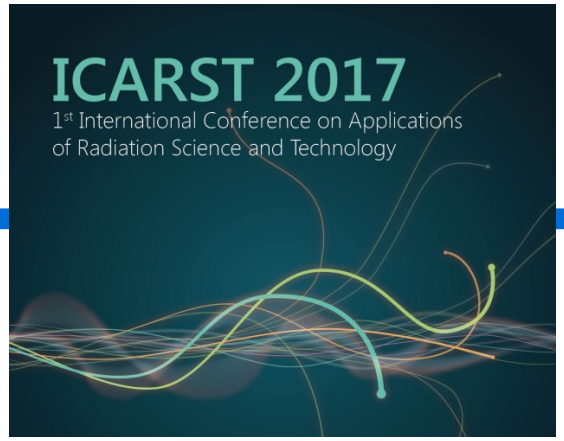


Recent Progress in Pulse Radiolysis

Detection Methods and their Application to Ionic Liquid-Based Systems for Closing the Nuclear Fuel Cycle

JAMES F. WISHART, Andrew R. Cook, David C. Grills, Bobby H. Layne

Chemistry Division, Brookhaven National Laboratory

– and the international community!

U.S. DEPARTMENT OF ENERGY | Office of Science

BROOKHAVEN NATIONAL LABORATORY

Importance of Pulse Radiolysis to Radiation Science and Technology

Fundamental radiation chemistry

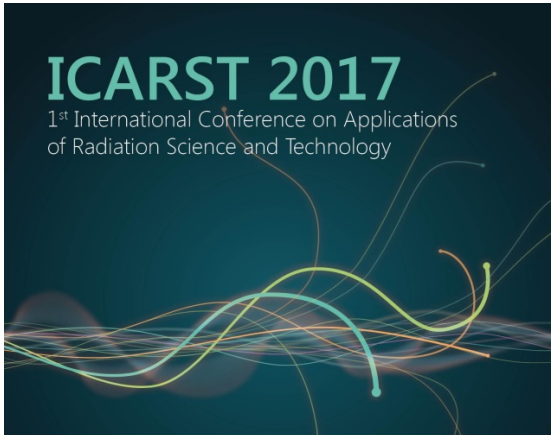
- Identities and reactivities of primary radiolytic species
- Kinetics and mechanisms of inhomogeneous reactions
- Evolution of reactive intermediates into radiolysis products

Applying radiation chemistry to larger problems

- Converting initial radiolytic species into useful intermediates

Reaction kinetics and mechanisms

- Radiolytic synthesis of advanced materials
- Polymerization; Advanced oxidation processes
- Destruction of pollutants and pathogens
- Understanding radical reactions in biology
- Electron transfer reactions in energy conversion
- Catalytic mechanisms for energy and materials



Recent Progress in Pulse Radiolysis

Ultrafast pulse radiolysis

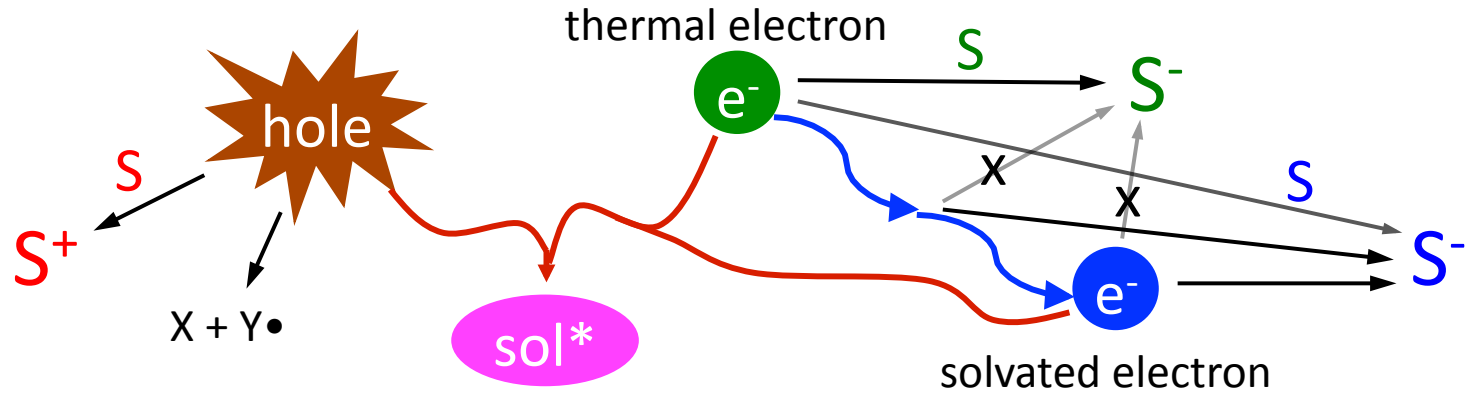
- Over the past 20 years, picosecond photocathode electron accelerators have enabled detailed study of fundamental radiolytic processes.
- Examples: early-time yields, electron-hole recombination, electron and hole scavenging in competition with solvation and proton transfer
- Better understanding of how radiolytic energy is deposited and subsequently redistributed by chemical reactions
- Fundamental radiation chemistry of organic solvents and ionic liquids

Experimental and detection methods

- Optical detection dispersed in wavelength, time or both (several labs)
- Time-resolved infrared (TRIR) (Brookhaven), rapid-scan IR (CEA Saclay)
- Simultaneous electrochemical/optical detection (U. Paris-Sud)

Primary Radiolytic Species Reactivity

Processes that control product distributions and fixation of radiolysis effects:



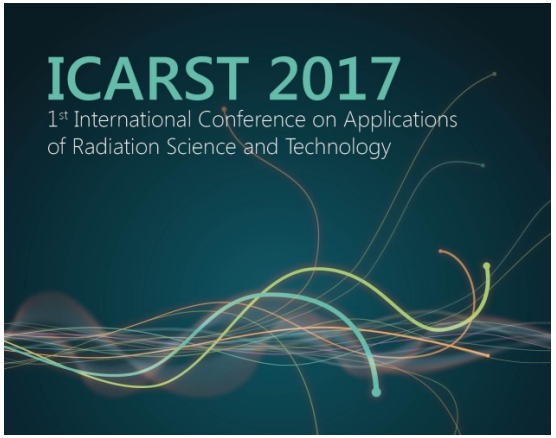
Electron (and hole) solvation dynamics

Pre-solvated electron scavenging

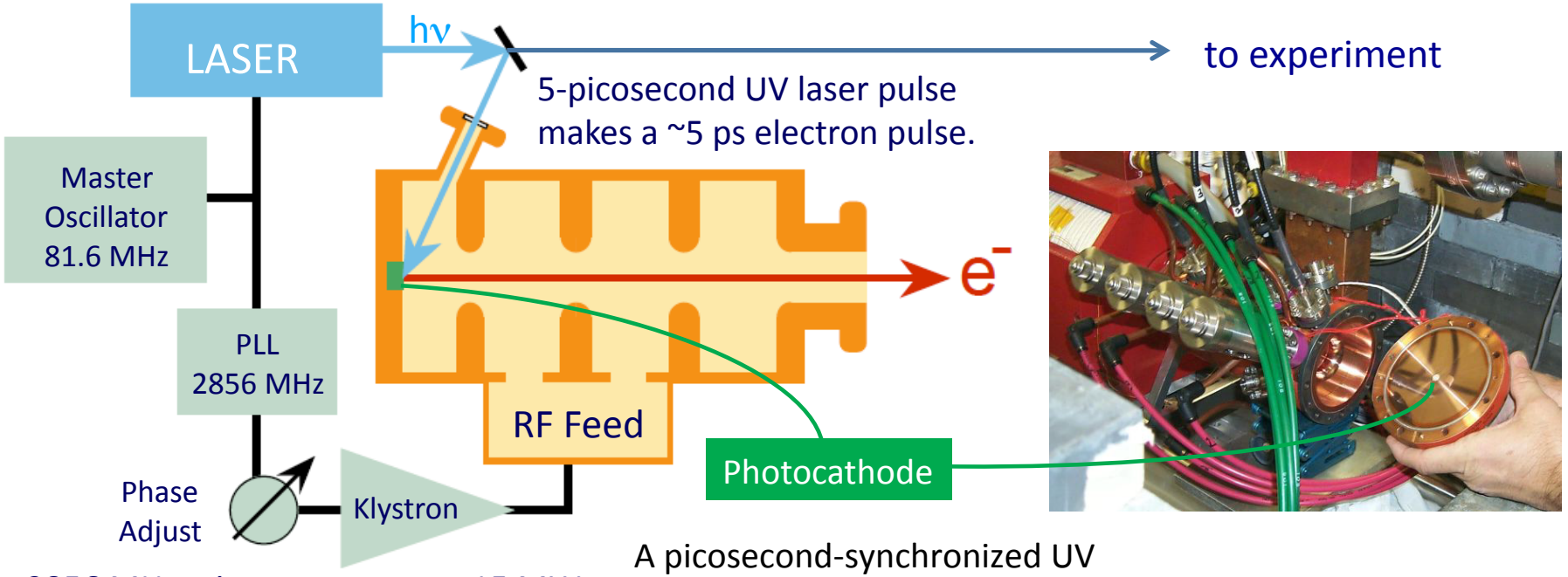
Solvated electron scavenging

Hole scavenging (prompt and diffusional) and intrinsic reactivity

Geminate and bulk recombination



Photocathode electron gun accelerators have made ultrafast radiolysis much more accessible

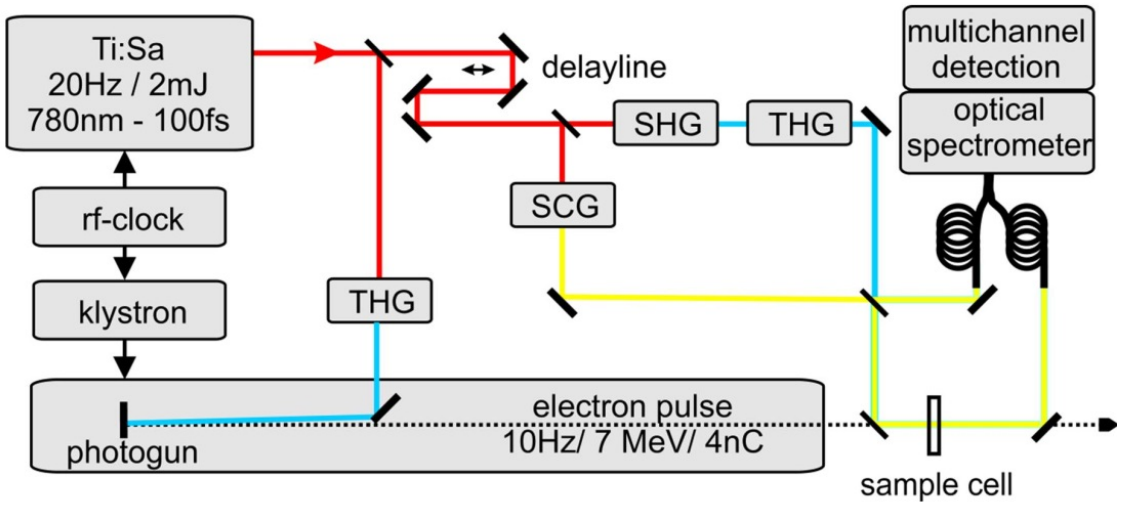


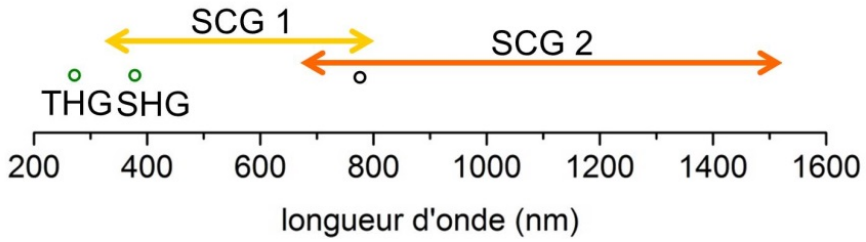
A picosecond-synchronized UV laser pulse generates photoelectrons, which are accelerated to 9 MeV by high fields (80 MV/m) in the **30-cm long** resonant-cavity structure.

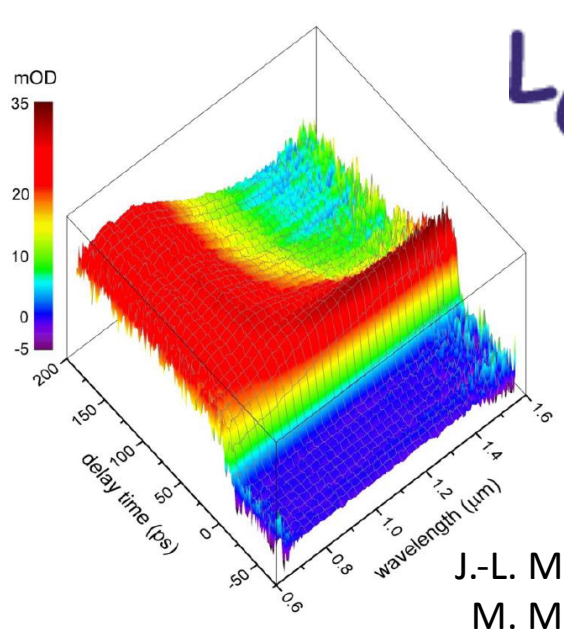
Picosecond facilities are located at: BNL, U-Paris Sud, Osaka U., U of Tokyo, Waseda U., (TU Delft and BARC in progress).

BNL LEAF Facilty: Wishart, Cook, Miller *Rev. Sci. Inst*. 75, 4359 (2004)

Picosecond continuum pulse-probe detection at the ELYSE facility (U. Paris-Sud, Orsay)







J.-L. Marignier
M. Mostafavi
U. Schmidhammer

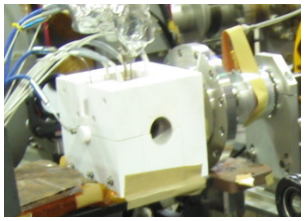
ELYSE:

- Pulse duration 5 - 15 ps
- Beam energy up to 9 MeV
- Charge per pulse up to 7 nC
- Dose per pulse ≈ 20 Gy
- Frequency up to 25 Hz

Also: streak camera transient absorption
Time range: 4 ps to 1 ms
240-850 nm

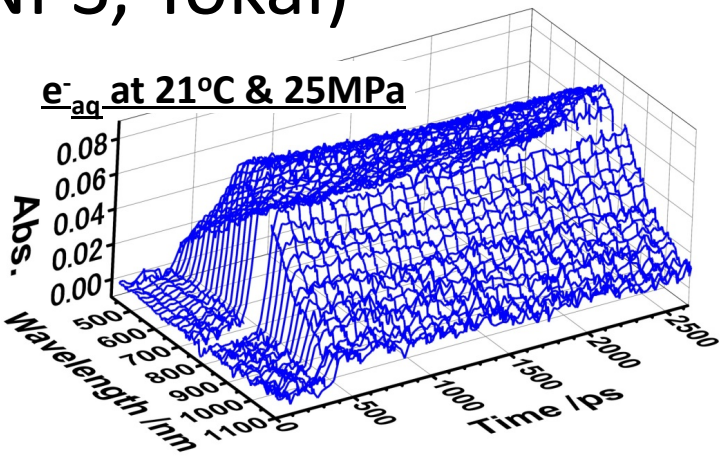
High temperature and pressure pulse-probe radiolysis at U. Tokyo (NPS, Tokai)

Rapid acquisition of 2D data : ***3 min/scan***
Wavelength : 430 — 1100 nm
Time : 0 — 2667 ps

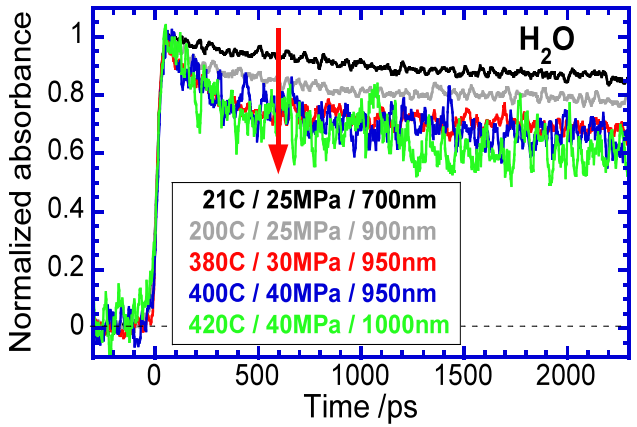


High temperature/pressure cell

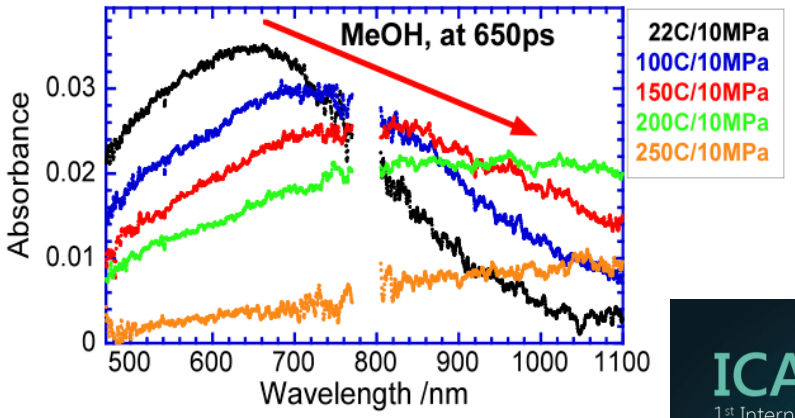
Up to 430°C, 40MPa



Practical work at extreme conditions (H_2O & MeOH)



Decay kinetics of e^-_{aq} in H_2O
up to supercritical state (>374°C, >22.1MPa)

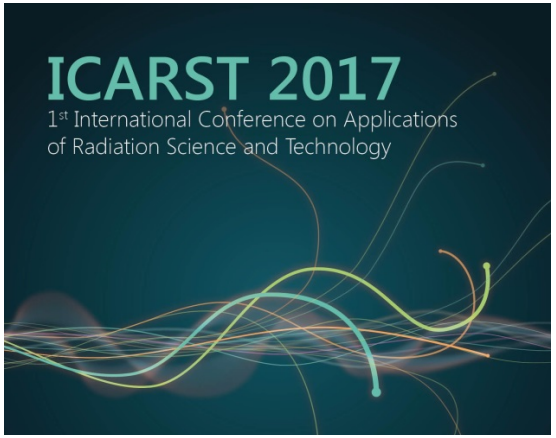


Spectra of e^-_{solv} in methanol
up to supercritical state (>239°C, >8.1MPa)

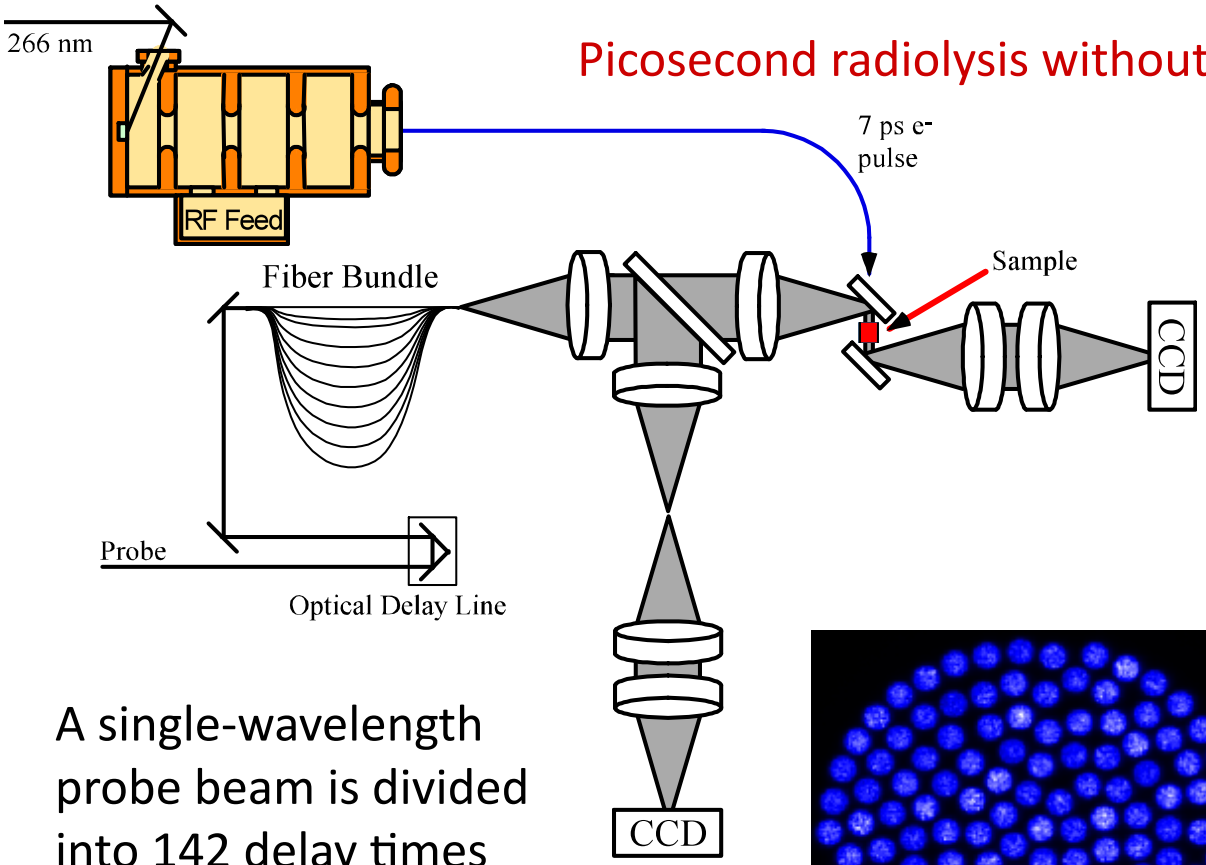
Rapid spur reaction in ps at HTHP

Destabilization of solvated electron at HTHP

Further HTHP studies : various polar liquids, and molten salts



Optical Fiber Single-Shot (OFSS) Picosecond Detection System at BNL's LEAF

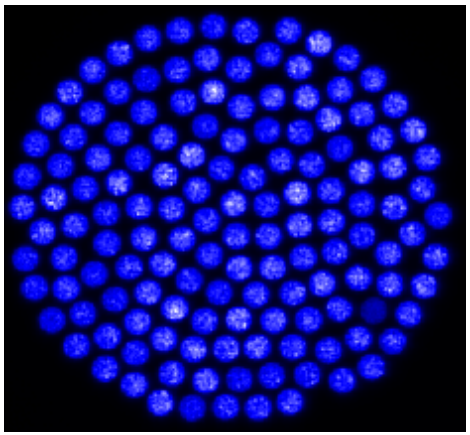


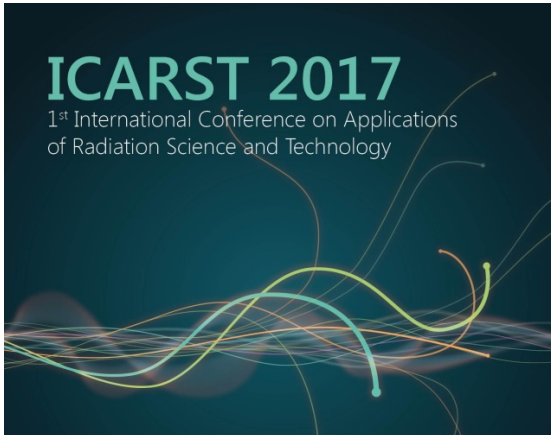
Picosecond radiolysis without needing huge samples

- Small sample volume (125 μL)
- Reduces consumption of precious samples
- Avoids needing to flow samples
- Can easily study viscous ionic liquids
- Can study transparent solids
  e.g., controlled pore glasses

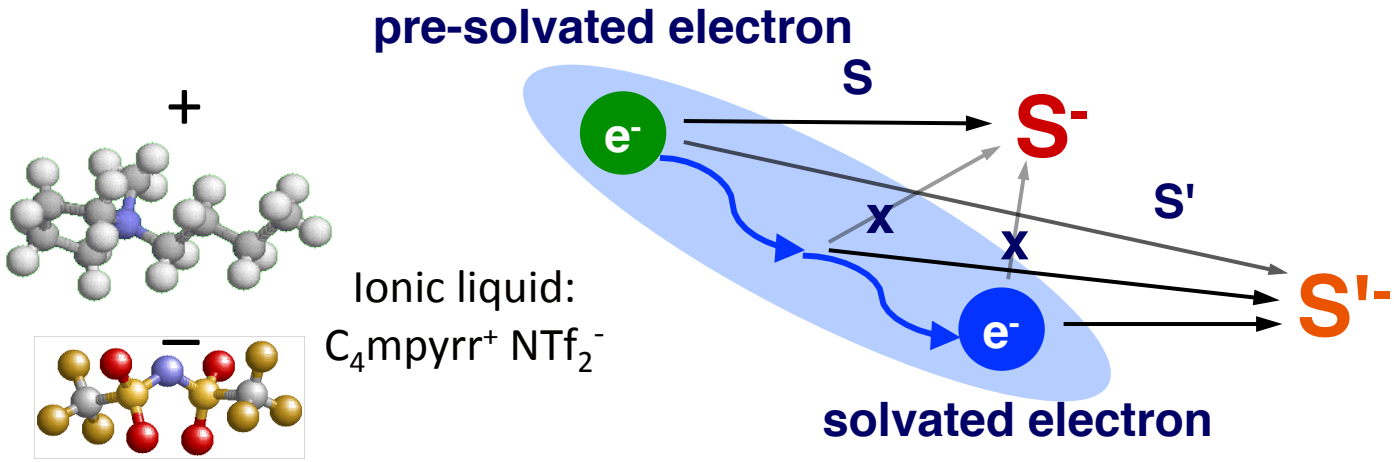
A single-wavelength probe beam is divided into 142 delay times spanning 5 ns

Cook, A. R.; Shen, Y., *Rev. Sci. Inst.* 2009, *80*, 073106

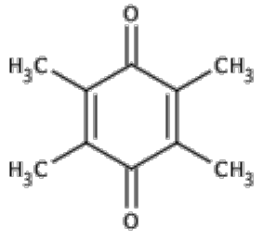




Pre-solvated electron reactivity is important in concentrated and viscous materials

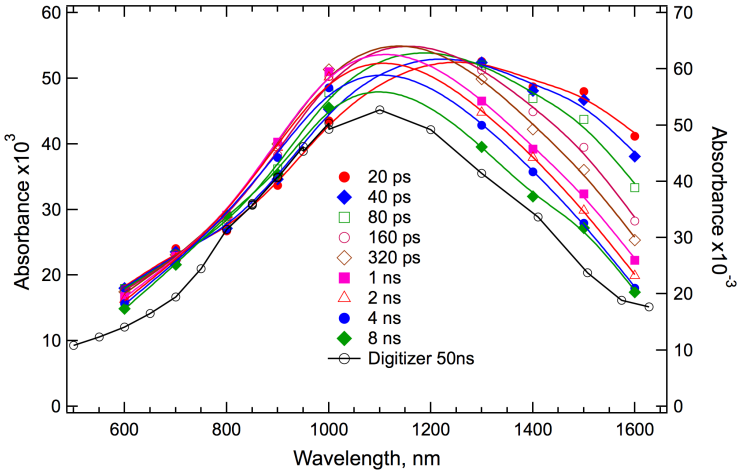


Scavenger **S**:

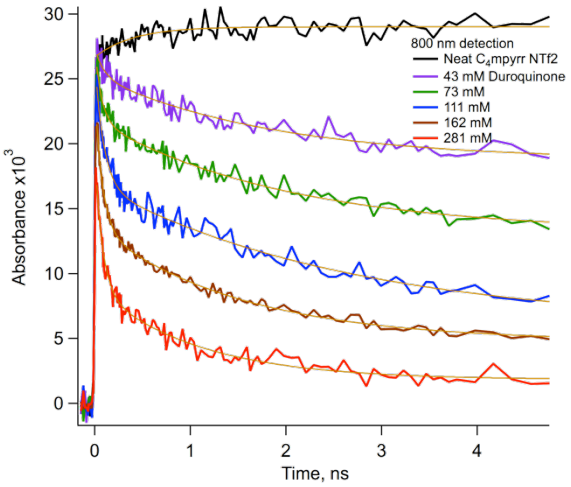


Duroquinone

Electron solvation

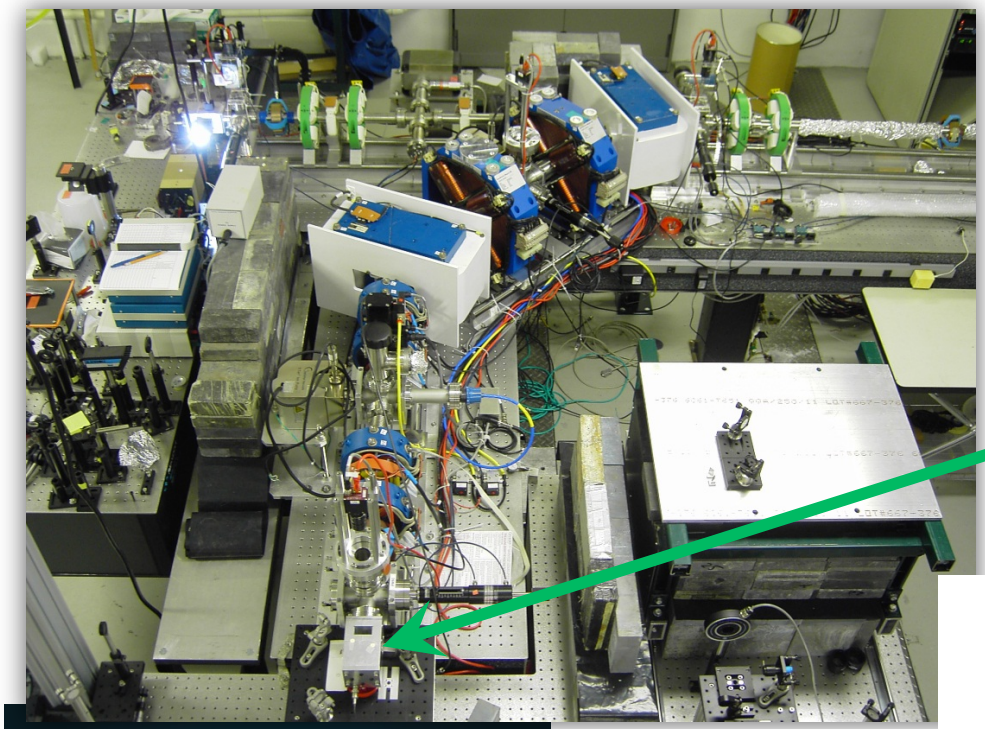


Electron scavenging

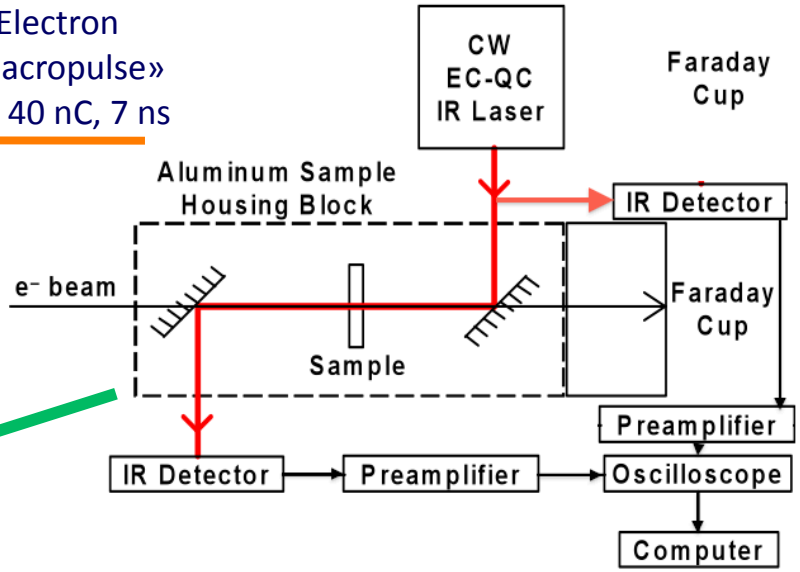


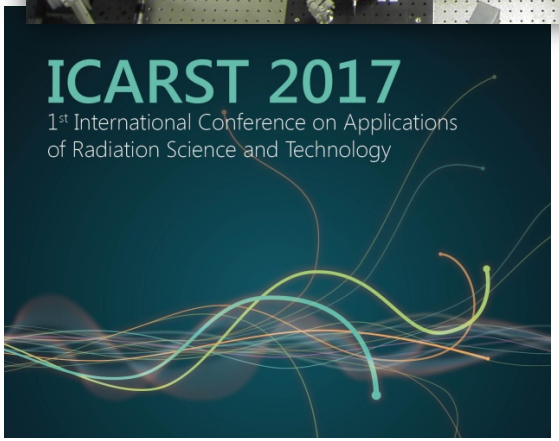
Faraday Discuss. 2012, *154*, 353-363.

Time-resolved mid-infrared detection pulse radiolysis at BNL: Transient Absorption and Step-Scan FTIR



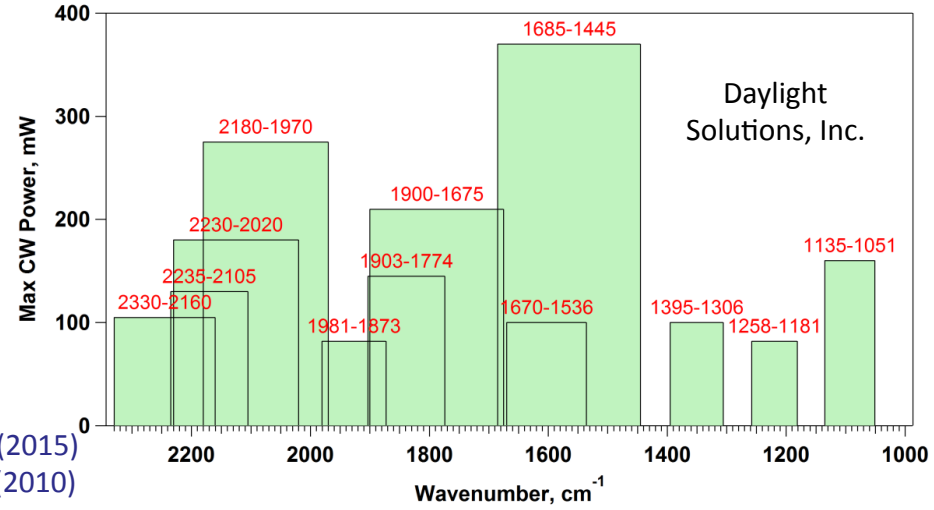
Electron «macropulse» 20 - 40 nC, 7 ns





Vibrational spectroscopy for structure-selective detection.

External cavity quantum cascade lasers (EC-QCL)

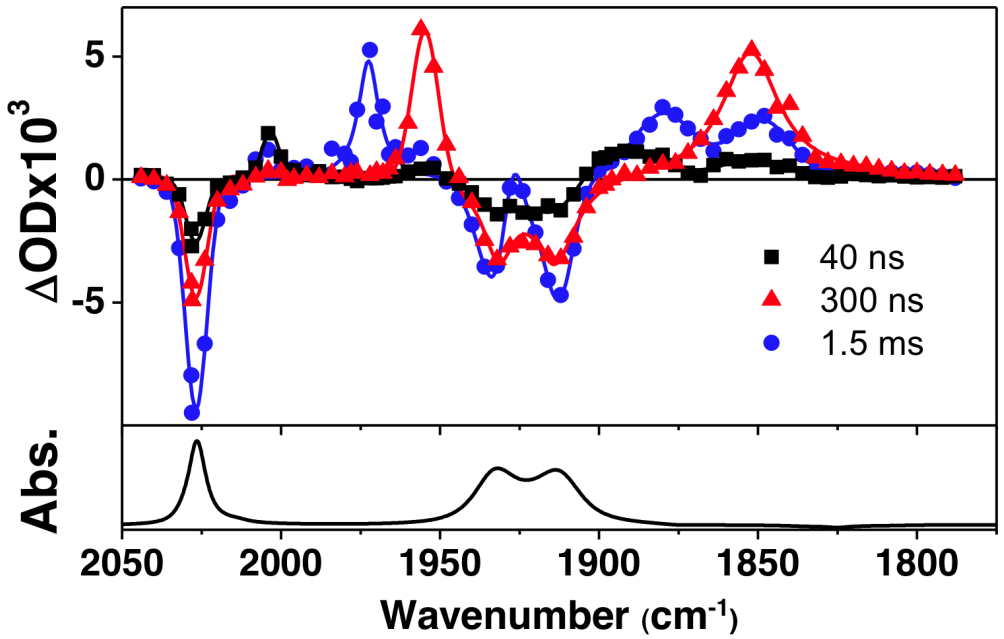


Rev. Sci. Instrum. 86, 044102 (2015)
Appl. Spectrosc. 64, 563-570 (2010)

Formation mechanism of a Mn-based CO_2 reduction catalyst revealed by mid-IR pulse radiolysis

Catalysis based on earth-abundant metals: Co, Ni, Fe, Mn.

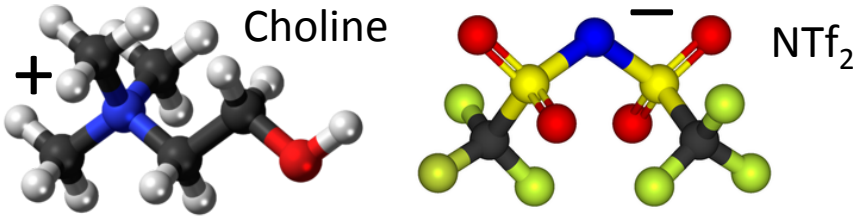
$$Mn(OC(O)H)(^tBu_2\text{-bpy})(CO)_3 \xrightarrow{PR} [Mn(OC(O)H)(^tBu_2\text{-bpy}^{\bullet-})(CO)_3]^- \xrightarrow[-HCO_2^-]{\tau=77\ ns} {}^{\bullet}Mn(^tBu_2\text{-bpy})(CO)_3 \xrightarrow[2k_{dim} = 1.3\times10^9\ M^{-1}s^{-1}]{+{}^{\bullet}Mn} [Mn(^tBu_2\text{-bpy})(CO)_3]_2$$



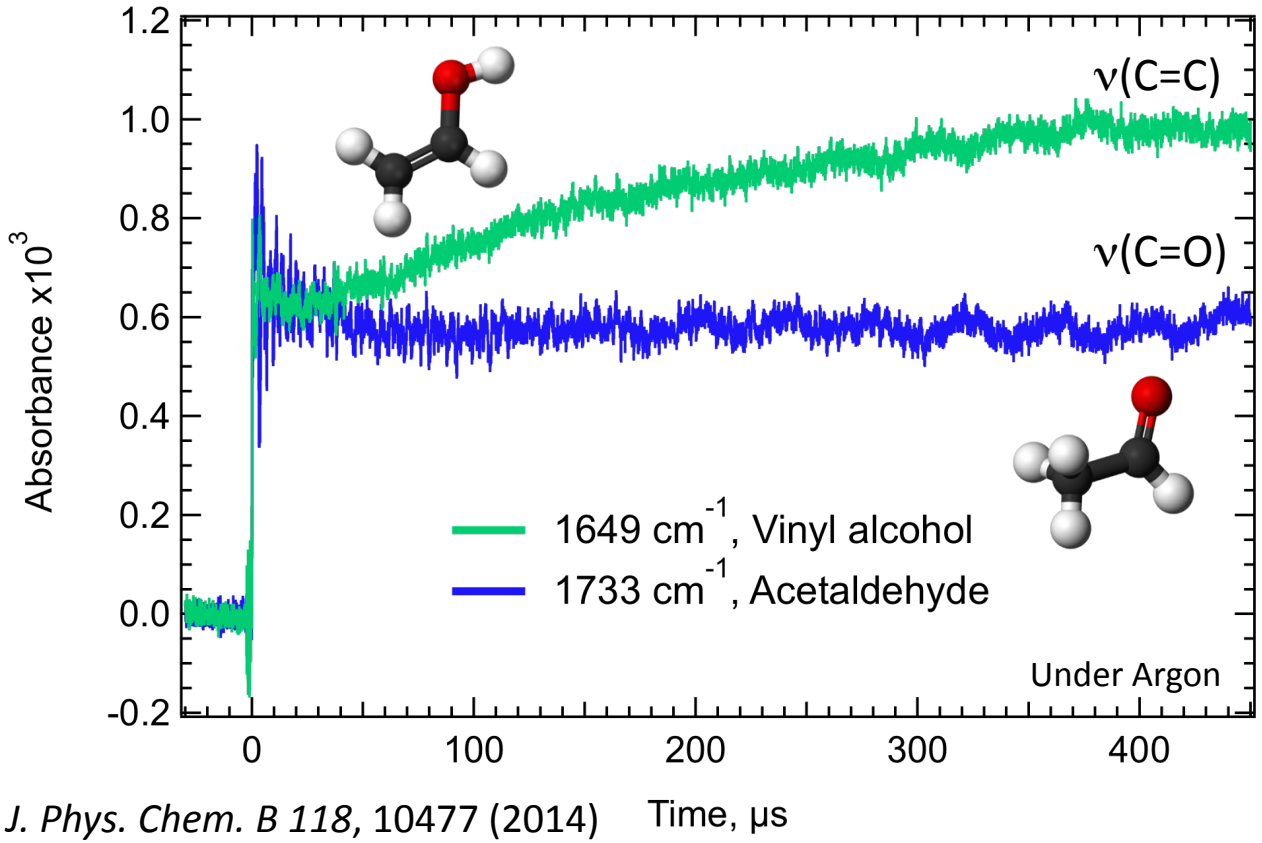
Grills, et al., *J. Am. Chem. Soc. 136,* 5563 (2014)

- HCO_2^- used as scavenger of ${}^{\bullet}CH_2CN$ radicals.
- Generates $CO_2^{\bullet-}$ reductant.

TRIR shows two N-C scission products in the radiolysis of choline NTf_2 ionic liquid



Time-resolved infrared permits detection *and quantification* of species impossible to detect by UV-Vis transient absorption.



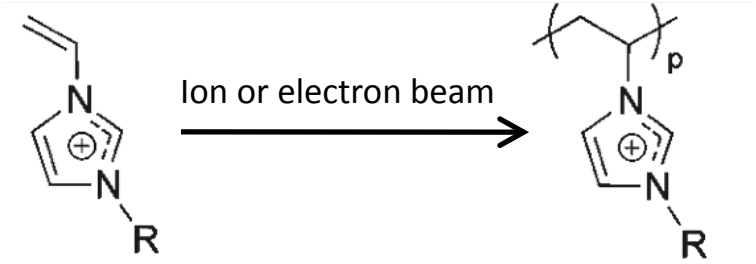
0.7 → 1.2

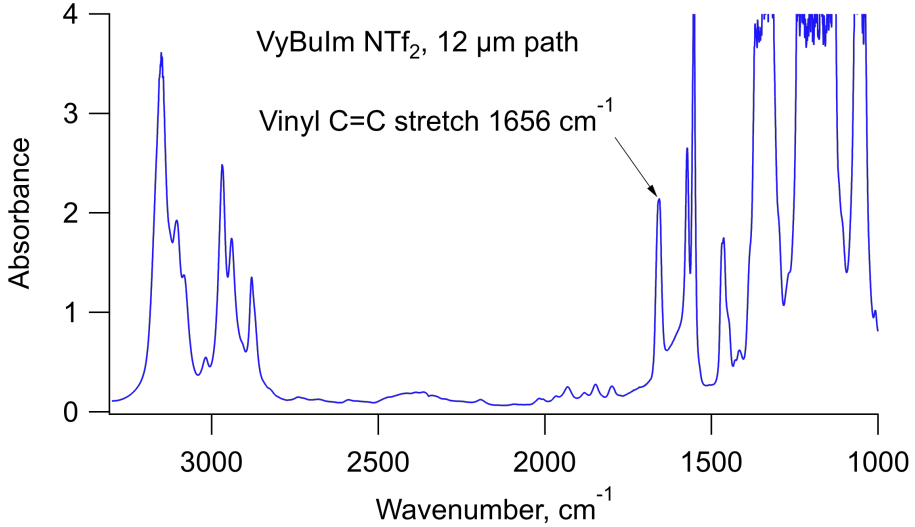
Yields per 100 eV

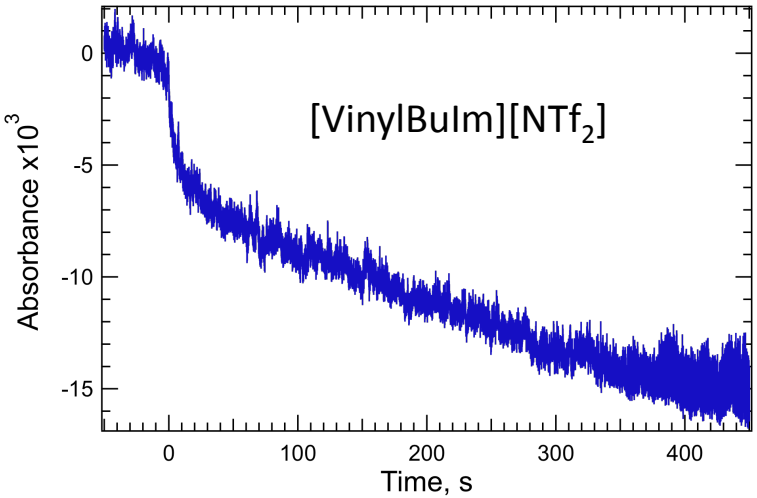
0.7

J. Phys. Chem. B 118, 10477 (2014)

Observing radiolytic IL polymerization by transient IR spectroscopy at LEAF

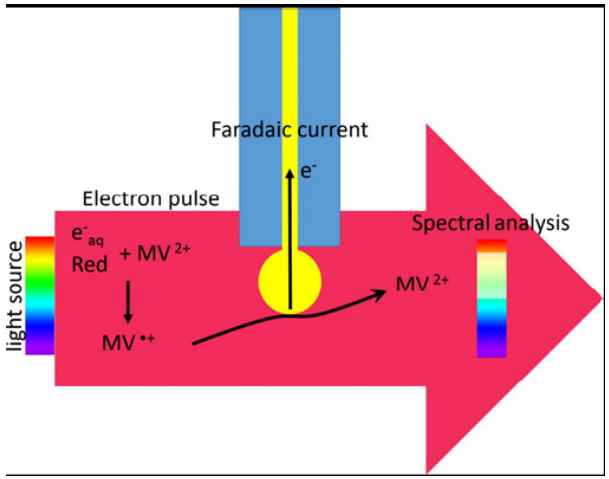




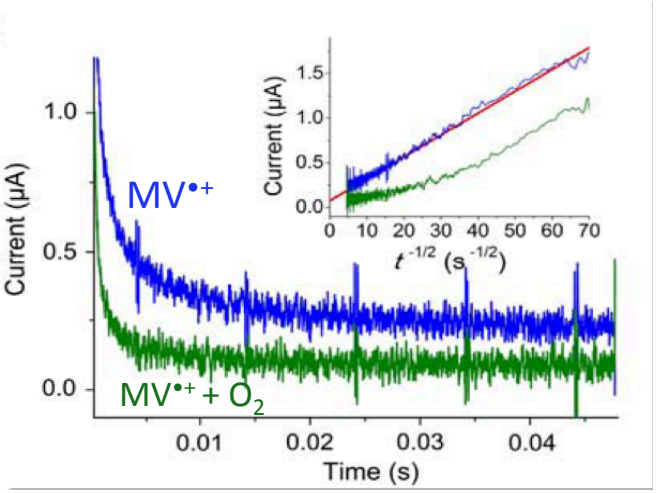


Rev. Sci. Instrum. 86, 044102 (2015)

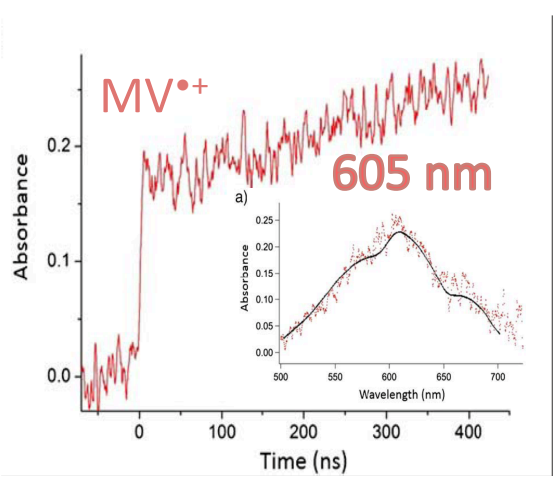
Simultaneous electrochemical and transient spectroscopic detection in pulse radiolysis



1mM MV^{2+}, 0.35M Na_2SO_4, 50mM isopropanol in H_2O



Transient electrochemical signal in presence and absence of oxygen

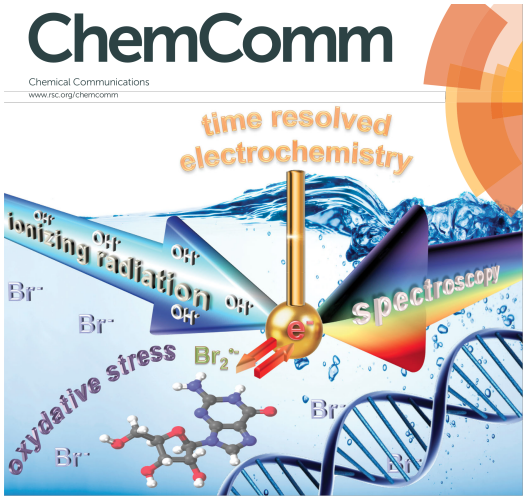


Evolution of the absorbance at 605 nm and transient absorption spectrum at 350 ns

UNIVERSITÉ PARIS SUD — LCP

Laboratoire de Chimie Physique

E. Maisonhaute (Paris VI),
J.-L. Marignier, M. Mostafavi
Electrochem. Comm., 2013, *35*, 149
Chem. Comm., 2015, *51*, 9089
Chem. Comm., 2016, *52*, 251



Current technical advances that will lead to future discoveries

Picosecond and shorter pulse radiolysis

- Diverse and evolving detection methods
- Pulse-pump-probe (excited states of radicals)
- Sub-psec manipulation of electron and light beams (Osaka)

Renaissance of transient vibrational spectroscopy

- IR: Time-resolved (BNL) and rapid-scan *in situ* (Saclay)
- Raman: Osaka, Notre Dame, planned for BNL, ELYSE

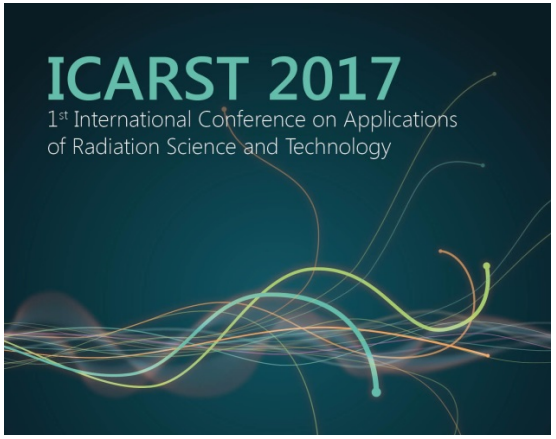
More abundant and better performing heavy ion sources

Advanced experiments with low-energy beams

- Surface-specific radiolysis and detection techniques

Computation:

- Simulations of radiolysis, electronic structure



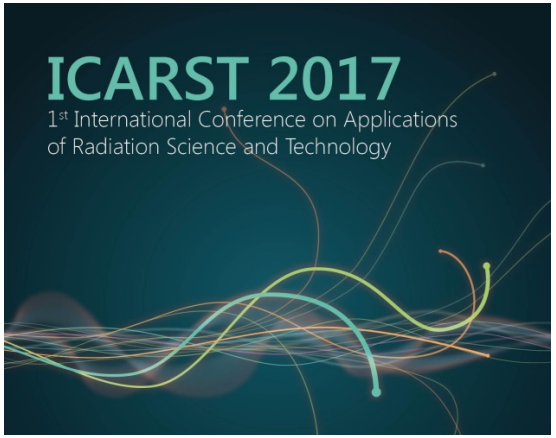
THANK YOU FOR YOUR ATTENTION!

Andrew Cook

David Grills

Bobby Layne

BNL: Tomasz Szreder, Alison Funston, Suraj Dhiman, Yoany Portilla

International Contributions: Mehran Mostafavi, Jean-Louis Marignier, Yosuke Katsumura, Hiro Minamimoto

This talk and use of the LEAF Facility of the BNL Accelerator Center for Energy Research were supported by the U. S. Dept. of Energy
Division of Chemical Sciences, Geosciences and Biosciences.