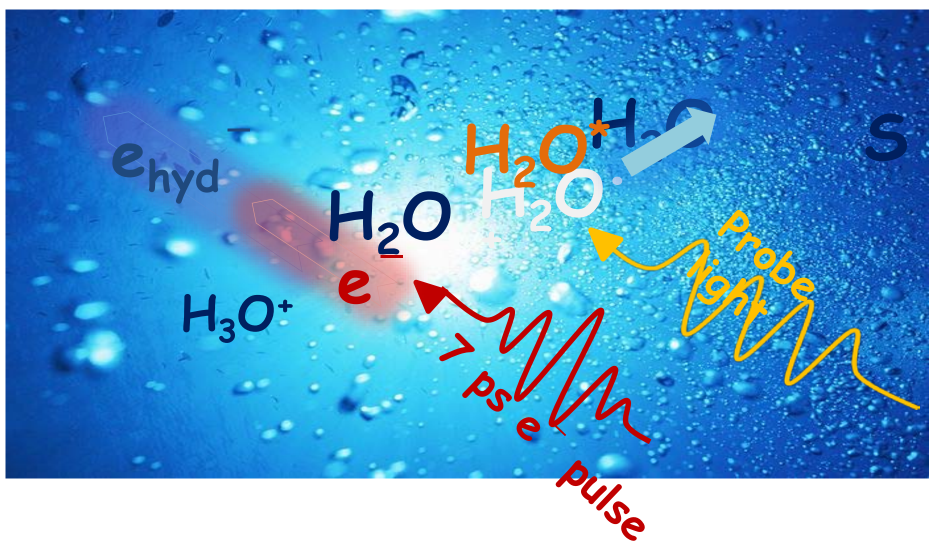
Requirements of New Tools for Challenges in Ultrafast Radiation Chemistry

Mehran MOSTAFAVI

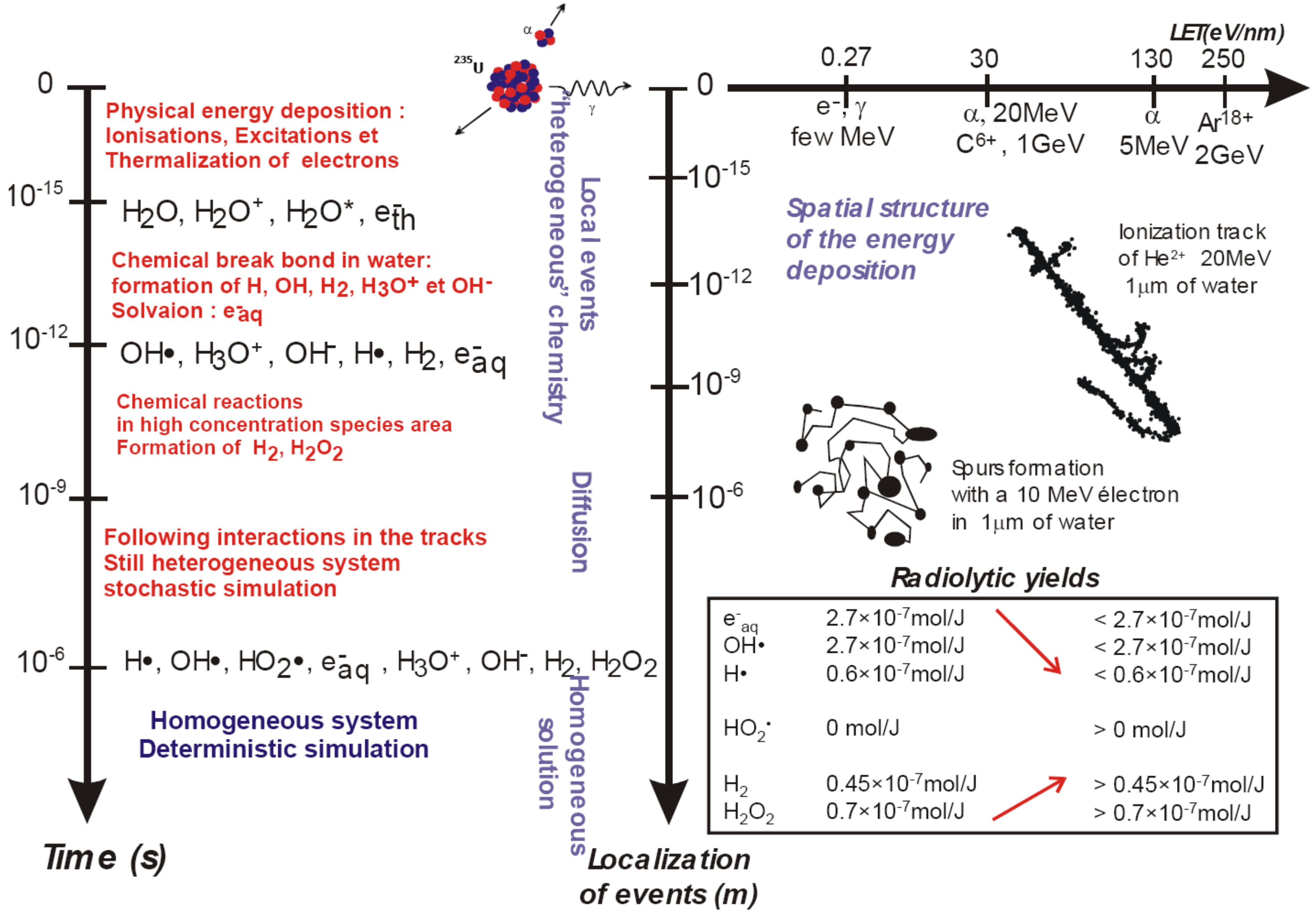
Laboratoire de Chimie Physique/ELYSE, CNRS / Université Paris-Sud

Orsay, France



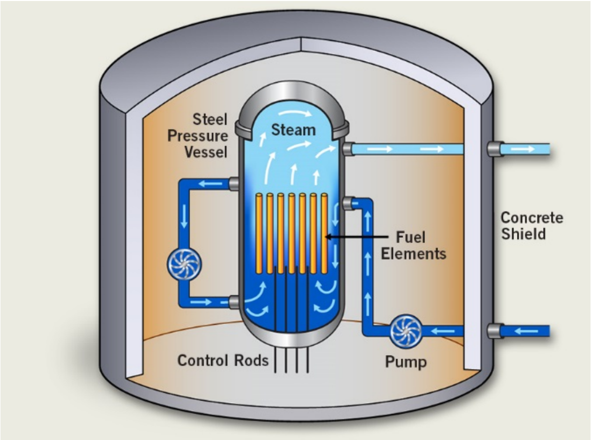
- Introduction to Radiation Chemistry
- Examples of new results and new challenges
- **New sources needed for Radiation Chemistry**

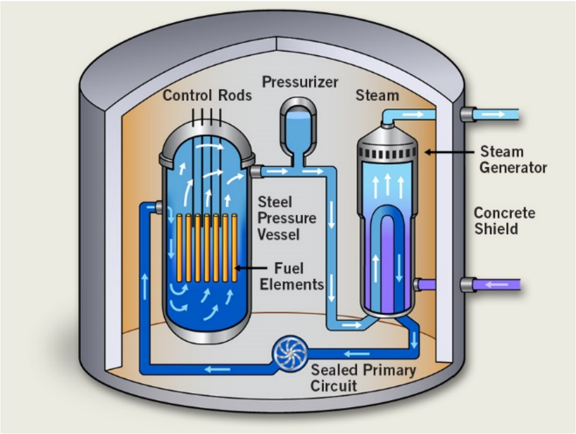
Water radiolysis : Time and LET dependent Radical Yield

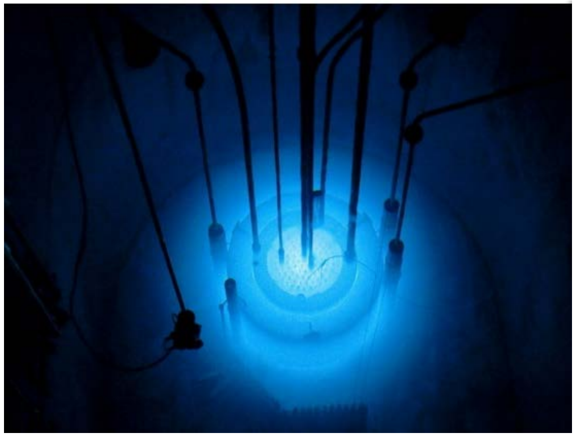


e^-_{aq}	2.7×10^{-7}mol/J	< 2.7×10^{-7}mol/J
$OH\bullet$	2.7×10^{-7}mol/J	< 2.7×10^{-7}mol/J
$H\bullet$	0.6×10^{-7}mol/J	< 0.6×10^{-7}mol/J
$HO_2^\bullet$	0 mol/J	> 0 mol/J
H_2	0.45×10^{-7}mol/J	> 0.45×10^{-7}mol/J
H_2O_2	0.7×10^{-7}mol/J	> 0.7×10^{-7}mol/J

Why radiolysis studies ? Nuclear Energy

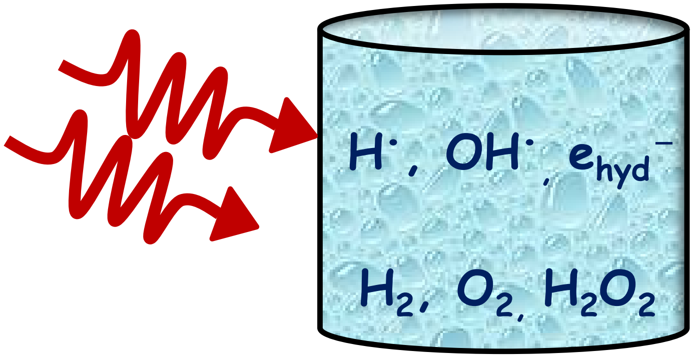






Industrial Nuclear Reactors

Boiling Water Reactor (BWR) & Pressurized Water Reactor (PWR)

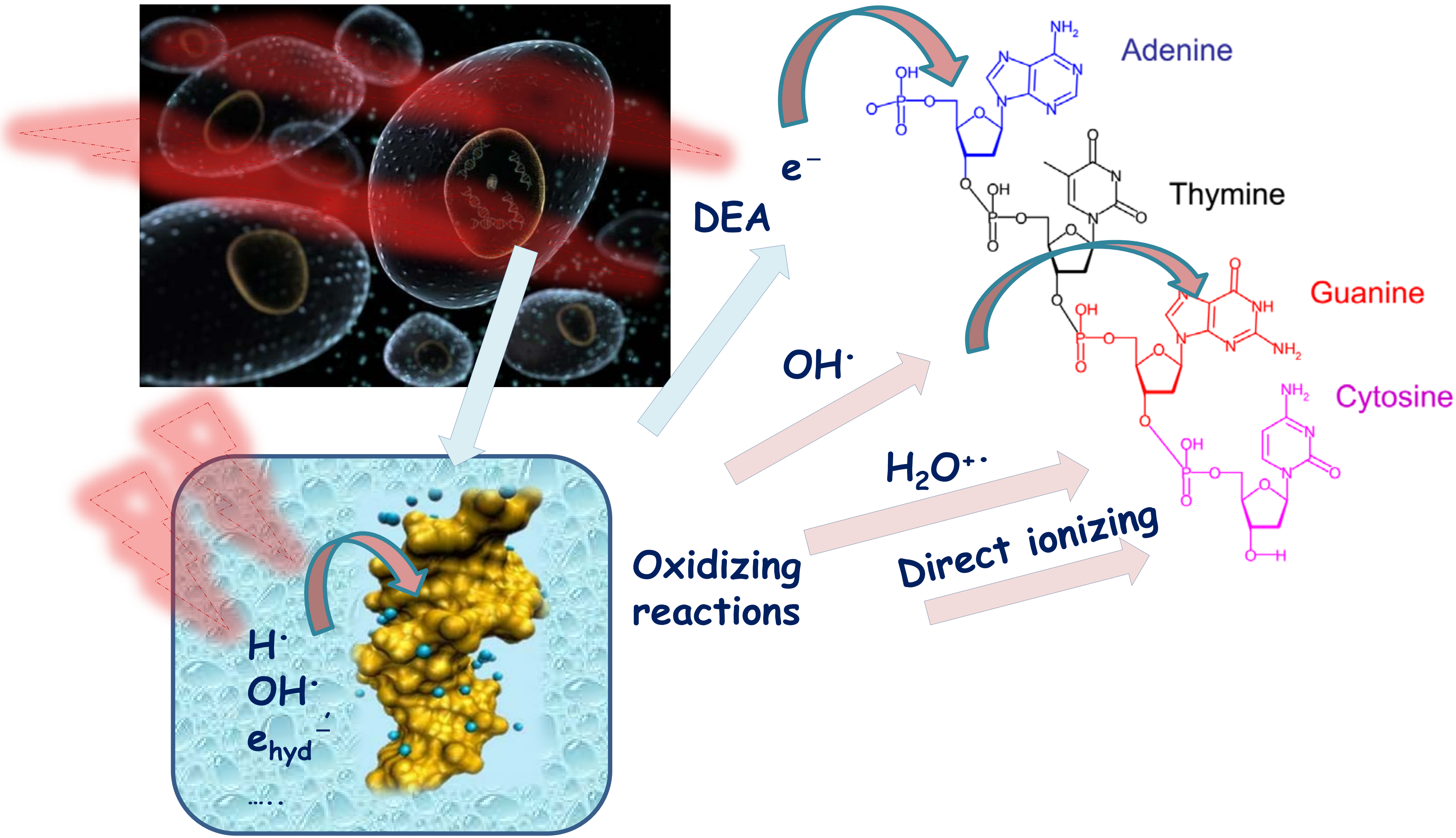


- Nuclear waste storage
- Spent fuel processing and reprocessing

Metal corrosion, polymer degradation & H_2 formation

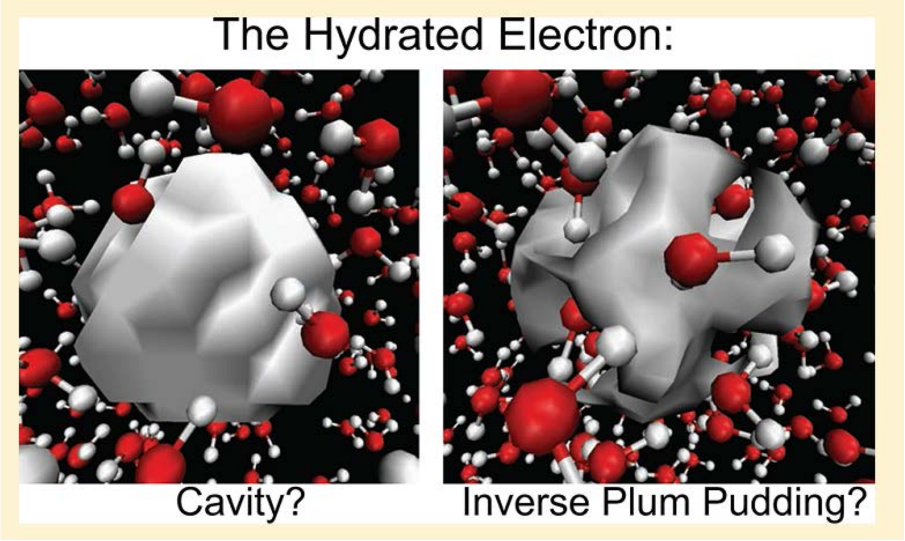
Why radiolysis studies ? Radiobiology and radiotherapy

Living body consists of 70-90 % water



Why water radiolysis ?

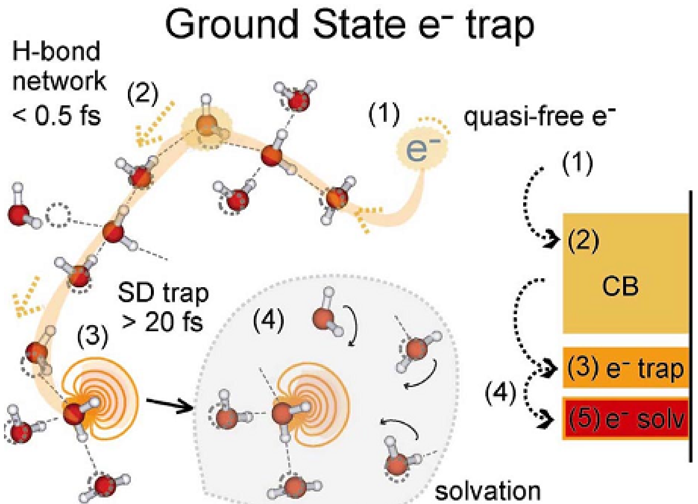
Fundamental interests: electron and proton transfer, radical reactivity and solvation dynamics



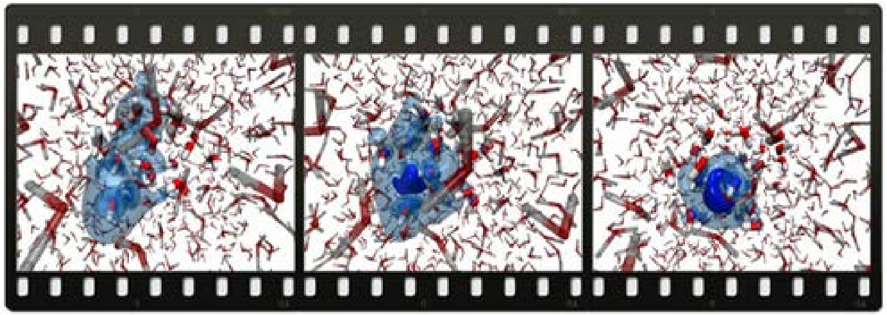
Does e_{hyd}^- occupy a cavity ?

Model for e_{hyd}^-

R. E. Larsen et al. Science. 2010, 329, 65.



Solvation dynamics of e^- in water



J. Savolainen *et al.* Nature Chem. 2014, 6, 697.
D. Nordlund *et al.* Phys Rev Lett. 2007, 99, 217406

First pulse radiolysis measurements

Hart and Boag's experiment (1963)

Using a μs pulse of 10 MeV electrons, Hart and Boag[15] obtained indisputable evidence of the existence of the hydrated electron as a distinct species of matter with an absorption spectrum of its own and other characteristic properties. The hydrated electrons were produced in high concentration in a quartz cell during the short duration of the pulse. These were traversed normally by light from a bright xenon arc, the cell walls being mirrored to effect multiple reflections to increase the light path. The resulting beam was then analysed by a monochromator set at 720 nm, the absorption maximum of the pale blue solution of the hydrated electrons, and finally it reached a shielded photomultiplier, whose amplified signal was recorded (Fig. 11.4).

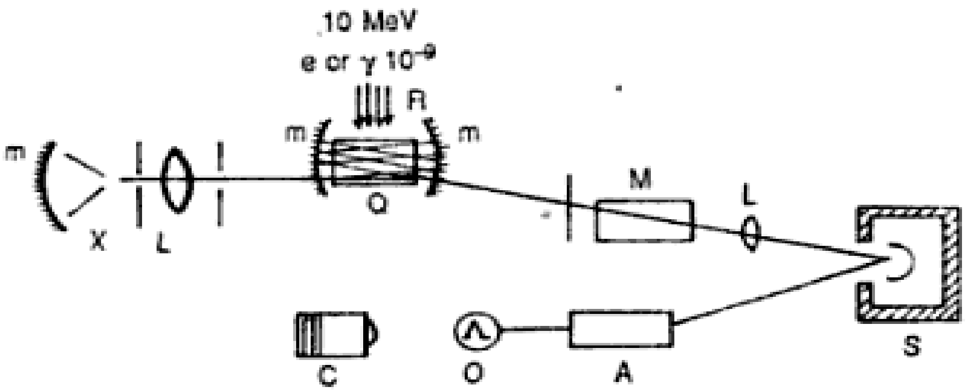
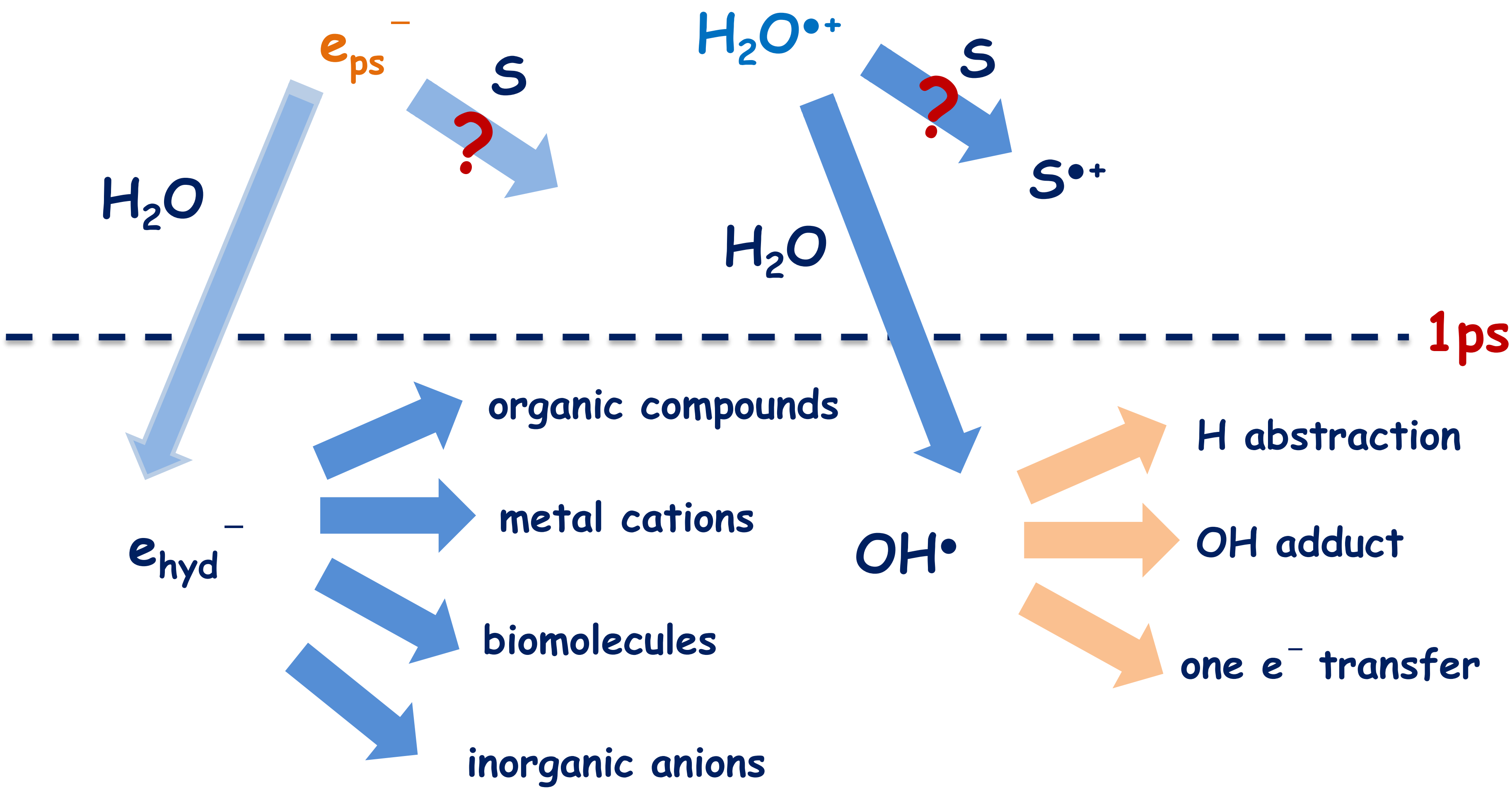


Fig. 11.4 Hart and Boag's pulse radiolysis set up for detecting the hydrated electron. m: Mirror; X: Xenon arc; Q: Lens; R: Radiation pulse; Q: Quartz cell with water; M: Monochromator; S: Shielded photomultiplier; A: Amplifier; O: Oscilloscope; C: Polaroid camera.

Reactivity of e_{hyd}^{-} and $OH^{\bullet}$ radicals

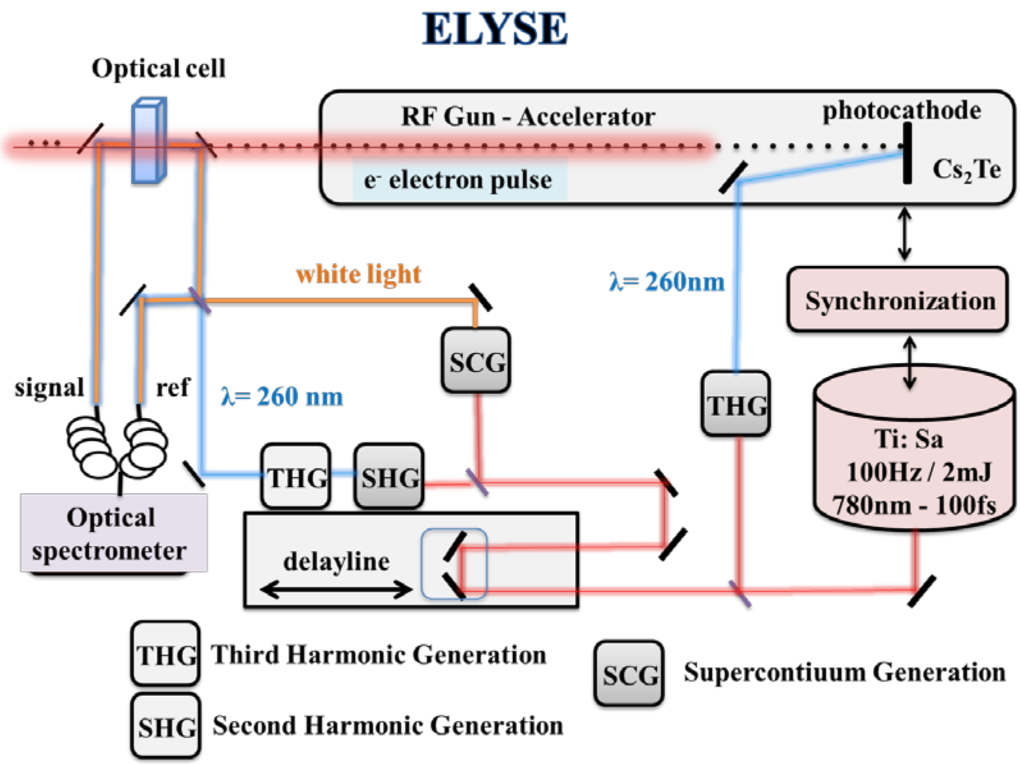


G. V. Buxton *et al.* Critical review of rate constant for reactions of hydrated electron, hydrogen atom and hydroxyle radicals in aqueous solutions. J. Phy. Chem. Ref. Data. 1988, 17, 2.

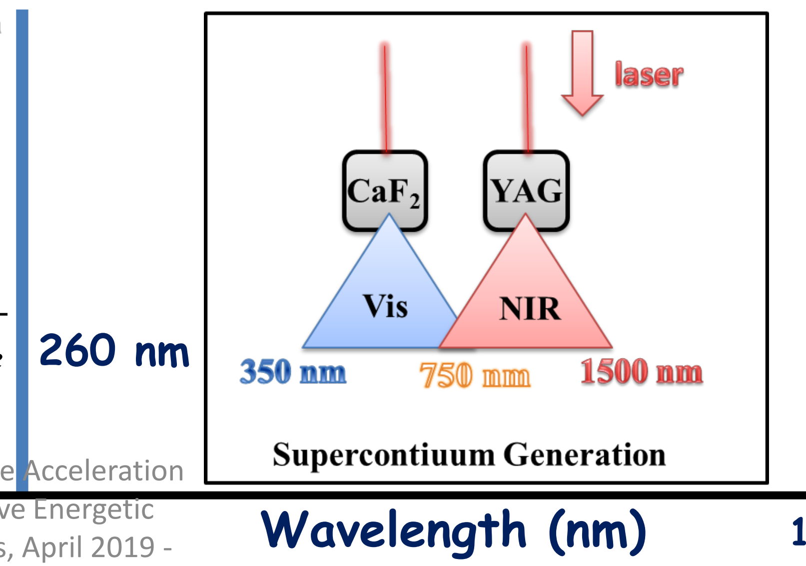
Orsay Picosecond Pulse Radiolysis Facility- ELYSE

Electron Pulse duration: 7 ps
Energy: 4 – 8 MeV
Charge: 1 – 6 nC
Frequency: 1 - 20 Hz

Picosecond pulse radiolysis - ELYSE

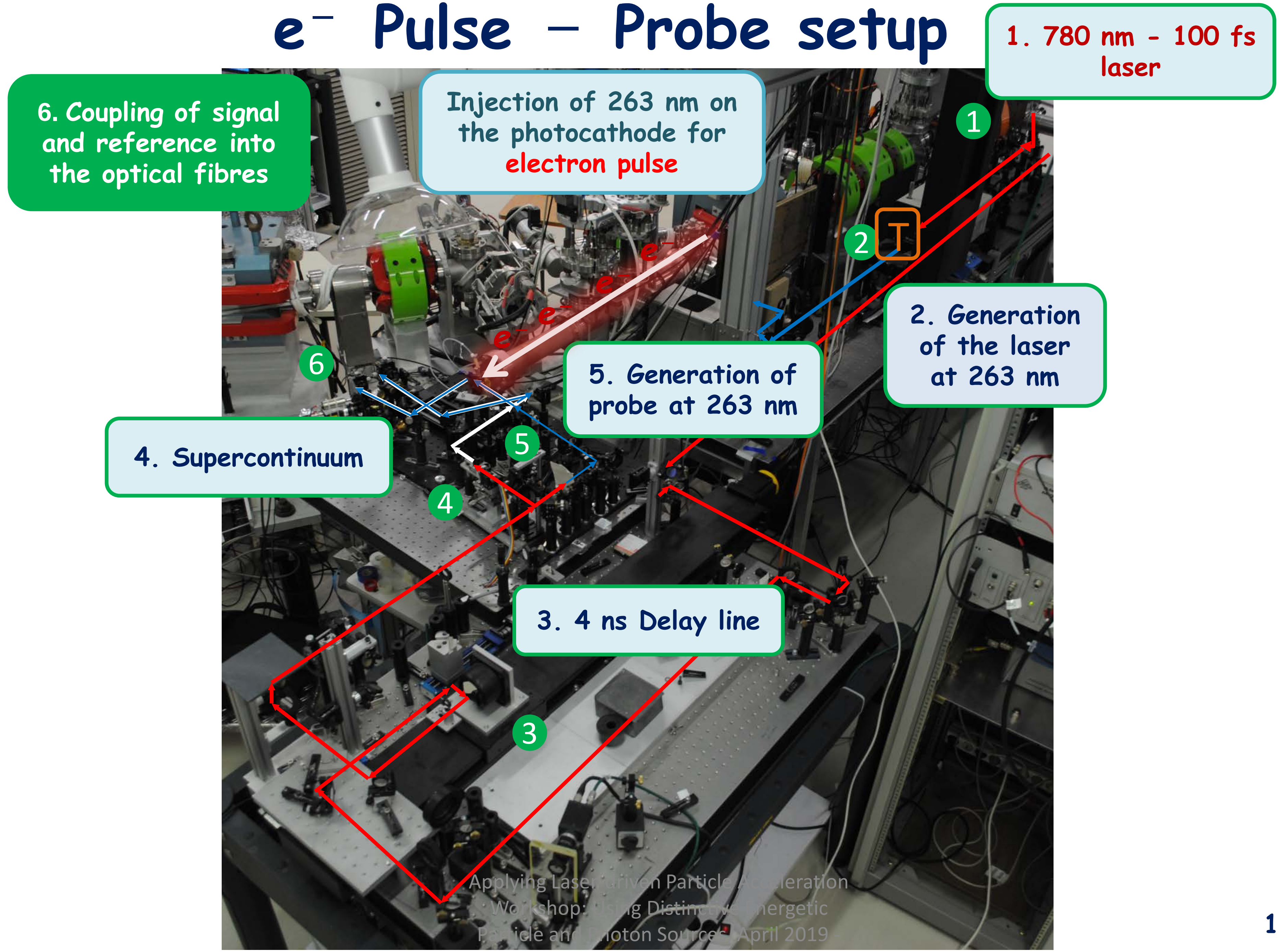


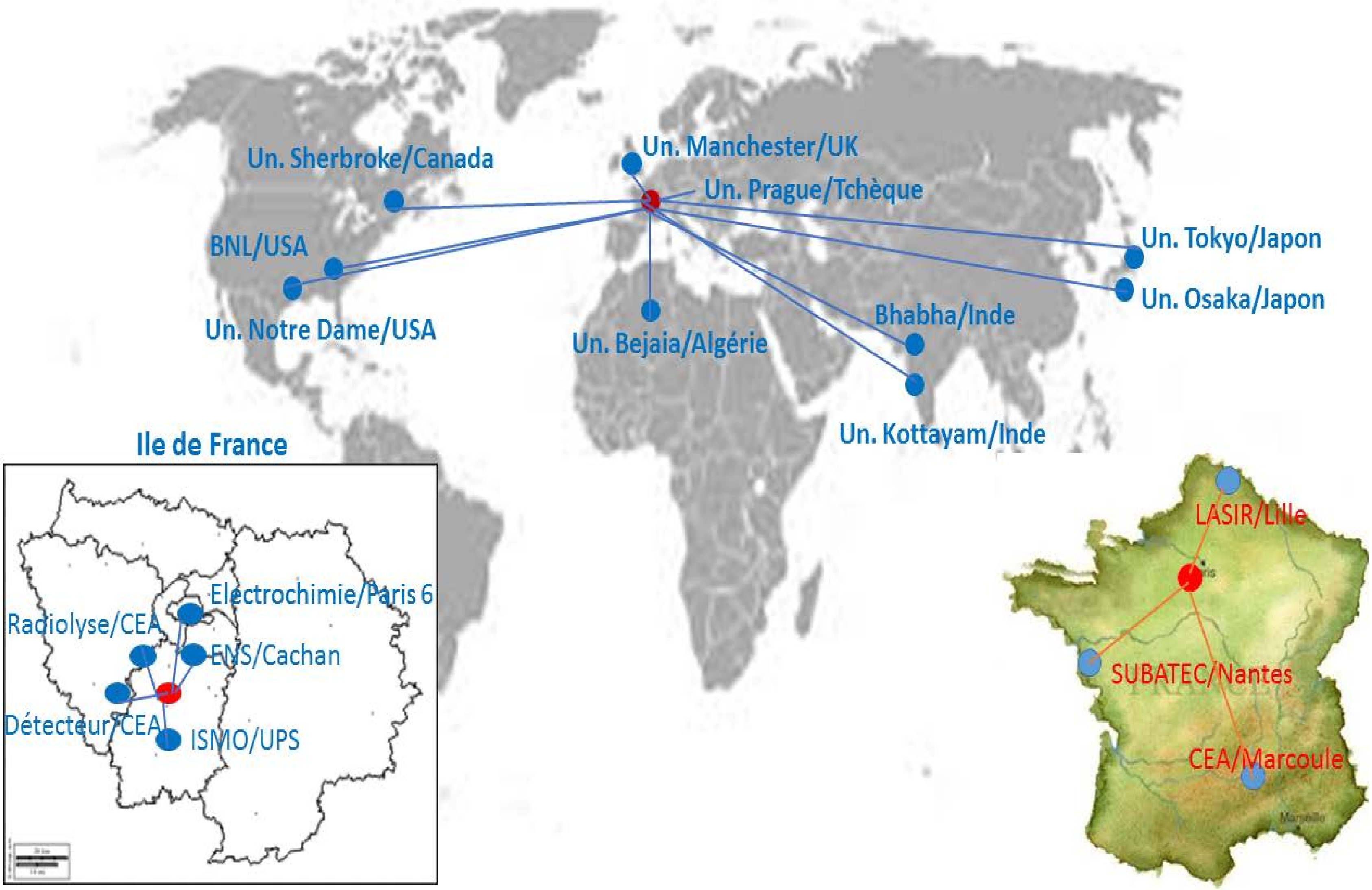
Probe light:



$$OD(\lambda,\Delta t) = \log\frac{I^{\circ}{}_{réf} - I_{dark}}{I^{\circ}{}_{sig} - I_{dark}} - \log\frac{I_{réf} - I_{dark}}{I_{sig} - I_{dark} - I_{cekove}}$$

e^- Pulse – Probe setup

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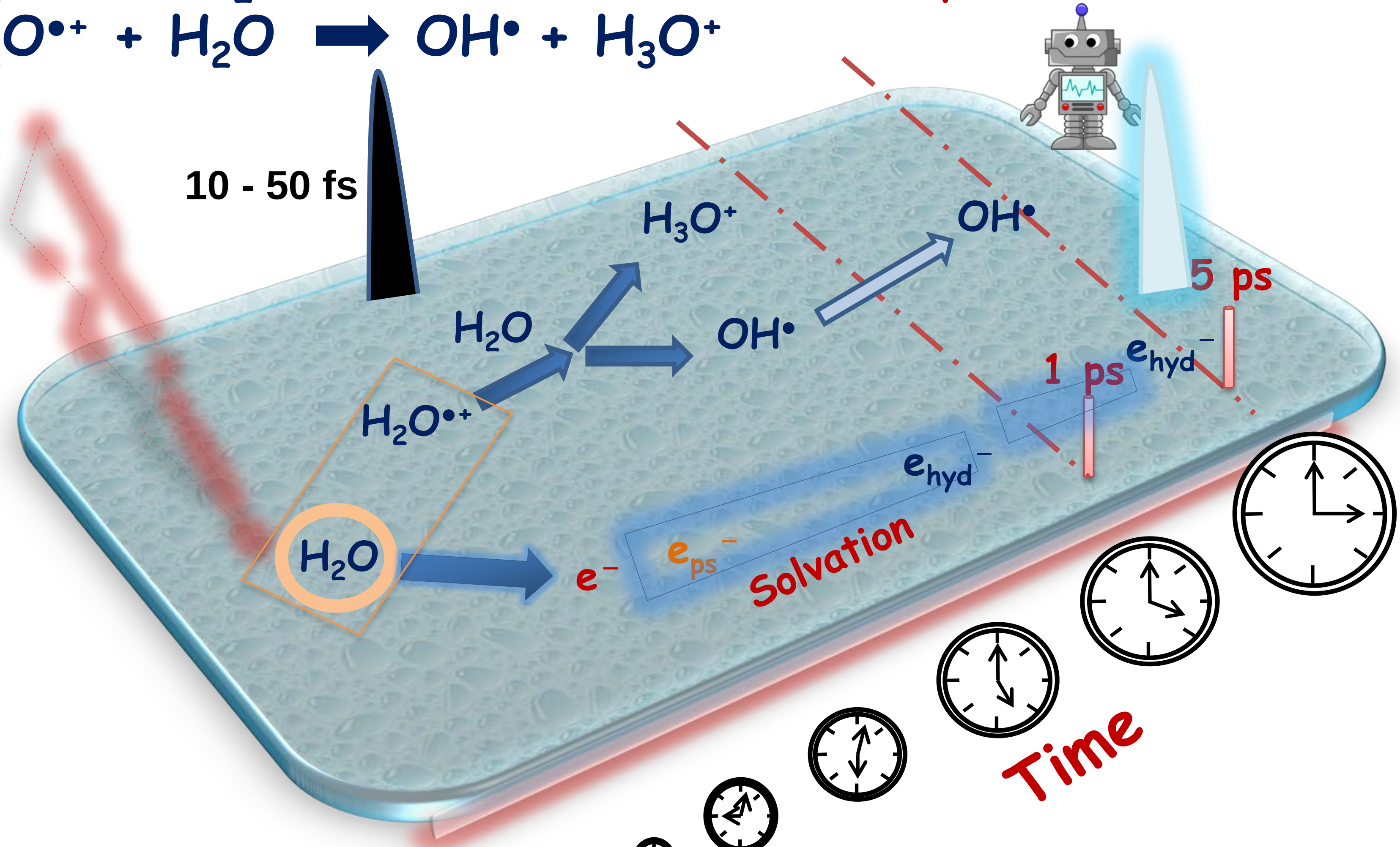
Bhabha/Inde
Un. Bejaia/Algérie
Un. Kottayam/Inde
Ile de France
Electrochimie/Paris 6
Radiolyse/CEA
ENS/Cachan
Détecteur/CEA
ISMO/UPS
LASIR/Lille
SUBATEC/Nantes
CEA/Marcoule

Reactivity of $H_2O^{\bullet+}$ in neat water

$H_2O \rightsquigarrow H_2O^{\bullet+} + e^-$

$H_2O^{\bullet+} + H_2O \rightarrow OH^\bullet + H_3O^+$

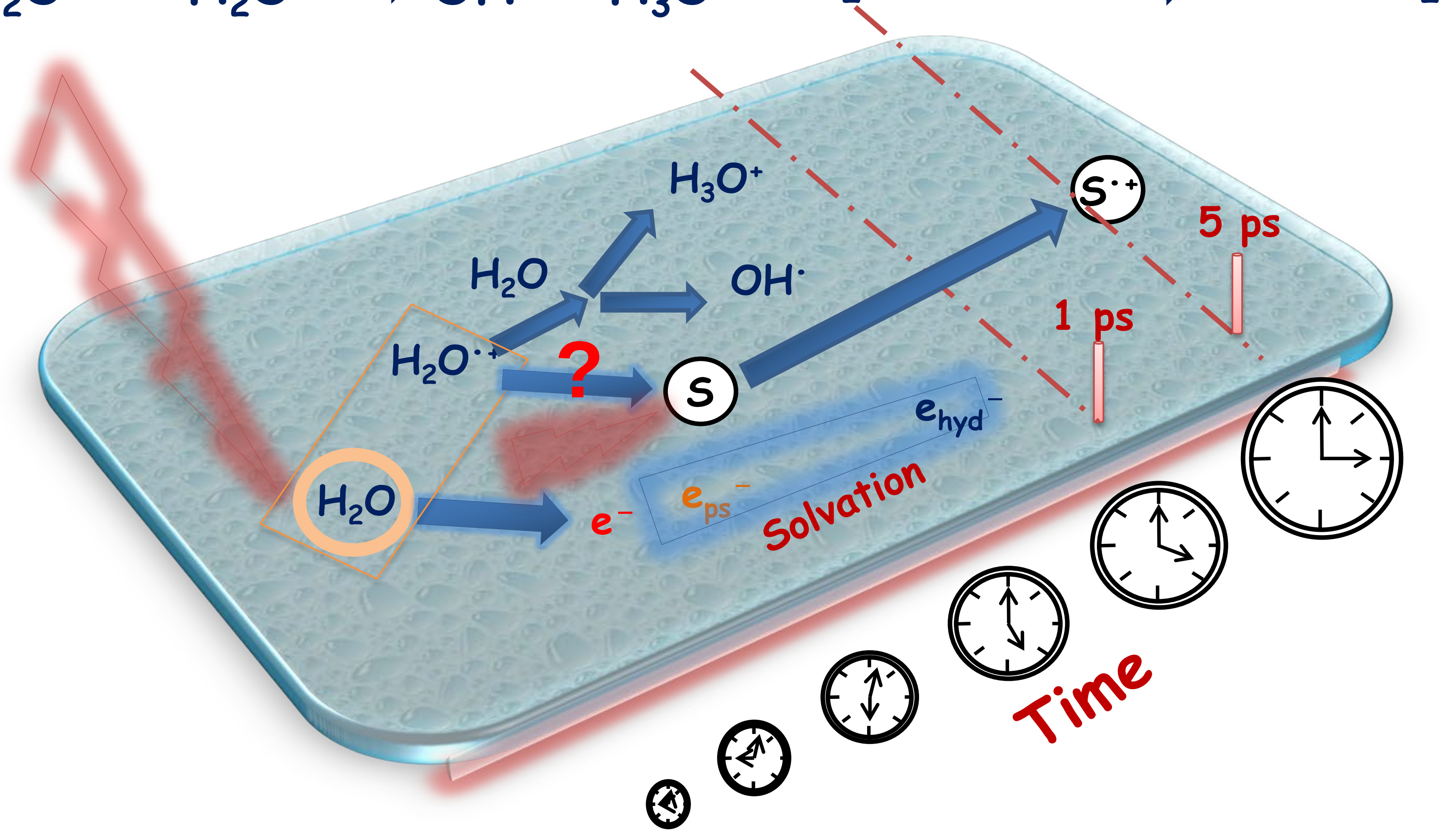


Reactivity of $H_2O^{\bullet+}$ in concentrated solutions

$H_2O \rightsquigarrow H_2O^{\bullet+} + e^-$

$H_2O^{\bullet+} + H_2O \rightarrow OH^{\bullet} + H_3O^+$

$H_2O^{\bullet+} + S \rightarrow S^{\bullet+} + H_2O$



Selecting solute S: H_2SO_4

Our Observable: Formation of $SO_4^{\bullet-}$ Radical

$$H_2O \rightsquigarrow H_2O^{\bullet+} + e^-$$

$$H_2O^{\bullet+} + H_2O \rightarrow OH^{\bullet} + H_3O^+$$

$$OH^{\bullet} + HSO_4^- \nrightarrow SO_4^{\bullet-} + H_2O$$

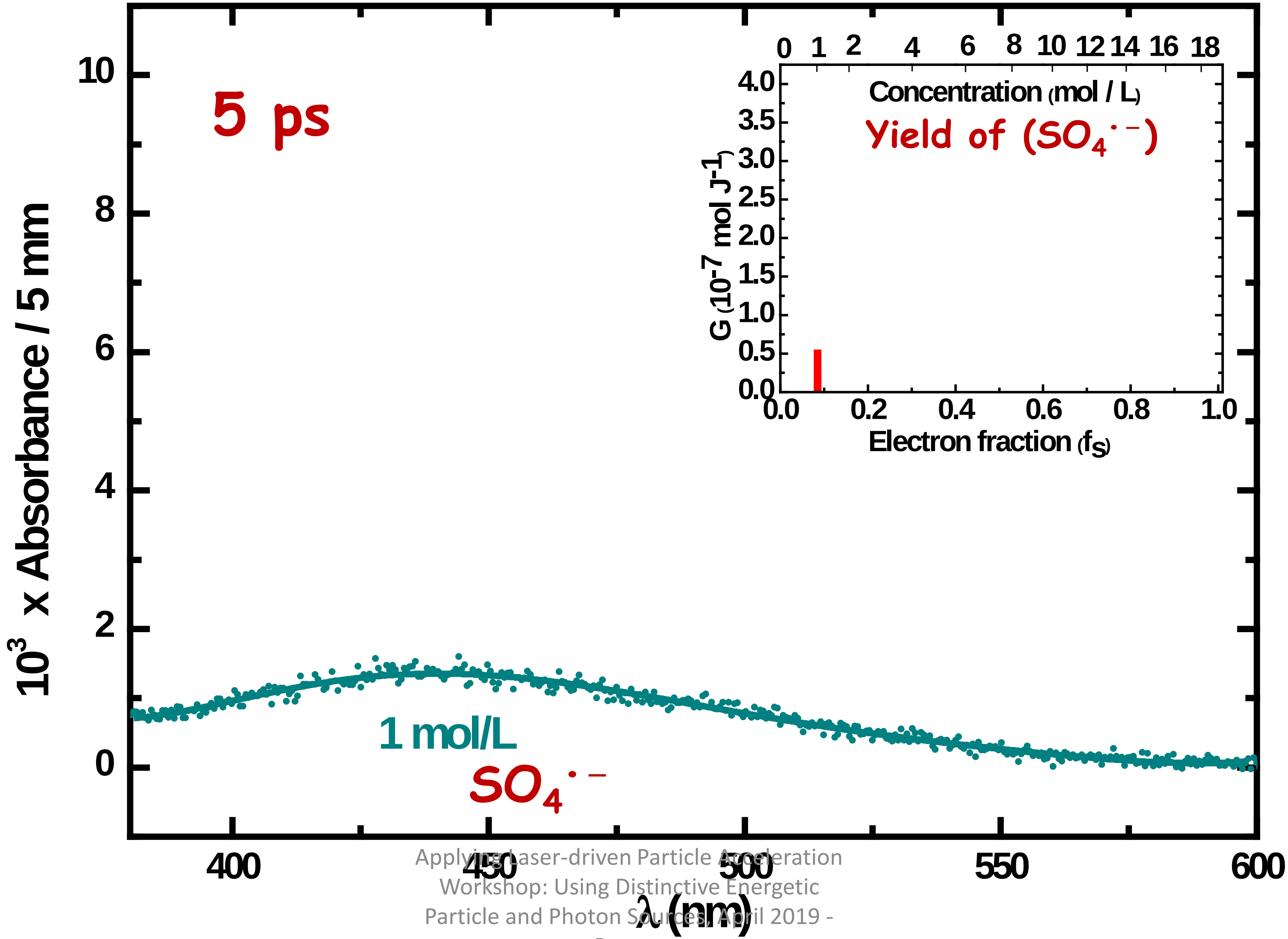
$k = 1.4 \times 10^7\ L\ mol^{-1}\ s^{-1}$

✓ Not occurring on ps time scale

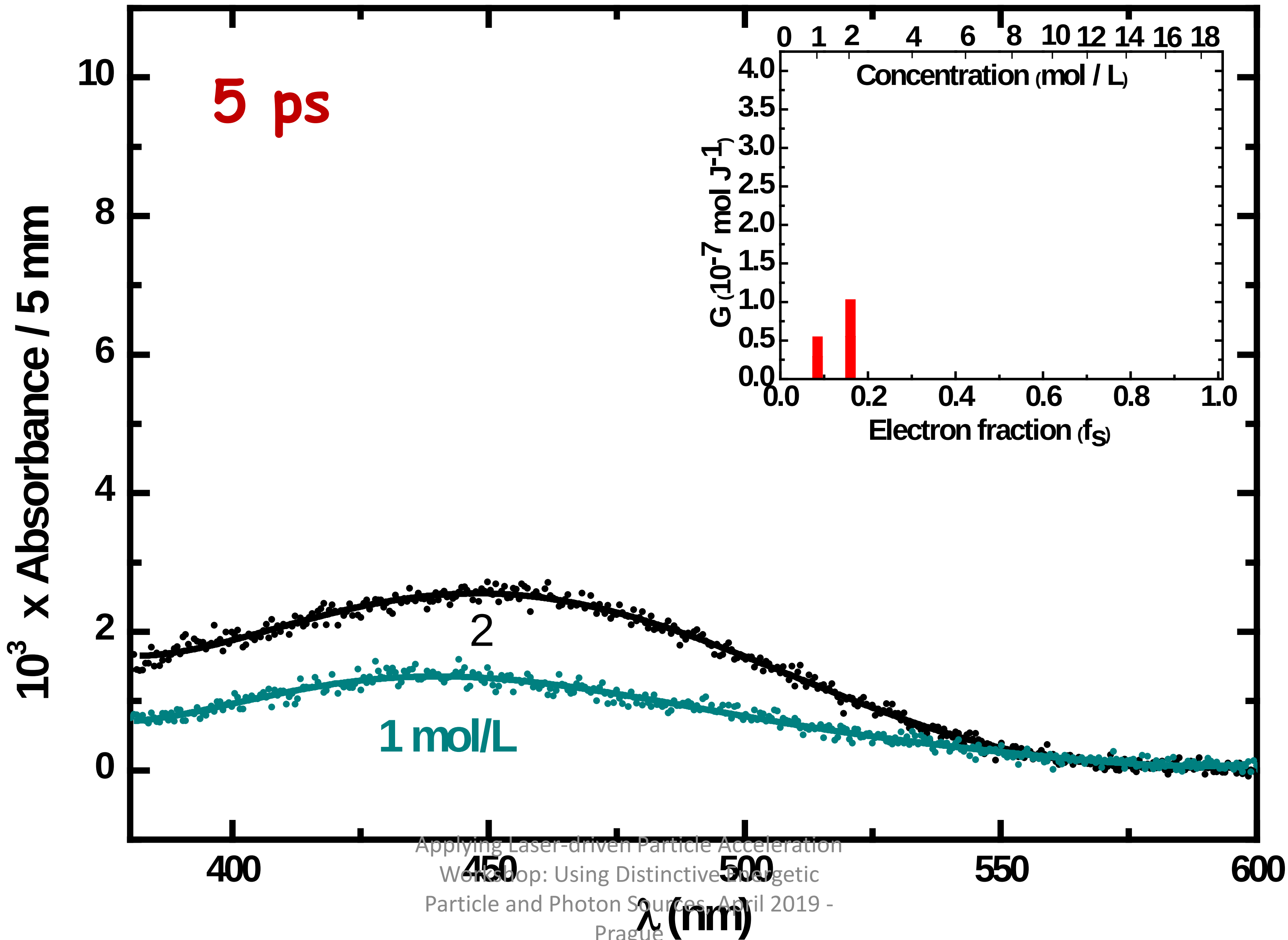
$$H_2O^{\bullet+} + SO_4^{2-} \xrightarrow{?} SO_4^{\bullet-} + H_2O$$

$$SO_4^{2-} \rightsquigarrow SO_4^{\bullet-} + e^-$$

Formation of $SO_4^{\bullet -}$ in solution H_2SO_4



Formation of $SO_4^{\bullet -}$ in solution H_2SO_4



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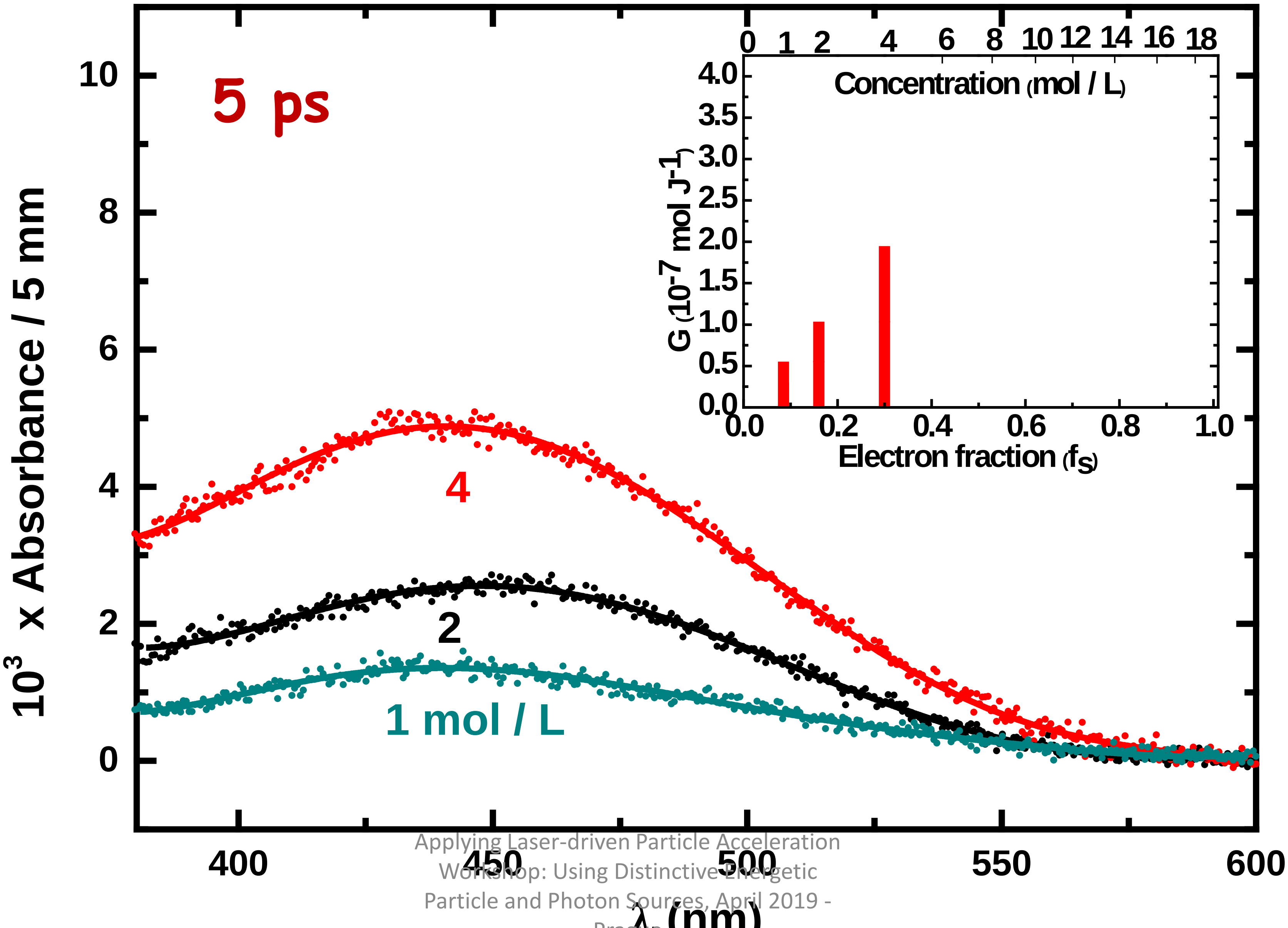
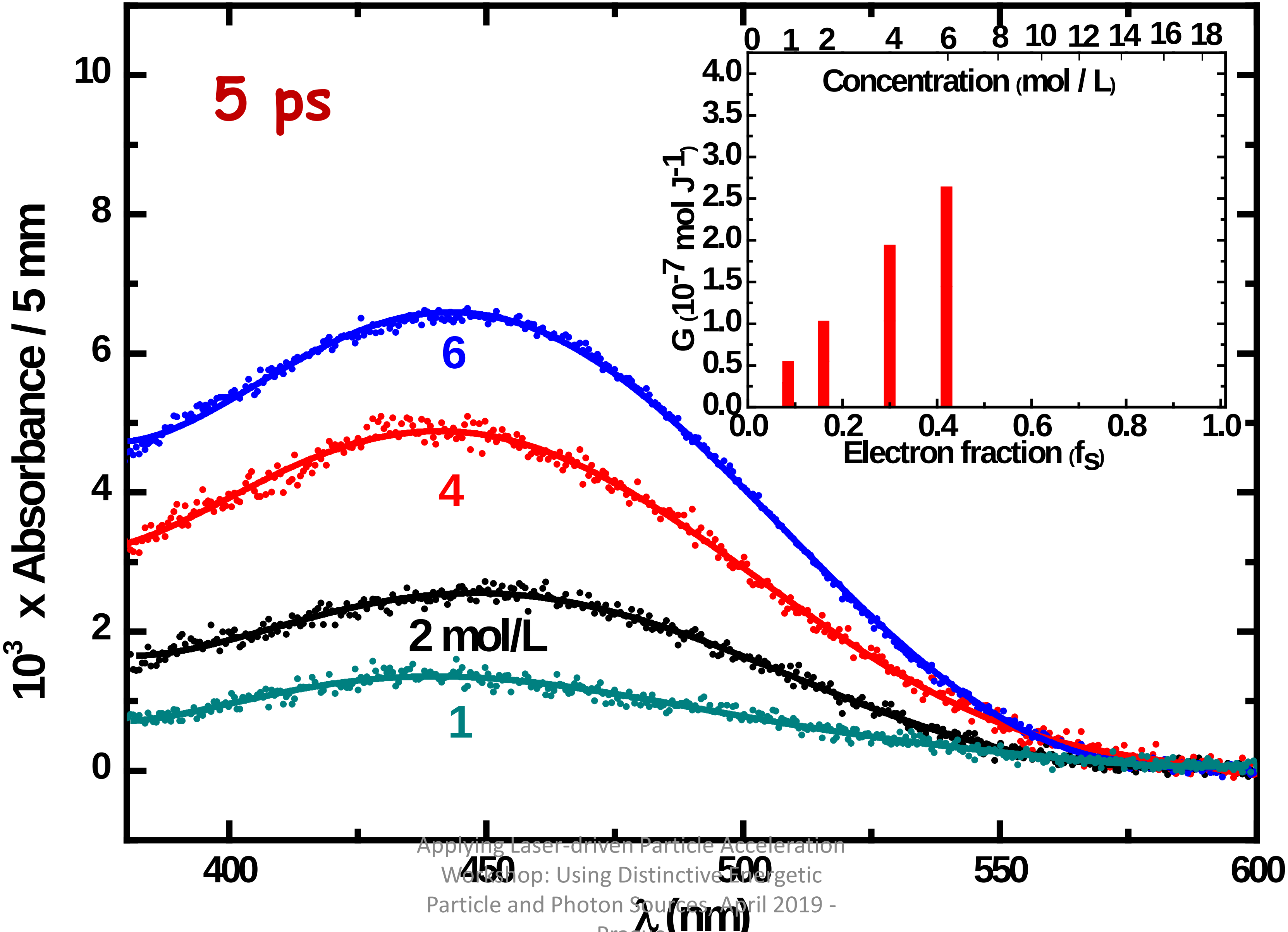
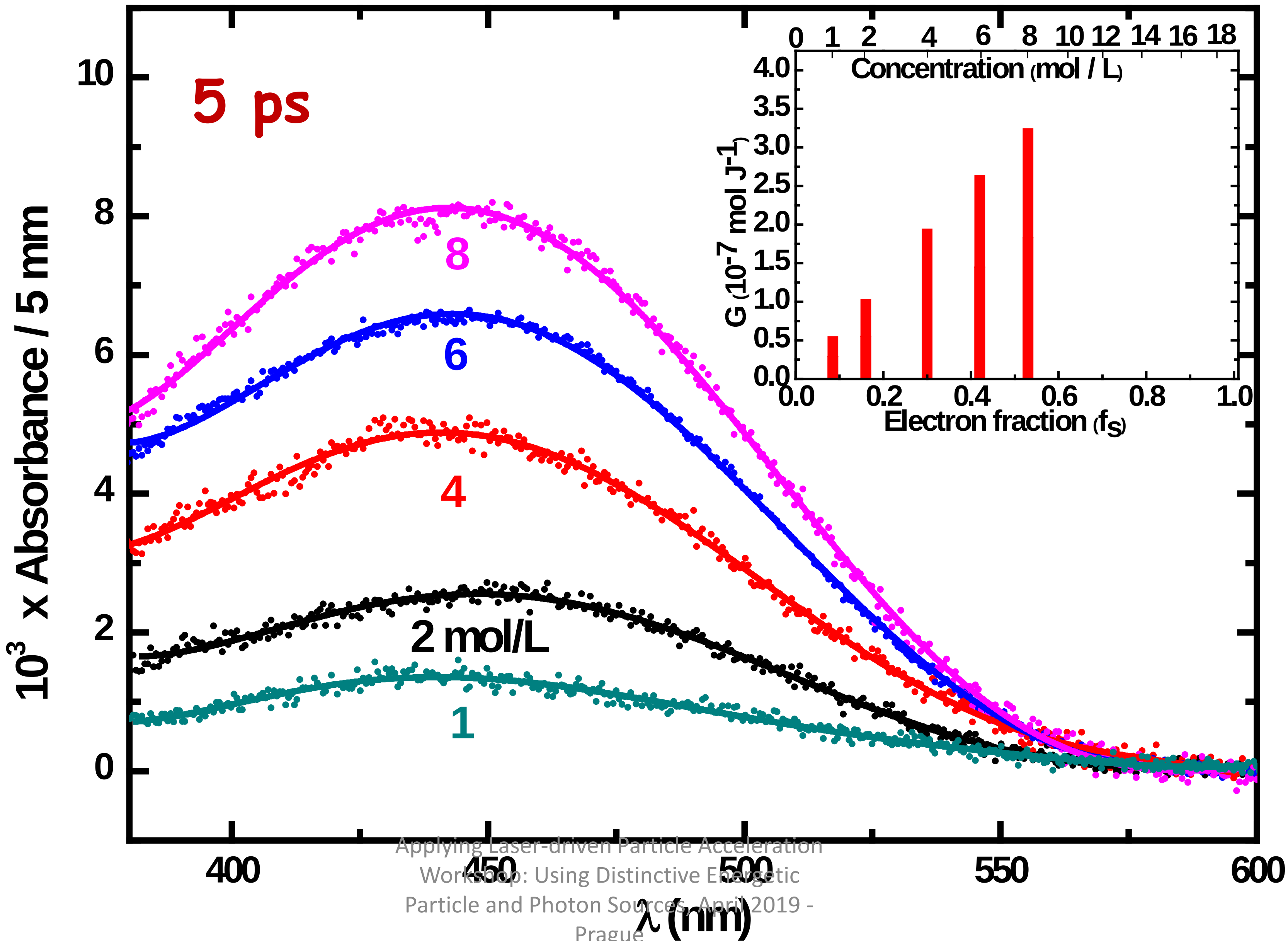


Formation of $SO_4^{\bullet -}$ in solution H_2SO_4



Formation of $SO_4^{\bullet -}$ in solution H_2SO_4



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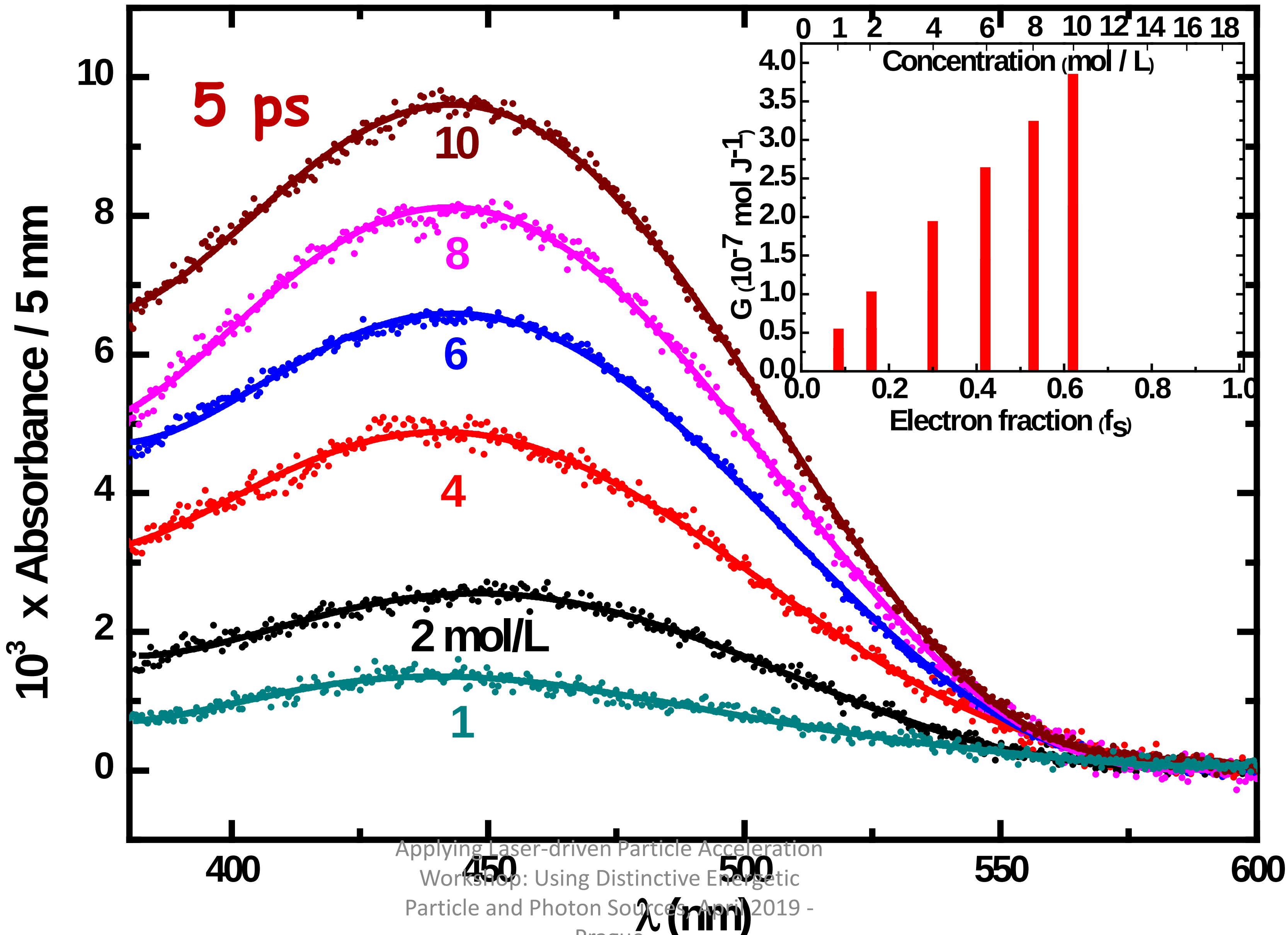

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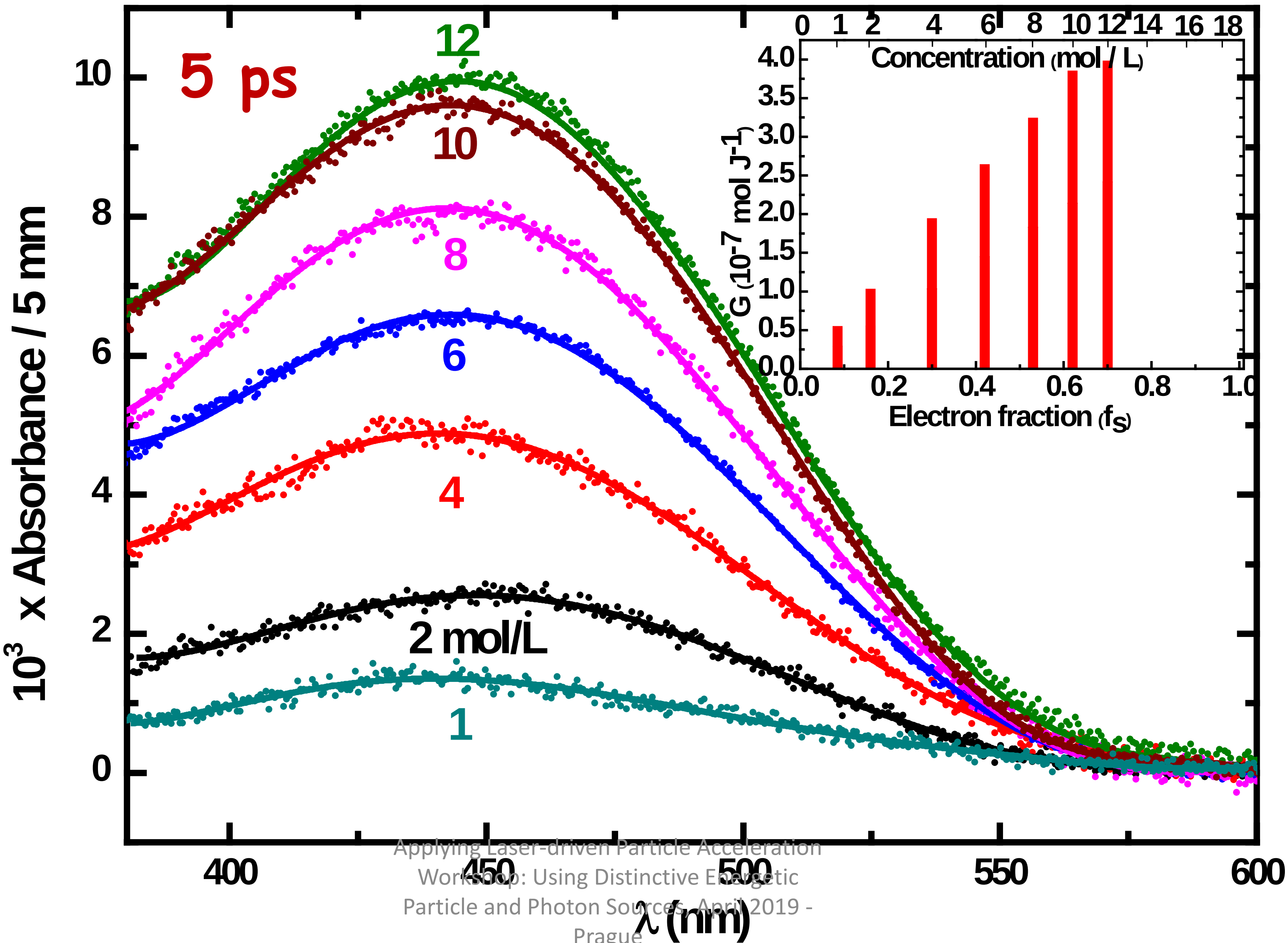

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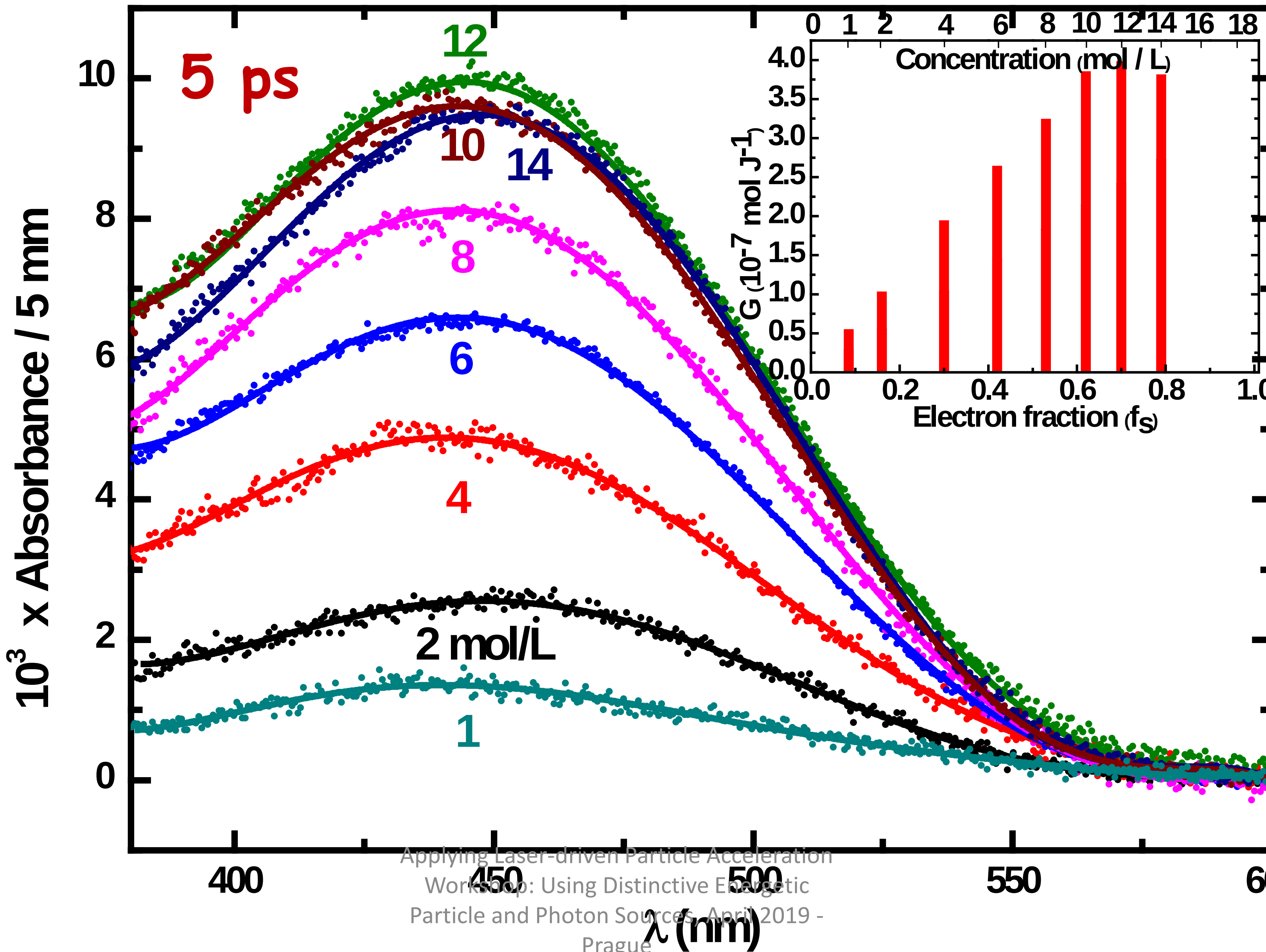

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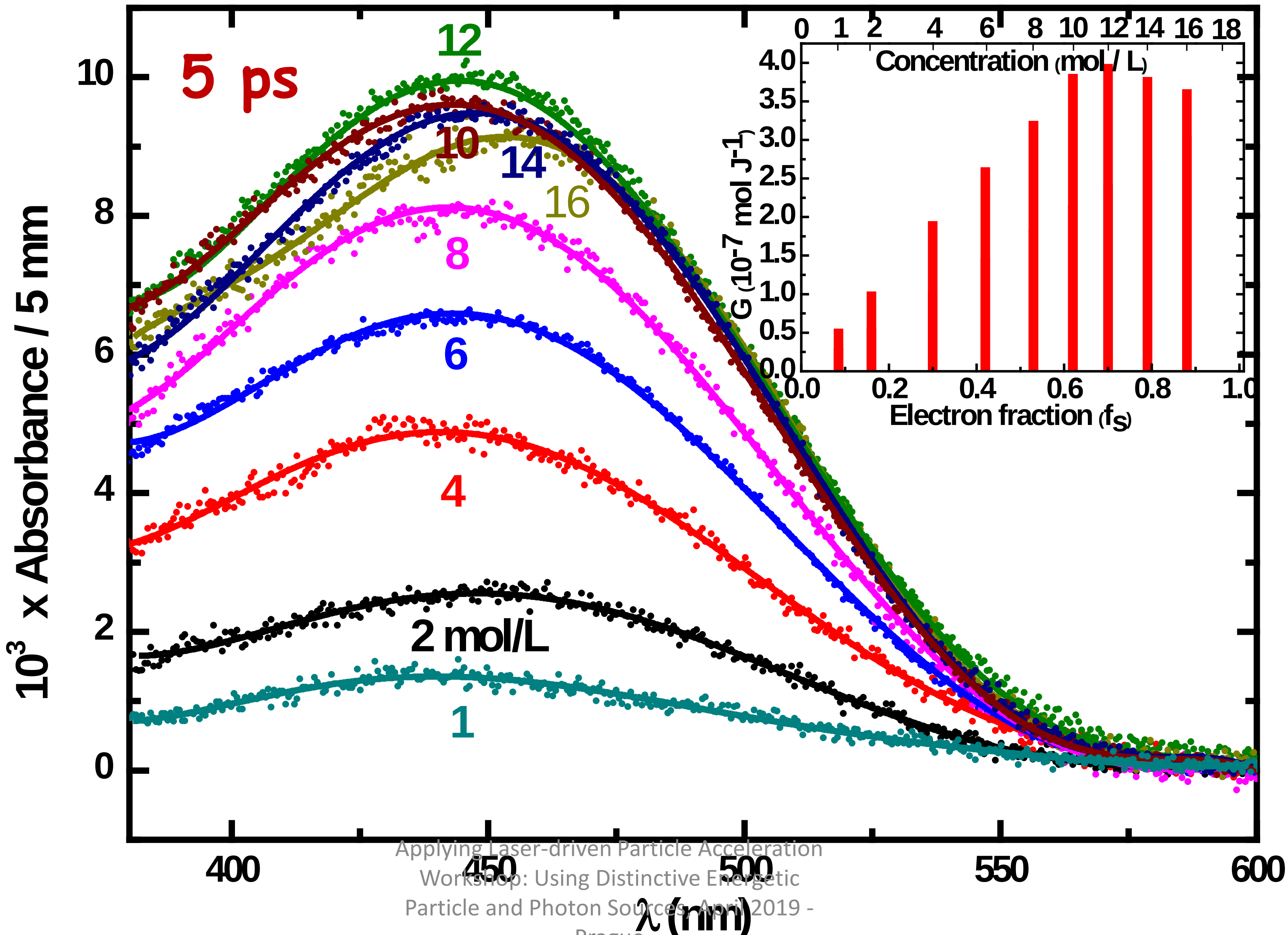

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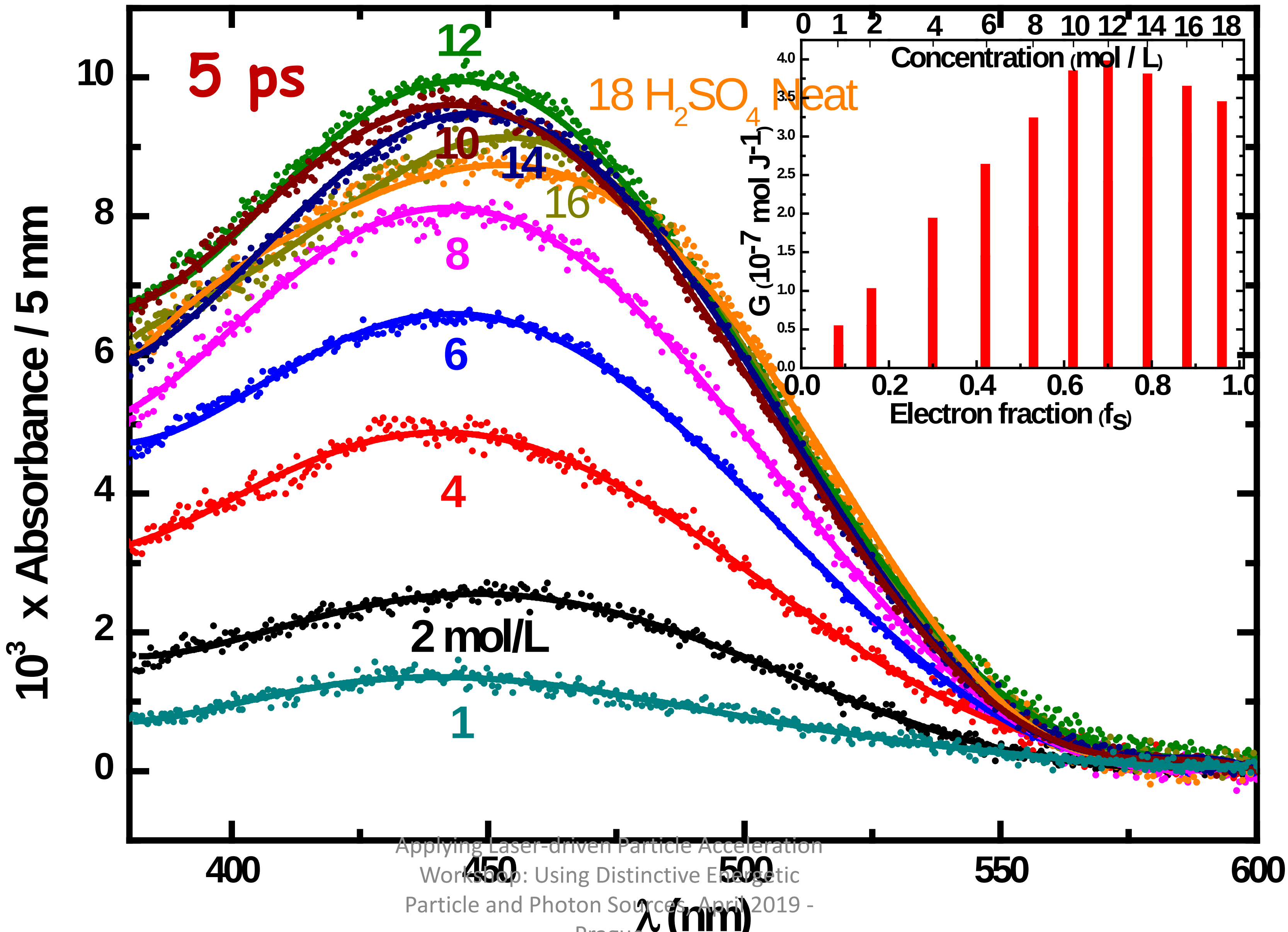

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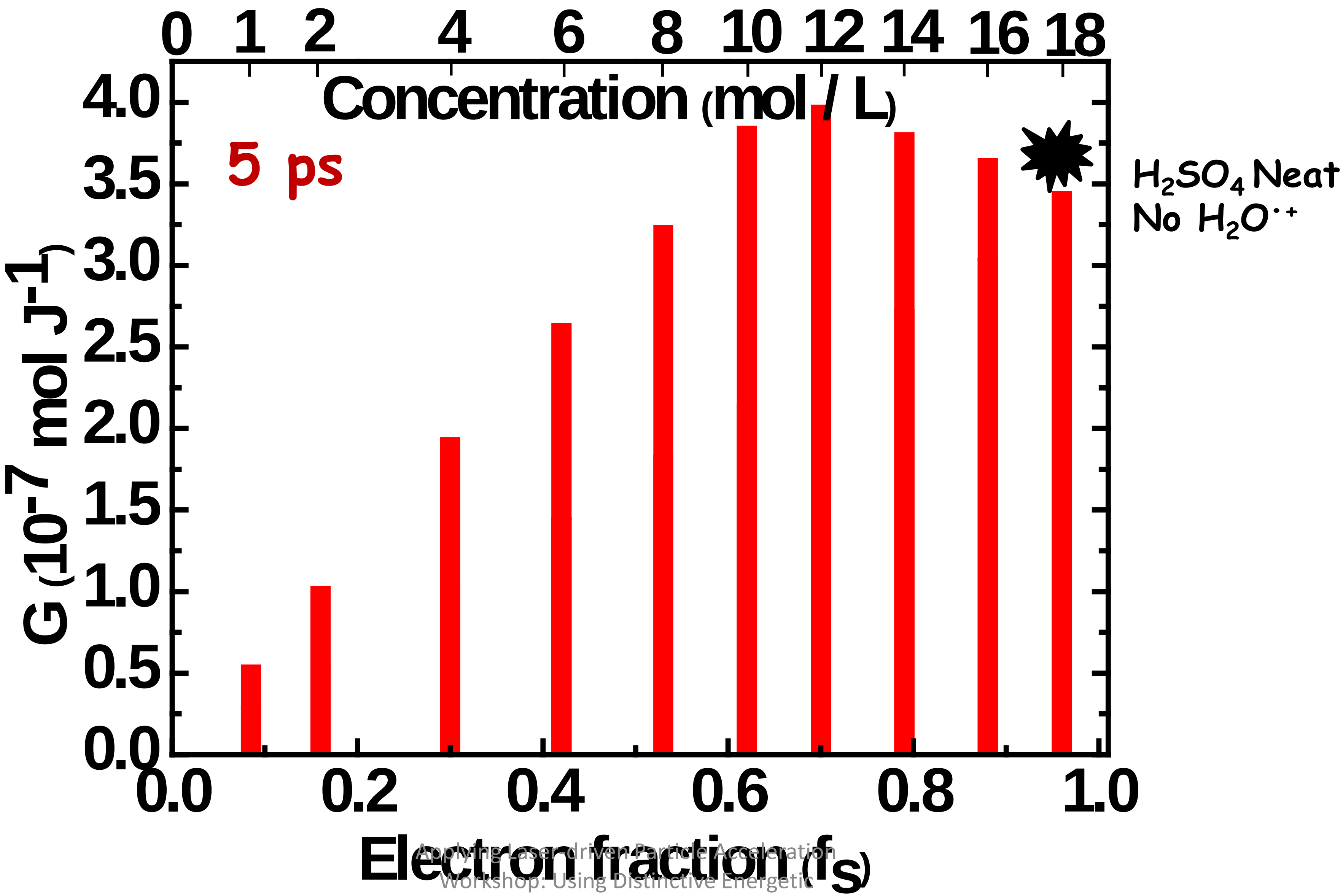
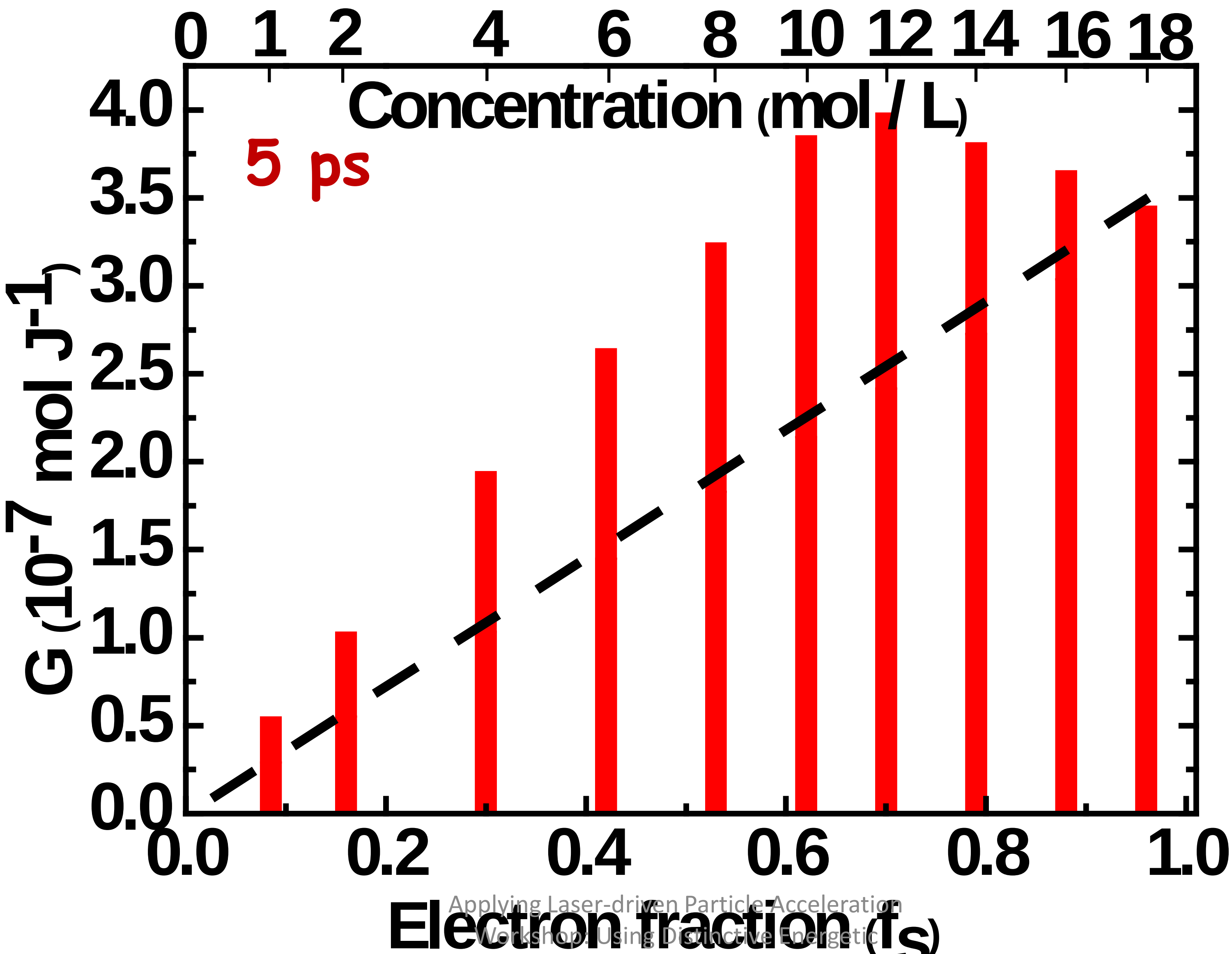
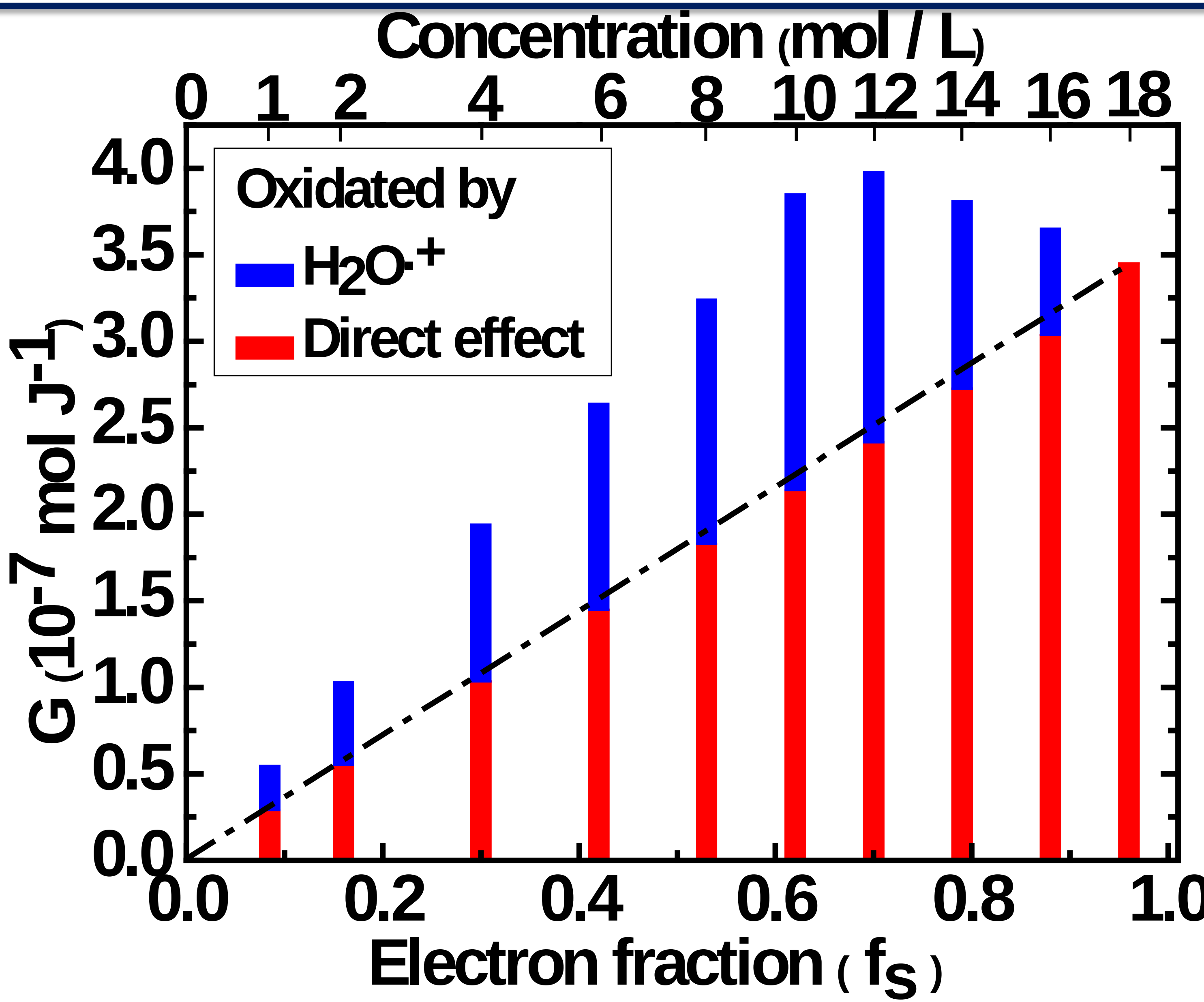


Formation of $SO_4^{\bullet -}$ in solution H_2SO_4



Reactivity of $H_2O^{\bullet+}$ in solution H_2SO_4



$H_2O^{\bullet+}$ a strong oxidizing species

Formation of $SO_4^{\bullet-}$ Radical

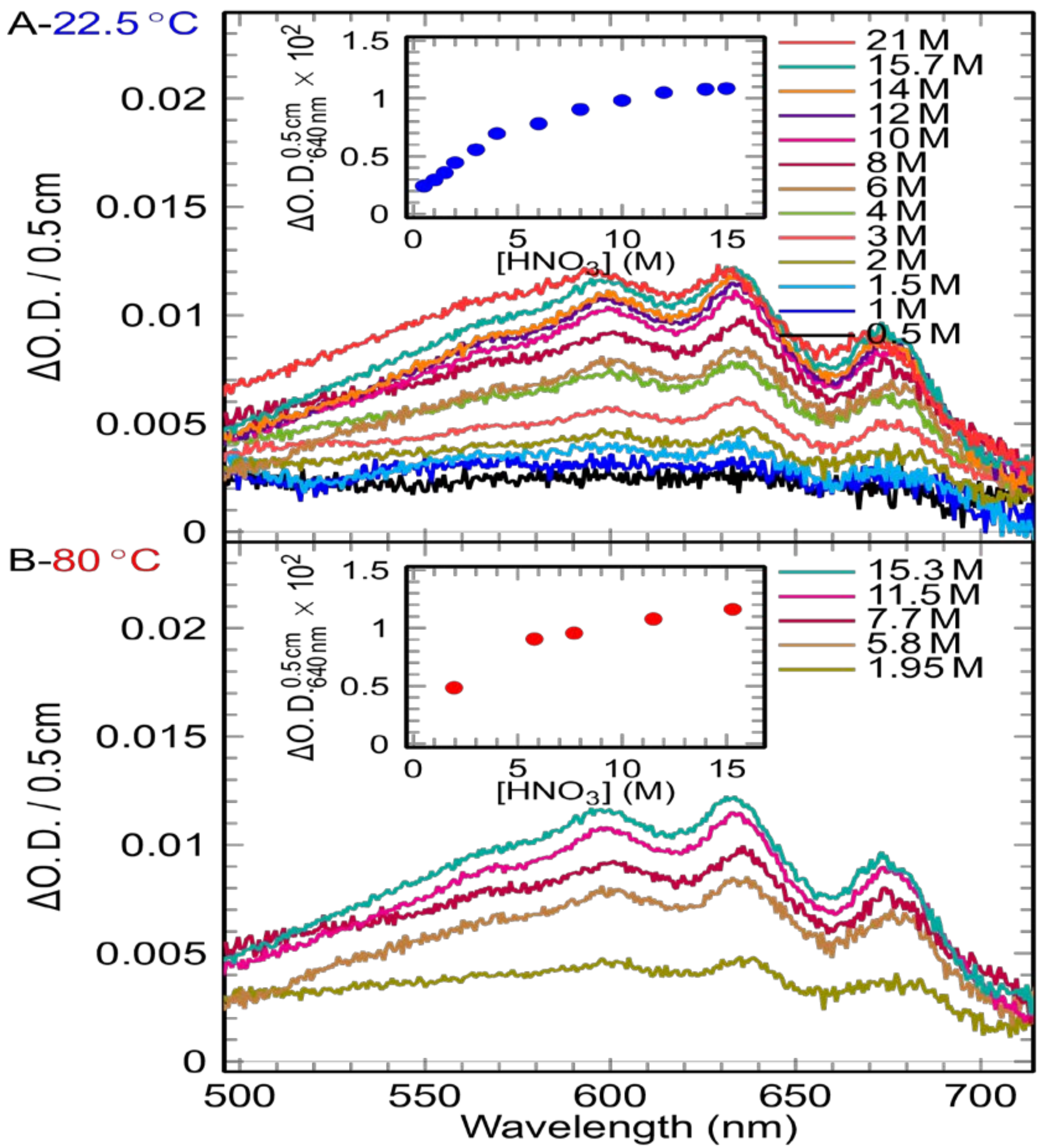
$$H_2O \rightsquigarrow H_2O^{\bullet+} + e^-$$

$$H_2O^{\bullet+} + H_2O \longrightarrow OH^{\bullet} + H_3O^{+}$$

$$H_2O^{\bullet+} + SO_4^{2-} \longrightarrow SO_4^{\bullet-} + H_2O$$

Nuclear Fuel retreatment in 8 M nitric acid solutions: Transient absorption : NO_3° detection at 7 ps

$$H_2O^{\bullet +} + NO_3^- \rightarrow H_2O + NO_3^{\bullet}$$

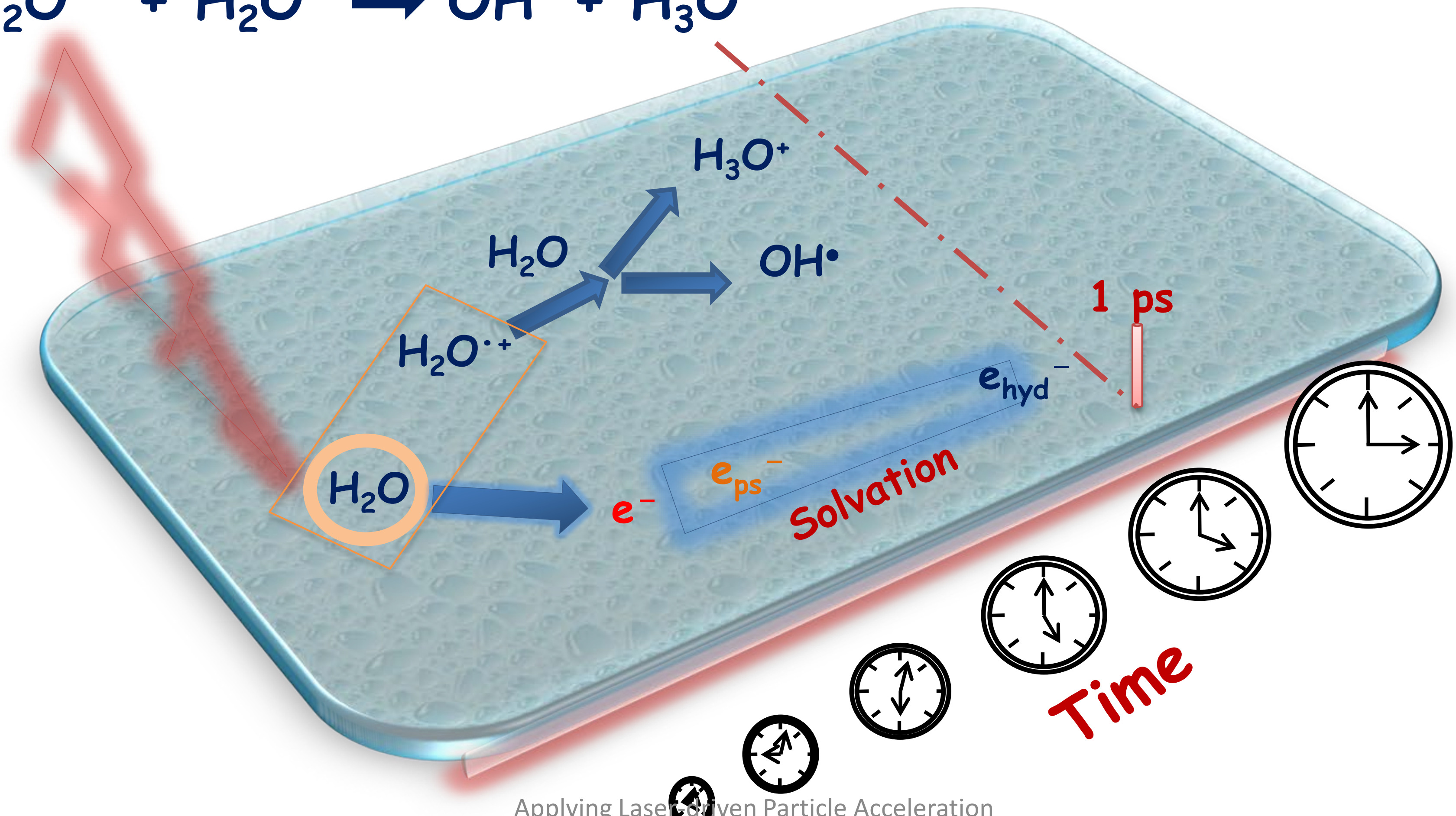


Dynamics of e_{ps}^{-} in neat water

$H_2O \rightsquigarrow H_2O^{\bullet+} + e^{-}$

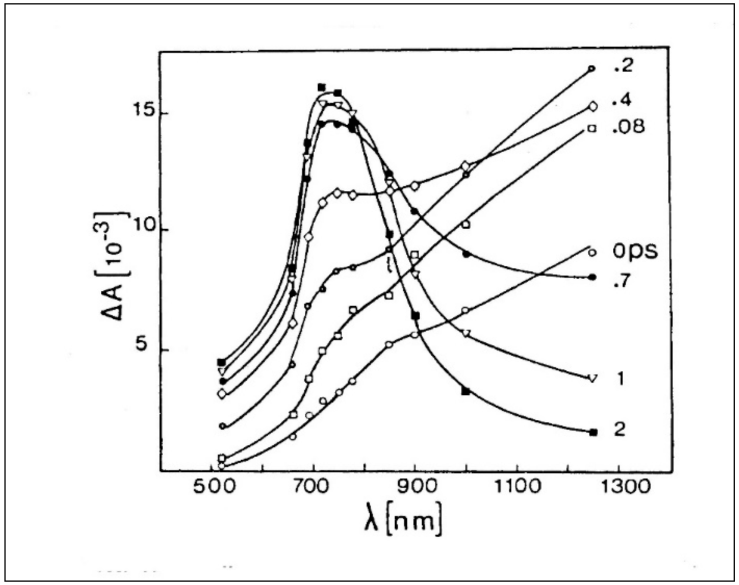
$e_{ps}^{-} + H_2O \rightarrow e_{hyd}^{-}$

$H_2O^{\bullet+} + H_2O \rightarrow OH^{\bullet} + H_3O^{+}$



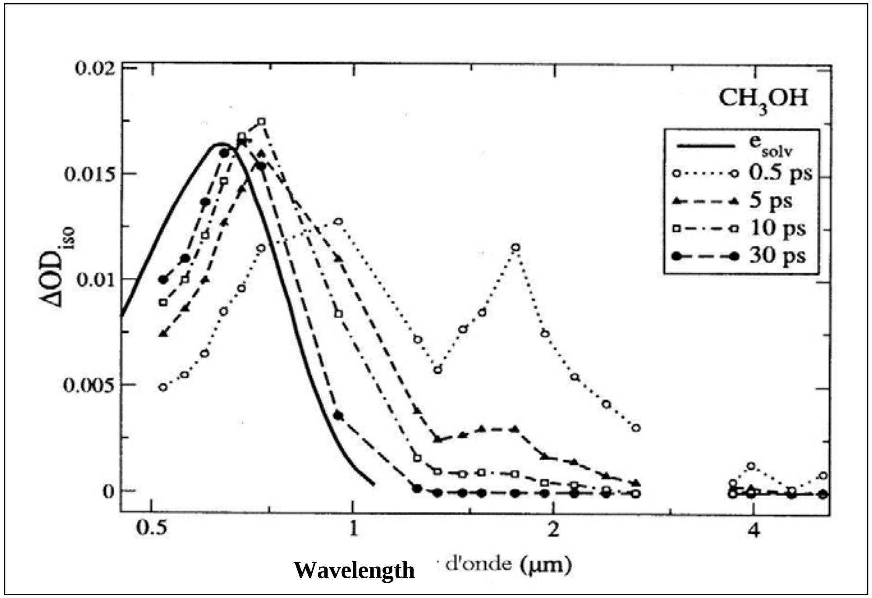
Solvation dynamics of electron in liquid

H_2O



A. Migus, Y. Gauduel, J.L.Martin, A. Antonetti, *Phys. Rev. Letters* (1987) *58*, 1559.

Methanol



T. Scheidth, R. Laenen, *Chem. Phys. Lett.* (2003) *371*, 445

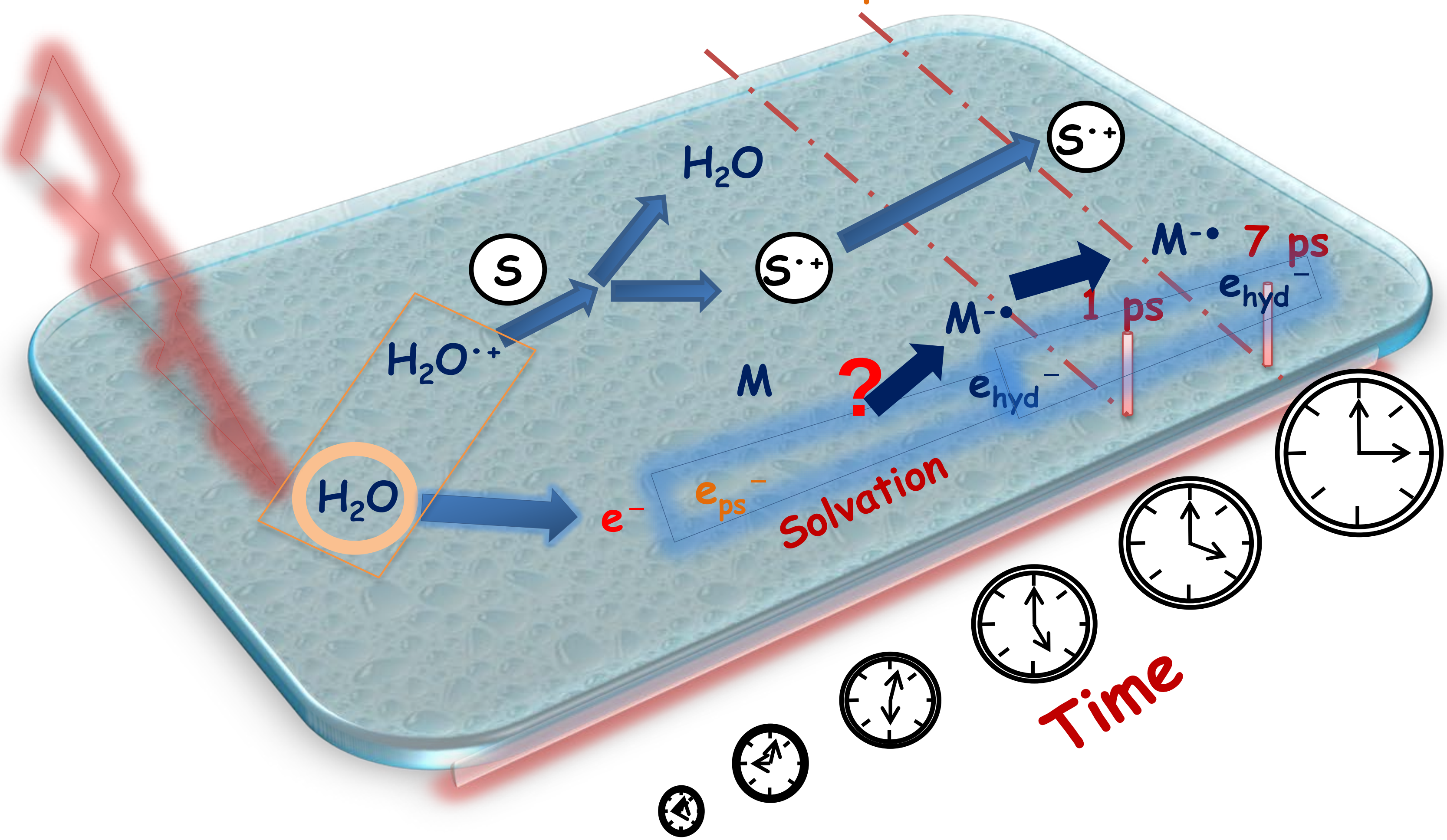
Reactivity of e_{ps}^- in solutions

$H_2O \rightsquigarrow H_2O^{\bullet+} + e^-$

$H_2O^{\bullet+} + H_2O \rightarrow OH^{\bullet} + H_3O^+$

$H_2O^{\bullet+} + S \rightarrow S^{\bullet+} + H_2O$

$e_{ps}^- + M \xrightarrow{?} M^{-\bullet} + H_2O$



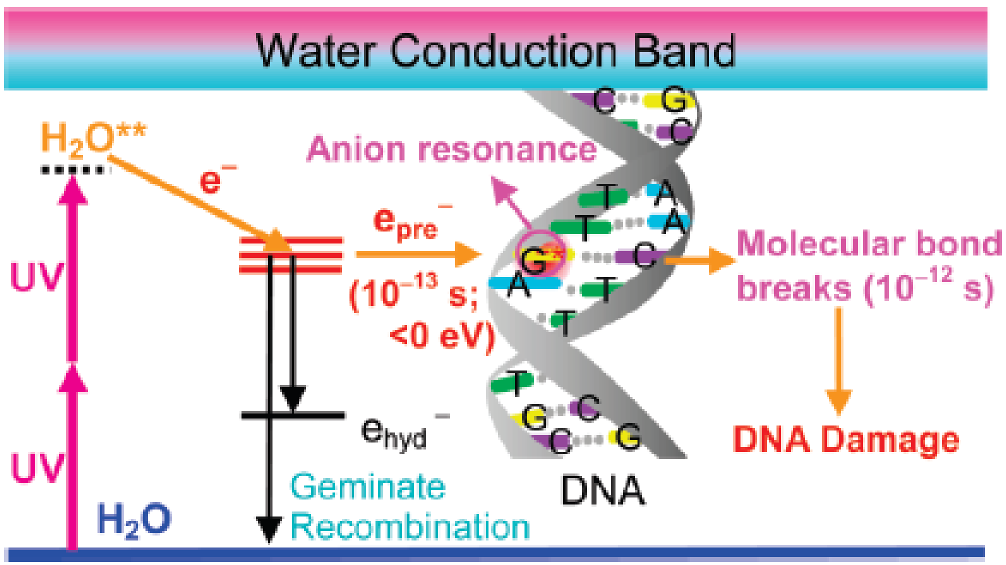
J|A|C|S COMMUNICATIONS

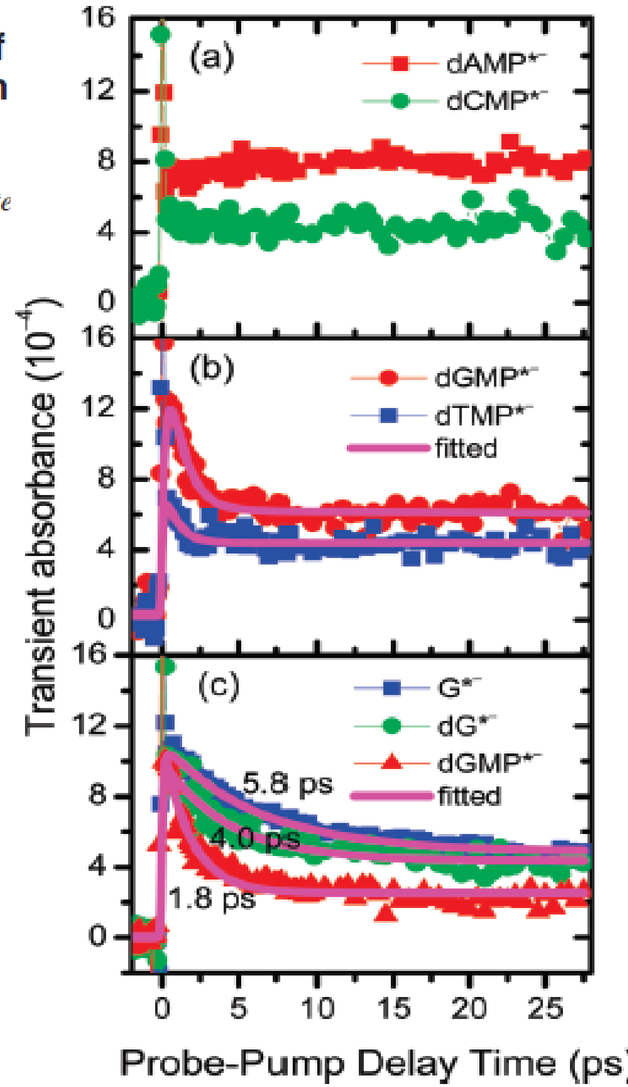
Published on Web 07/27/2009

Bond Breaks of Nucleotides by Dissociative Electron Transfer of Nonequilibrium Prehydrated Electrons: A New Molecular Mechanism Reductive DNA Damage

Chun-Rong Wang, Jenny Nguyen, and Qing-Bin Lu*

Department of Physics and Astronomy and Departments of Biology and Chemistry, University of Wate
200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada





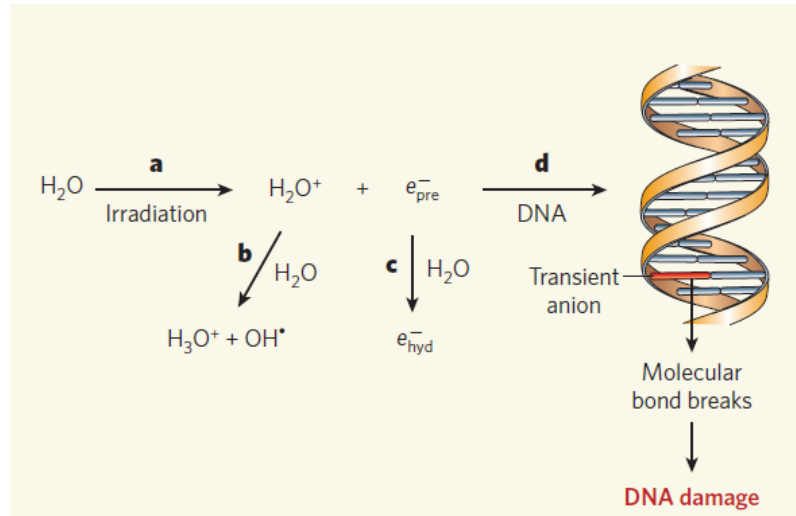
NATURE|Vol 461|17 September 2009

BIOLOGICAL CHEMISTRY

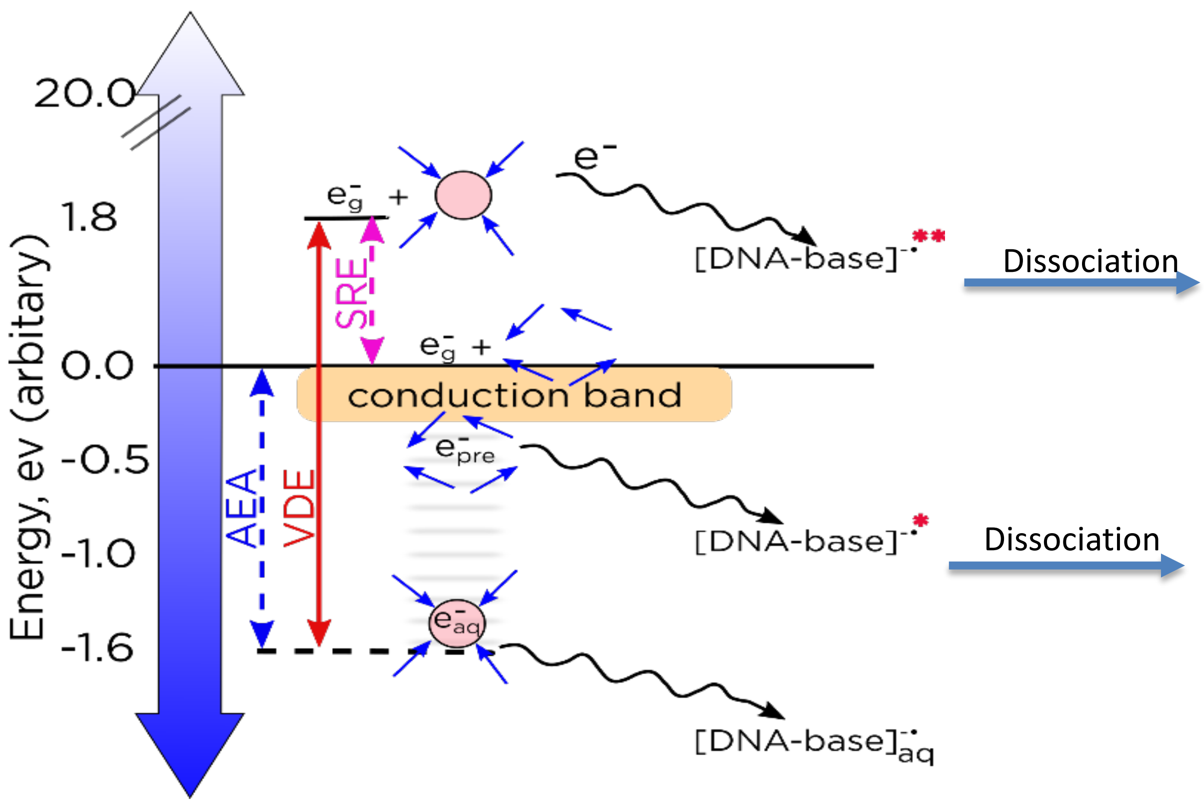
Beyond radical thinking

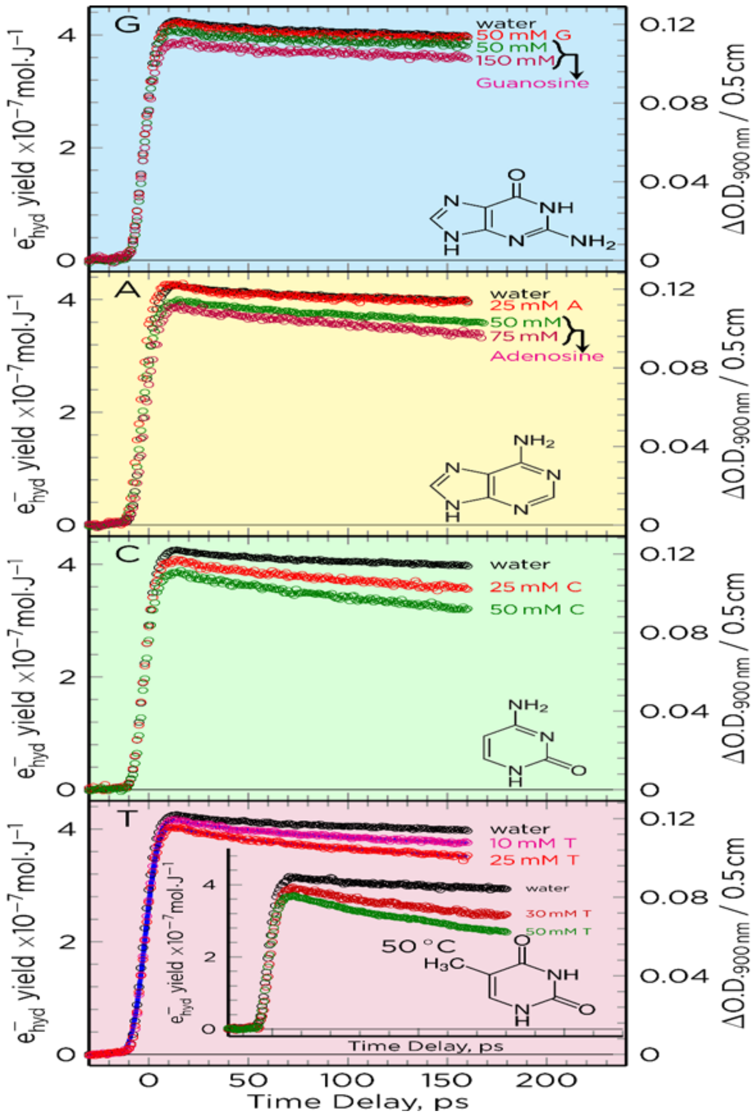
Léon Sanche

Radiation-induced DNA damage has been attributed to hydroxyl radicals, which form when water absorbs high-energy photons or charged particles. But another product of water's radiolysis might be the real culprit.



Question: Dose pre-hydrated electron reaction produce an excited state undergoing dissocoation?

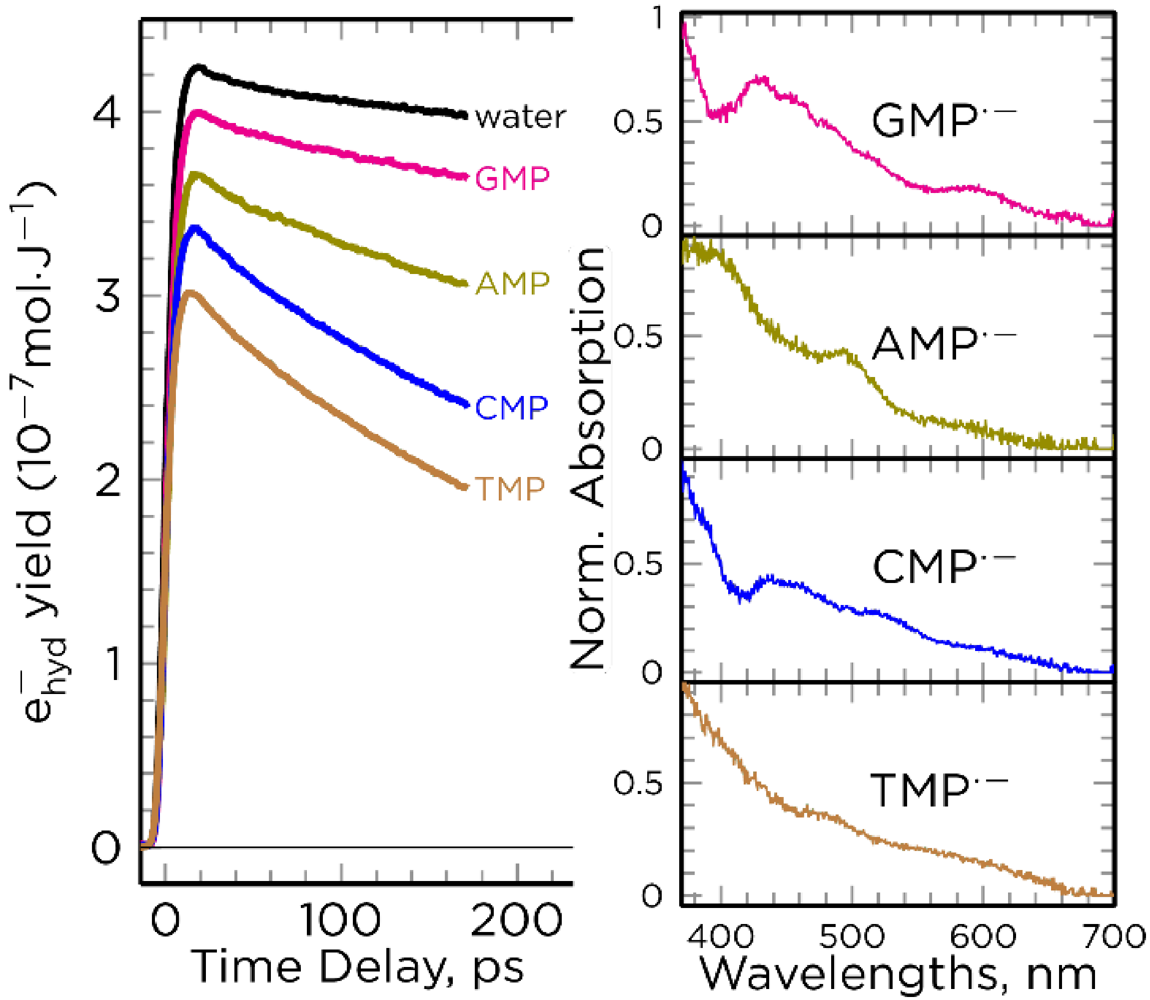




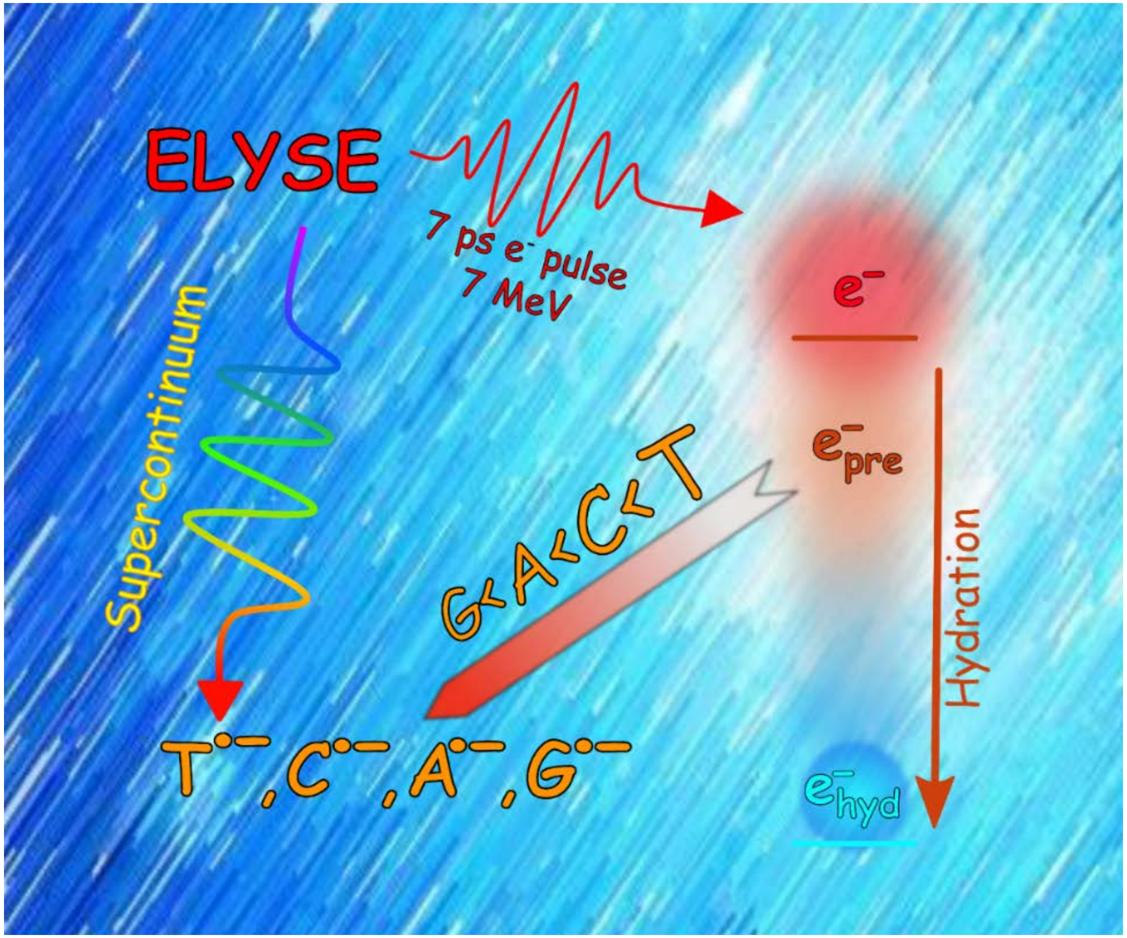
DNA bases scavenger of prehydrated electron?

- ✓ No reaction between prehydrated electron and Guanine and adenine
- ✓ With higher concentration Guanosine and Adenosine react in low amount with prehydrated electron
- ✓ Cytosine and Thymine are more efficient electron scavenger
- ✓ By increasing the temperature Thymine reacts more efficiently with prehydrated electron

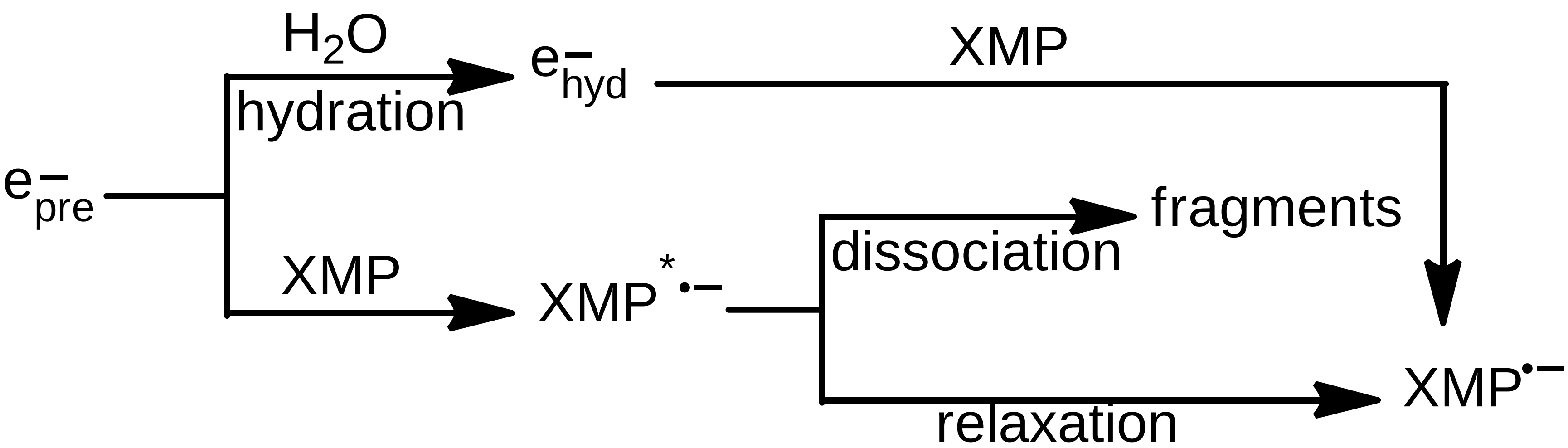
Nucleotides radical anions ($GMP^{•-}$, $AMP^{•-}$, $CMP^{•-}$ and $TMP^{•-}$) observed at 7 ps



Kinetics of e_{hyd}^- and the absorption spectral of the anion observed at 7 ps in the presence of 250 mM nucleotides in water


ELYSE
7 ps e- pulse
7 MeV
Supercontinuum
e-
e-pre
Hydration
G<A<C<T
T•-,C•-,A•-,G•-
e-hyd

Reactivity of e_{pre}^- and e_{hyd}^- with XMP and possible decay excited anions $XMP^{*\bullet -}$

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RESEARCH ARTICLE | CHEMISTRY

Reactivity of prehydrated electrons toward nucleobases and nucleotides in aqueous solution

Jun Ma[1], Furong Wang[1], Sergey A. Denisov[1], Amitava Adhikary[2] and Mehran Mostafavi[1,*]

+ See all authors and affiliations

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DOI: 10.1126/sciadv.1701669

Science Advances
Vol 3, No. 12
01 December 2017
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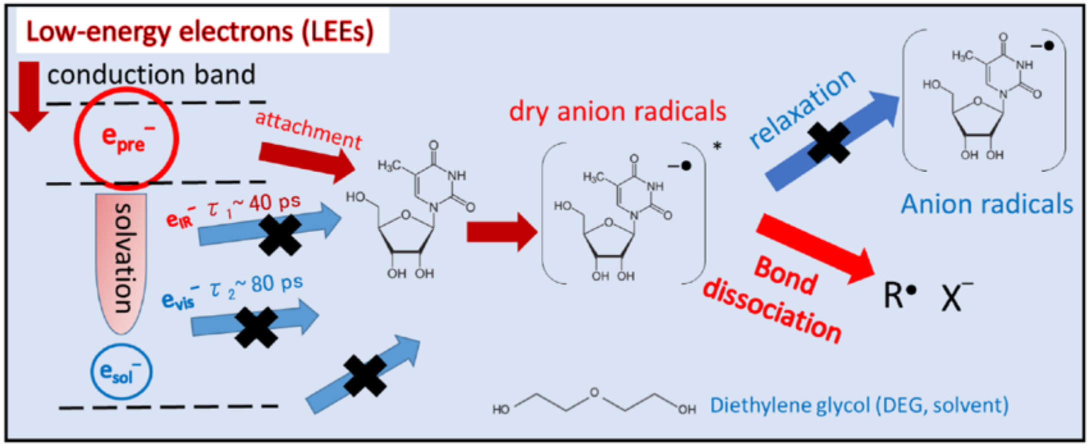
Vibration states of the solvent molecules affecting DEA process



nature COMMUNICATIONS

Article | OPEN | Published: 09 January 2019

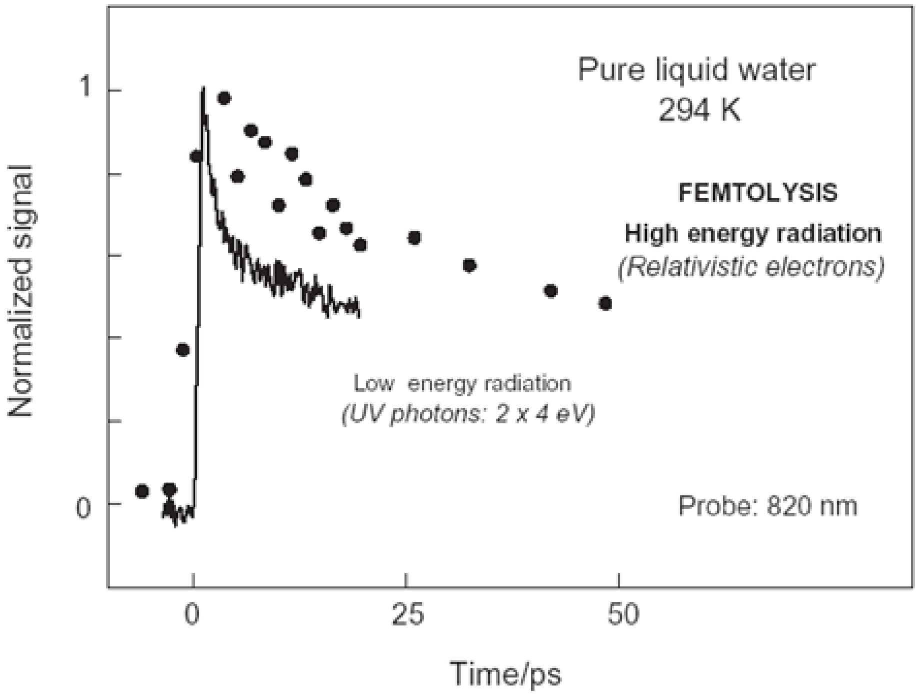
Observation of dissociative quasi-free electron attachment to nucleoside via excited anion radical in solution

Jun Ma, Anil Kumar, Yusa Muroya, Shinichi Yamashita, Tsuneaki Sakurai, Sergey A. Denisov, Michael D. Sevilla, Amitava Adhikary, Shu Seki & Mehran Mostafavi

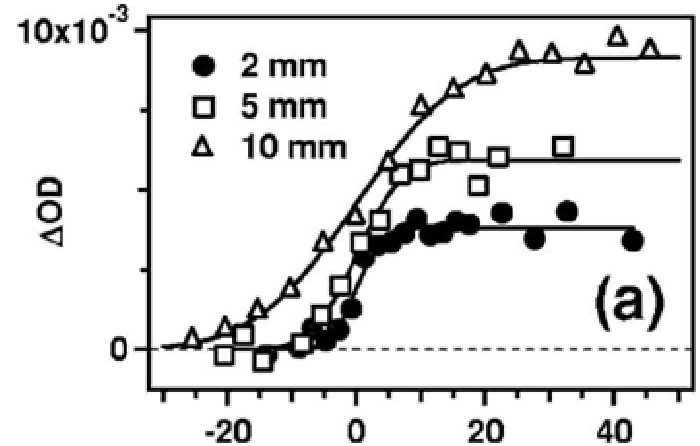
- Introduction to Radiation Chemistry
- Examples of new results and new challenges
- Pulsed source in Radiation Chemistry
- **New sources for Radiation Chemistry**

Chalenges of new source of electron bunch

Electron pulses (1.5-20 MeV) generated by a terrawatt laser wakefield accelerator

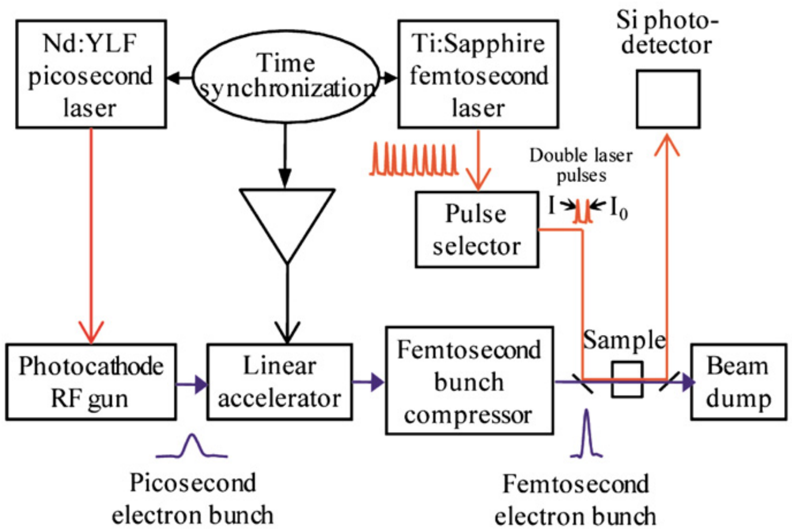


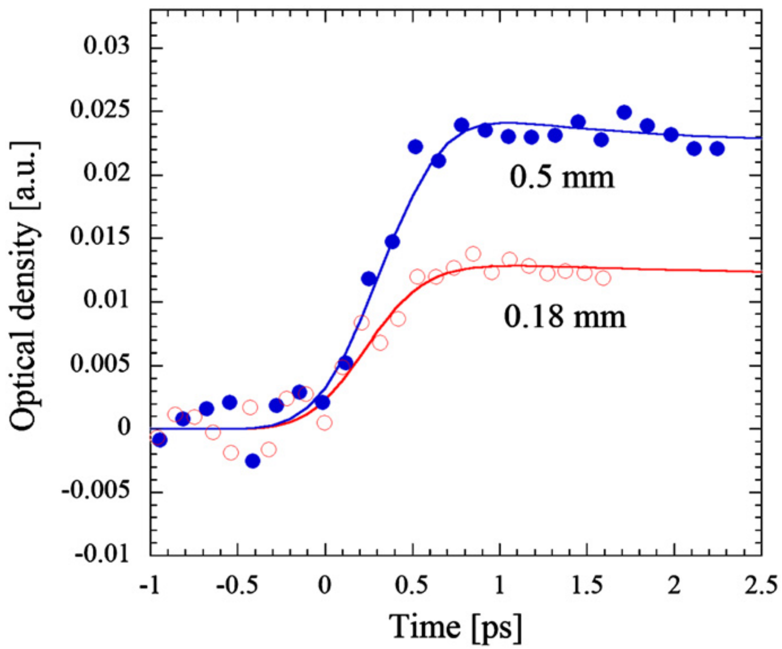
Brozek-Pluska, Beata, David Gliger, Abdeslem Hallou, Victor Malka, and Yann A. Gauduel. 2005. *Radiat. Phys. Chem.* 72 (2-3):149-157.



Oulianov, Dmitri A., Robert A. Crowell, David J. Gosztola, Ilya A. Shkrob, Oleg J. Korovyanko, and Roberto C. Rey-de-Castro. 2007. *J. Appl. Phys.* 101 (5):053102-9.

Ultrafast pulse radiolysis : Recent development with 200 fs time resolution still conventionnal method unsing photocathod

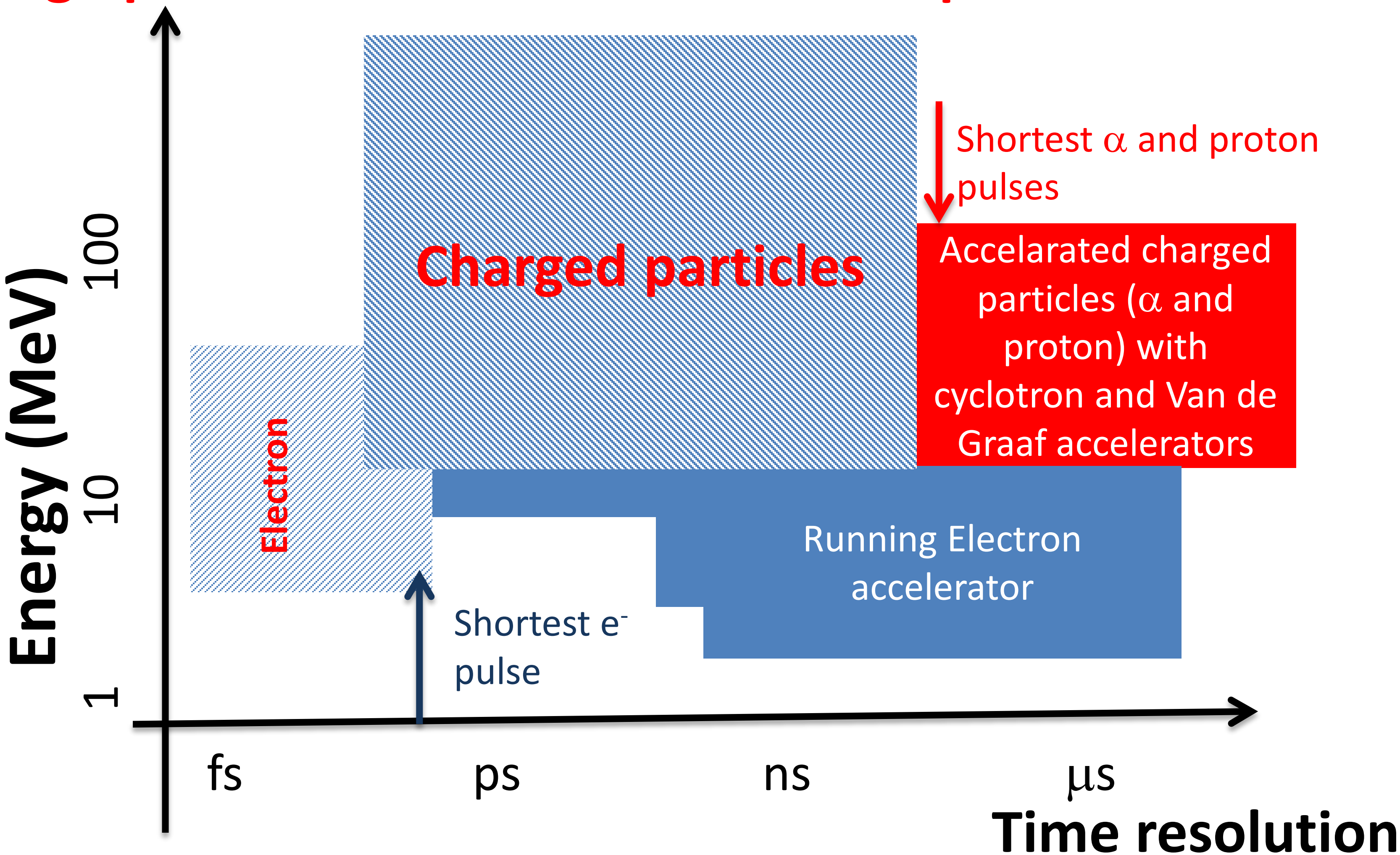




The electron bunch produced by the RF gun synchronized the electrons are emitted from the photocathode in the presence of a strong RF electric field.

Sample thicknesses of 0.18 and 0.5mm.The probe at 800 nm J. Yang et al. NuclearI nstruments and Methods in Physics Research A 2011

Missing pulsed sources for Radiation Chemistry: help of high power laser driven accelerated particles



- Mono-kinetics particle beam a few MeV to few 10 MeV
- Dose per pulse > 0.1 Gy
- Pulse duration less than 50 fs

Electron bunches requirements for pump-probe pulse radiolysis

- **Mono-kinetics electron beam with**
Ranging from a few MeV to few 40 MeV

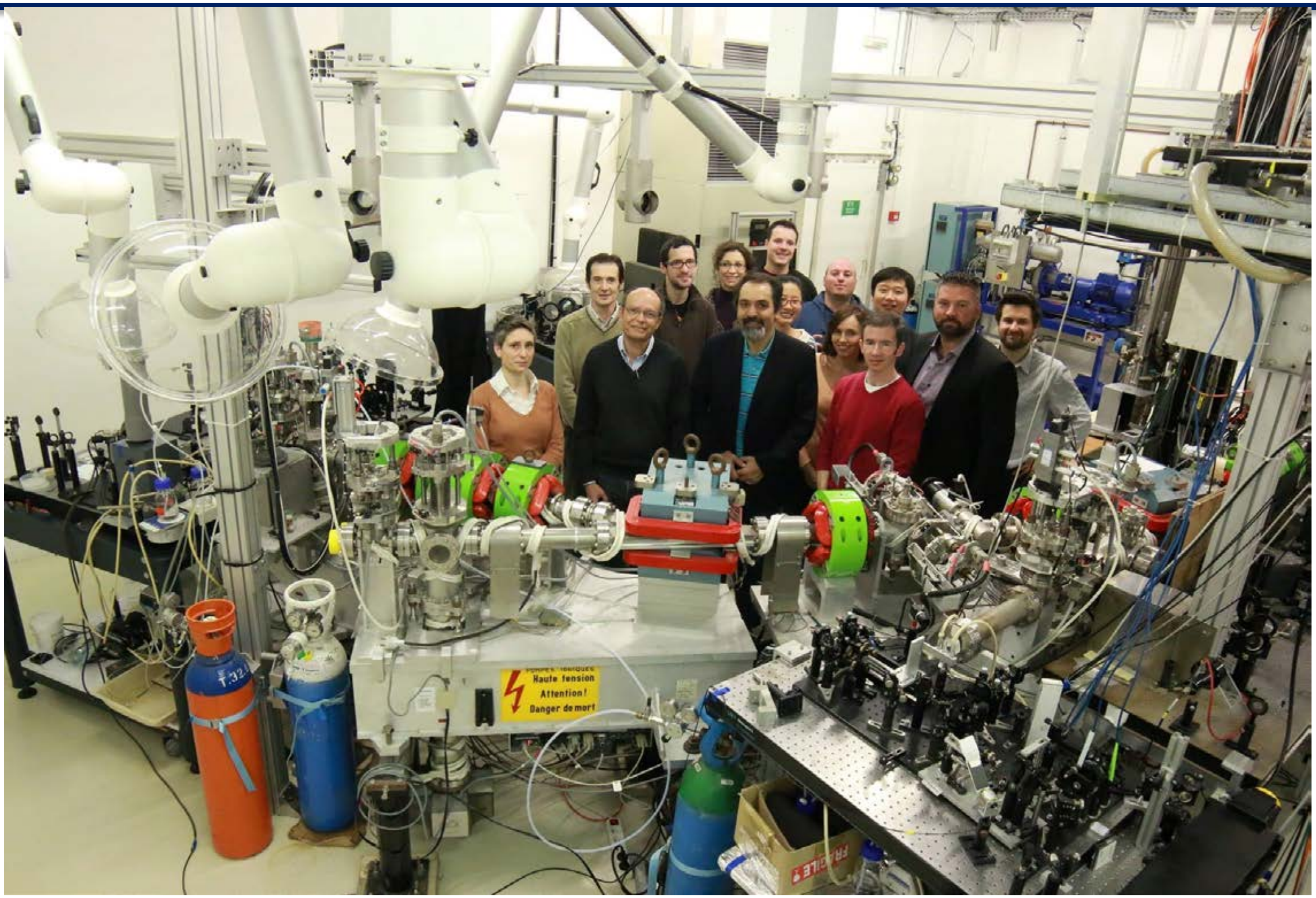
- **Dose per electron pulse > 0.5 Gy (0.5 J/Kg)**

- **Pulse duration less than 100 fs**

- **Frequncy of at least 100 Hz**

- **Beam size less tha 100 microns**

-Optical path 200 μm to 1 mm (detection).



Thanks for your attention !