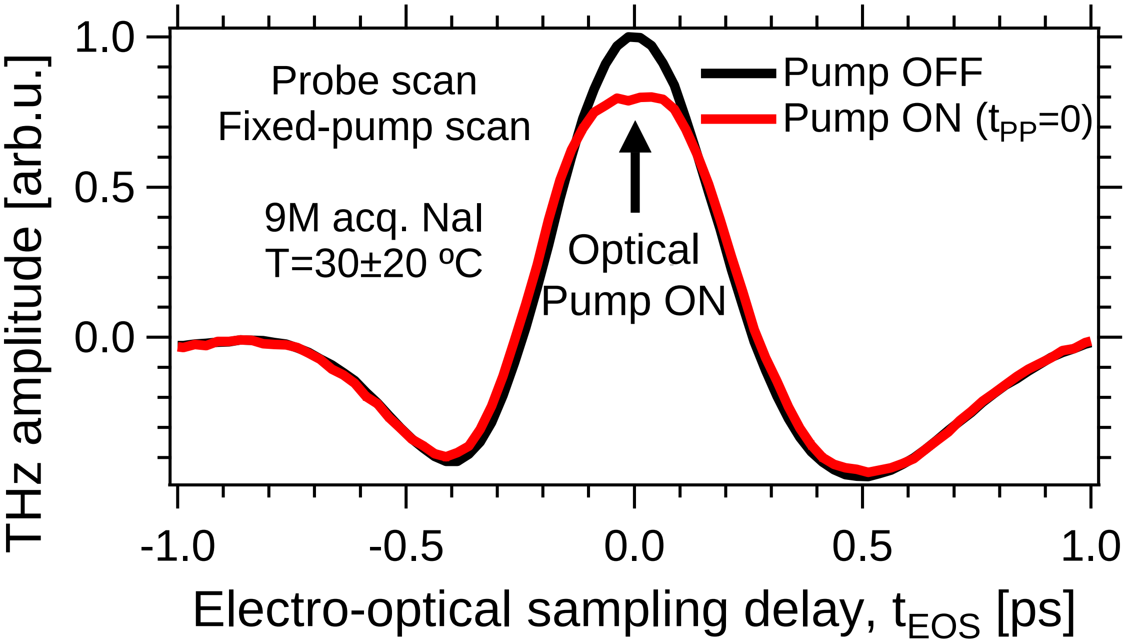

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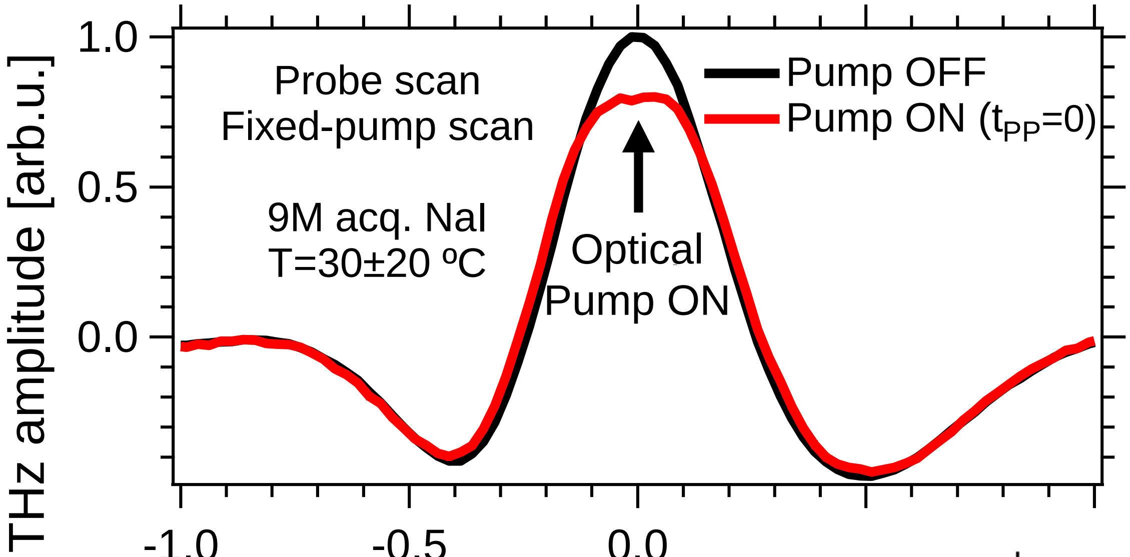
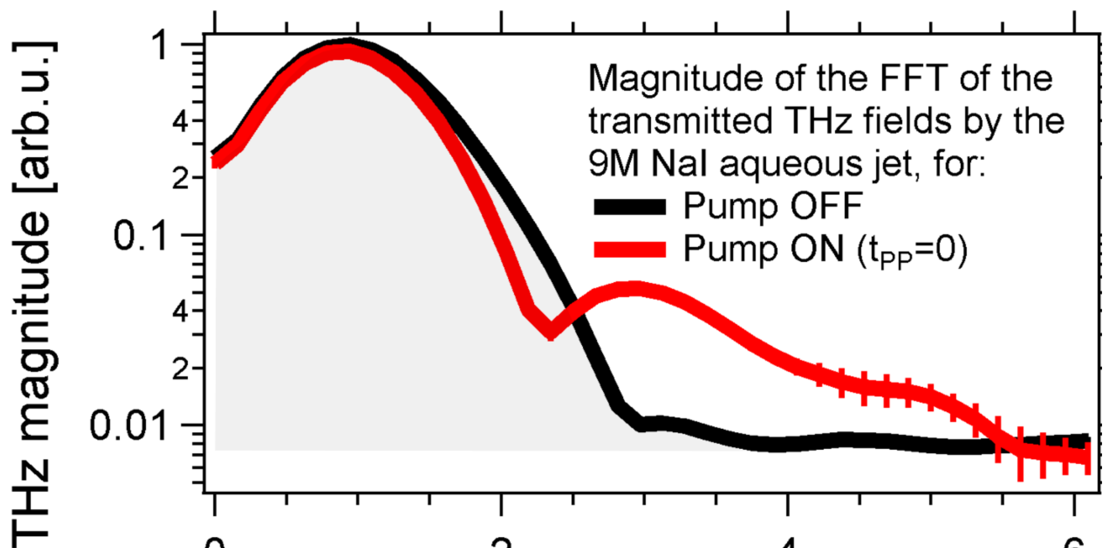
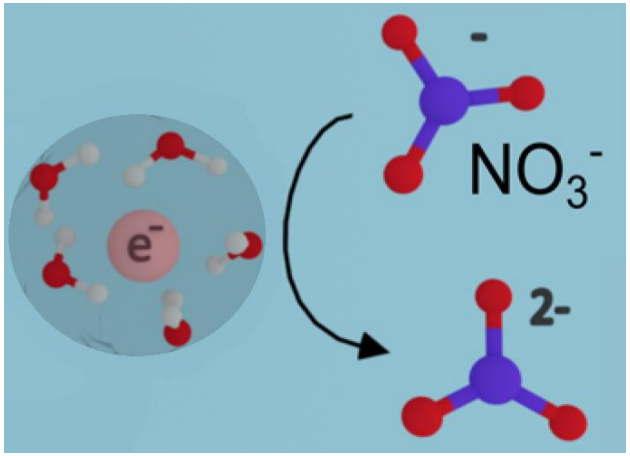


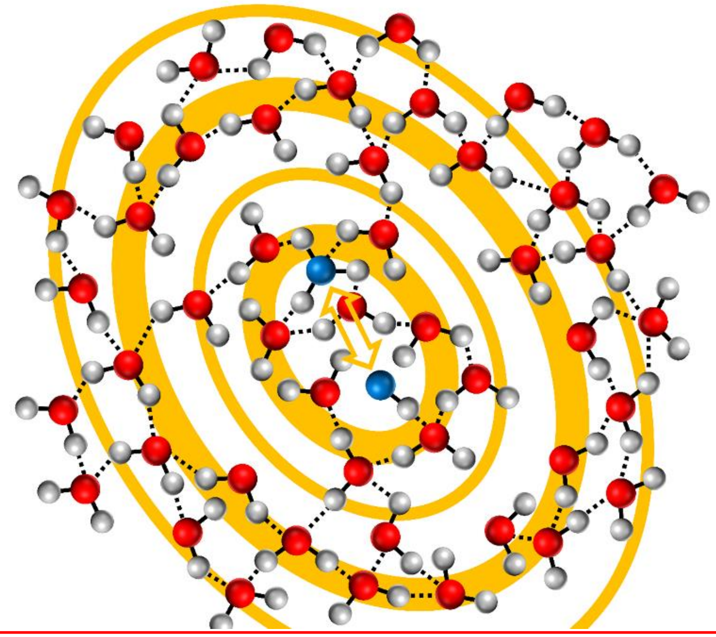


THz probes water dynamics associated to pulse photo-ionization of pure water

PNAS 120, e2216480120, 2023

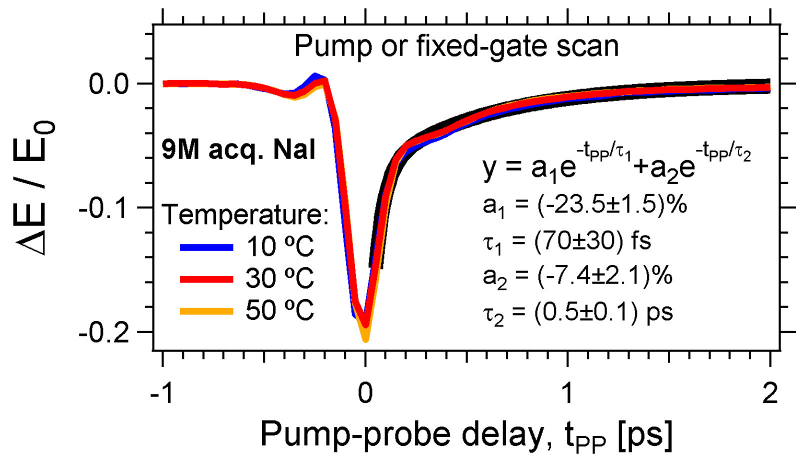


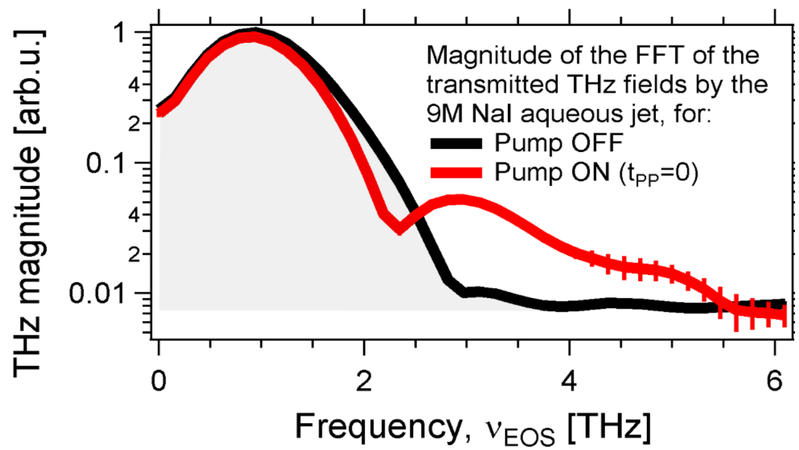
Adapted from PNAS 120, e2217035120, 2023



+NaI: Large (20%), fast (70 fs) THz modulation, pulse-shaping and freq. up-shift

APL Photonics 7, 121302, 2022





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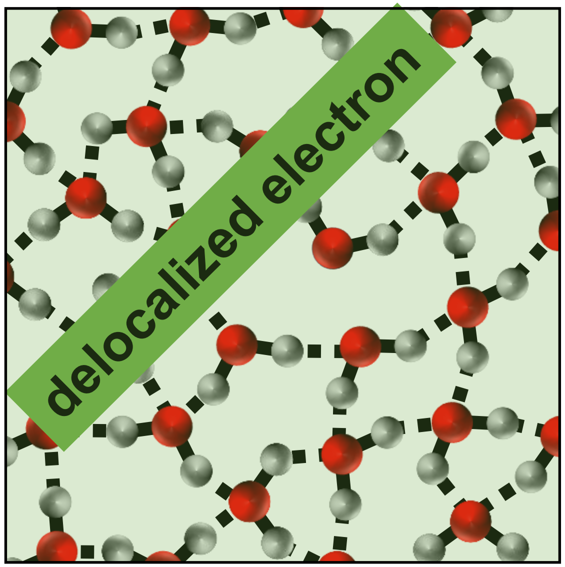

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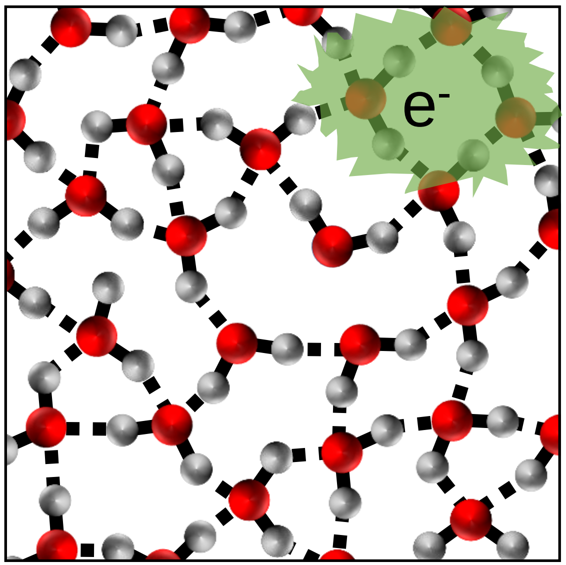

“fill void” (r~2.5 Å), lifetime~100μs

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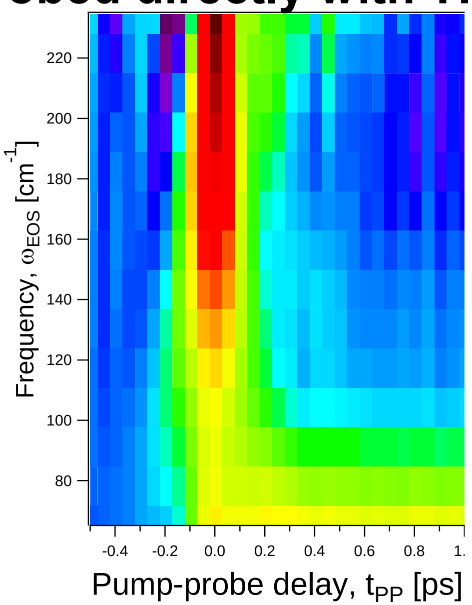

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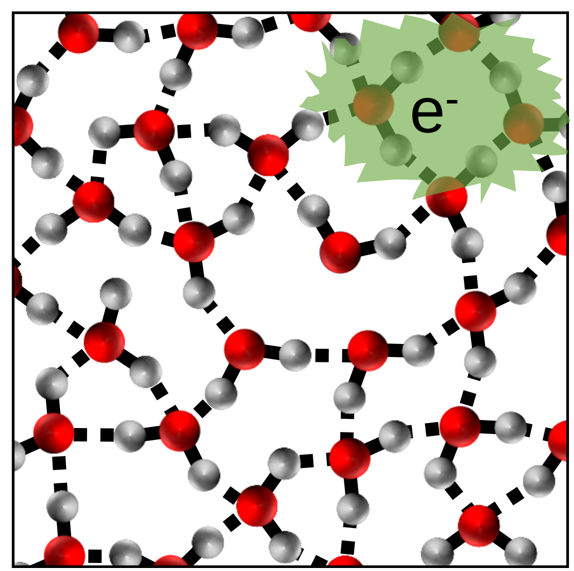

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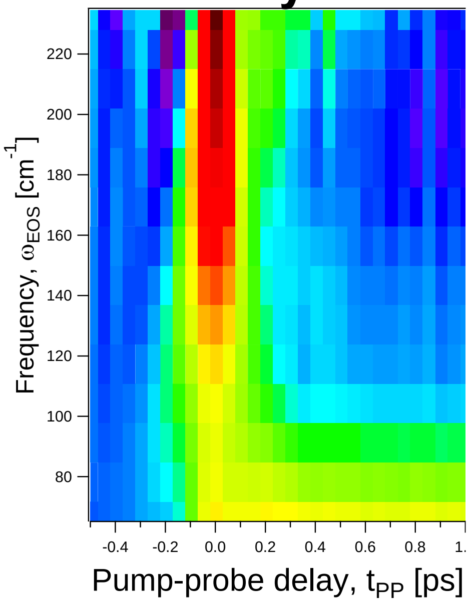

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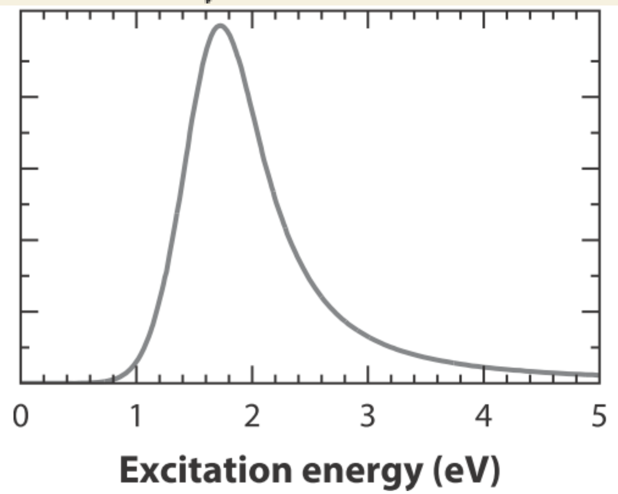
Electron localization (>0.3 ps)
→ Probed at NIR-VIS frequencies

Annu. Rev. Phys. Chem. 2017. 68:447–72



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“Direct” band gap of liquid water?

- What is the minimum excitation energy required to generate delocalized electrons: 8-12eV, 100-150nm?
- Electron affinity: 0 to 1.2eV? [Nat. Com. 9, 247, 2018]

➢ Relevant, e.g., as a **fundamental physical question** (electronic properties of liquid water), for **chemistry** (electrons used in reactions), and **biology** (electrons source of DNA damage).

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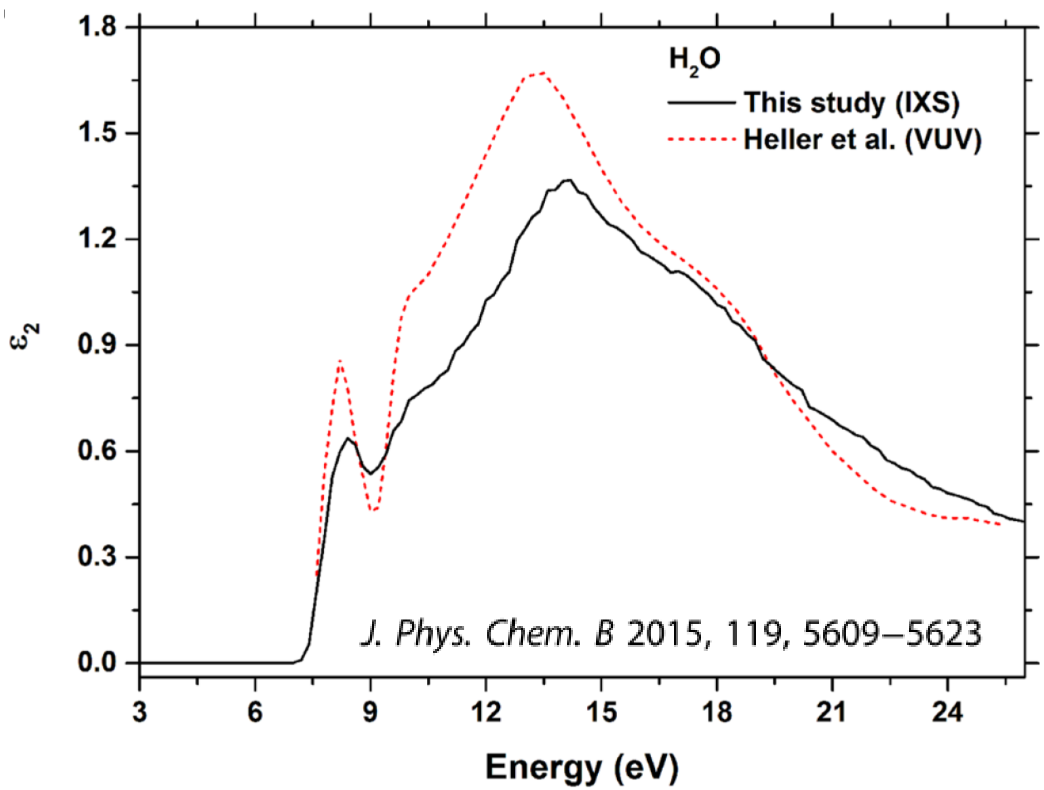

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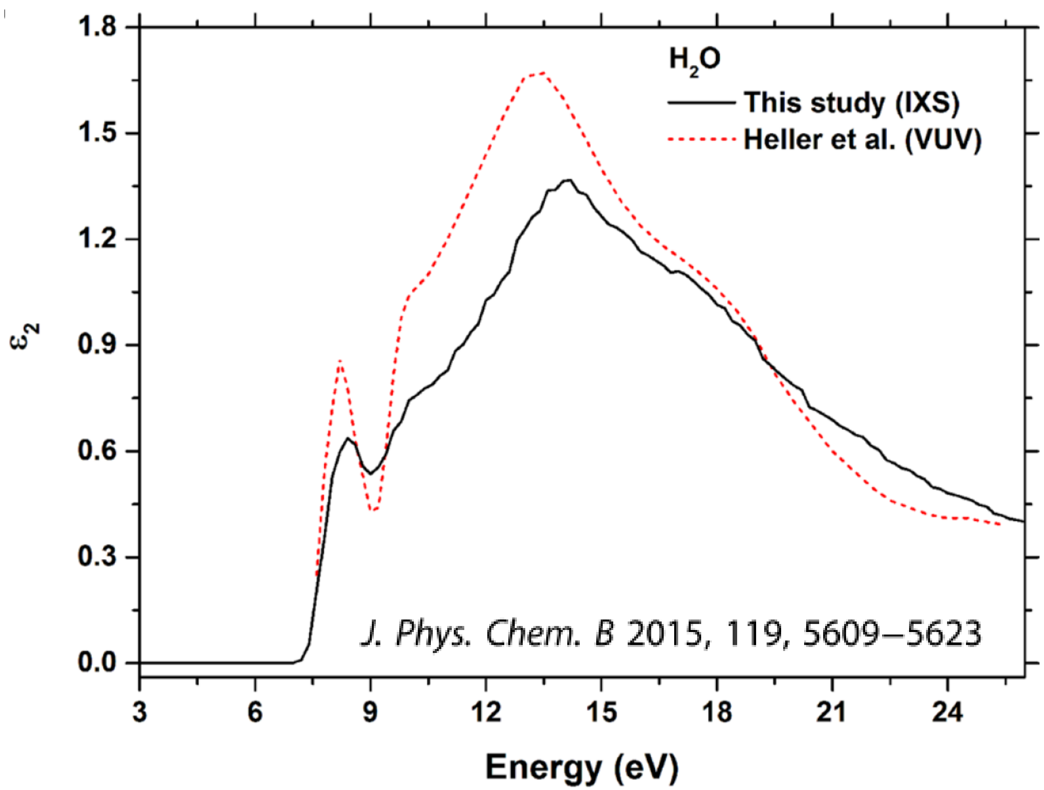

Pump-Probe:
Direct photoionization of water and count generated e^-

Pump: ARIA 100-150 nm

Probe: VIS/NIR laser(~800nm)

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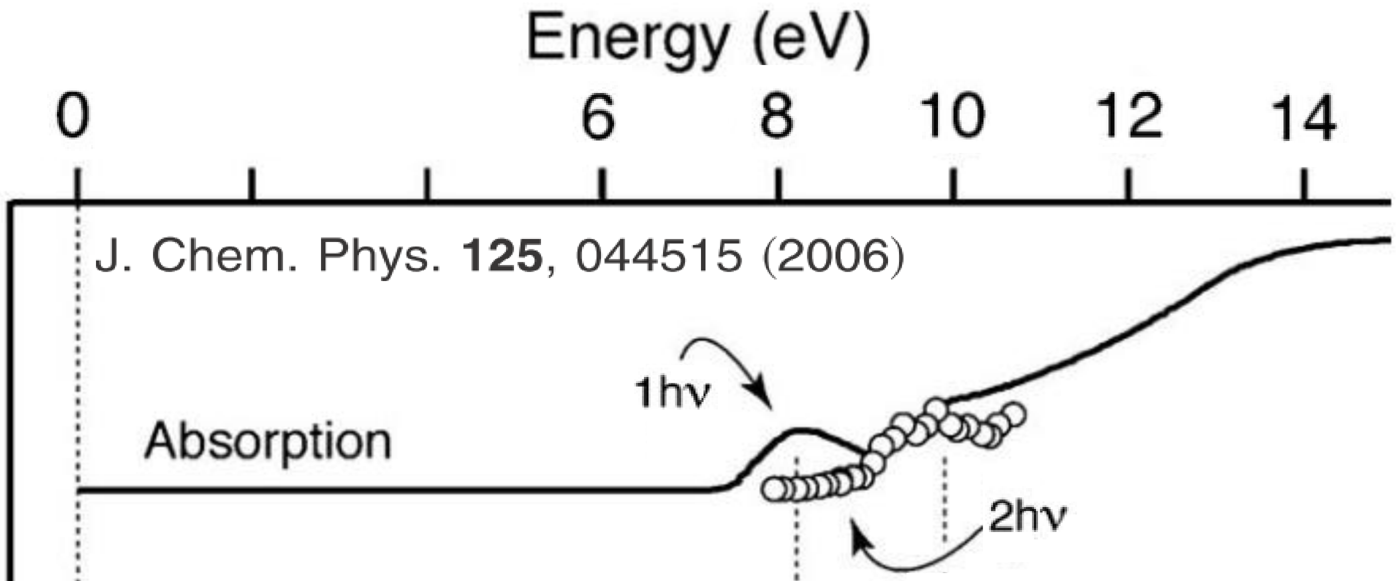
Probe: VIS/NIR synchronized pulsed laser(~800nm, ~100fs) (broad absorption by e^-_{aq} → laser **color not critical**)

Abs. H_2O at 10 eV ~250k cm^{-1}
Pen. Depth ~40 nm
Detect probe change **~10mOD**
[C=OD/(~15k cm^{-1}·40nm)]:
→ need generate ~**167mM e^-_{aq}**

Pump: **tunable 100-150 nm**
Length: **50-250fs**
(<250 fs for dynamics; <0.1eV bandwidth excitation → >50fs).
Exc. H_2O: 167mM e^-_{aq}/55.4M ~ **$3\cdot10^{-3}$** x $3.35\cdot10^{22}$ H_2O/cm^3 ~ $1\cdot10^{20}$ H_2O/cm^3 x 10eV/ph. x J/eV ~ **162J/cm³** x 40nm→**Φ~0.65mJ/cm²**

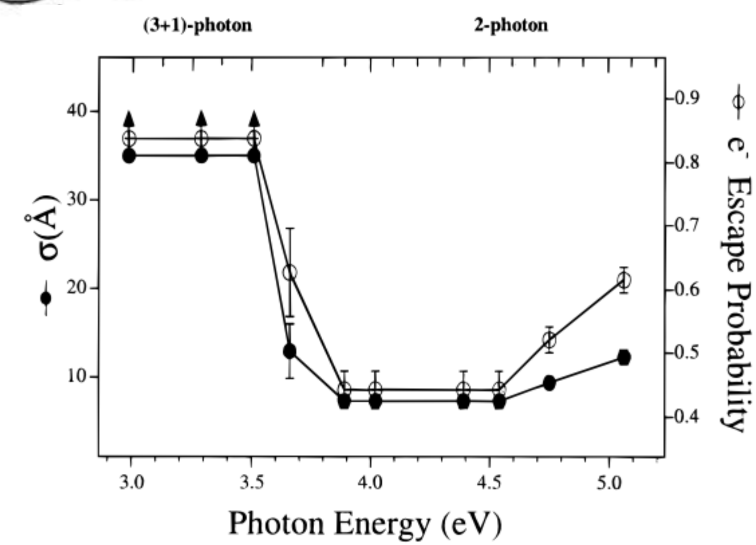
+39C heat/pulse: Rep. rate must be < 100 MHz (liquid jet preferable)

Cannot be done with multiphoton!



Especially revealing is a comparison of the 3.0 eV multiphoton ionization with the 4.5 eV excitation, where one expects the same final energy (9 eV), but obtains vastly different geminate

J. Phys. Chem., Vol. 100, No. 45, 1996



Acknowledgements

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Deutsche Forschungsgemeinschaft
German Research Foundation

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Kristina Tschulik
Paolo Cignoni

Clara Saraceno
Celia Millon*
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MPIK Heidelberg
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Mike Klopf

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Nidhi Adhlakha*

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former

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THANK YOU !!!

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