Radiation induced reactions of liquids in ps time range and in supercritical conditions

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Topics

(I) Ultra-fast pulse radiolysis system at NERL

(II)Pulse radiolysis of supercritical water and alcohols

Acknowledgement

Coworkers

Linac Division (Univ. of Tokyo)

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MEXT (Ministry of Education, Culture, Sports Science and Technology)

"Fundamental R&D program on water chemistry of supercritical pressure water under radiation field"

Construction of
a ultra-fast pulse radiolysis system
and
its application

Ultra-fast pulse radiolysis system

Projects;

BNL (LEAF), Univ. of Pari-Sud (Elyse),

Univ. of Tokyo, Sumitomo Heavy Industries, Waseda Univ., Osaka Univ.

Shanghai Institute of Applied Physics, Bhabha Atomic Res. Centre (approved)

$\leq$ **~ps pump-and-probe;**

Laser photocathode rf-gun & ***fs laser***

Photochemistry

Time resolution in laser photolysis

pico second $\rightarrow$ femto second

no velocity difference in sample

Radiation chemistry

Time resolution in pulse radiolysis

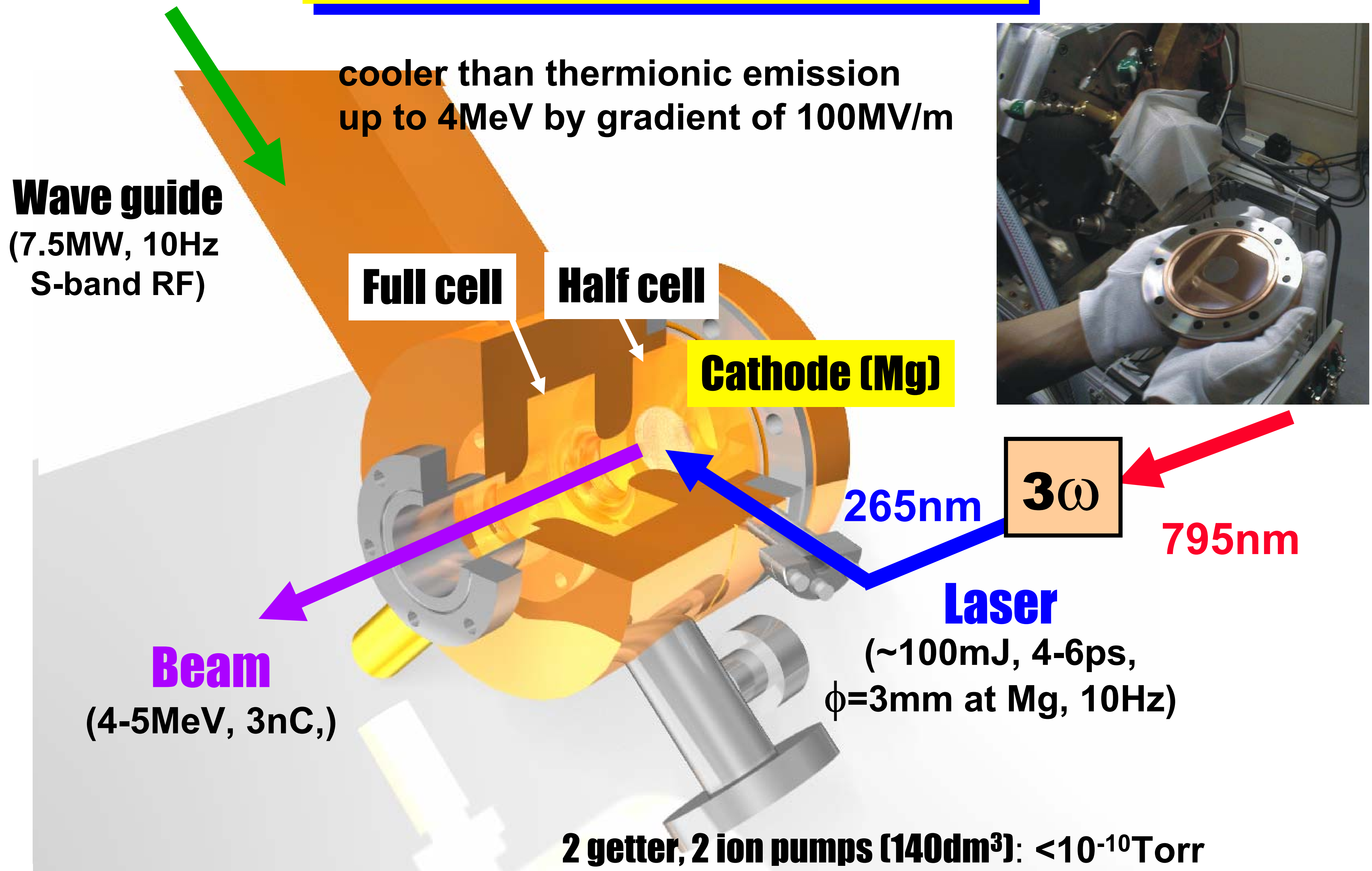
Velocity difference in sample

relativistic electron: ***c***

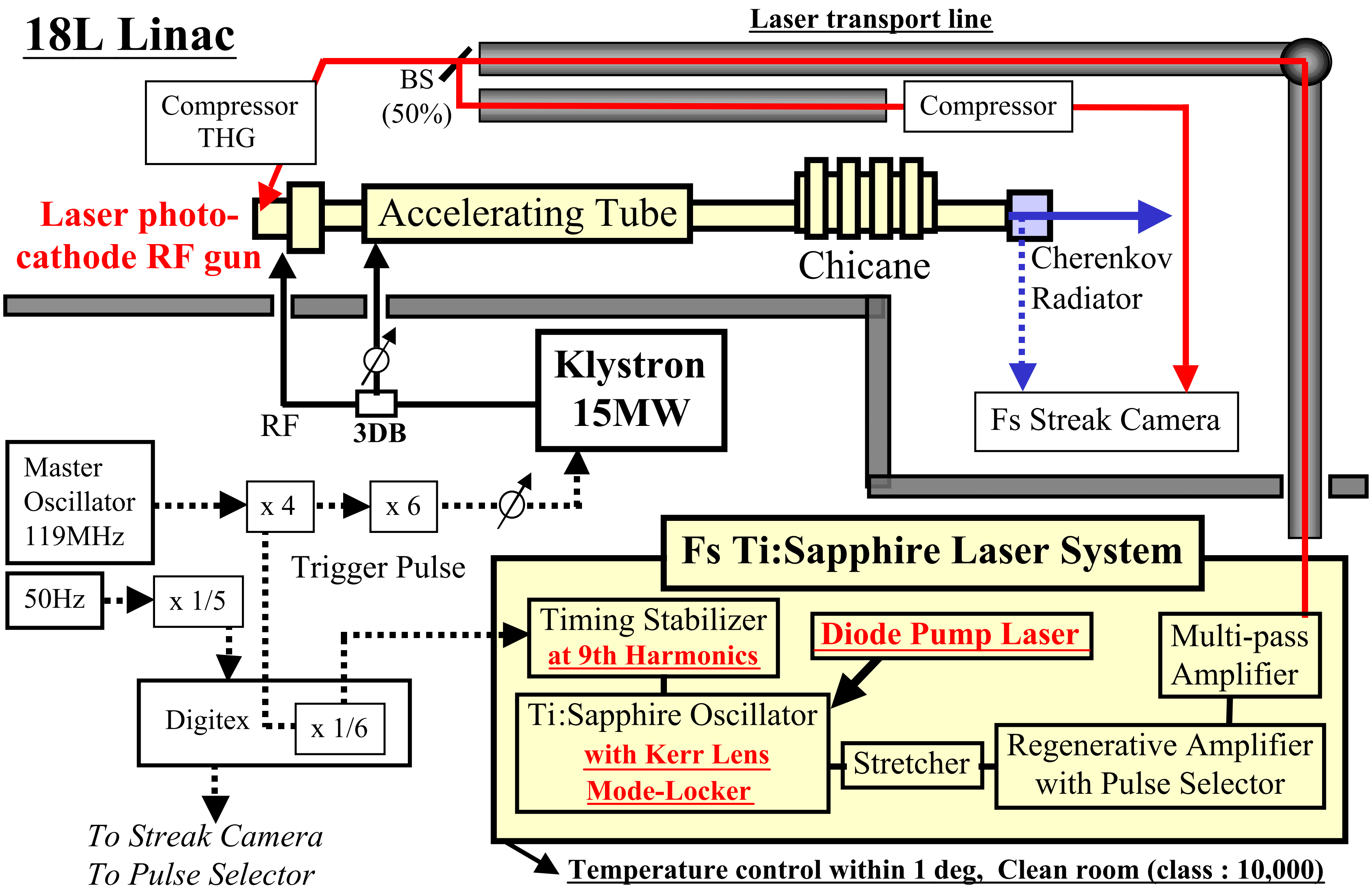
laser pulse: ***c/n*** (n: reflective index)

1 mm H_2O = 1 ps

Photocathode RF-Gun

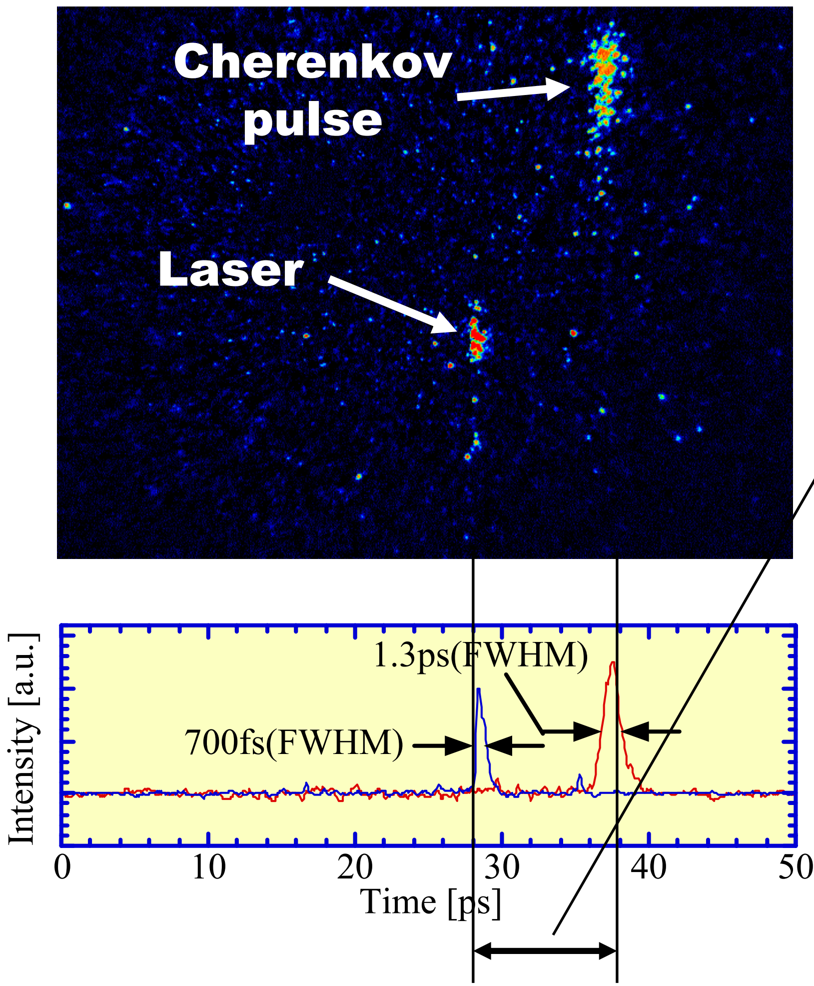


Ultrafast Pulse Radiolysis System at NERL

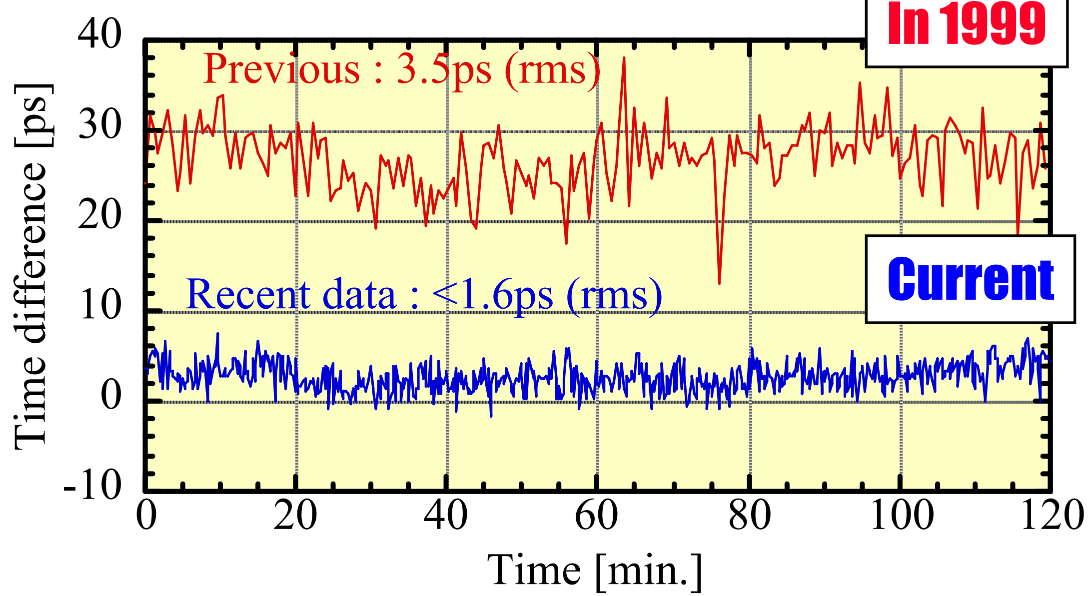


Precise synchronization

Synchronization between electron beam and laser measured by FESCA



Synchronization experiment



Improvement

***pulse to pulse jitter*: <500fs(rms)**

- **Stabilized RFs ← passive mode-lock**
- **Simulation by PARMERA : 330fs(rms)**

long time drift

(1) Cooling system for ACC: *ΔT < 0.01K*
(2) Temp. control in rooms: *ΔT < 0.5K*
(3) N_2 gas in 50m transport line ← vacuum

Time resolution vs. cell length

Growth of hydrated electron at 700 nm

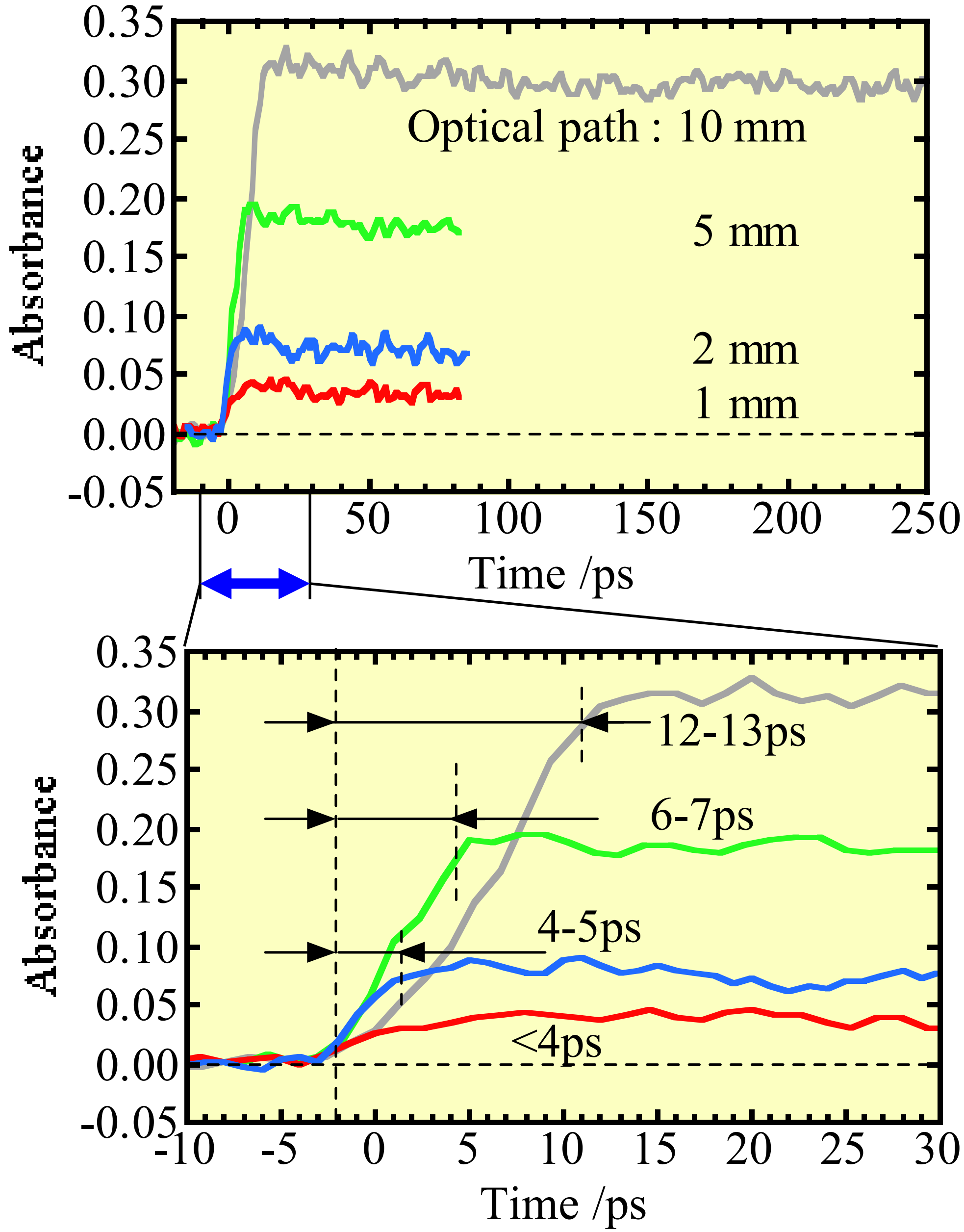
l /mm	10	5	2	1
O.D. S/N	0.32 15	0.19 10	0.08 5	0.04 3
Dose	40Gy	47Gy	50Gy	50Gy
Time resol. /ps	12-13ps measured 12.2ps calculated	6-7ps 7.2ps	4-5ps 5.2ps	<4ps 3.2ps

Time resolution: δ_{total}

$\delta_{total} = \delta_{diff} + (\delta_E^2 + \delta_L^2 + \delta_{sync}^2)^{1/2}$

dominant factor: δ_{diff}

← refractive index n=1.33

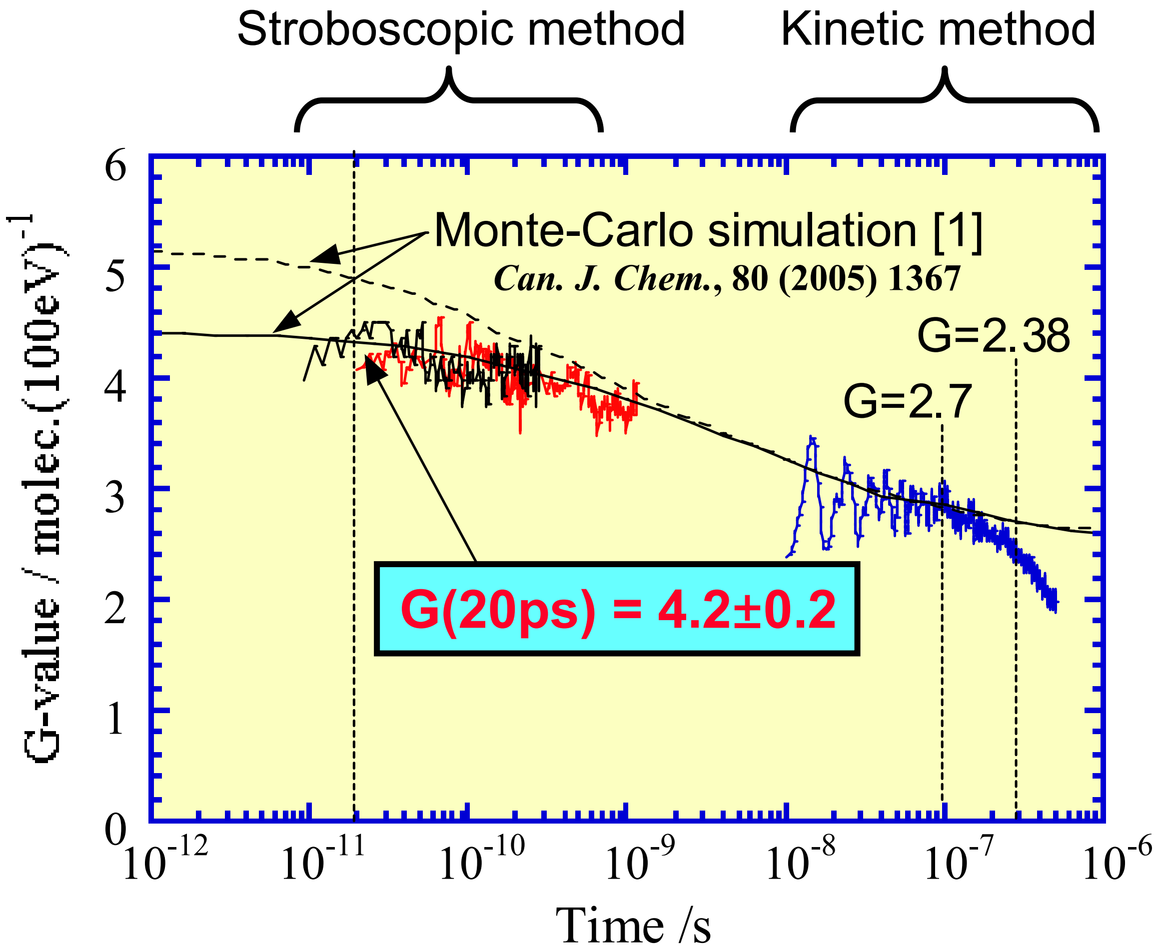


Re-evaluation of $G(e^-_{aq})$ at ps time

Primary G=2.7; *established*
reported Initial G : 4.0~4.8

		G (time)
1970	Tront	---
1973	Tront	4.0 (30ps)
		4.0 (30ps)
1973	ANL	4.1 (200ps)
1975	Tront	4.6 (dry)
1976	ANL	4.6 (100ps) 4.1 (1ns)
1985	Hokkaido	4.8 (30ps)
1996	NDRL & ANL	4.8 (100ps)
1999	ANL	4.0 (time zero)

$G(e_{aq}^-)$ measured at 795 & 633nm
Pump & Probe at 795nm
Kinetic measurement at 633nm with a He-Ne laser

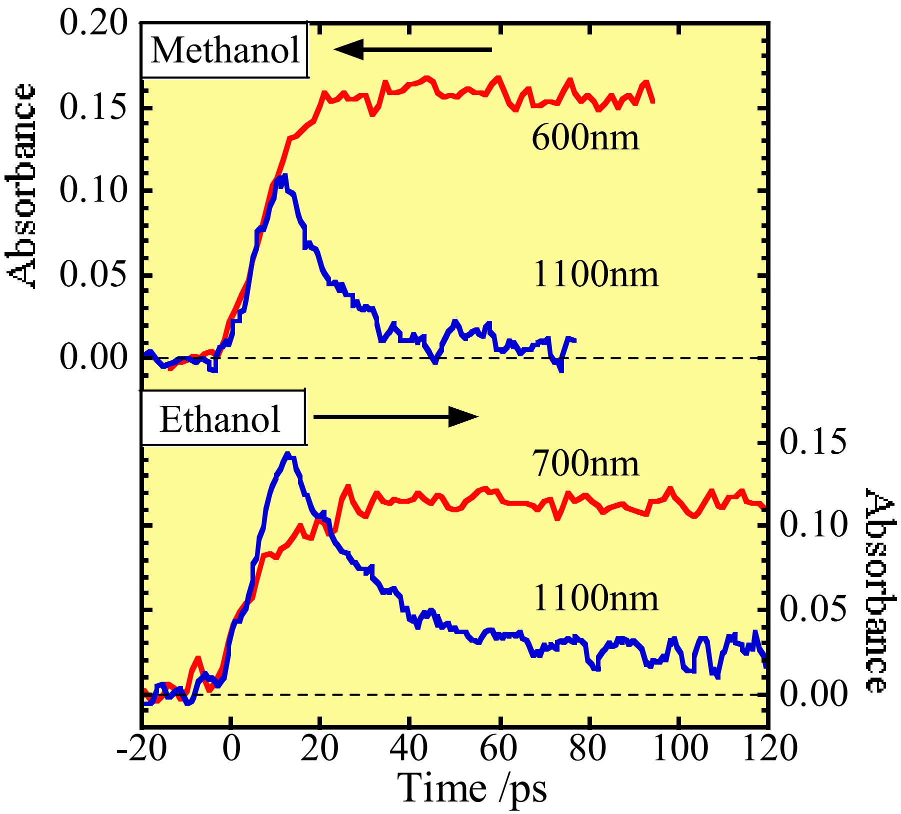


Y. Muroya, M. Lin, G. Wu, H. Iijima, K. Yoshii, T. Ueda, Y. Katsumura; *Radiat. Phys. Chem.*, **72,** 169-172 (2005)

G of solvated electron in alcohols

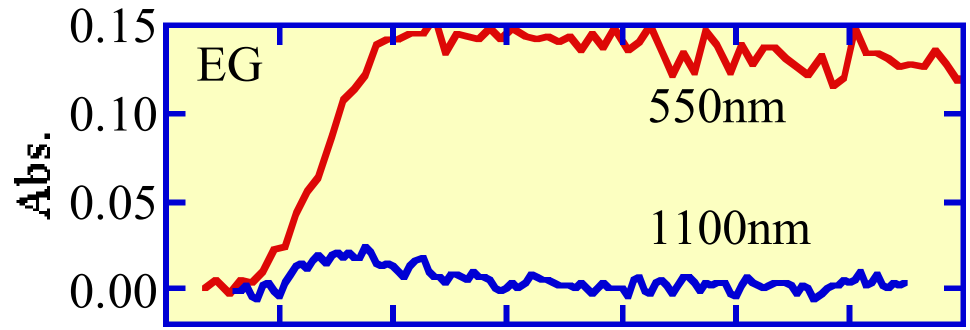
Procedure of G-value determination

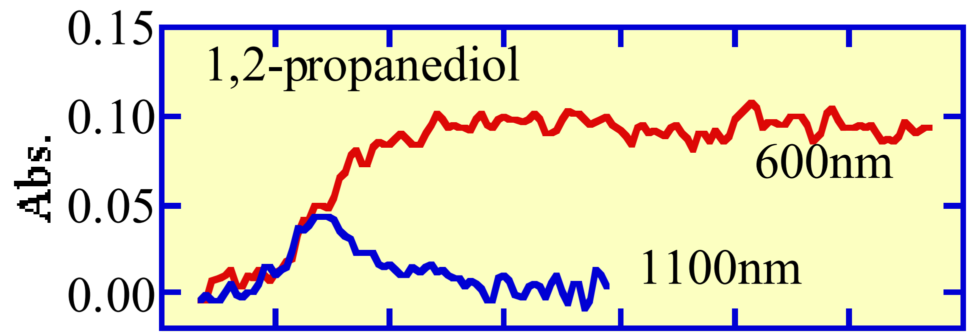
(1) H_2O measurement at 700nm
(2) Dose calculation
(3) Alcohols measurement at λ_{max}



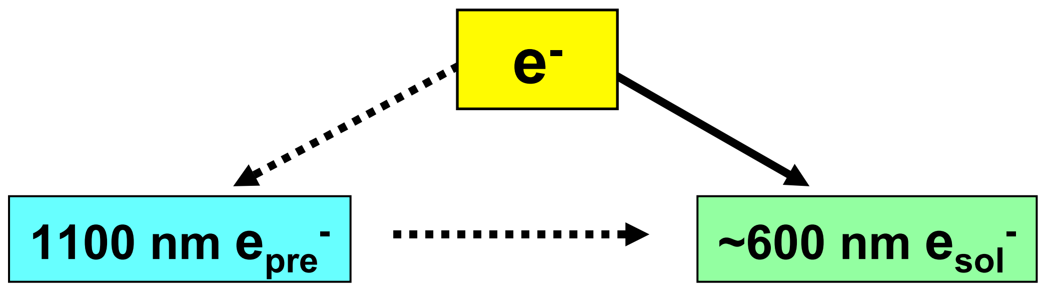
Dose : 37Gy

G(MeOH) = 4.1 @50ps
G(EtOH) = 3.6 @50ps





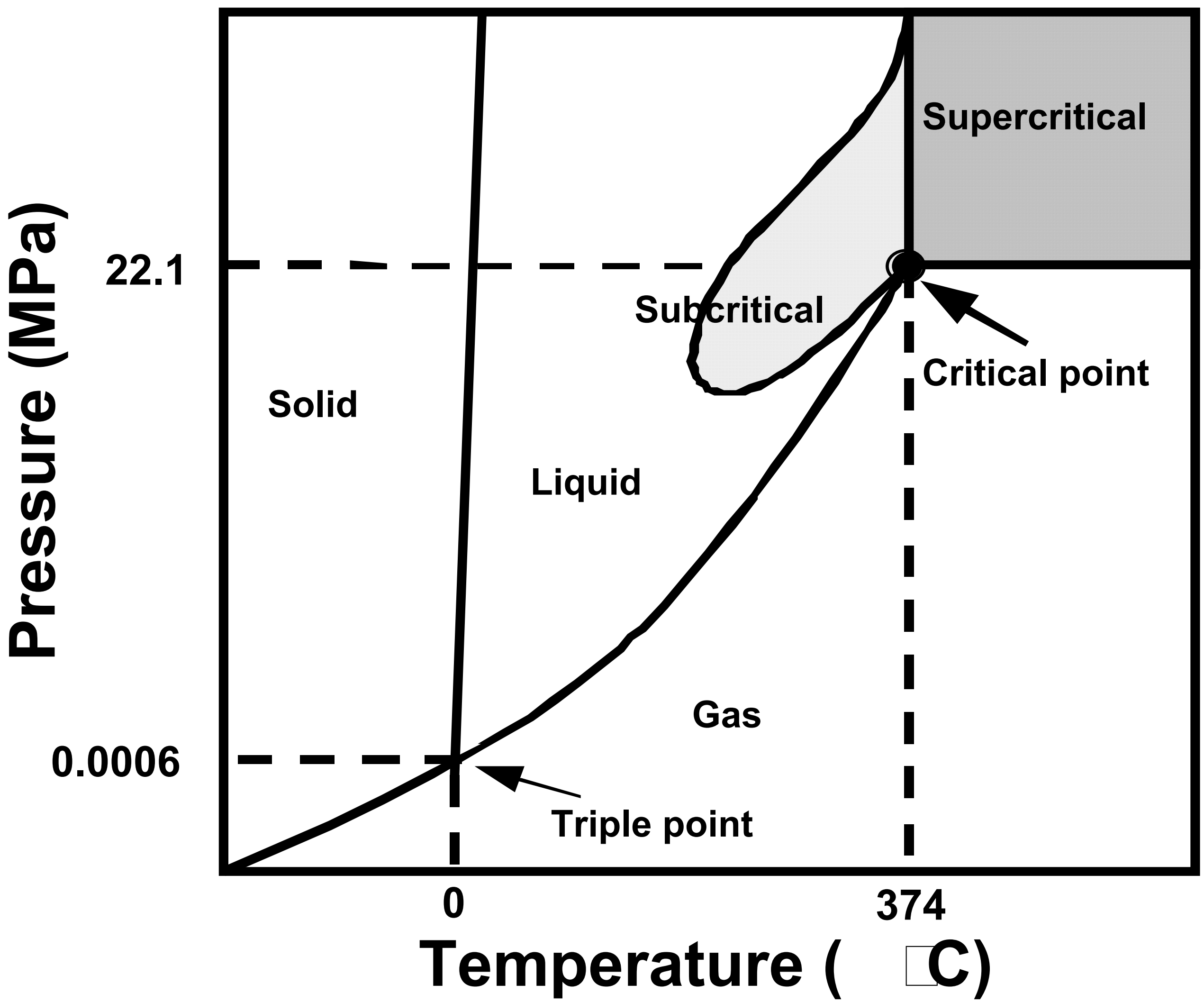
OD at 1100nm is smaller



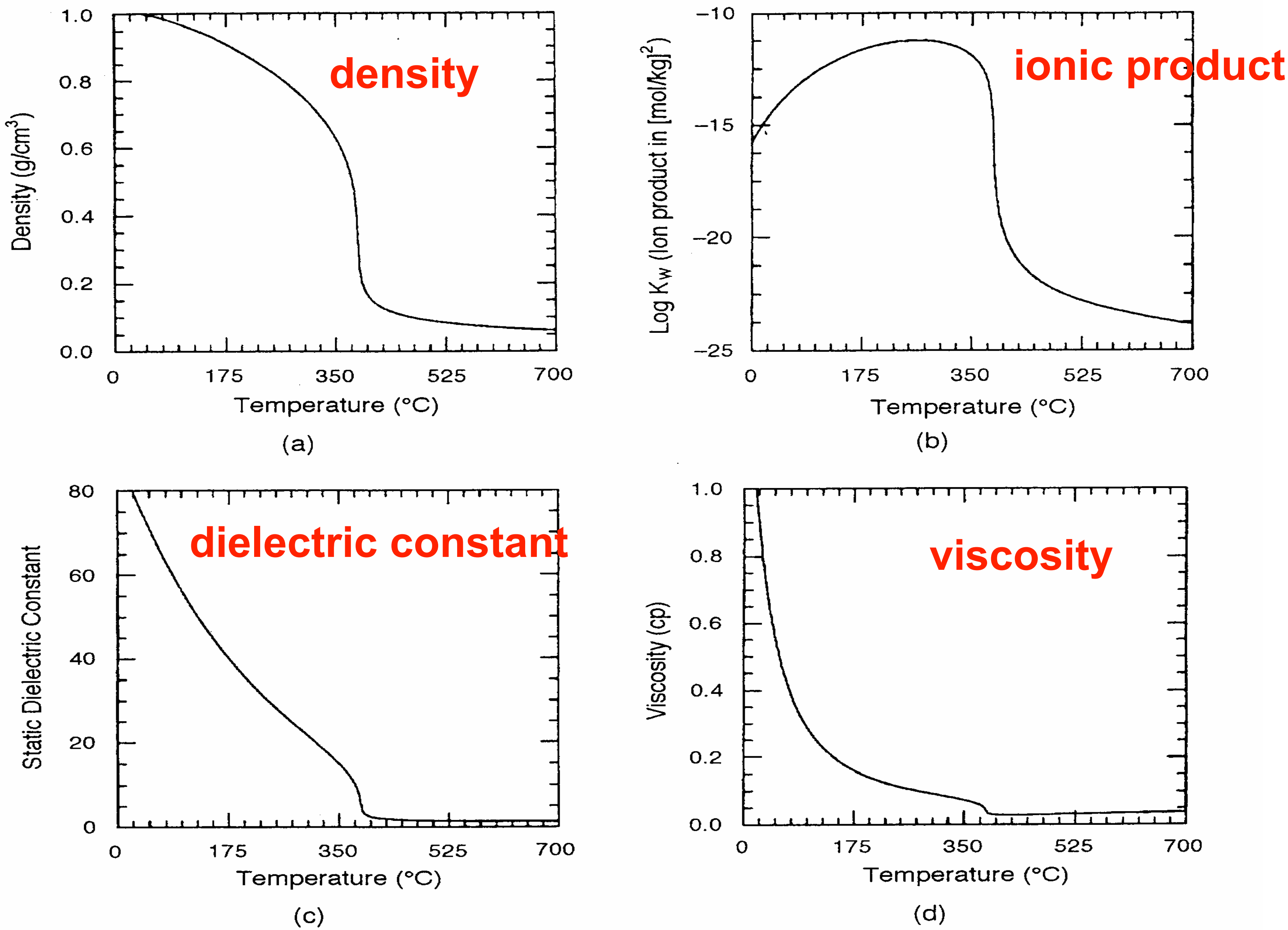
Radiation chemical study on supercritical water

What is supercritical water (SCW)?

$T_c > 374\ °C,\ P_c > 22.1\ MPa$



Temperature dependence of some water properties at 250 bar



Application of SCW

(1) *Chemical reactions*

- high solvency of organics, tunable conc. of H^+ and OH^-

(2) *Hydrothermal synthesis* - solubilities

(3) *Waste oxidation*; SCWO (supercritical water oxidation)

- quick (sec - minute) and complete (>99.9%),
  PCB, dioxin, chemical weapon …
- high solvency of organics and oxygen

(4) *Radioactive waste reductions*

- high solvency of organics and oxygen; solubilities

(5) *Biomass conversion* - high solvency of organics

(6) *Plastic degradation* - high solvency of monomers

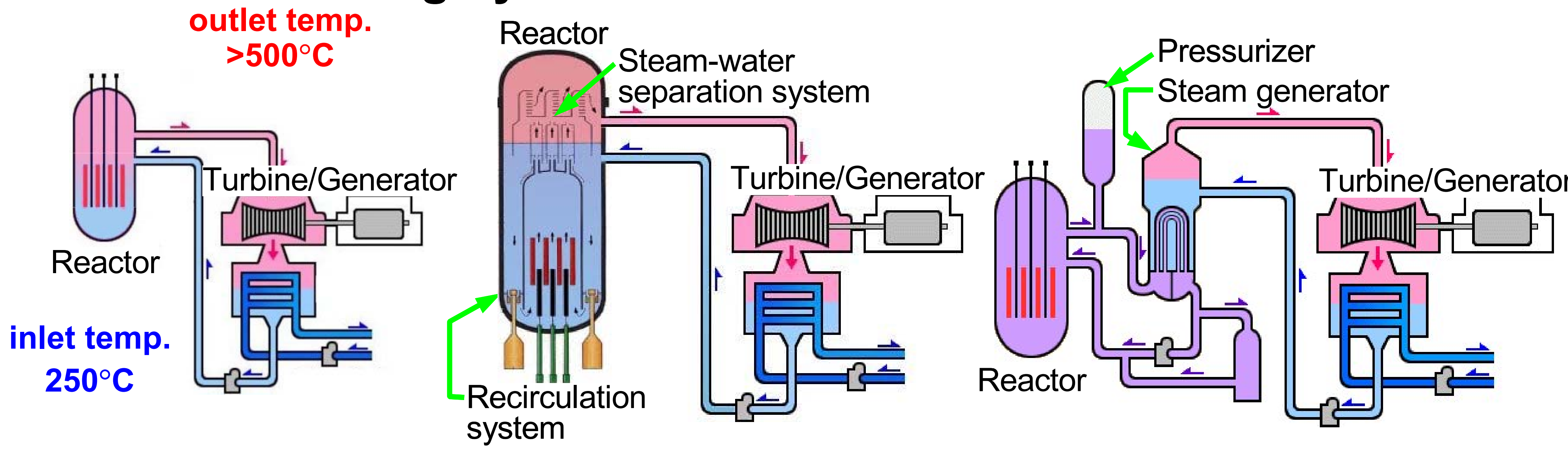
(7) *Synthesis of nano-particles* - low solubility of salts

(8) *Supercritical water-cooled reactor*

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



SCWR **ABWR** **PWR**

Importance of the radiation chemistry of SCW

(1) *Chemical reactions in SCW & SCF*

T (°C), *p* (Mpa), ρ, pKw, ε, viscosity, diffusion…

(2) *Interests from radiation chemistry*

ε (dielectric const), Onsager radius…

(3) *Fundamental data for SCWO*

OH , HO_2 reactions

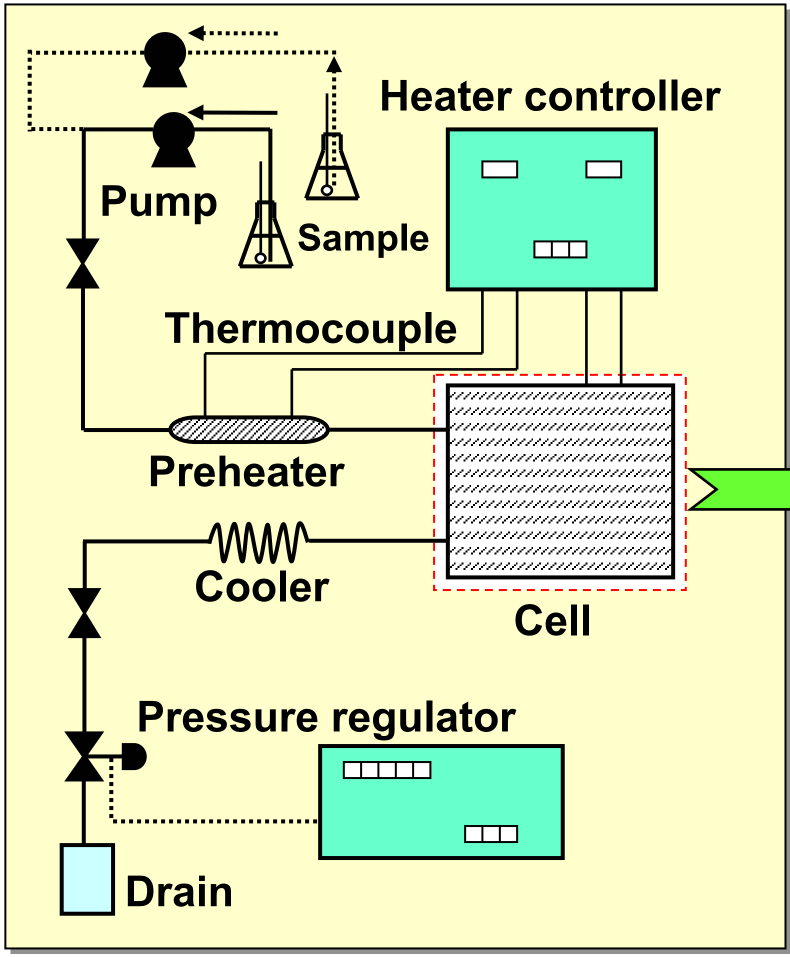
(4) *Theoretical subjects*

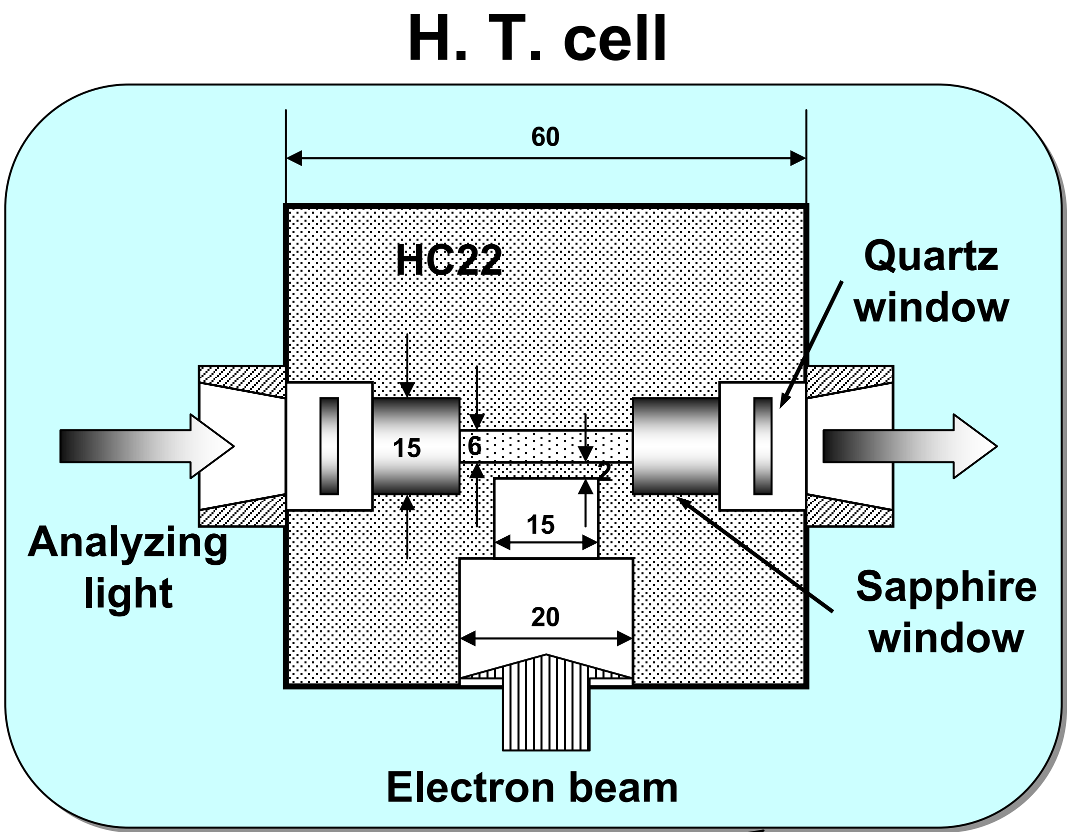
solvation, spectrum change, hydrogen bond, reaction…

(5) *Development of supercritical water-cooled reactor*

G-values of water decomposition, rate constants

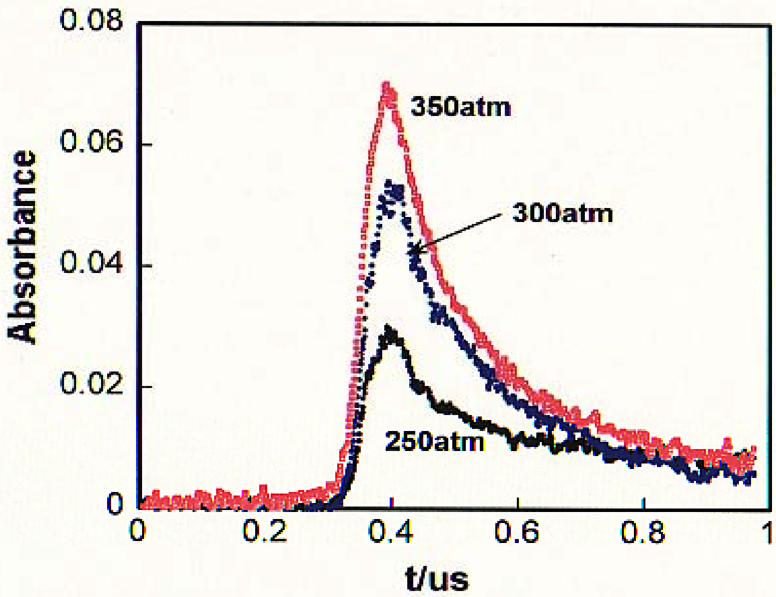
Experimental set-up





Pressure: 40 MPa
Temperature: 500 °C

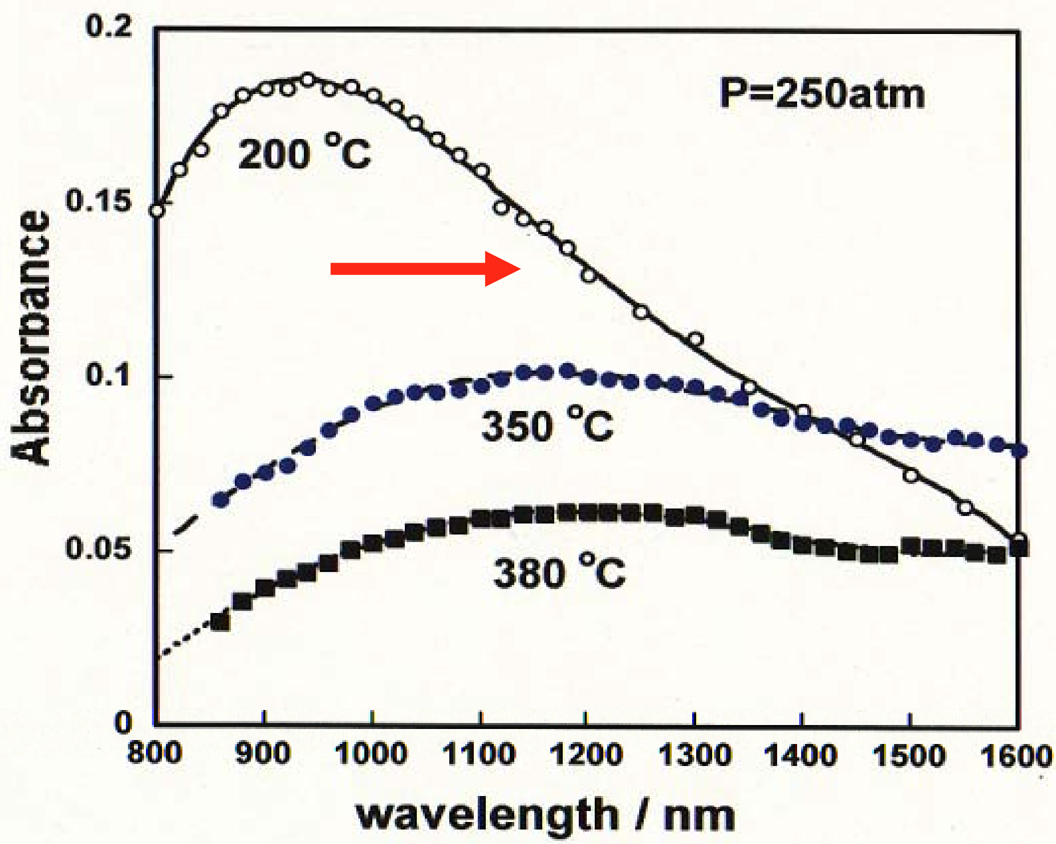
Hydrated electron; e_{aq}^-



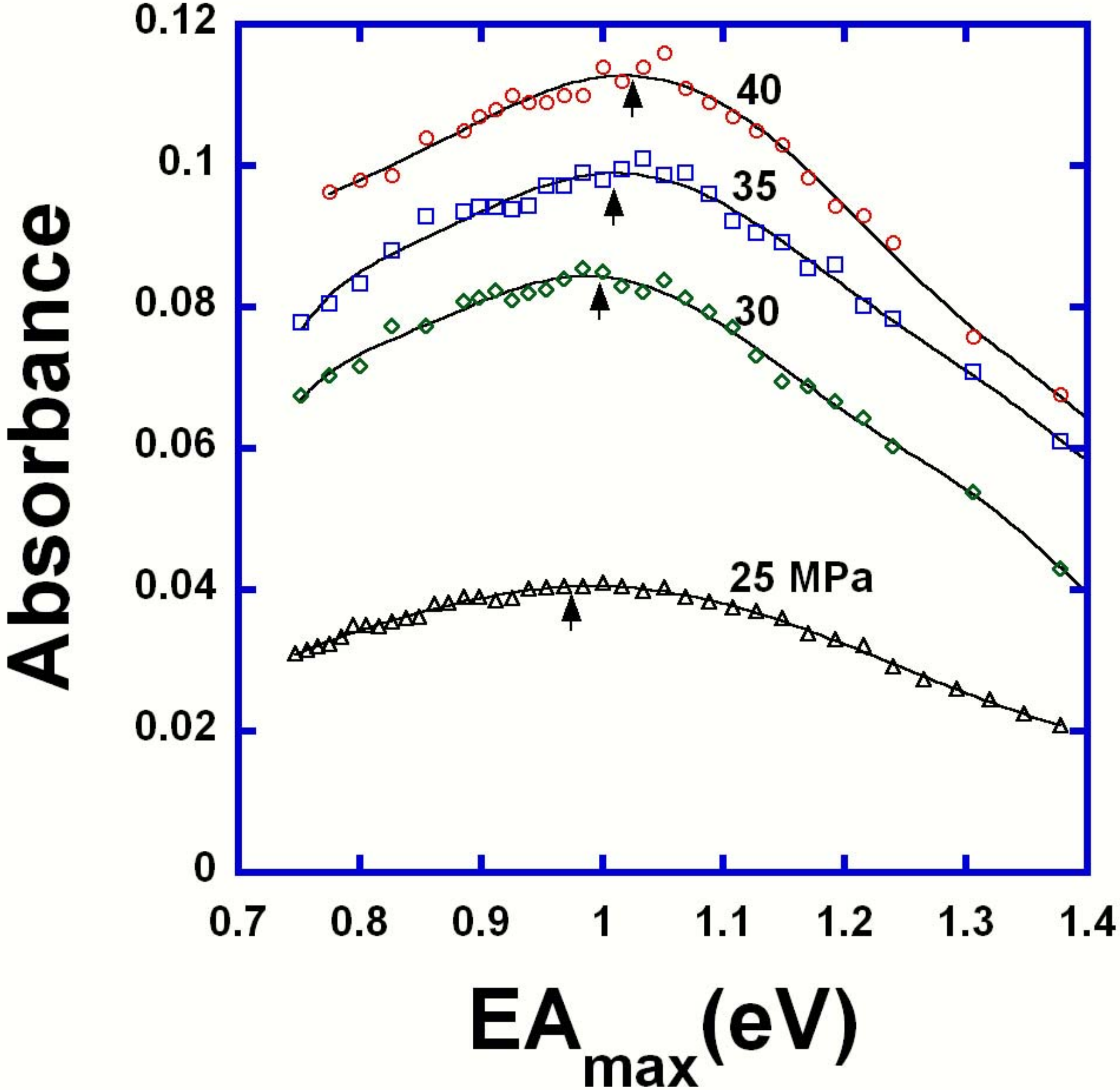
Time profiles of e_{aq}^- in supercritical water D_2O at 400°C.

54Gy/pulse, 1200 nm

Peak position shifts with temperature
At room temp.; 720 nm
→ 380 °C; ≈ 1200 nm
Water density is not normalized

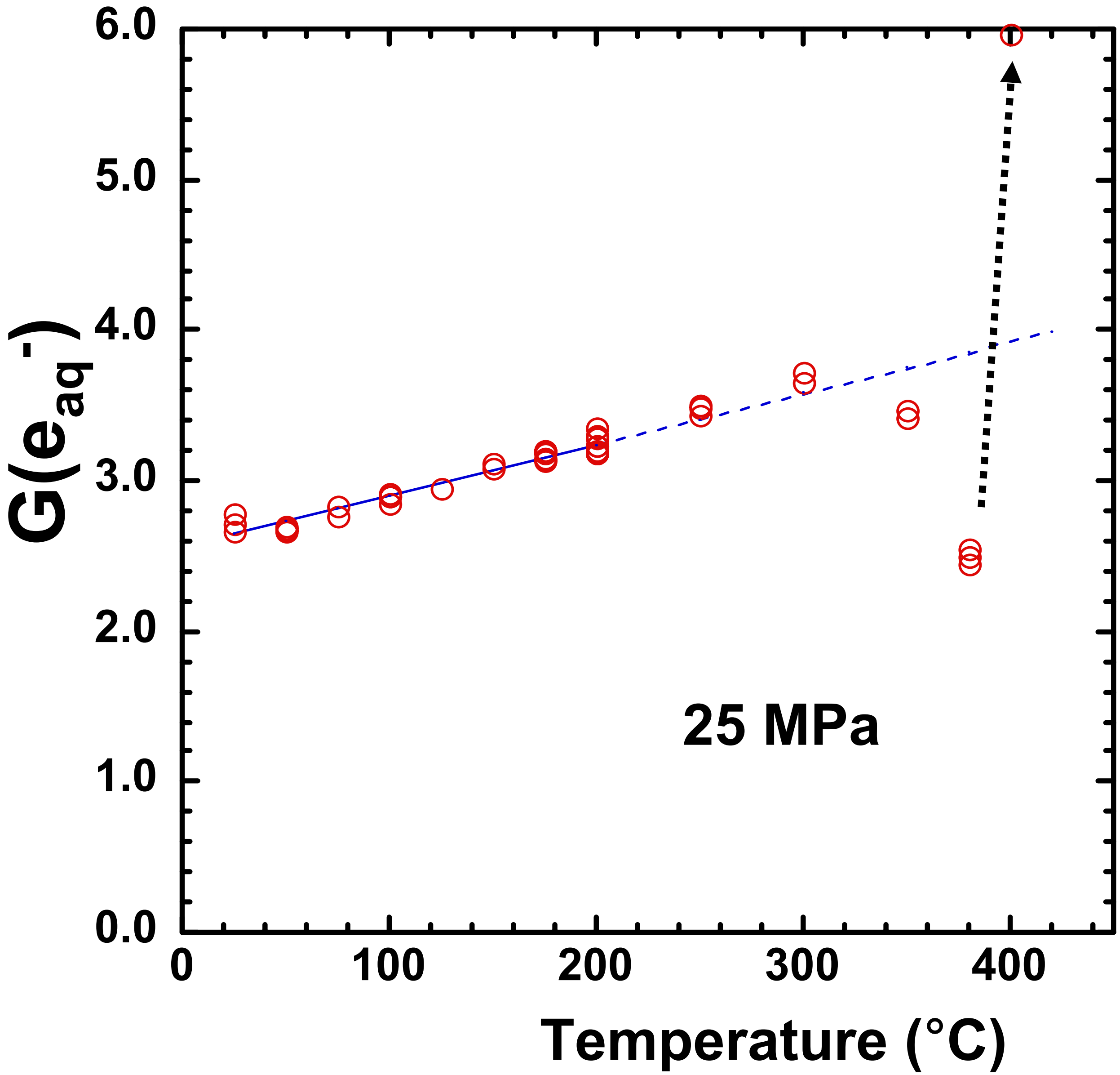


Absorption spectra of e^-_{aq} at 400 °C

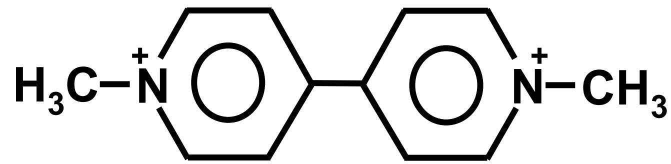


Solvation is controlled by the density; number of the surrounding water molecules.

$G(e^-_{aq})$ vs. temperature for hydrated electron



sample:
0.5 mM MV^{2+}
0.1 M tert-BuOH

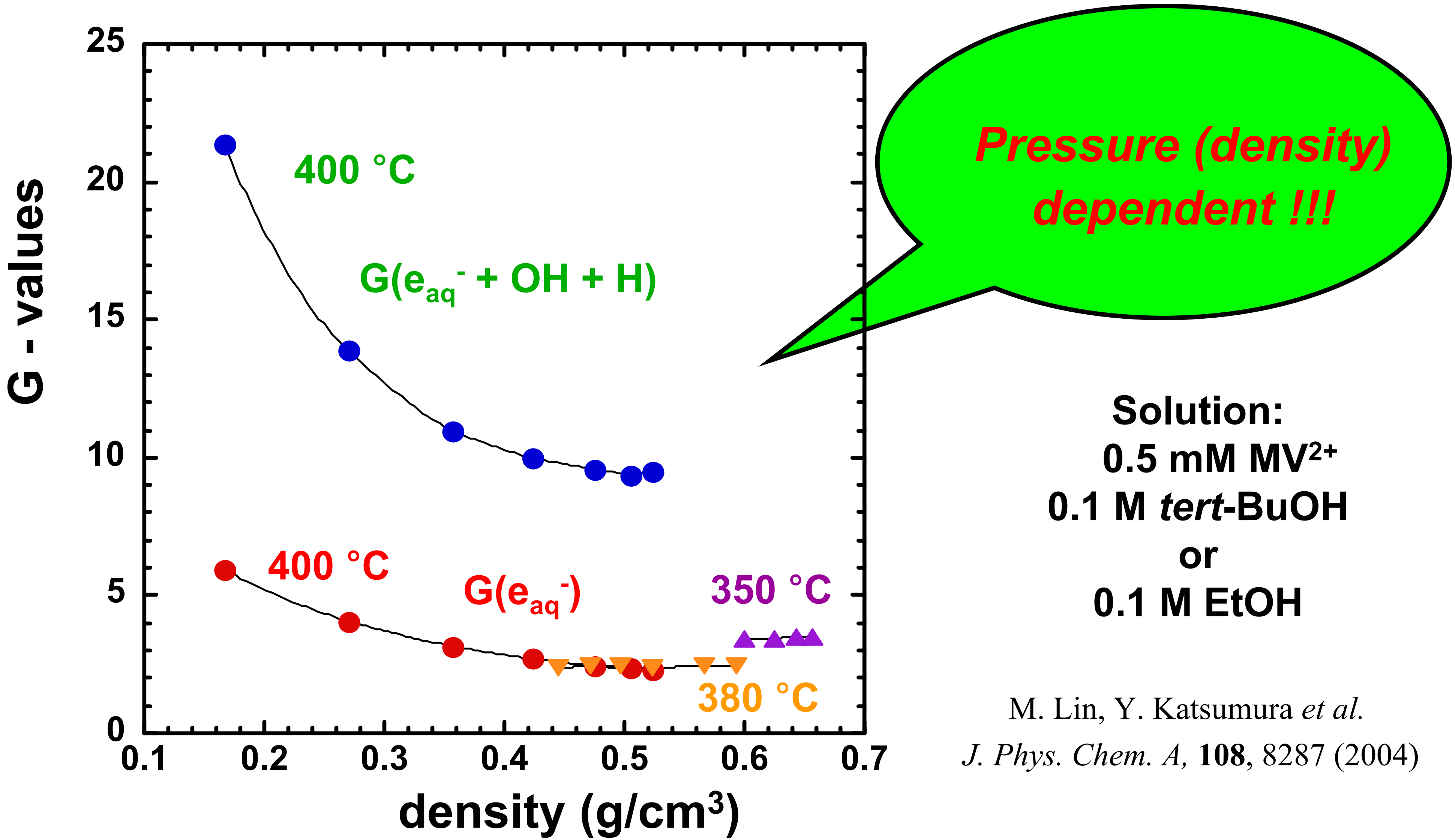


MV^{2+}

Methyl Viologen

M. Lin, Y. Katsumura *et al.*
J. Phys. Chem. A, **108**, 8287 (2004)

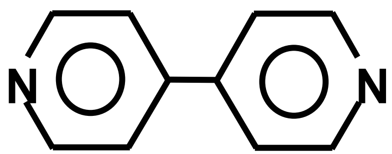
Pressure (density) dependence of G-values



Solution:
0.5 mM MV^{2+}
0.1 M *tert*-BuOH
or
0.1 M EtOH

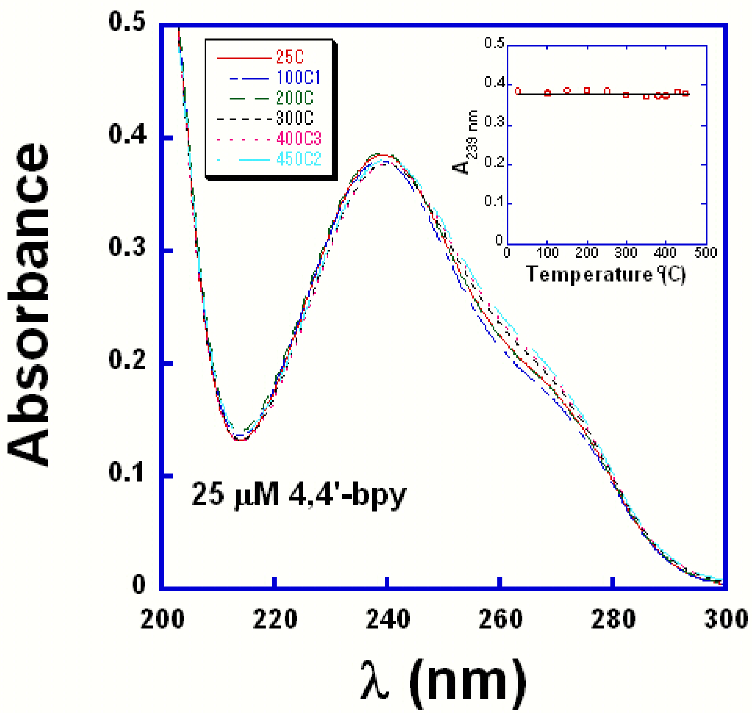
M. Lin, Y. Katsumura *et al.*
J. Phys. Chem. A, **108**, 8287 (2004)

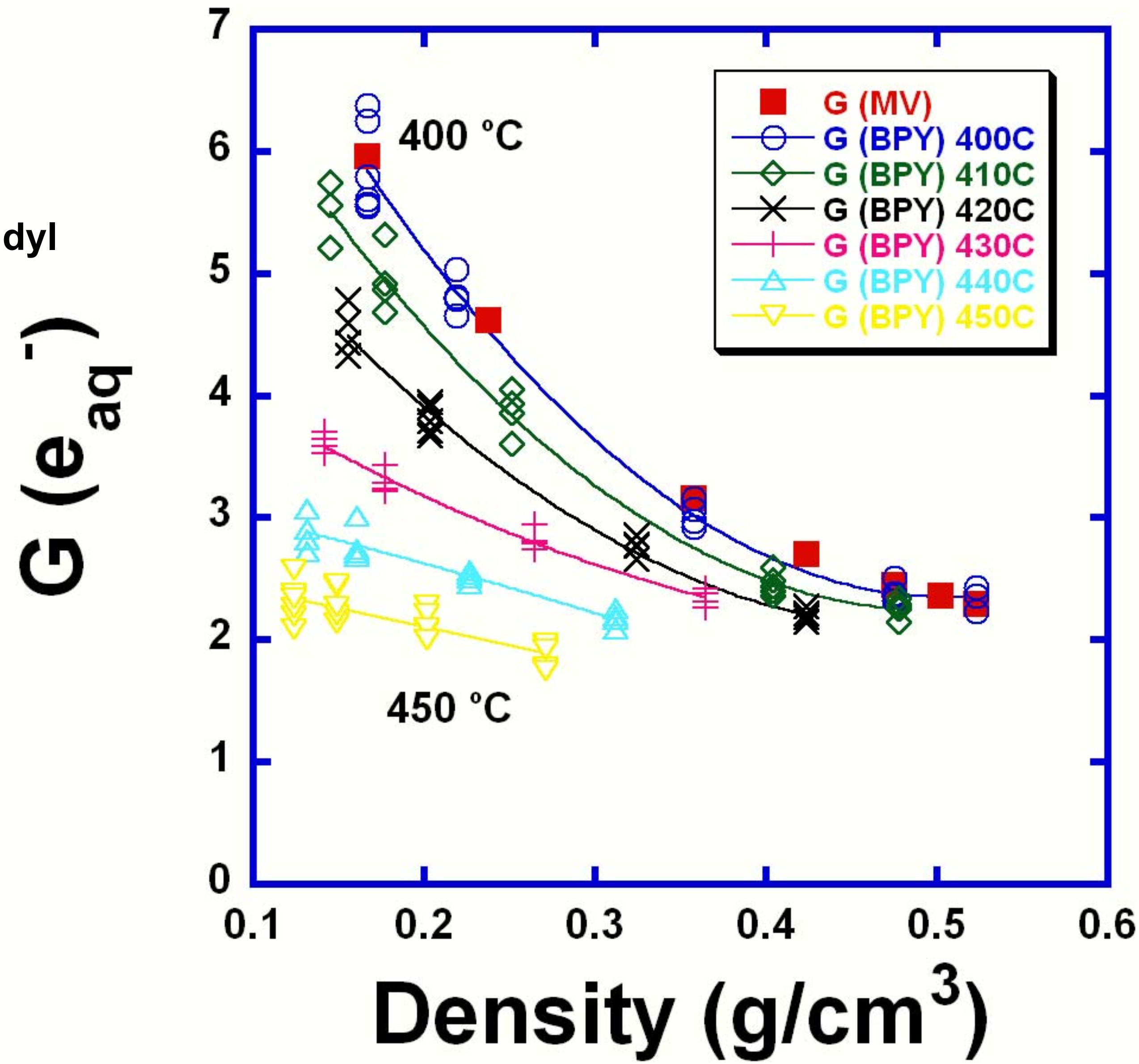
Density dependence of G-values up to 450 ℃



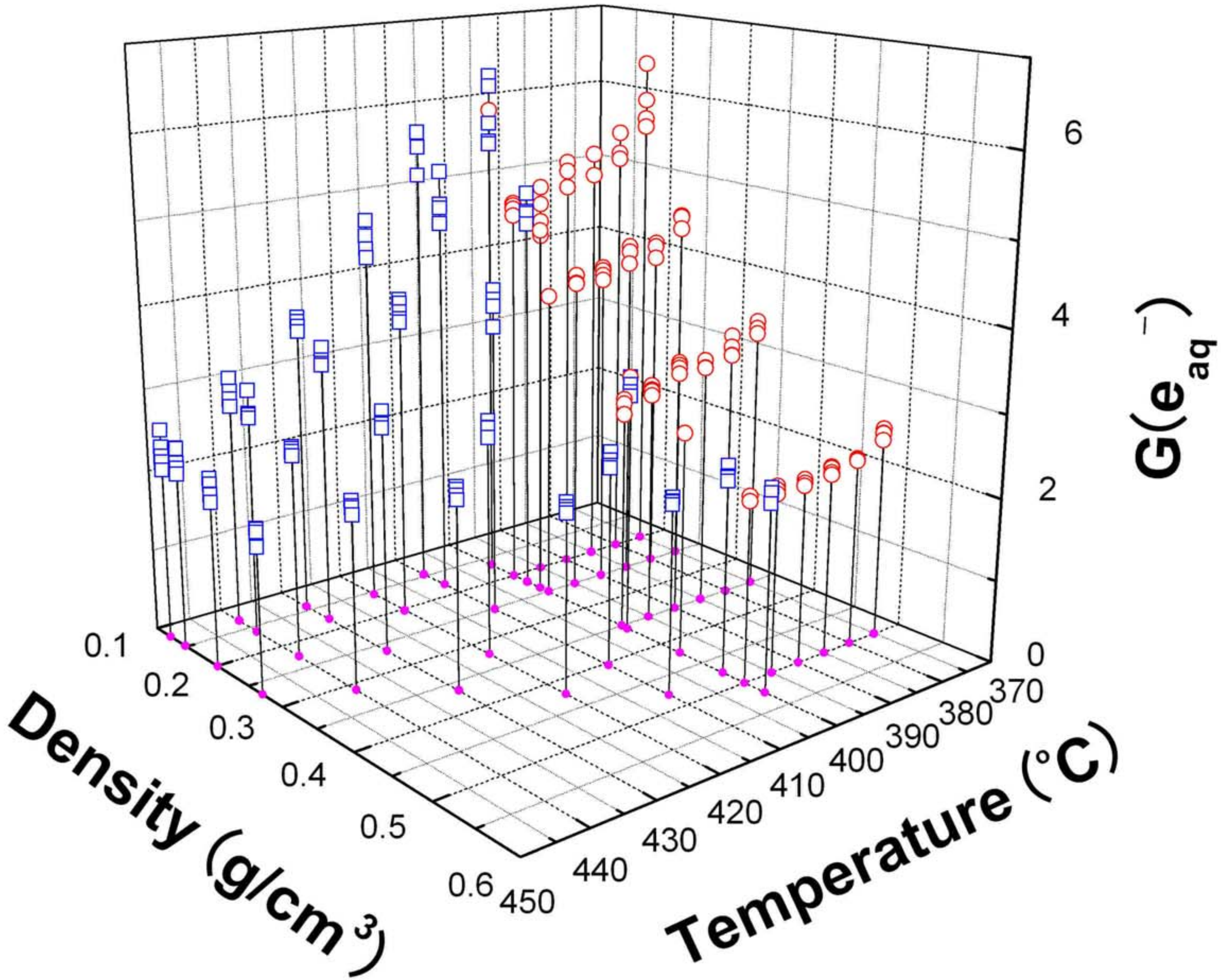
BPY

4, 4'-bipyridyl





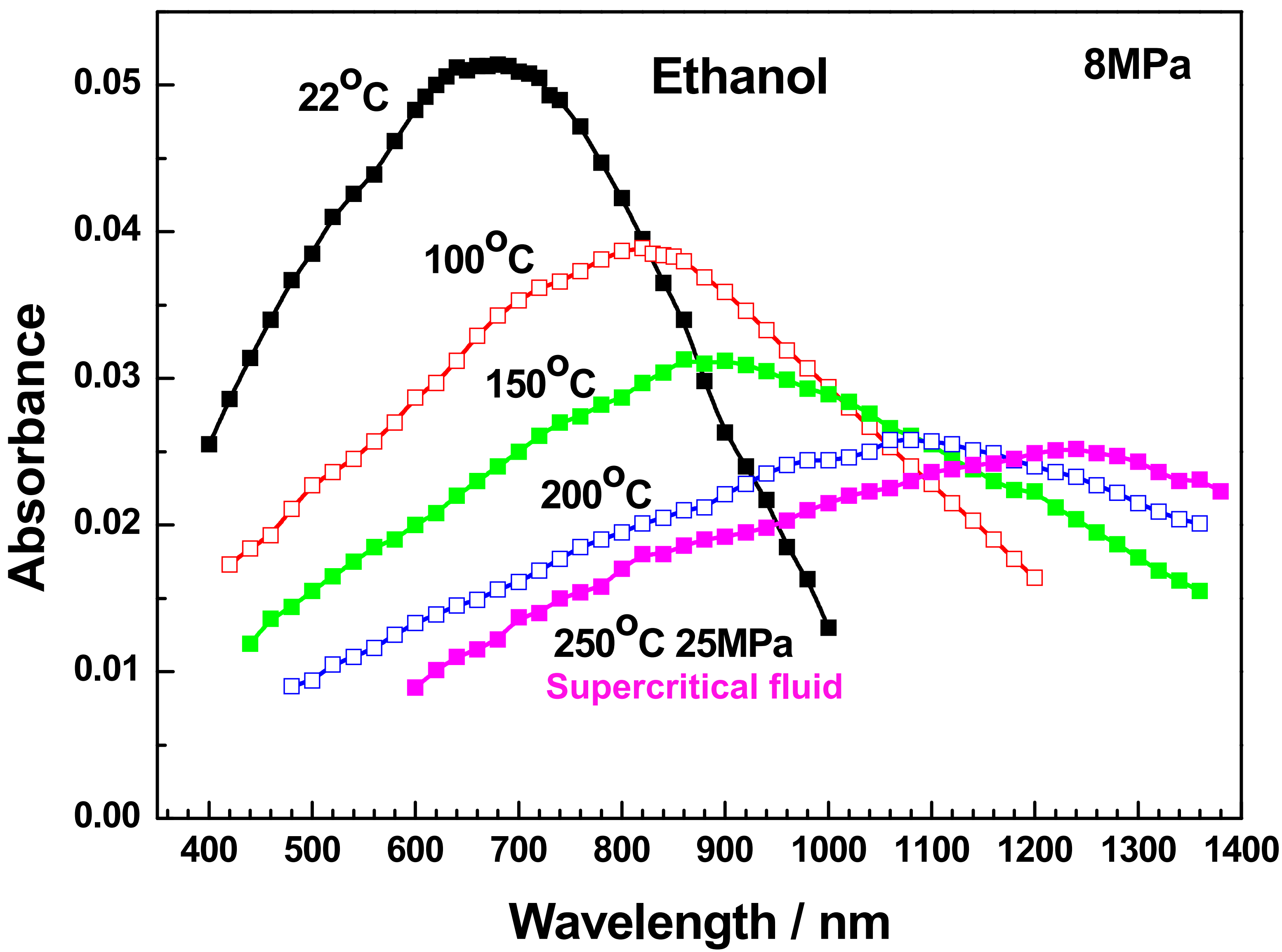
$G(e^-_{aq})$ as functions of density and temperature



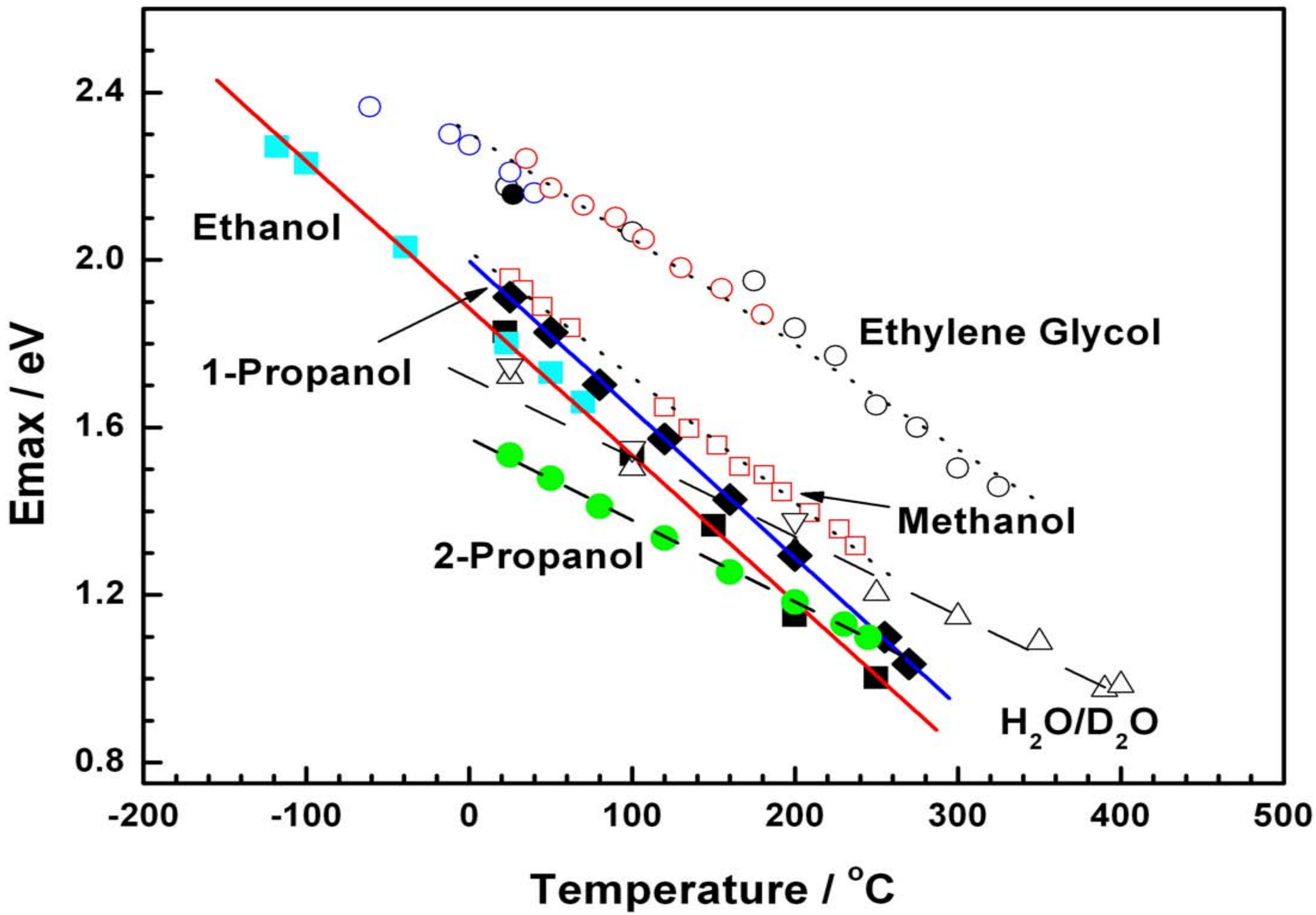
Critical points for several compounds

compound	Tc (°C)	Pc (MPa)	ρ (g/cc)
H_2O	374.2	22.1	0.322
methanol	239.5	8.10	0.272
ethanol	240.8	6.15	0.276
1-propanol	263.6	5.18	0.274
2-propanol	235.2	4.76	0.273
CO_2	31.1	7.38	0.468

Absorption spectra of e^-_{sol} in ethanol



Peak shifts of solvated electrons in different alcohols



Thank you for

your kind attention !