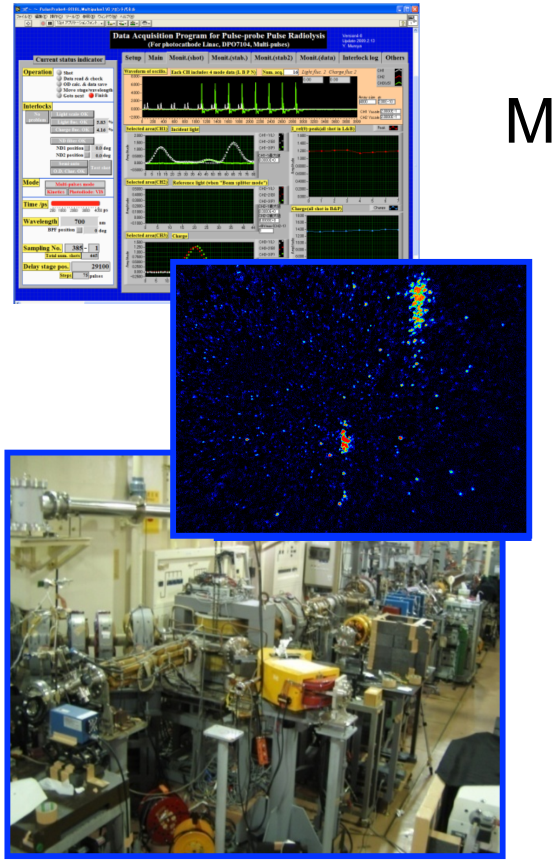
Symposium; *Radiation Chemistry: the Marie Curie's heritage*

November 15 and 16, 2011, Maison de la Chimie, Paris, France

Water Radiolysis under Extreme Condition



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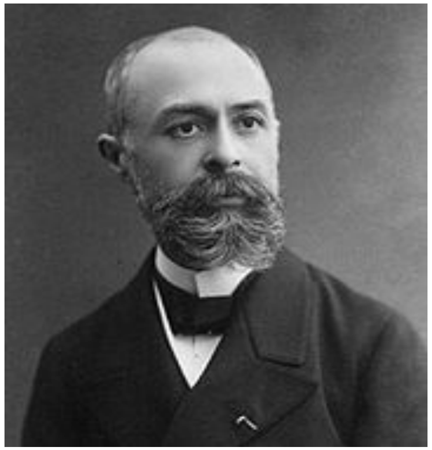
Content

(1) Brief history on radiolysis of water
& High temperature water radiolysis
(2) Experimental
(3) Observation of energy minimum for the absorption peak of e^{-}_{sol} at fixed density
(4) Ultrafast pulse radiolysis study at HTHP
(5) Summary
(6) Future perspectives

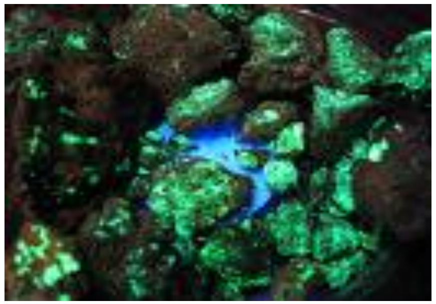
1895 Wilhelm Conrad Röntgen

X-rays

1896 Antoine Henri Becquerel



radioactivity



Maria Skłodowska-Curie and Pierre Curie: Ra 1898

J. Belloni,
"Historic landmarks in radiation chemistry since early observations by Marie Skłodowska-Curie and Pierre Curie"
***NUKLEONIKA*, *56*, 201-211 (2011)**

C. R Acad. Sci. Paris, 1899, 129, 823

CHIMIE. — *Effets chimiques produits par les rayons de Becquerel.* Note de M. P. CURIE et de Mme CURIE, présentée par M. Becquerel.

« Les rayons émis par les sels de baryum radifères très actifs sont capables de transformer l'oxygène en ozone.

C. R Acad. Sci. Paris, 1901, 132, 768

Sur la radio-activité induite et les gaz activés par la radium.

*The release of **hydrogen** and **oxygen** by **aqueous solutions** of radium salt was observed by Pierre Curie and Andre Debierne.*

$H_2^+O + OH- = H_2O + OH$

$H_2^-O + H^+ = H + H_2O$ $\qquad 2OH = H_2O_2$

First observation of radiolysis of water !!

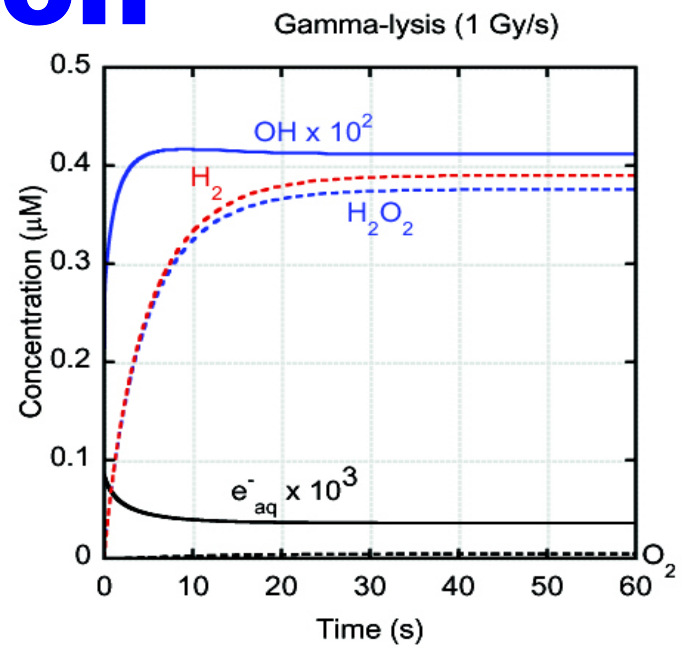
Contradiction

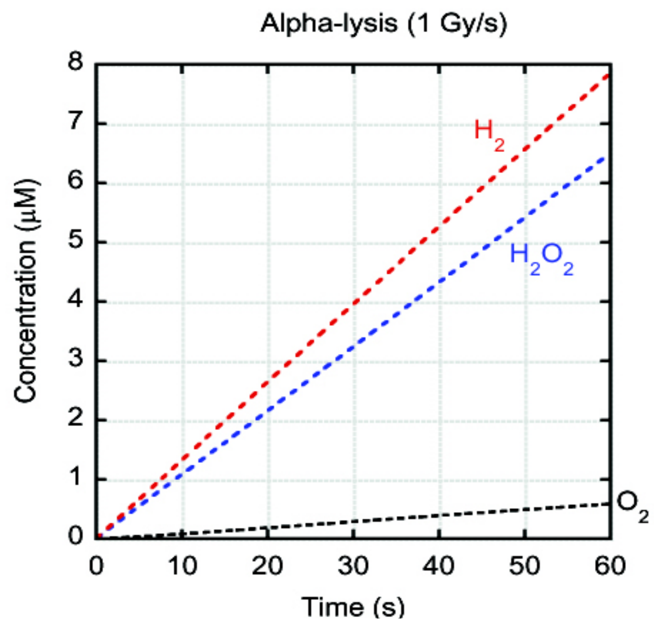
1901 **Curie & Debierne**
Continuous gas formation in radium salt solution
→ decomposition of water

1920s
No gas formation in water irradiated with X-ray
→ apparent no decomposition

Different types of radiation have different effects toward water decomposition

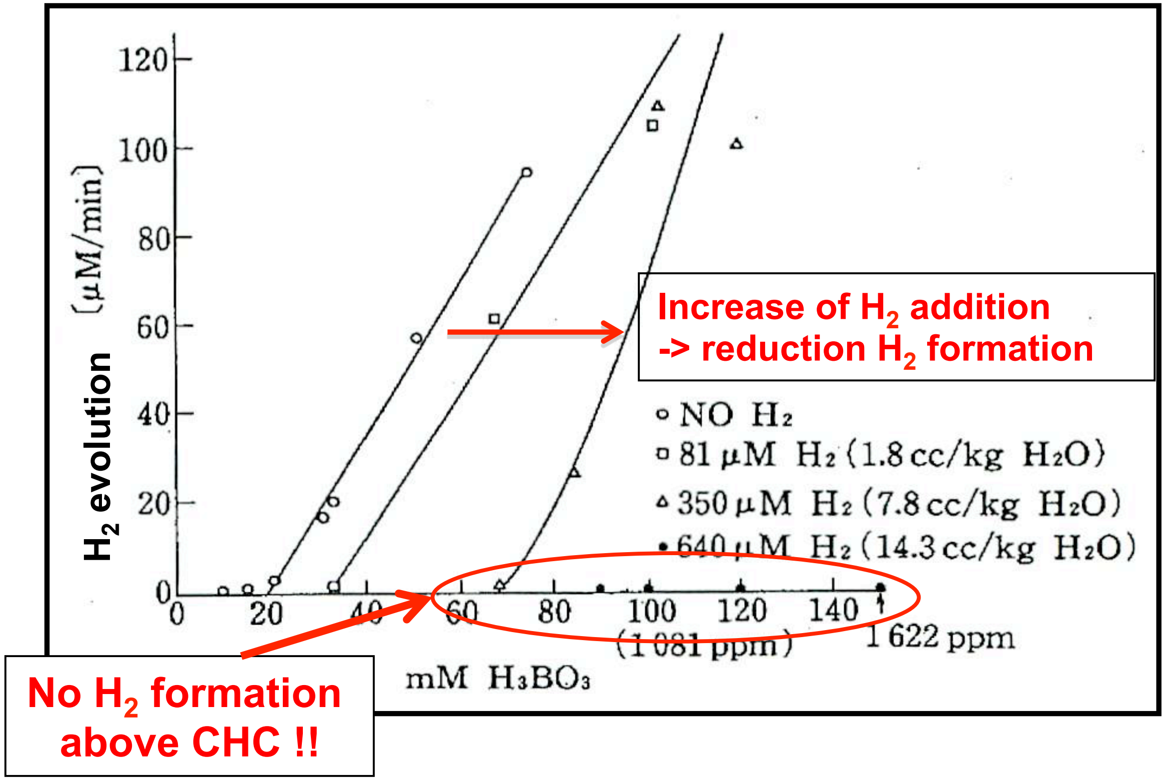
G-values	$-H_2O$	e^-_{aq}	OH	H	H_2O_2	H_2	HO_2
γ -ray	4.1	2.7	2.8	0.56	0.68	0.45	~0.01
α -ray	2.65	0.06	0.24	0.21	0.985	1.3	0.22

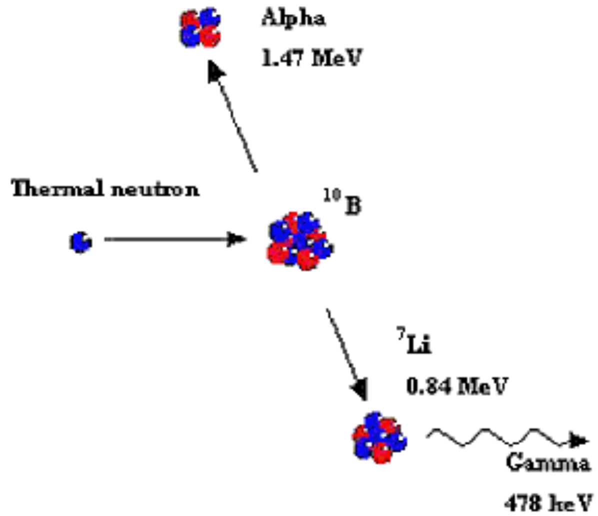




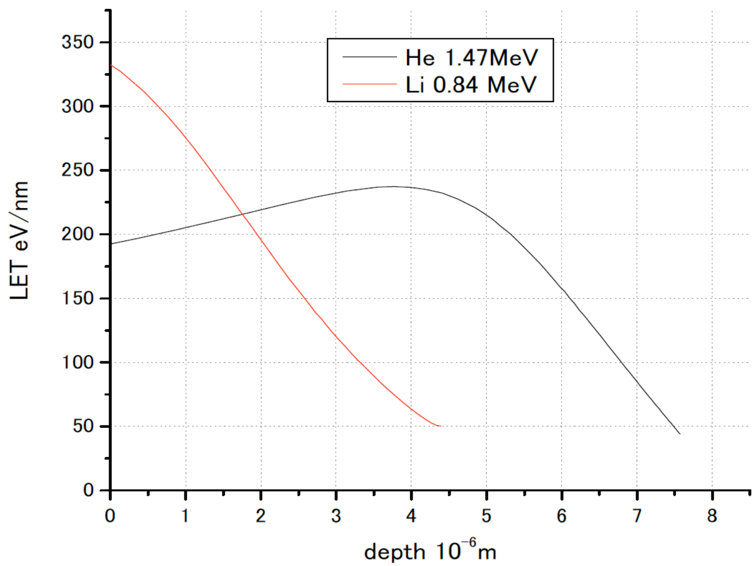
Inhibition of α-radiolysis by H_2 addition

The decomposition of Light and Heavy Water Boric Acid Solutions by Nuclear Reactor Radiations
by. E. J. Hart, W. R. McDonell and S. Gordon
Peaceful use of Atomic Energy in 1955





$^{10}B + {}^{1}n \rightarrow {}^{7}Li + {}^{4}He + photon$



Coolant water in PWR
-> 25 cc/kg STP H_2 addition

Discovery of hydrated electron

Nature **197**, 45 (1963)

J. W. Boag and E. D. Hart

Absorption Spectra of 'Hydrated' Electron

May 15, 1962
a few days before
Ed's departure to Israel

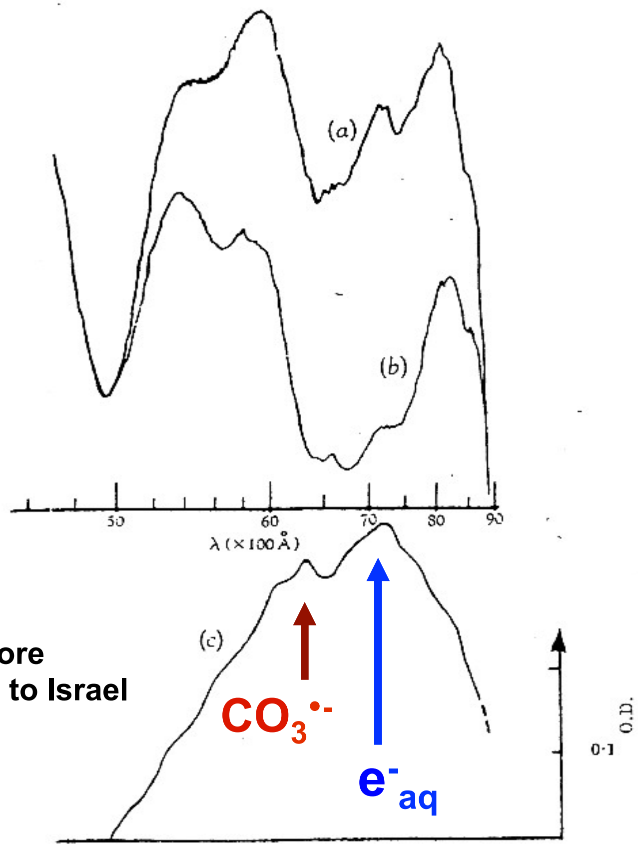


Fig. 1. Transient absorption in 0·5 M aqueous solution of sodium carbonate. *a*, Densitometer trace of part of a spectrogram taken through unirradiated solution (the peaks are due to the sensitizers in the emulsion); *b*, densitometer trace of same part of spectrum taken simultaneously with a 2 μsec electron pulse (*c*. 4 k.rads); *c*, difference curve

J. Am. Chem. Soc., **84**, 4090-4095 (1962)

The pulse radiolysis is a powerful and useful technique.

Nature **197**, 47 (1963)

J. P. Keene

Optical Absorption in Irradiated Water

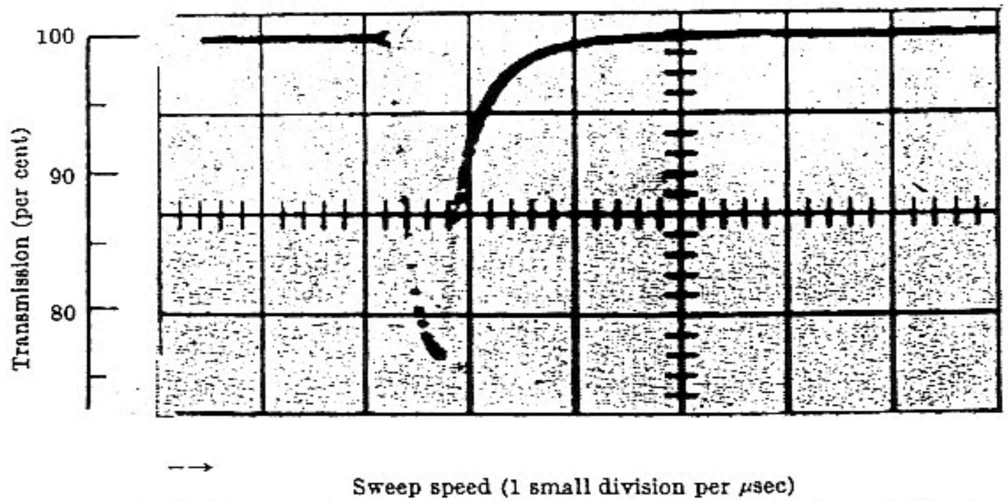
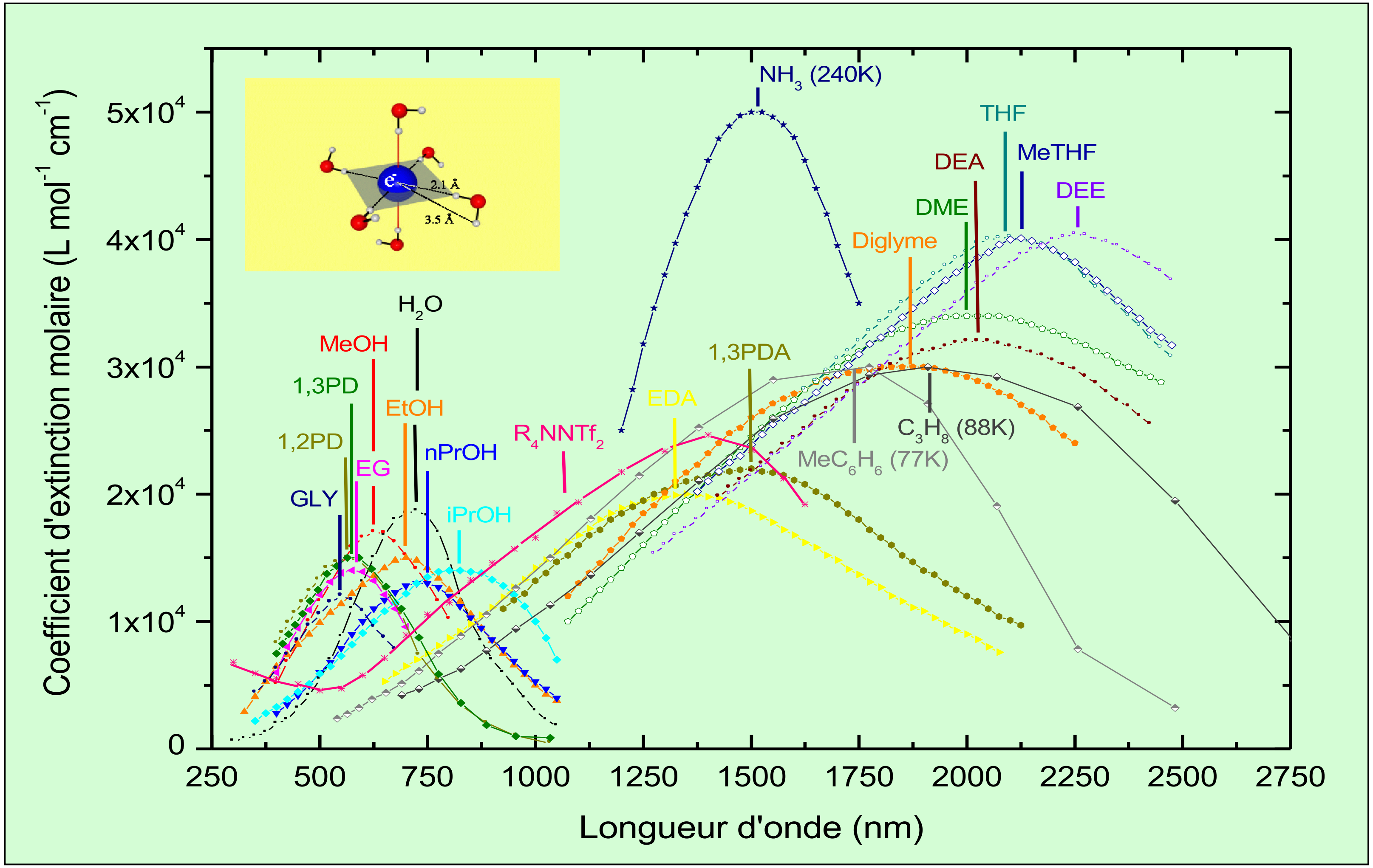


Fig. 3. Optical transmission of de-aerated water at 5430 Å before, during and after a 2 μsec electron pulse

At the Harrogate Congress in August, 1962 Dr. Keen reported his absorption measurements using photomultiplier and oscilloscope. The paper was submitted in August, 1962 but not published until 5 January, 1963.

Solvated electrons (e_{sol}^-)

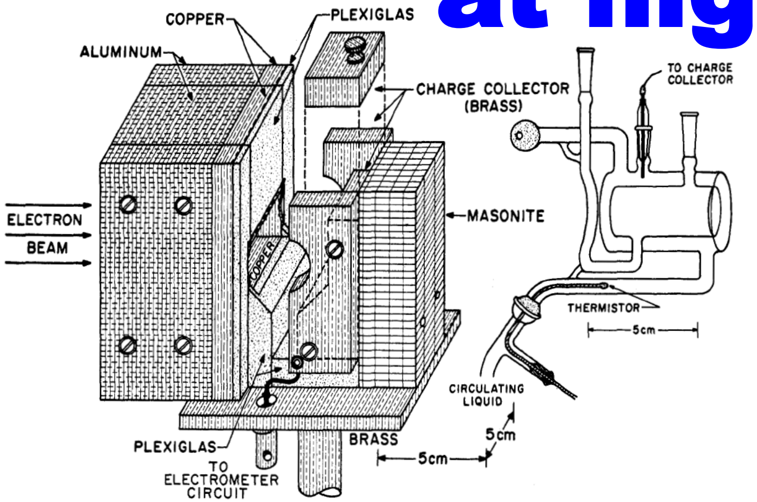


L. M. Dorfman and J. F. Galvas, in *Radiation Research. Biomedical, Chemical and Physical Perspectives*, 1975

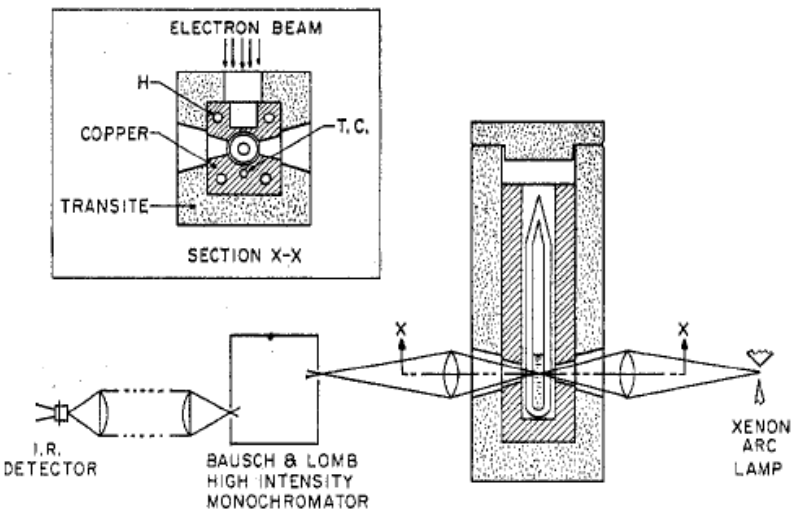
Hydrated electron at elevated temperatures

- subcritical and supercritical water -

Hydrated electron at high temperatures

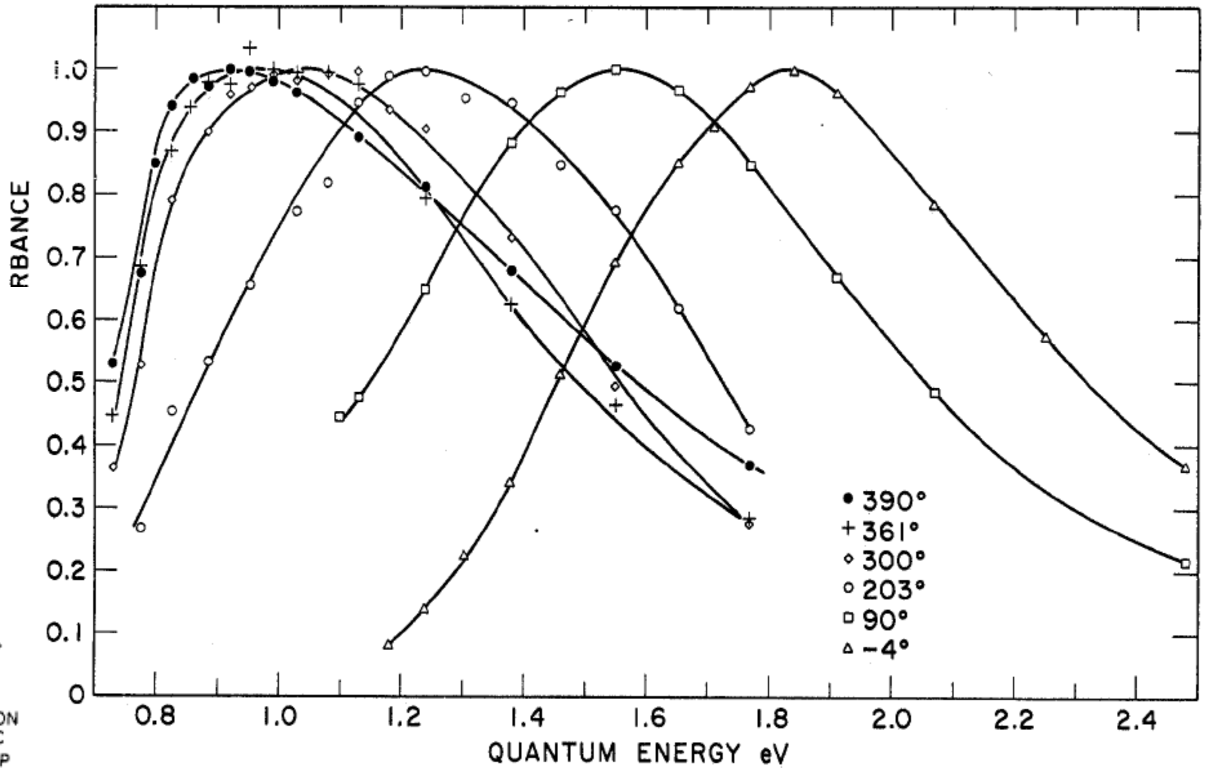


Temperature range -4 to 90 °C for H_2O



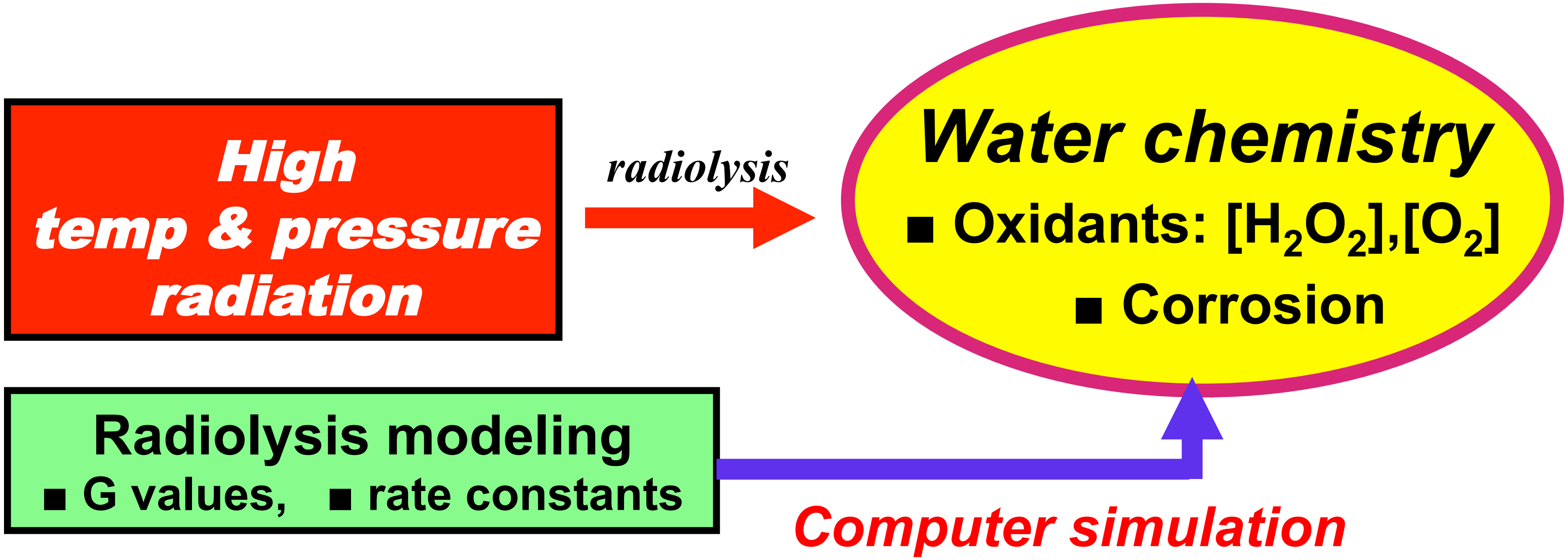
Temperature range 203 to 390 °C for D_2O

The absorption band of hydrated electron shifts to lower energy range (longer wave-length) with increasing of temperature.



Hart et al; *J. Phys. Chem.*, **75**, 2798 (1971)

Water chemistry in 1980-1990s



Hydrogen injection, **NMCA** (Noble Metal Chemical Addition),

Canada: **Dixson, Elliot, Quellette, Stuart**

Denmark: **Sehested**

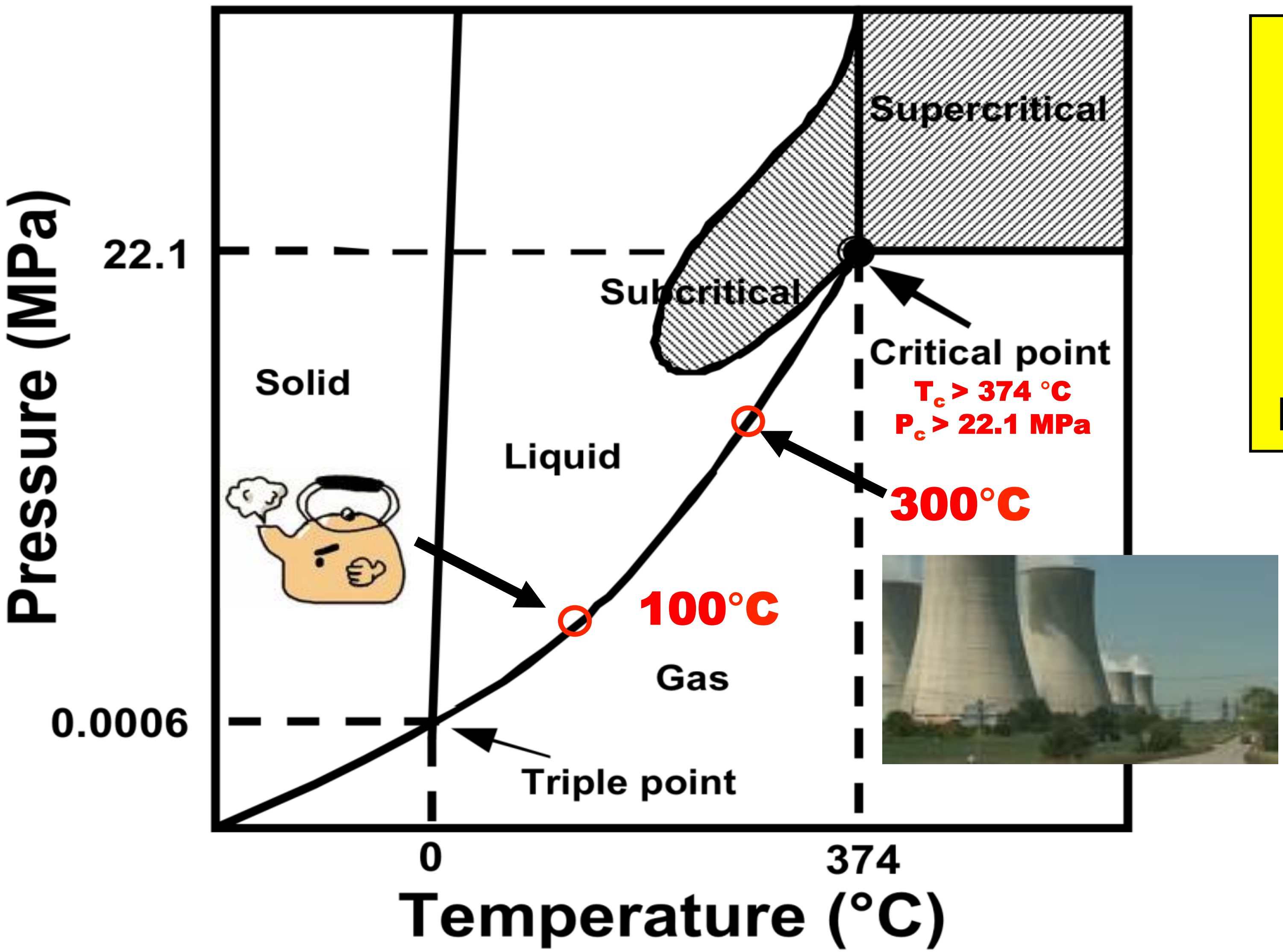
France: **Hickel, Pastina**

Japan: **Ishigure, Shiraishi, Katsumura**

Sweden: **Christensen**

UK: **Burns, Buxton, Sims, Stuart**

Phase diagram of water



H_2O
Tc: 374.1 °C
Pc: 22.1 MPa

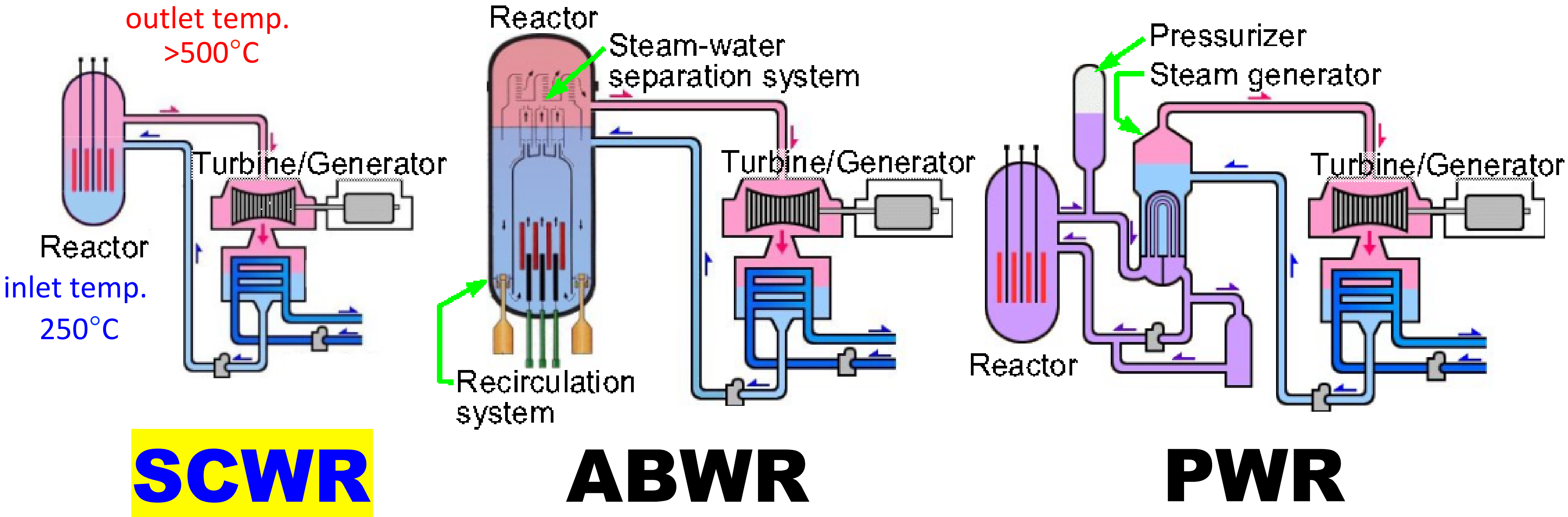
D_2O
Tc: 370.7 °C
Pc: 21.67 MPa

Supercritical Water Cooled Reactor (SCWR)

- High thermal efficiency (≥44%)
- Compact, small volume and simple structure
- Proven technologies (LWRs & SCW fossil plants)

→ highly ranked in economics

Proposed by Prof. Oka in 1989 (Waseda Univ.)



Hydrated electron in water

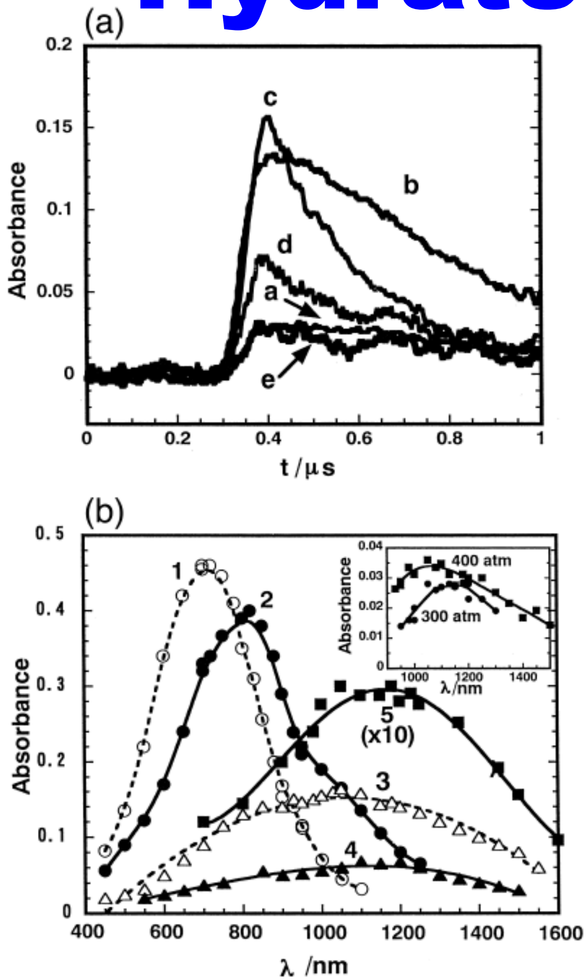
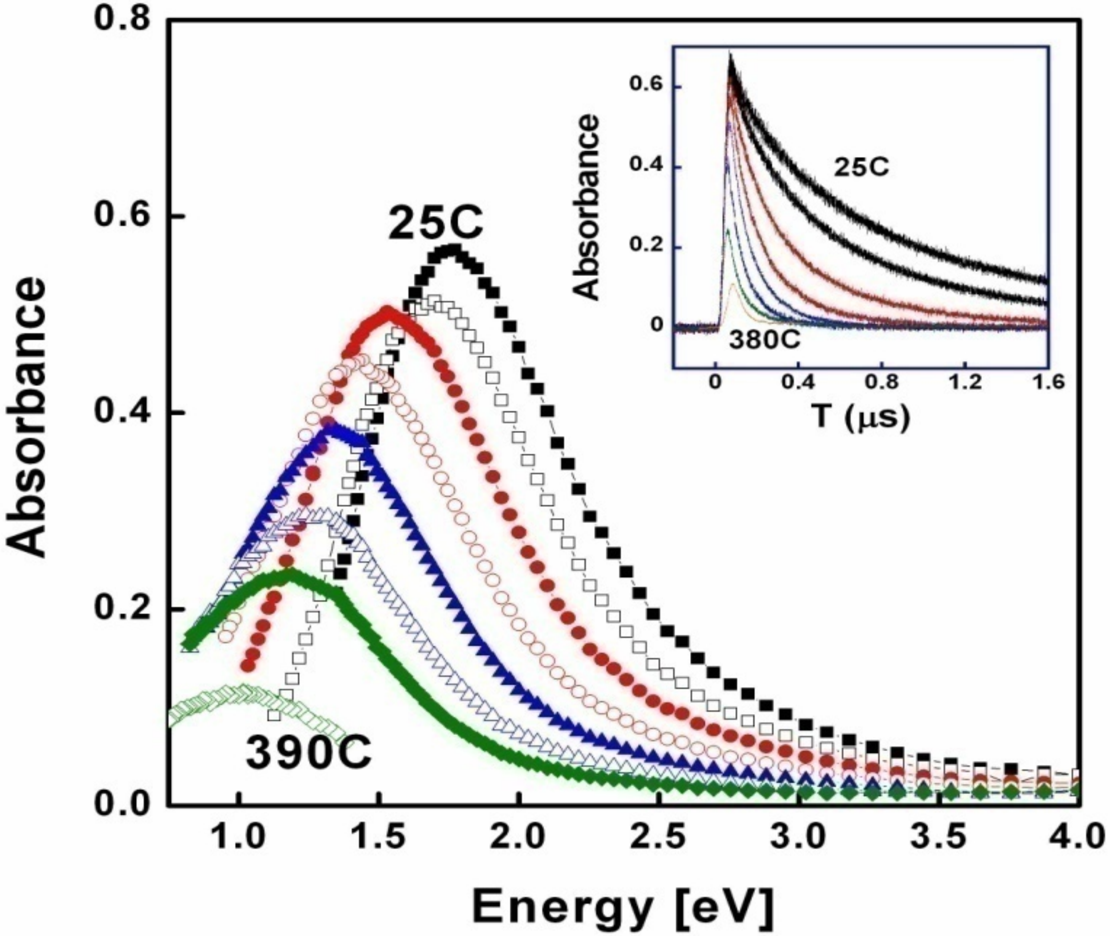


Fig. 2. (a) Time profiles of e^-_{aq} at 1100 nm in D_2O. 46 Gy/pulse. a. 25°C, 1 atm; b. 100°C, 100 atm; c. 250°C, 200 atm; d. 350°C, 250 atm; e. 400°C, 350 atm. (b) Absorption spectra of e^-_{aq}. Conditions for curves 1–5 are the same as for curves a–e in (a). Inset: Spectra of e^-_{aq} at 400°C under pressures of 300 and 400 atm.

Wu, Katsumura, Muroya and Terada; *Chem. Phys. Lett.*, ***325***, 531–536 (2000)

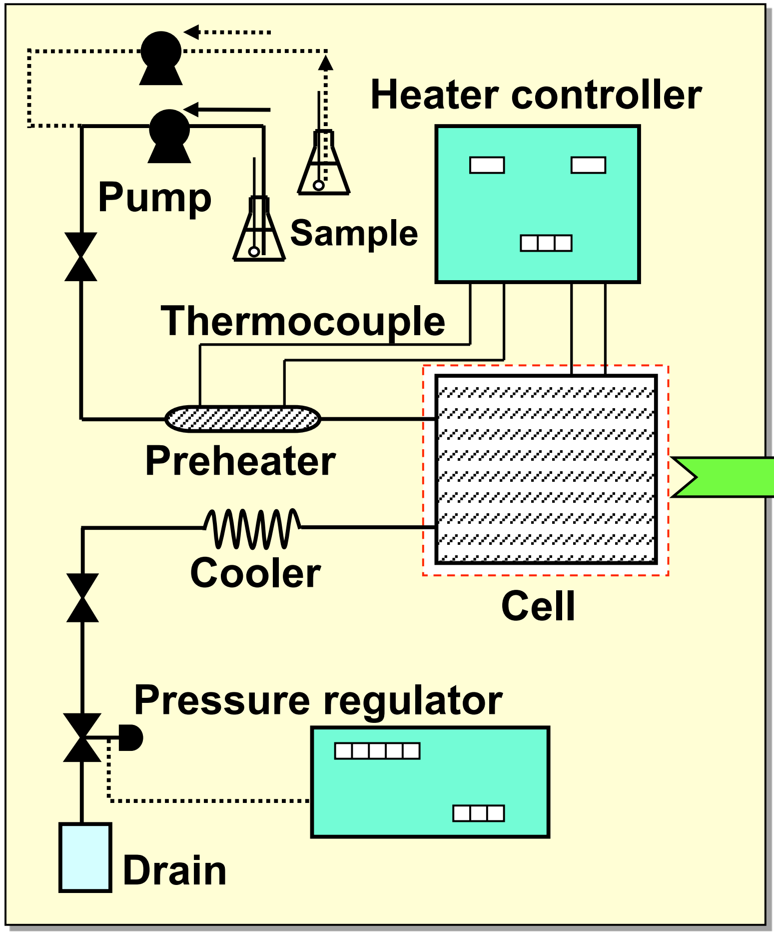


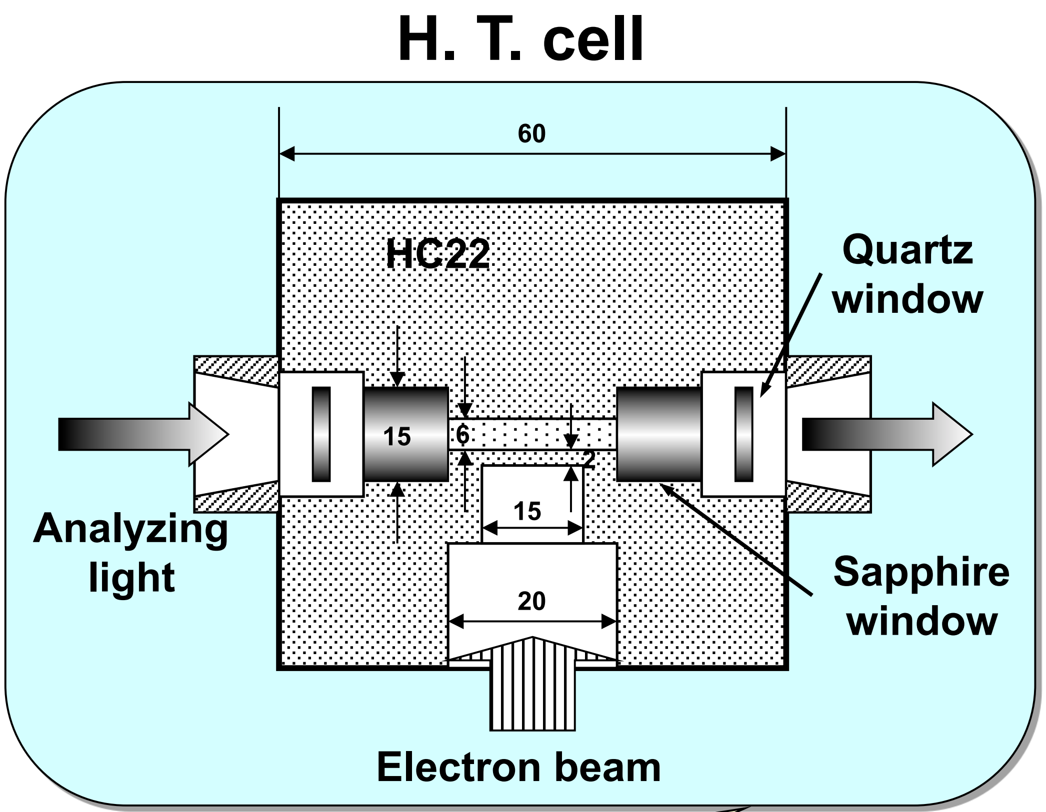
The normalized absorption spectra of the hydrated electron in D_2O in the presence of 0.2 M *tert-butyl* alcohol at different temperatures.

Lin, Kumagai, Lampre, Coudert, Muroya, Boutin, Mostafavi, and Katsumura *J. Phys. Chem. A*, **111**, 3548 (2007)

Experimental

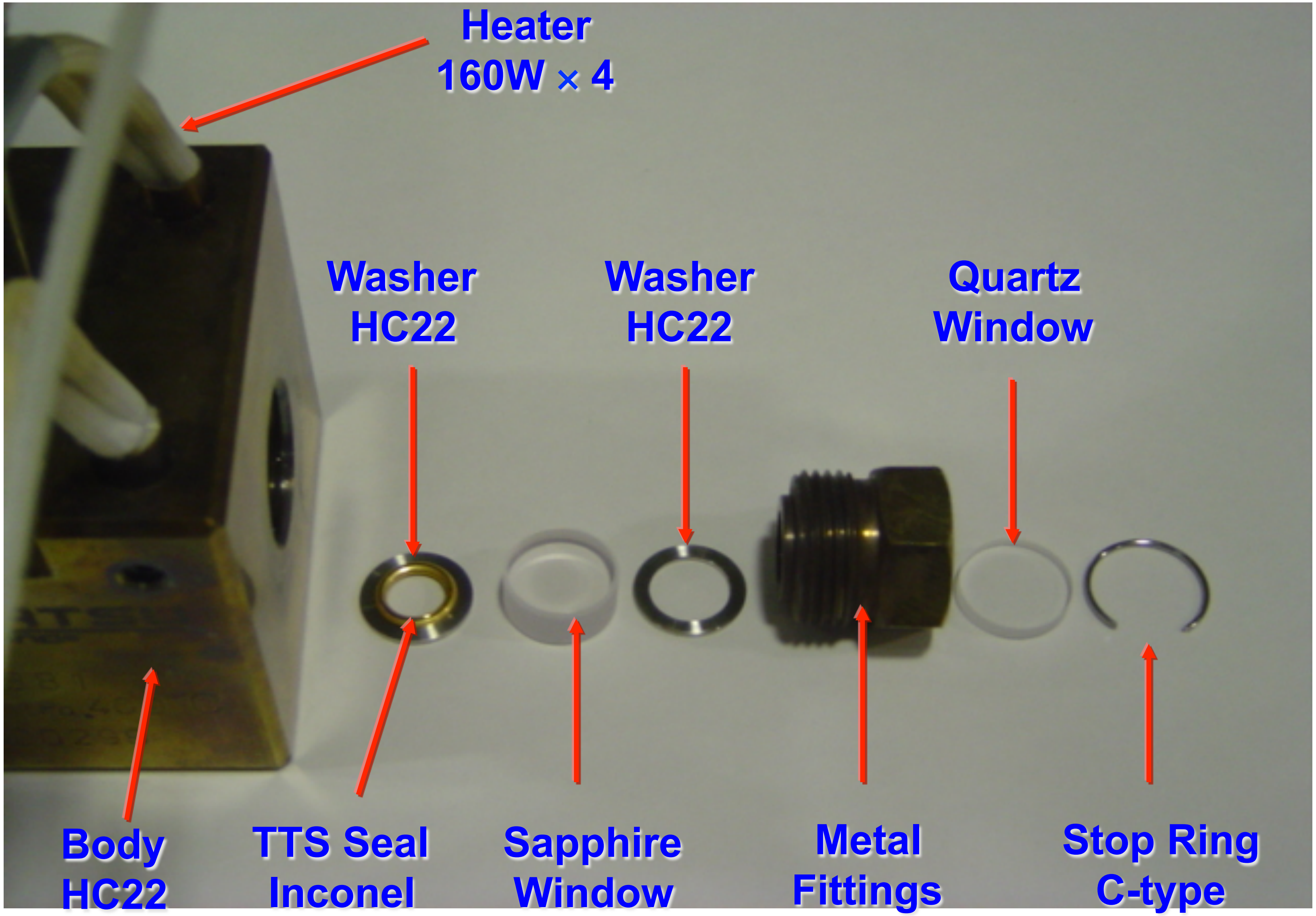
Experimental set-up





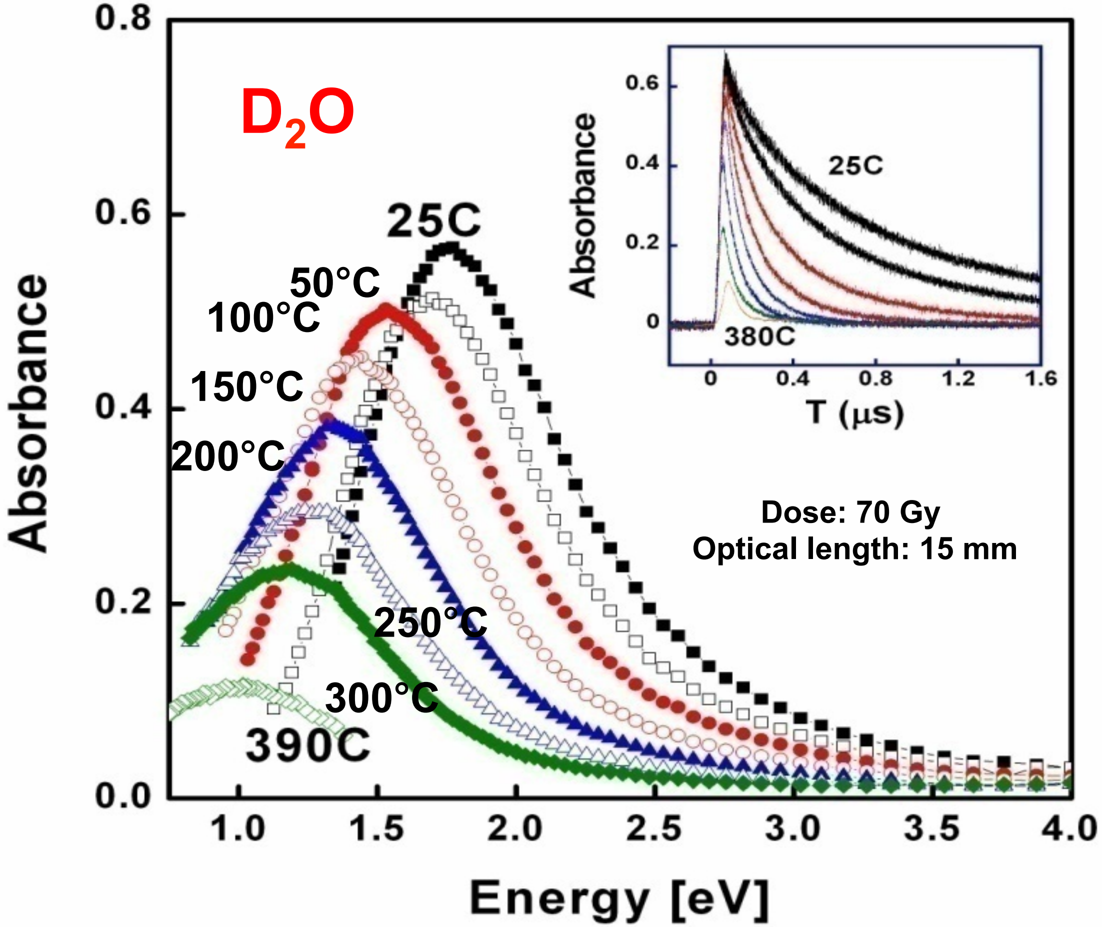
Pressure: 40 MPa
Temperature: 400 ºC

Window structure



Observation of energy minimum for the absorption peak of e^-_{aq}

Hydrated electron in water



H_2O	D_2O
Tc: 374.1 °C	Tc: 370.7 °C
Pc: 22.1 MPa	Pc: 21.67 MPa

Two findings

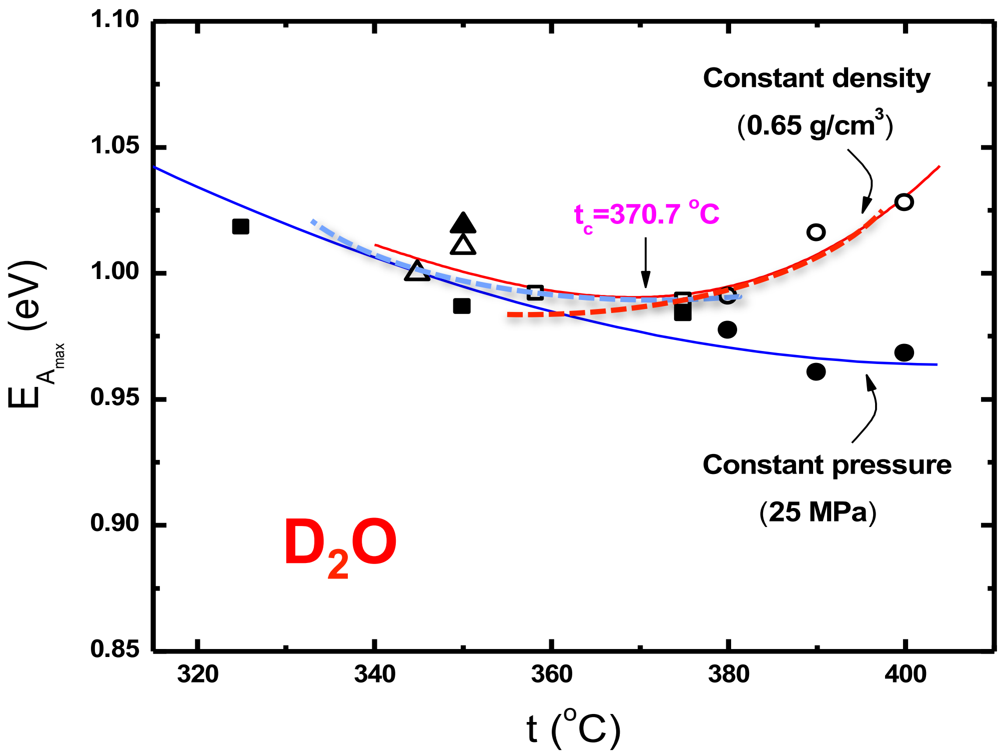
(1) The absorption spectra of the hydrated electron shift to lower energy (longer wavelength) with increasing temperature.

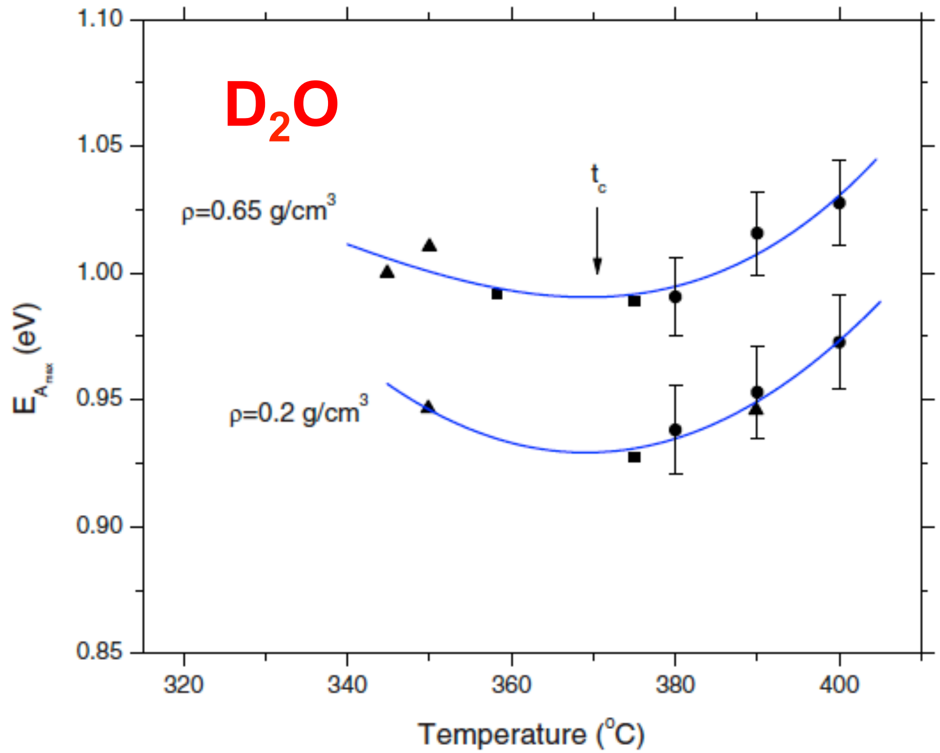
(2) The decay of the hydrated electron becomes faster with increasing temperature.

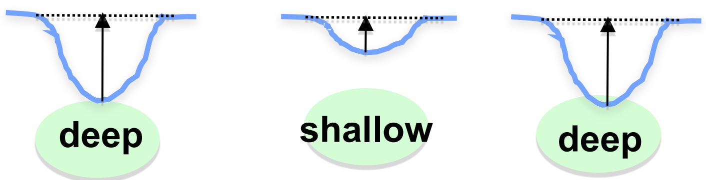
The normalized absorption spectra of the hydrated electron in D_2O in the presence of 0.2 M *tert-butyl* alcohol at different temperatures.

M. Lin, Y, Kumagai, I. Lampre, F.-X. Coudert, Y. Muroya, A. Boutin, M. Mostafavi, and Y. Katsumura
J. Phys. Chem. A, 111, 3548 (2007)

Constant density or pressure







at ρ = 0.2 g/cm^3,
from 22.14 MPa at 376 ºC
to ~26.4 MPa at 400 ºC

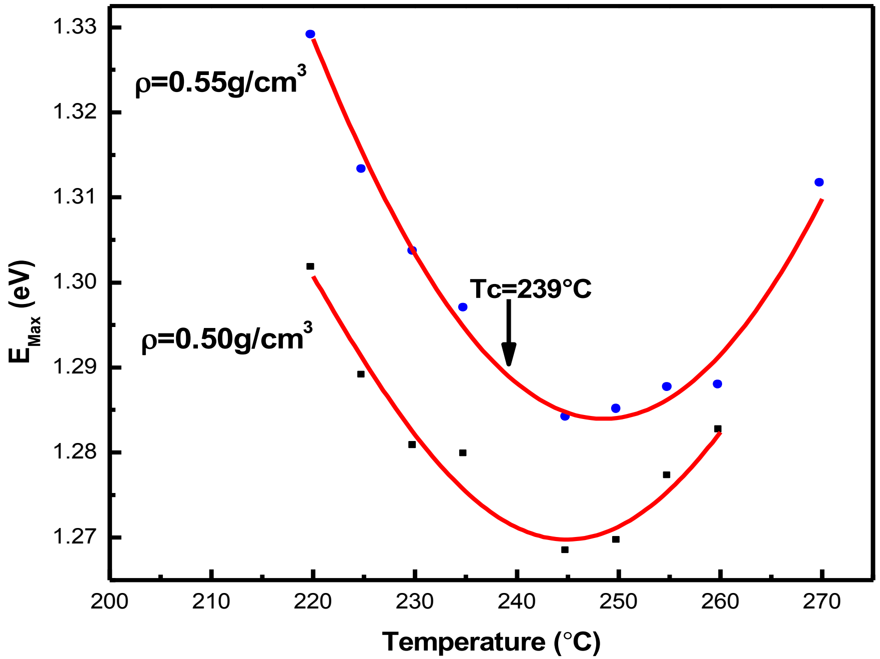
J-P. Jay-Gerin, M. Lin, Y. Katsumura, H. He, Y. Muroya, J. Meesungnoen, *J. Chem. Phys.*, 129, 114511 (2008)

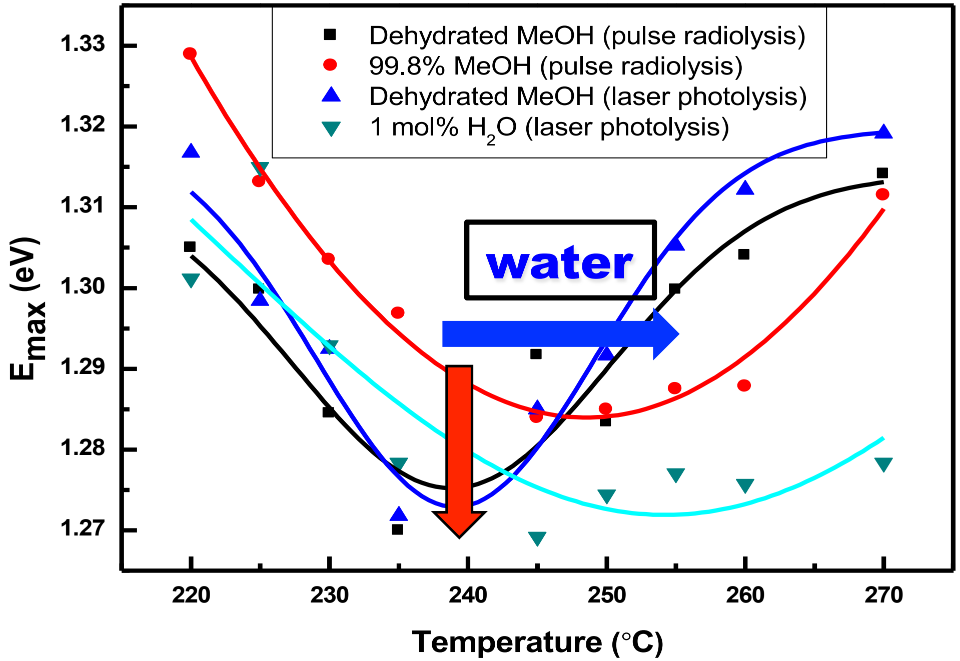
Why minimum?

Temperature: structure breaking (decrease the potential energy)

Pressure: structure making (increase the potential energy)

Solvated electron in methanol at fixed density





***E*Amax as the function of temperature in sub- and supercritical methanol at two fixed densities**

Having minimum! But not at T_c! Due to water?!

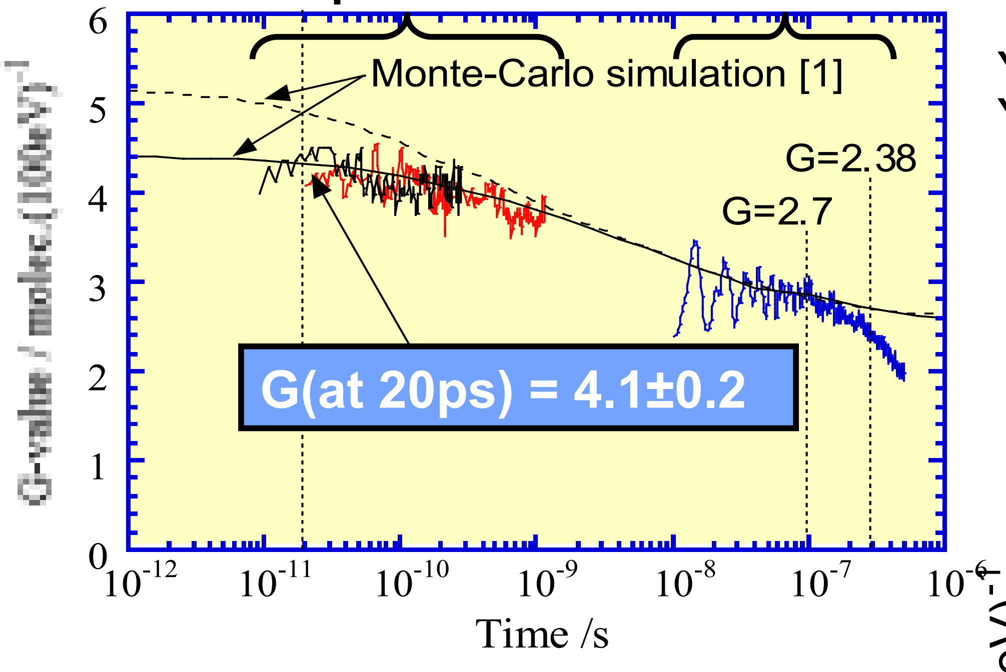
Water content effect on the E_{max} in sub- and supercritical methanol at fixed density 0.55g/cm^3.

- **Yes! For dehydrated MeOH, at T_c!**
- **More water, T_{min} increases.**
- **Two methods are consistent.**

Y. Yan, Y. Katsumura, M. Lin, Y. Muroya, S. Yamashita, K. Hata, J. Meesungnoen, and J.-P. Jay-Gerin, *Can. J. Chem.*, 88: 1026–1033 (2010)

Ultrafast Pulse Radiolysis System
for HTHP experiment

Re-evaluation of $G(e^-_{aq})$ at ps time



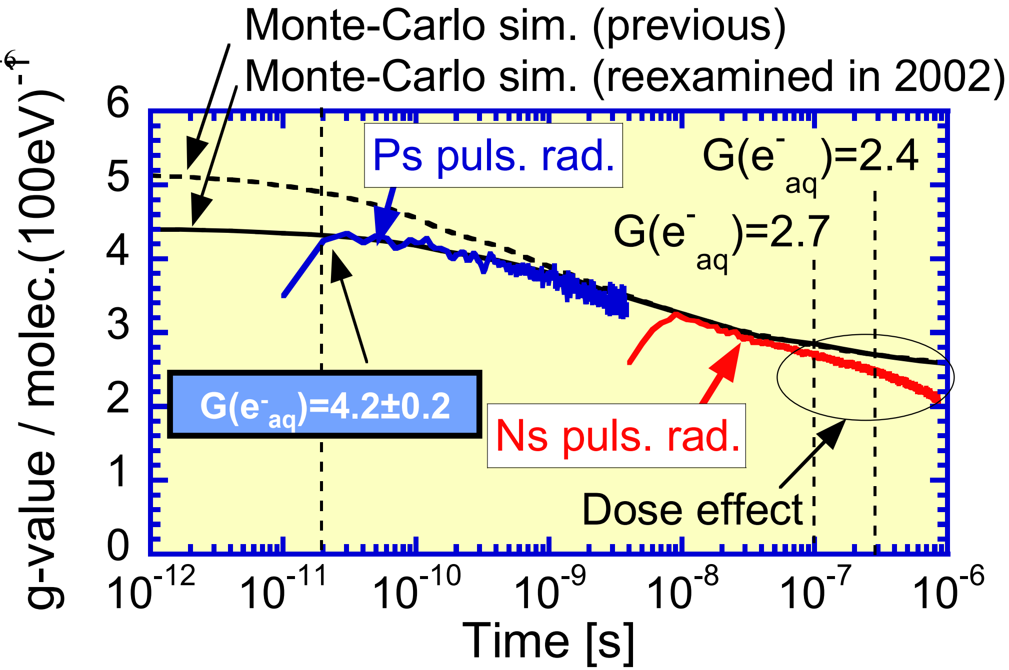
Y. Muroya, M. Lin, G. Wu, H. Iijima, K. Yoshii, T. Ueda, Y. Katsumura; *Radiat. Phys. Chem.*, 72, 169-172 (2005)

[1] Y. Muroya, J-P. Jay-Gerin, Y. Katsumura *et al.*; *Can. J. Chem.*, 80 1367 (2002)

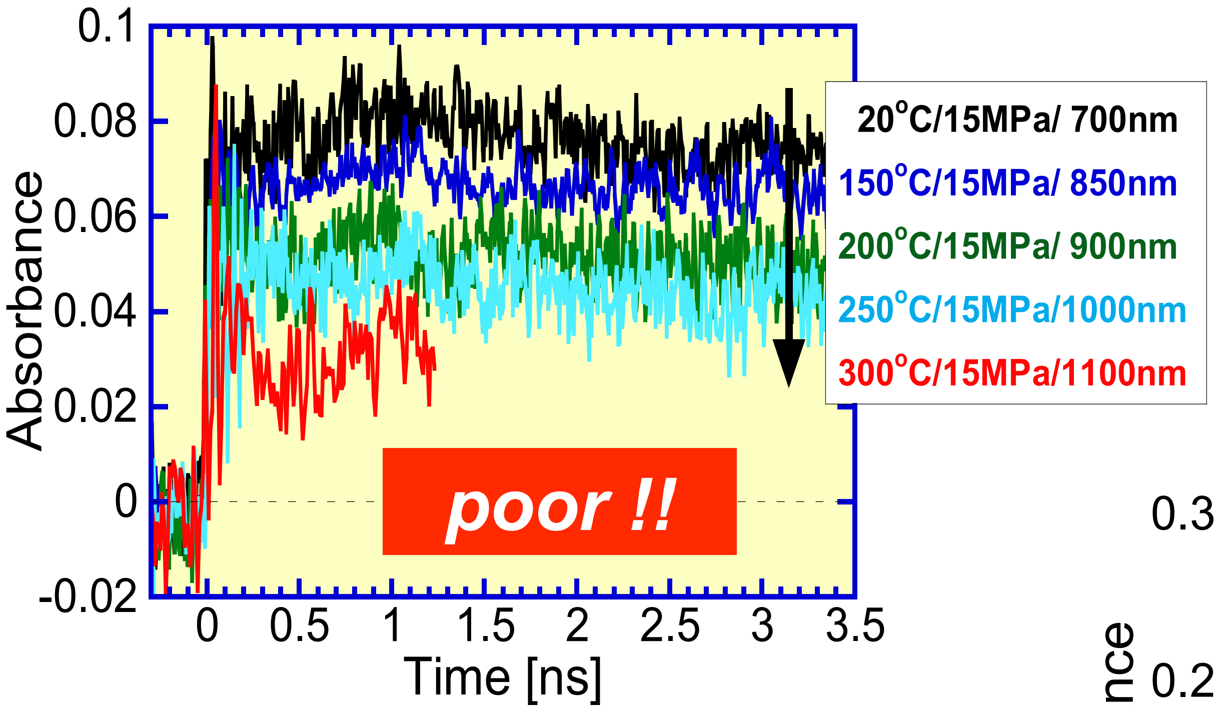
$G(e_{aq}^-)$ measured at 795 & 633nm

Pump & Probe at 795nm, 5 & 18 mm cell

Kinetic measurement at 633nm with a He-Ne laser



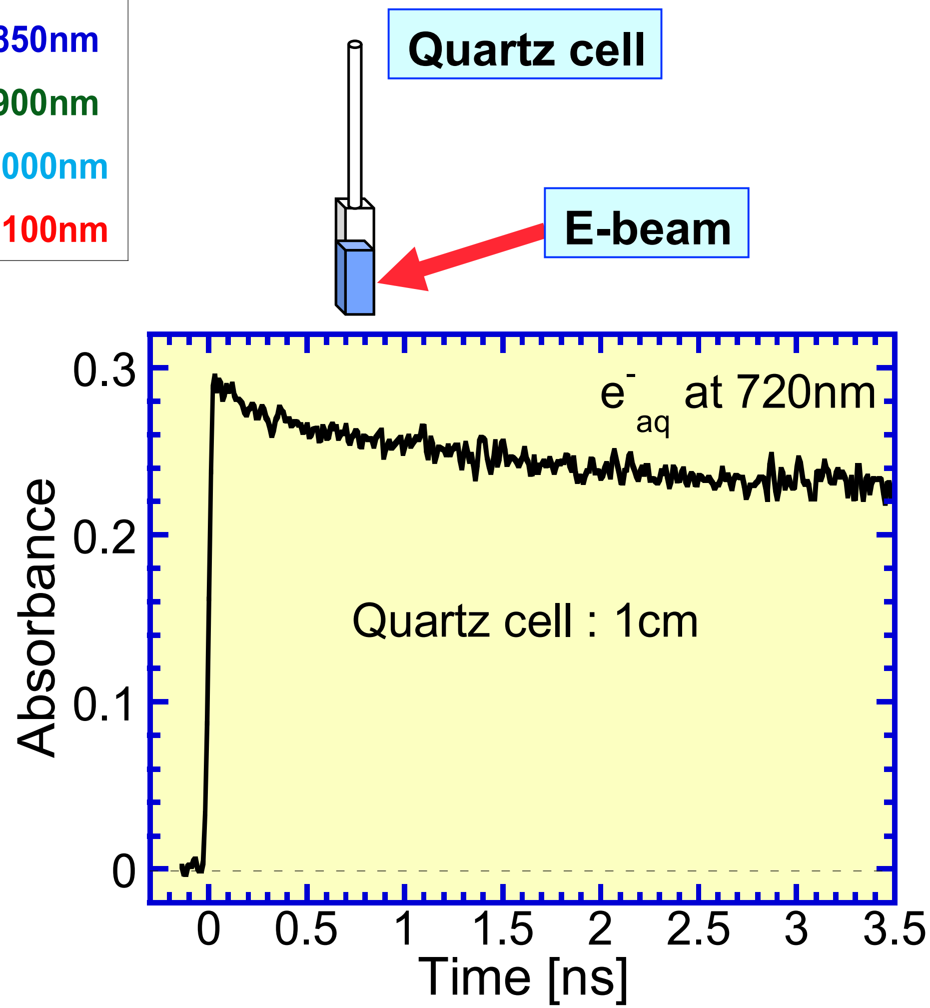
First HTHP ps pulse radiolysis (in 2008)



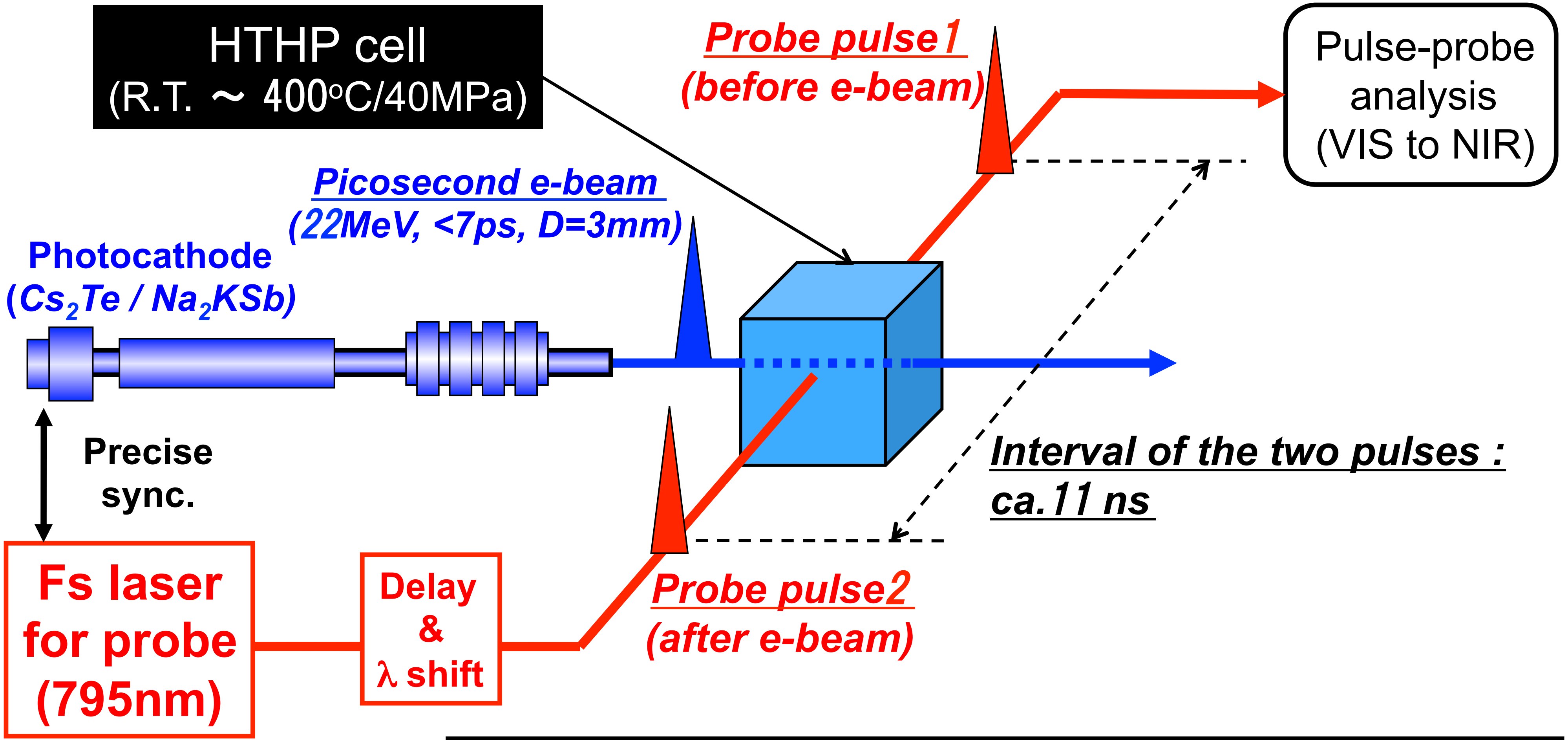
e^-_{aq} at elevated temperatures
(HTHP cell)

REQUIREMENTS
(1) Increase of charge
(2) Improve the S/N ratio

e^-_{aq} at room temperature
(1cm quartz cell)



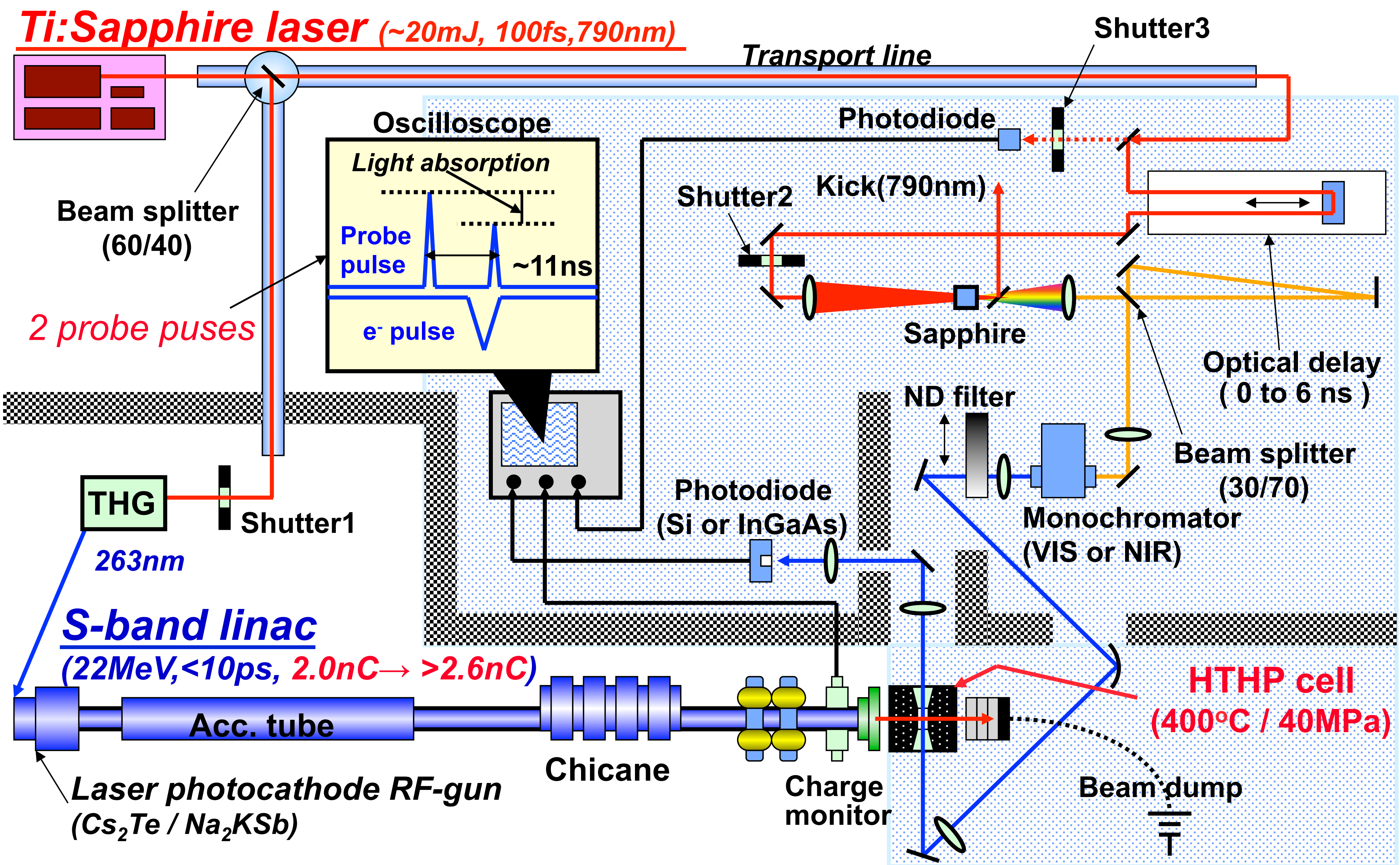
HTHP ultrafast pulse radiolysis system (2009)



Improvement

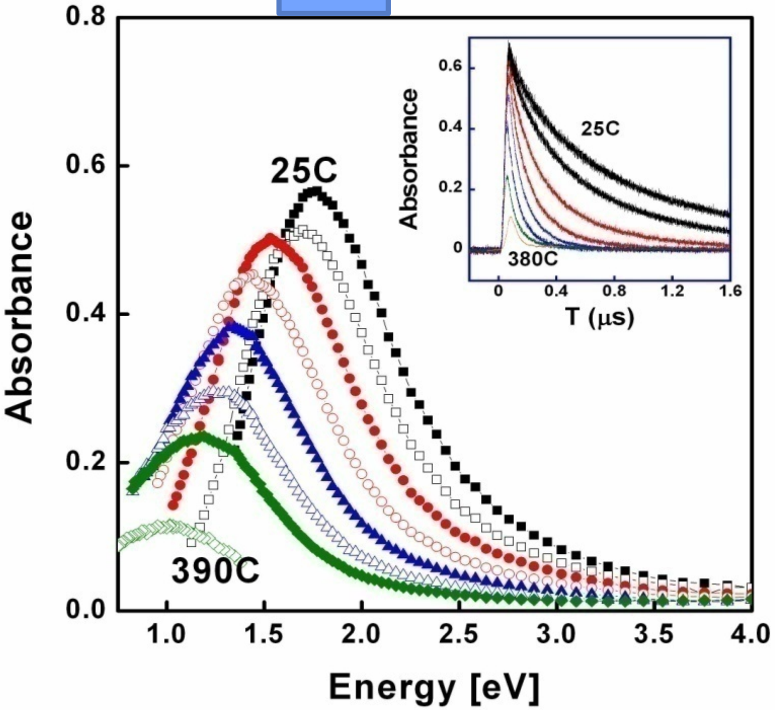
- *Charge: 2.0nC → 2.6nC/bunch*
- *A double probe-pulses with 11 ns interval for suppression of the relative instability between I_0 and I*

HTHP ultrafast pulse radiolysis system (2009)

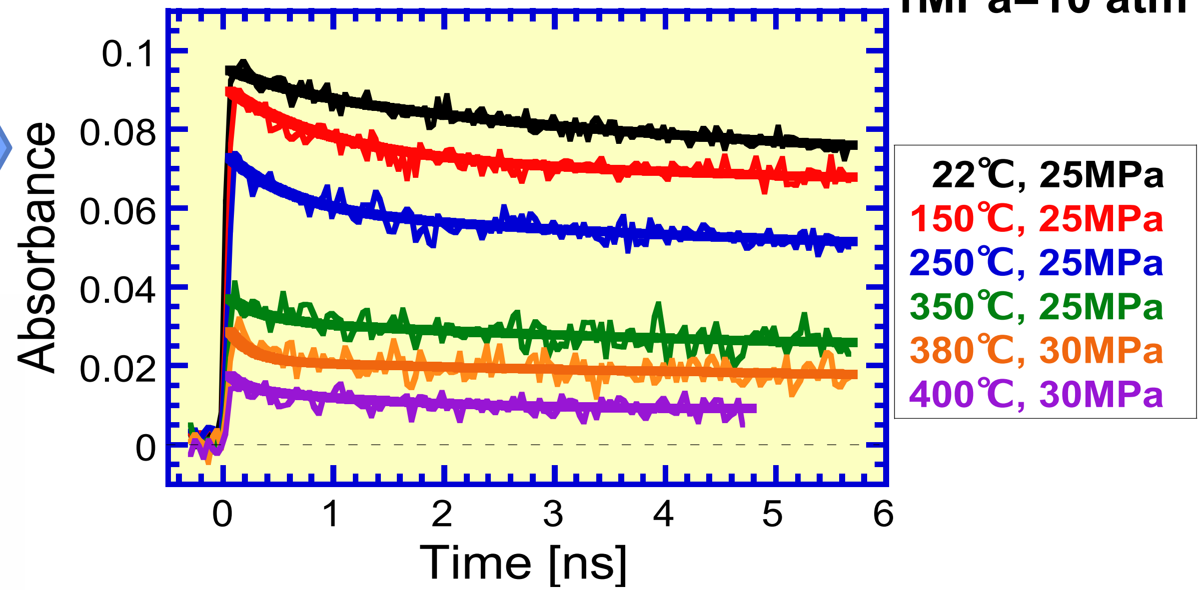


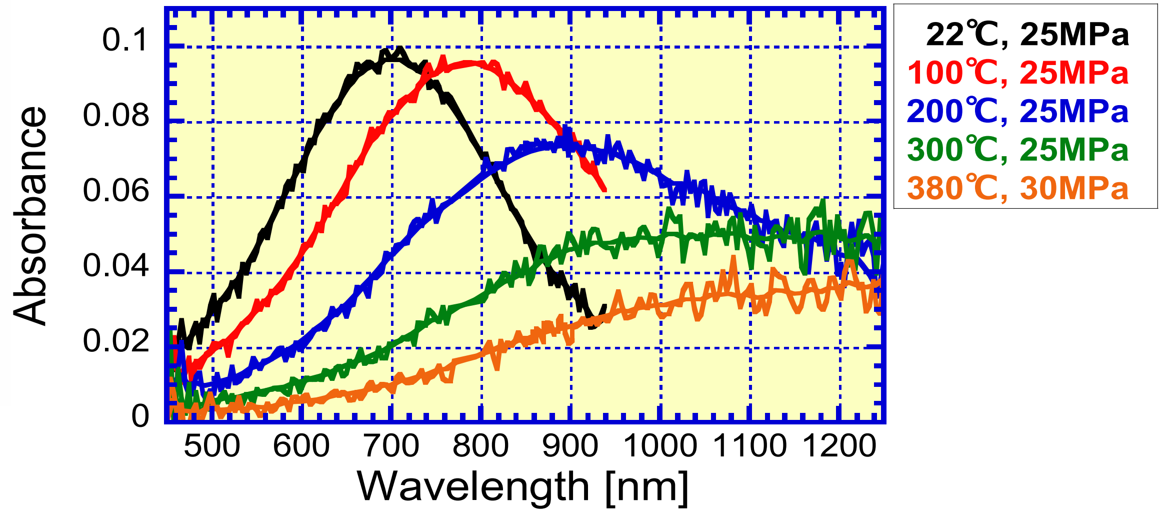
Measurement from ns to ps (2009)

Time resolution 200 times higher

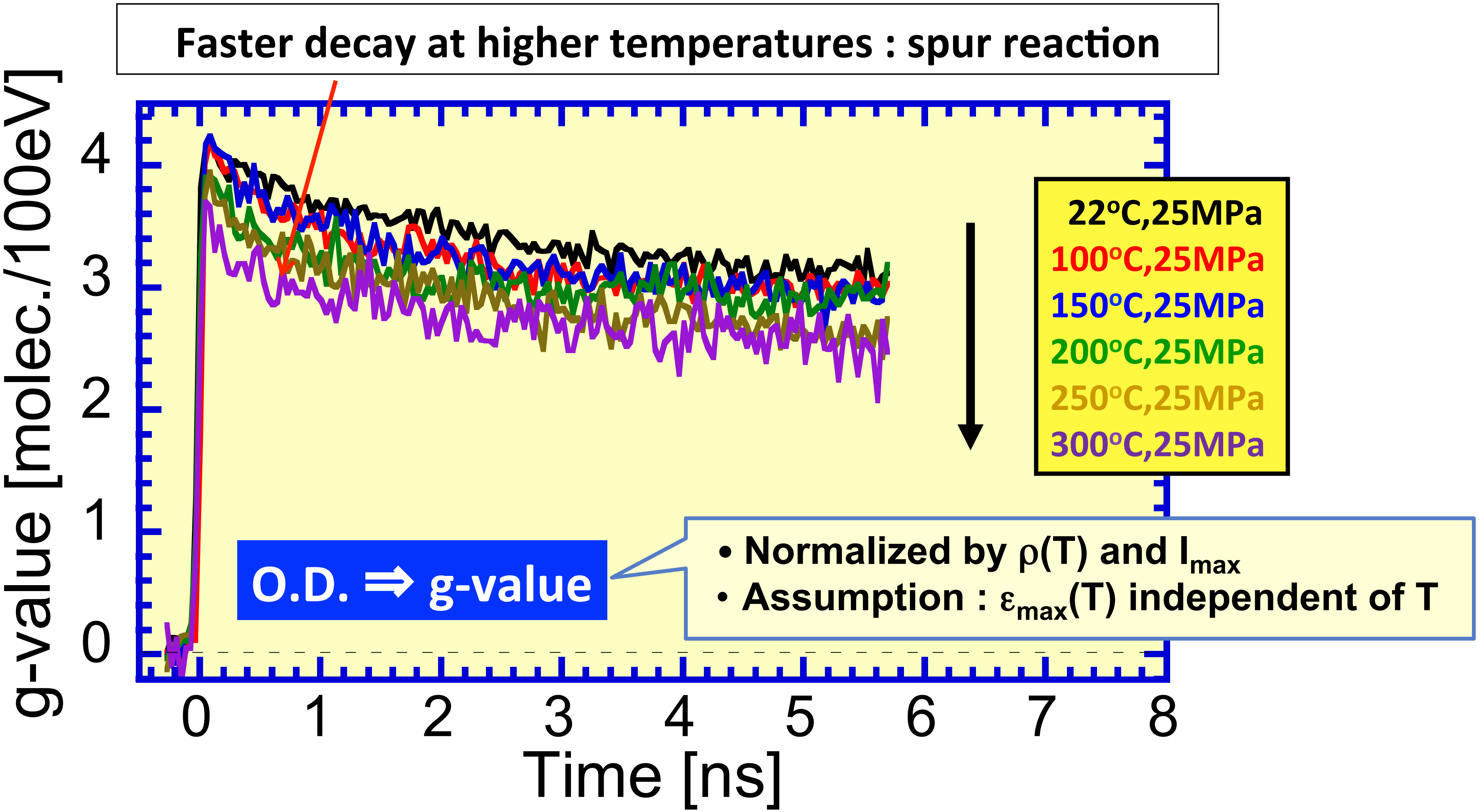


1MPa=10 atm



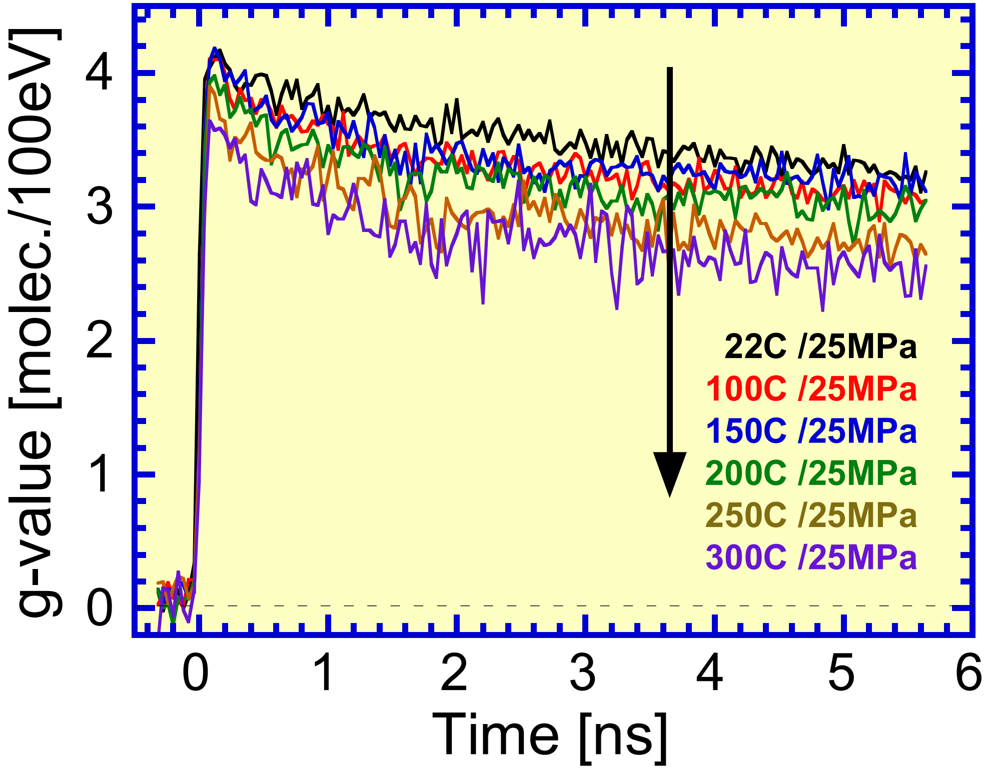


Time dependent g-values of e^-_{aq}

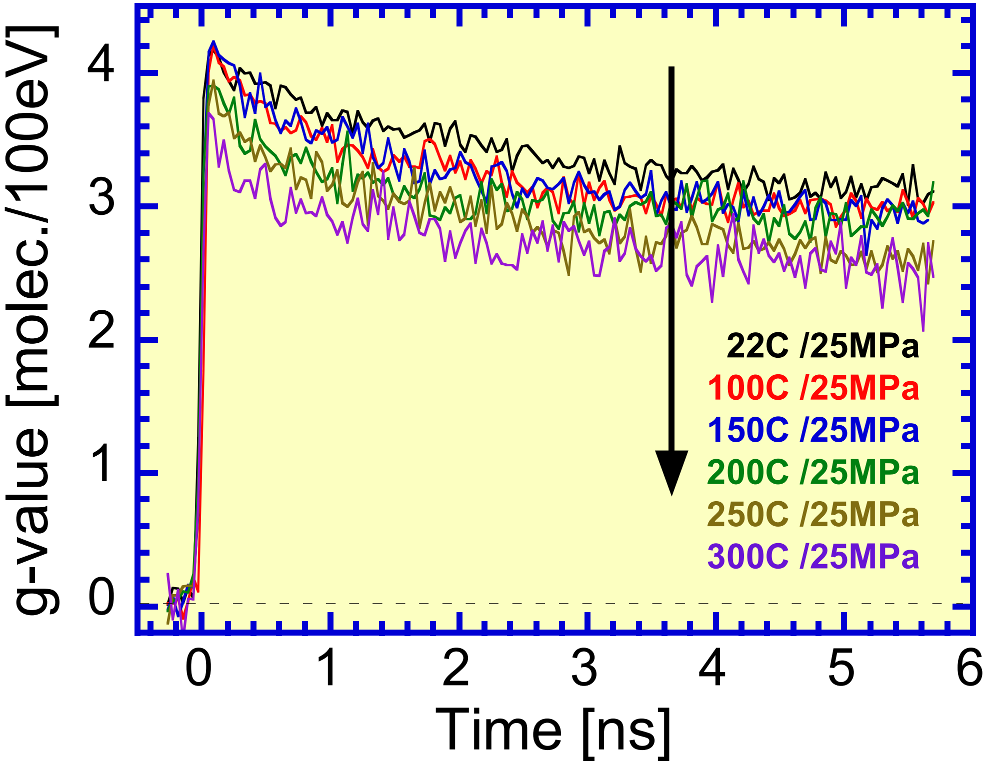


Isotope effect e^-_{aq} in D_2O and H_2O

In D_2O



In H_2O



- **The decay in a few ns slightly slower in D_2O than H_2O (ca.5%)**
  - **- Tendency is similar to previous reports**

(Chenovitz 1988, Jonah 1990, Bartels 2001)

Temperature dependent decay of e^-_{aq}

Spur reactions	rate const. /10^{10} $M^{-1}s^{-1}$
$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-$	0.54
$e_{aq}^- + OH \rightarrow OH^-$	3.0
$e_{aq}^- + H_3O^+ \rightarrow H + H_2O$	2.3
$e_{aq}^- + H \rightarrow H_2 + OH^-$	2.5
$H + H \rightarrow H_2$	1.3
$OH + OH \rightarrow H_2O_2$	0.53
$OH + H \rightarrow H_2O$	3.2
$H_3O^+ + OH^- \rightarrow 2H_2O$	14.3

Spur reactions for decreasing $g(e^-_{aq})$

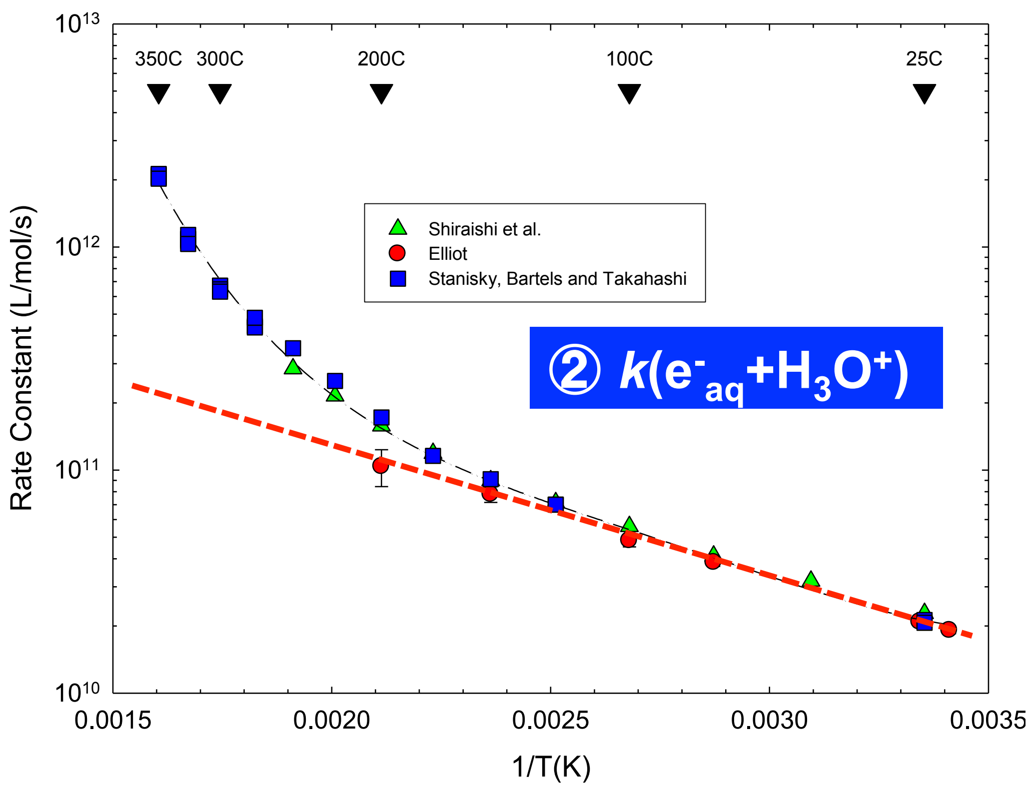
$$e^-_{aq} + OH \rightarrow OH^- \quad (1)$$

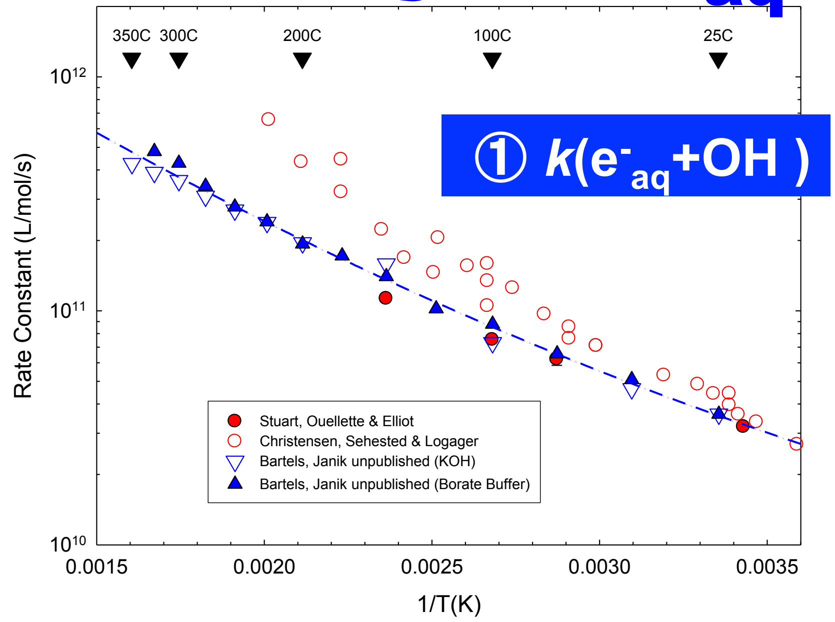
$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \quad (2)$$

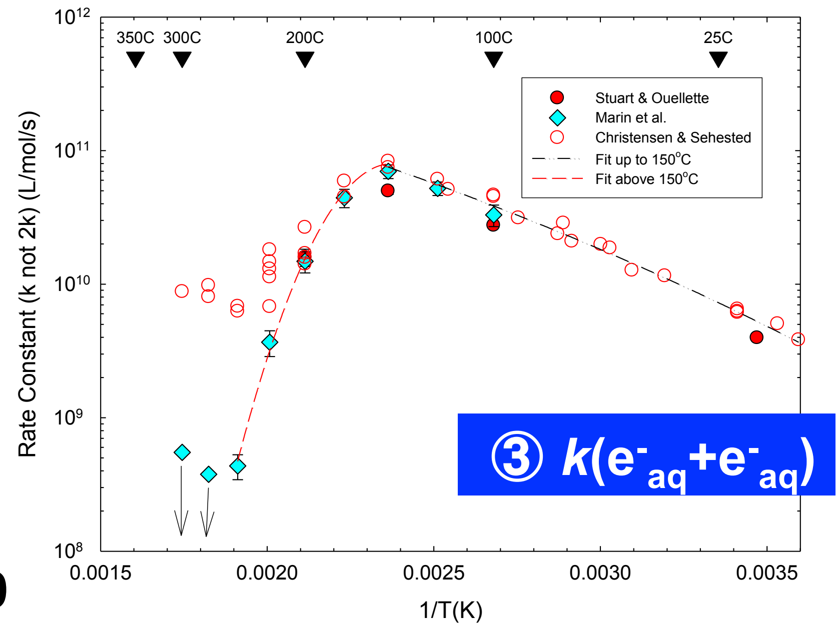
$$e^-_{aq} + e^-_{aq} + 2H_2O \rightarrow H_2 + 2OH^- \quad (3)$$

Temperature dependent decay of e^-_{aq}

k(e^-_{aq} + H_3O^+) is accelerated significantly at elevated temperatures (*k*> 10^{12})







A.J.Elliot, D.M. Bartels et al, AECL report, 2009

Temperature dependent decay of e^-_{aq}

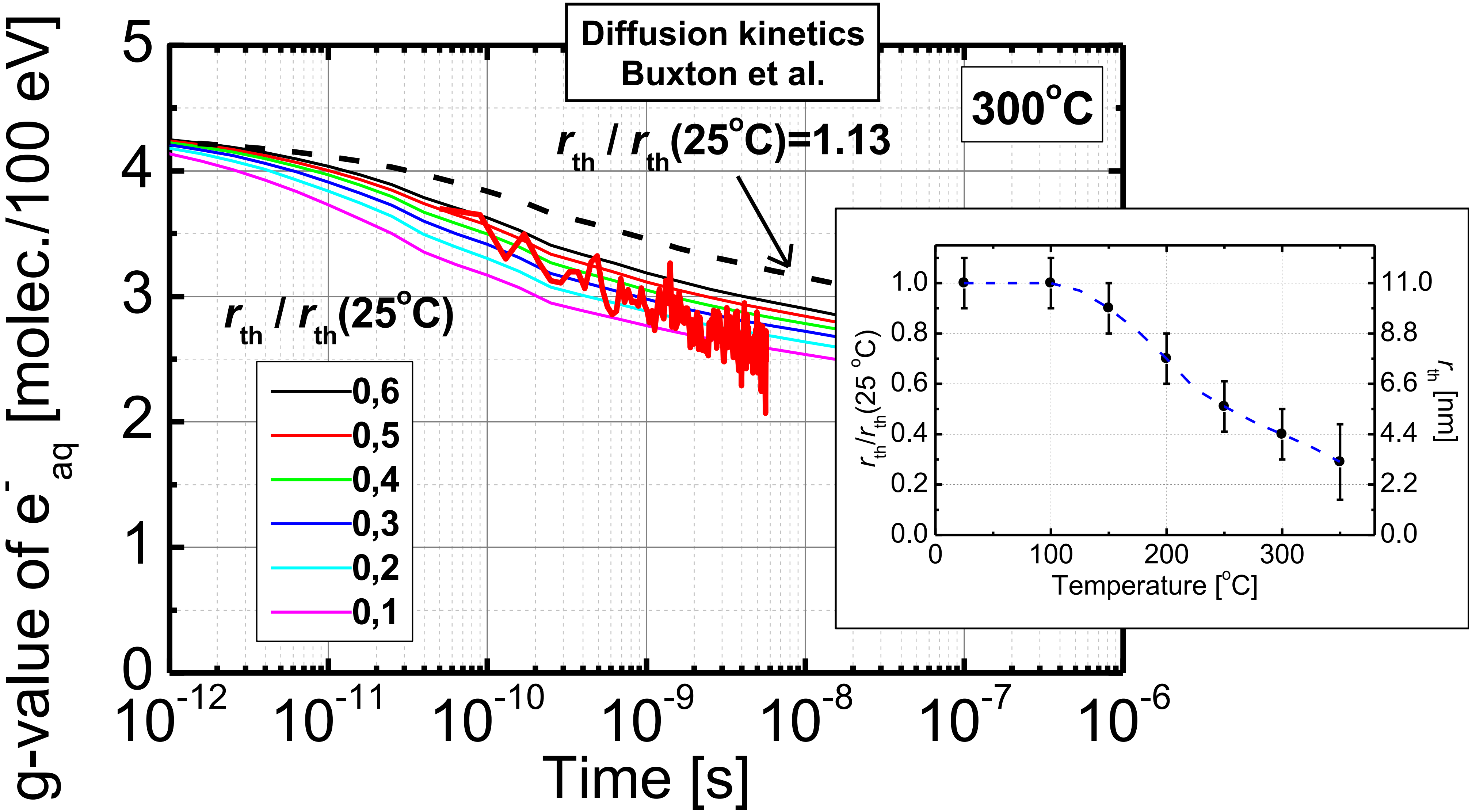
Possible reactions for decreasing $g(e^-_{aq})$

$$e^-_{aq} + OH \rightarrow OH^- \quad (1)$$
$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \quad (2)$$
$$e^-_{aq} + e^-_{aq} + 2H_2O \rightarrow H_2 + 2OH^- \quad (3)$$

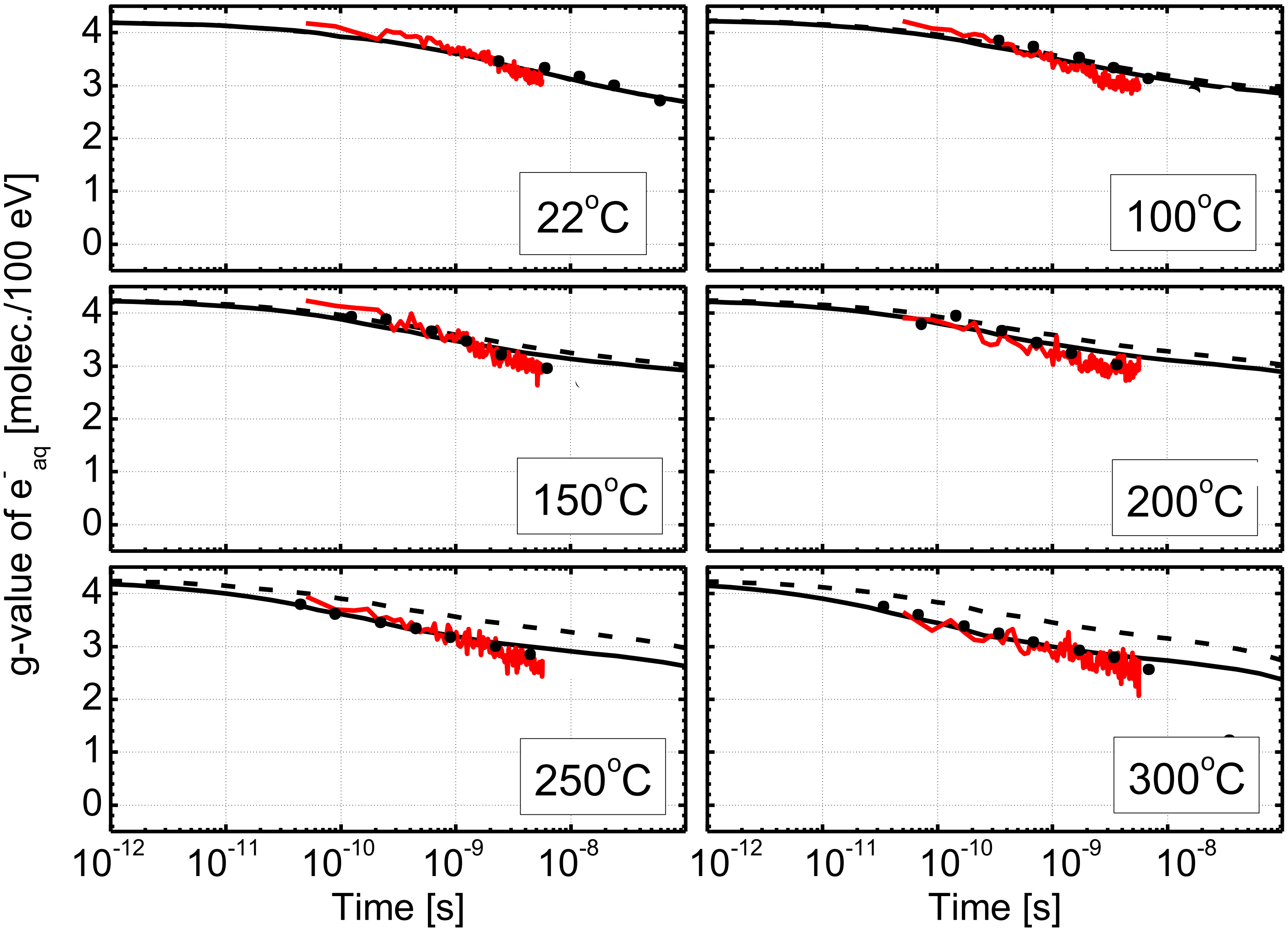
The reaction (2) plays an important role

→ **Monte Carlo calculation in collaboration with Sherbrooke Gr. (Prof. Jay-Gerin)**

Thermalization distance of e^-_{aq} at 300 °C

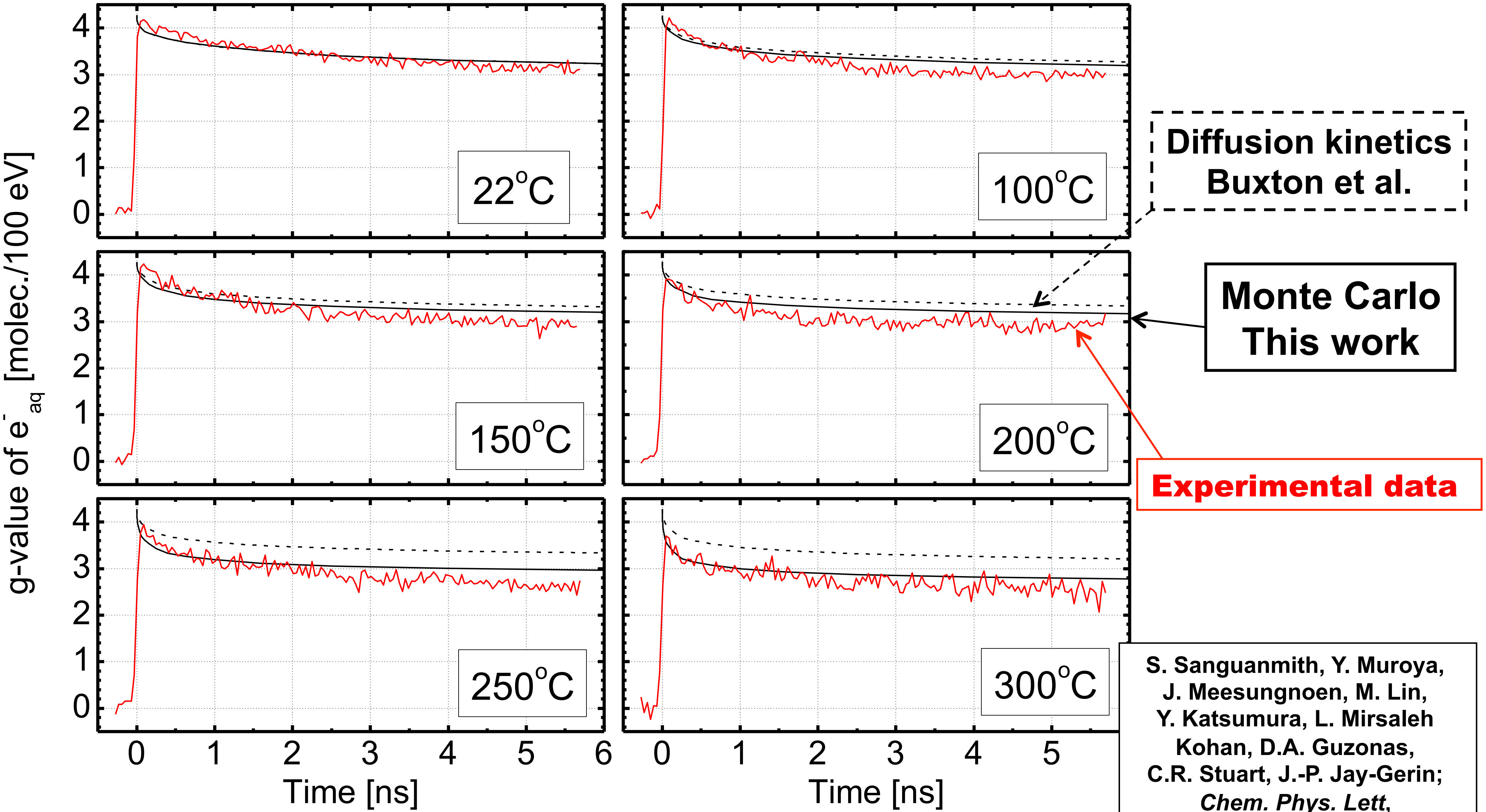


Time dependent $g(e^-_{aq})$ in H_2O up to 300°C; comparison with Monte-Carlo



● Scavenging experiment with MV^{2+}

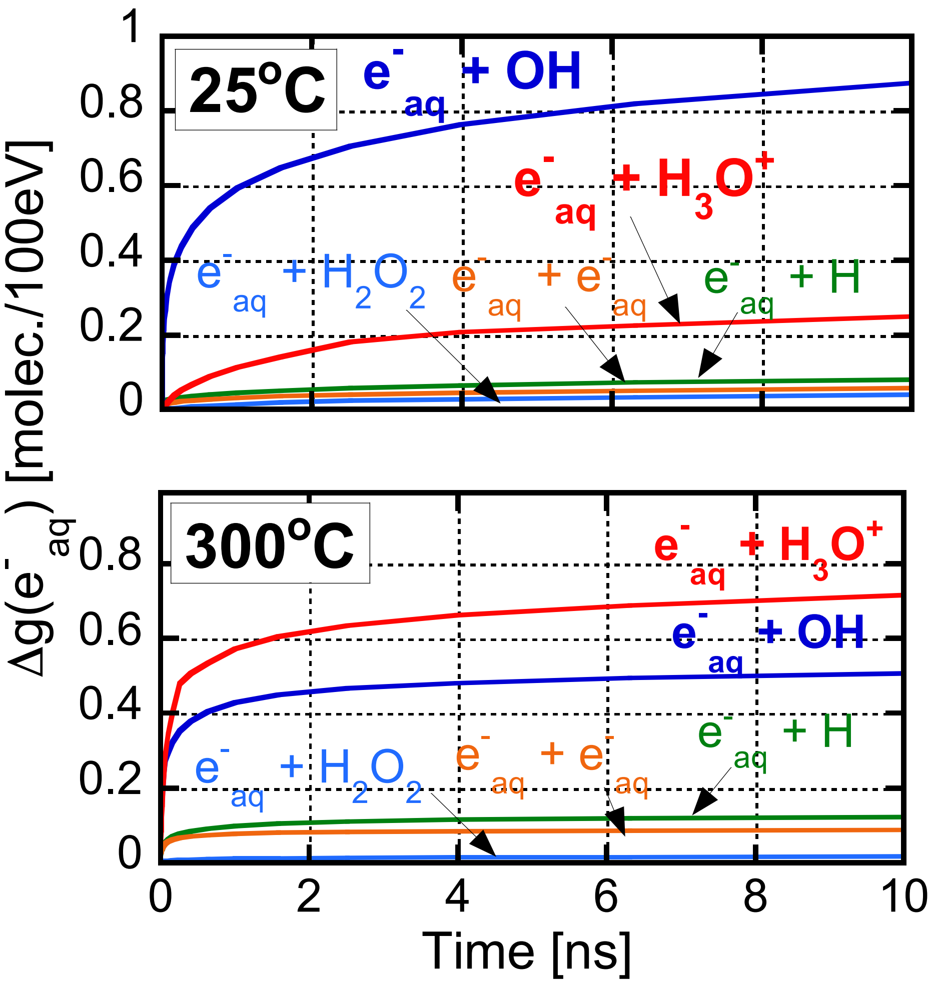
Time dependent g(e^-_{aq}) in H_2O up to 300°C; comparison with Monte-Carlo



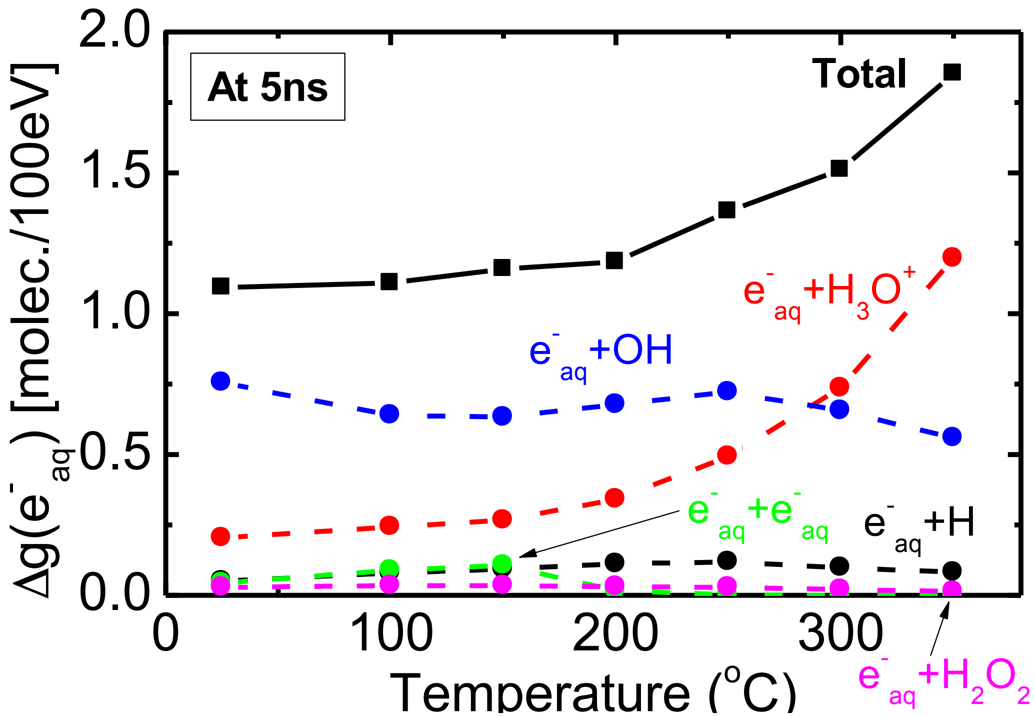
S. Sanguanmith, Y. Muroya, J. Meesungnoen, M. Lin, Y. Katsumura, L. Mirsaleh Kohan, D.A. Guzonas, C.R. Stuart, J.-P. Jay-Gerin; *Chem. Phys. Lett*, 508, 224 (2011)

Contribution of spur reactions

Time dependence

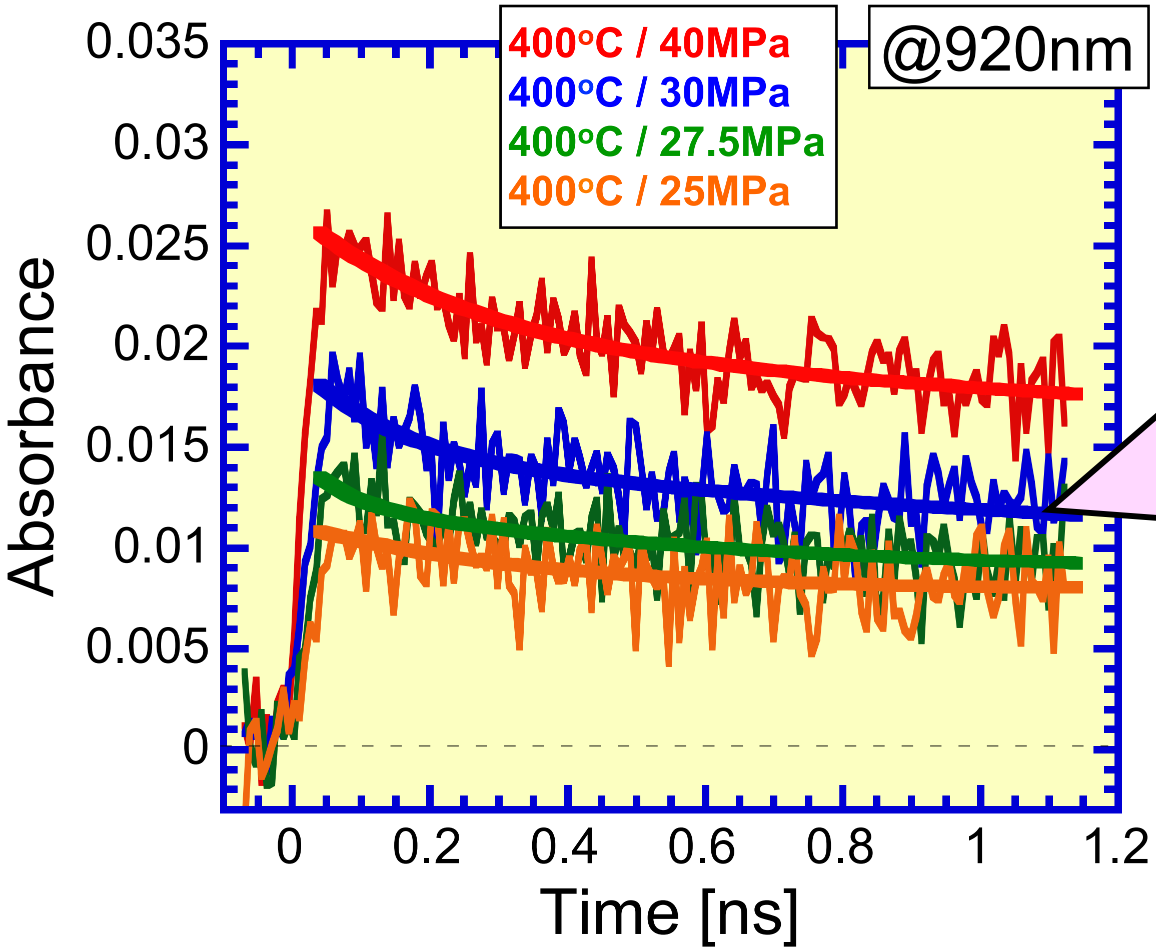


Relative contribution



Pressure (density) dependence at 400°C in SCW

Pres.: 40 → 25 [MPa]
⇒ ρ: 0.58 → 0.18 [g/cc]



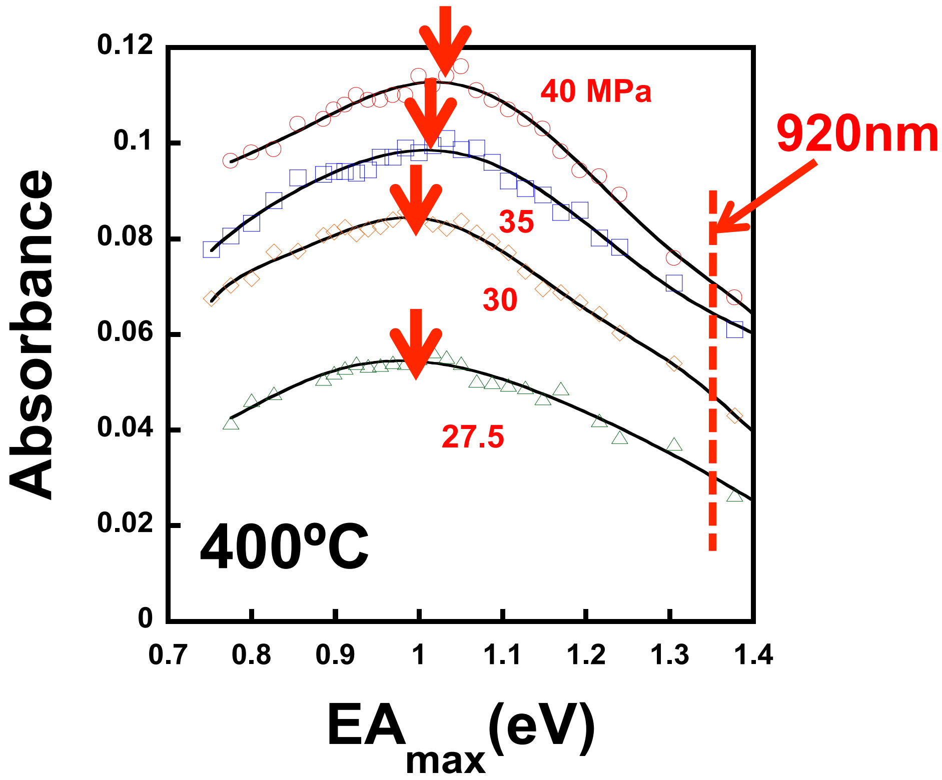
Long lived components after 1ns

40 MPa : 75%
30 MPa : 71%
27.5MPa : 69%
25 MPa : 71%

Fast component is almost independent of pressure

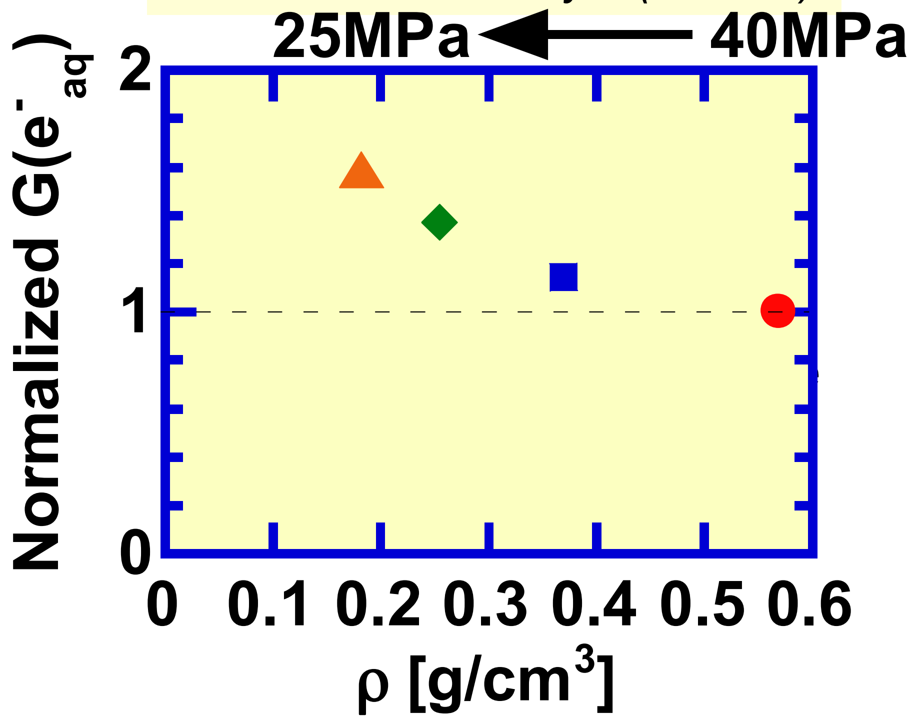
Density effects on the G(60ps) at 400°C

Absorption spectra at 400°C at different P obtained by *nanosecond pulse radiolysis*



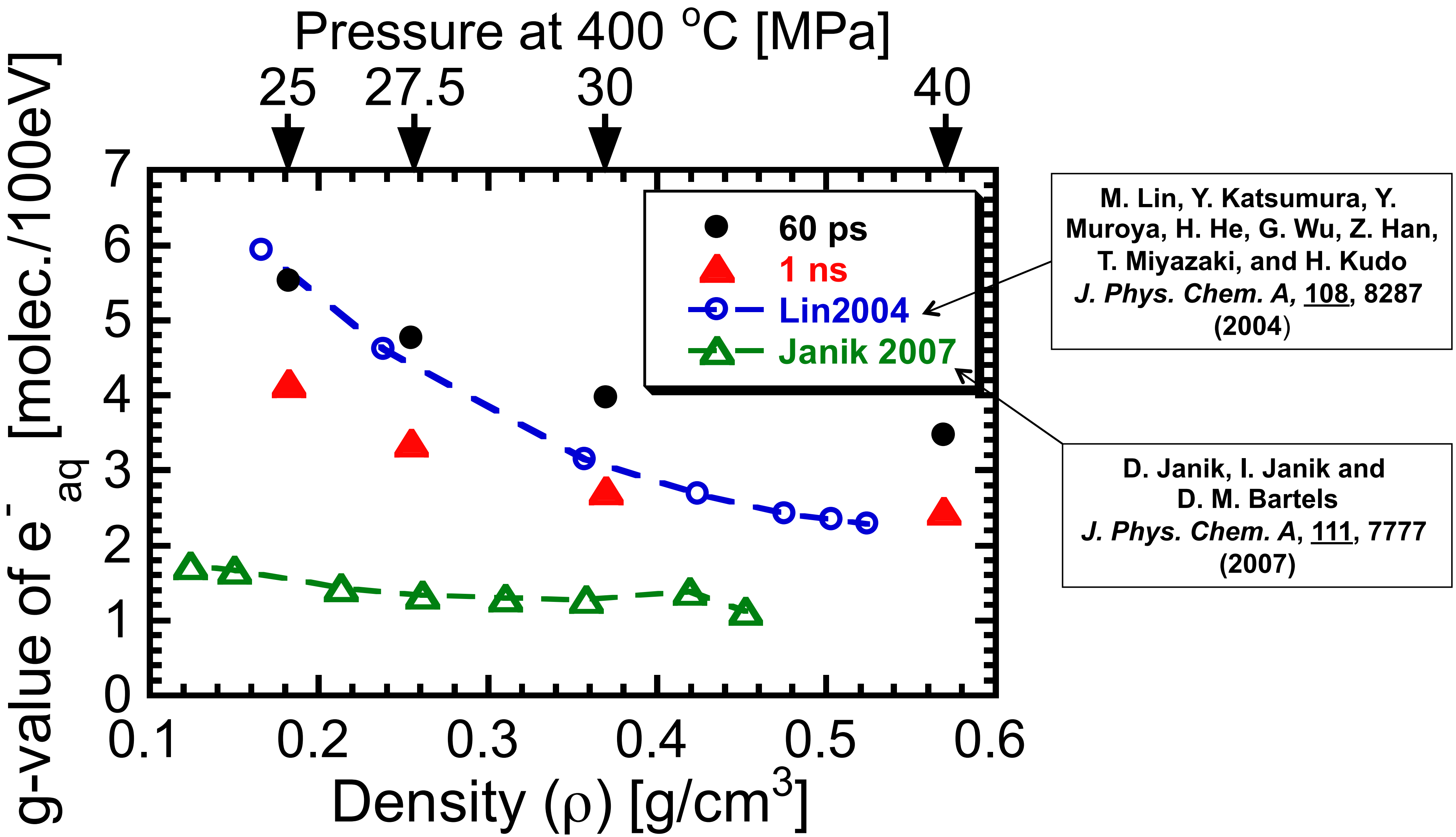
Relative G(e^-_{aq}) at 60ps vs. density of water

Note : ε_{max} independent on P normalized by G(40MPa)



- ***Picosecond yield showed strong density dependence***
  - Consistent with nanosecond exp. using scavenger

Pressure dependence of $g(e^-_{aq})$ in D_2O at 400°C



Summary

We have investigated pulse radiolysis study on water and alcohols at elevated temperatures up to 400°C.

(1) Solvated electrons in alcohols at elevated temperatures

(2) Observation of energy minimum for the absorption peak of e^-_{sol} at fixed density

(3) Ultrafast pulse radiolysis study at HTHP

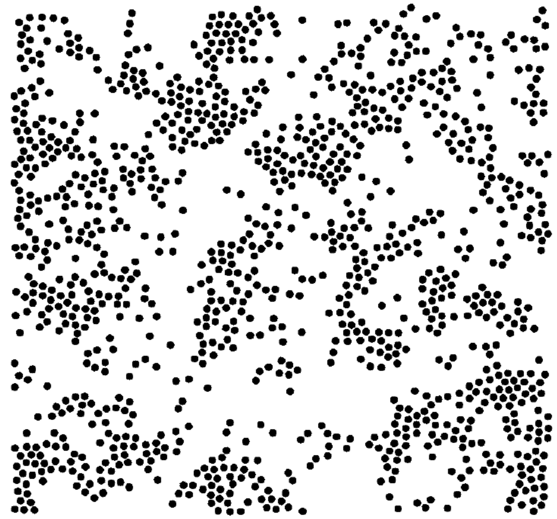
1. Optical spectra, fast spur reaction kinetics
2. Isotope effects in H_2O and D_2O exists, but small.
3. Monte Carlo simulation
4. Initial yield of e^-_{aq} strongly depends on pressure (density) at supercritical state at 400°C
5. Good agreement between scavenging evaluation and direct observation

Future perspectives

Higher *temperatures* above 400, 500 and 600 °C
Higher *pressures* above 40 MPa -> GPa
Higher *time resolution*: ps -> fs

Supercritical water

- **lower hydrogen bonds**
- **clustering structure**
- **beyond the frame of the traditional water radiolysis**



Configurational snapshot of a pure 2D Lennard-Jones SCF at $T_r \approx 1.17$ and $r_r \approx 0.86$.
S. C. Tucker, et al. *JPC B* 1998, *102,* 2437

-> new approaches
Quantum Calculation, Molecular Dynamics

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