Performance and application of ultrafast pulse radiolysis system using laser photocathode rf-gun combined with fs laser

Jul. 26th, 2004
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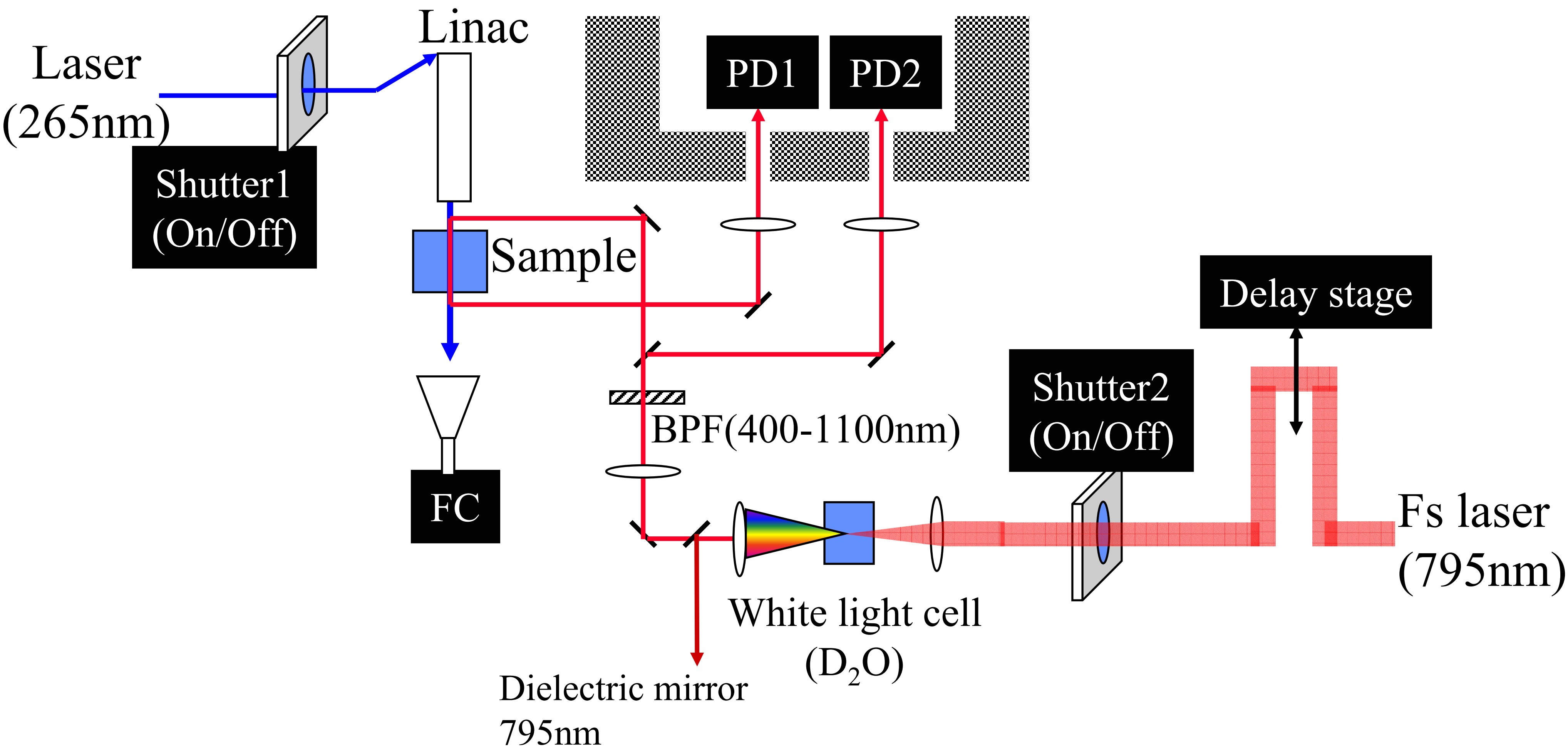
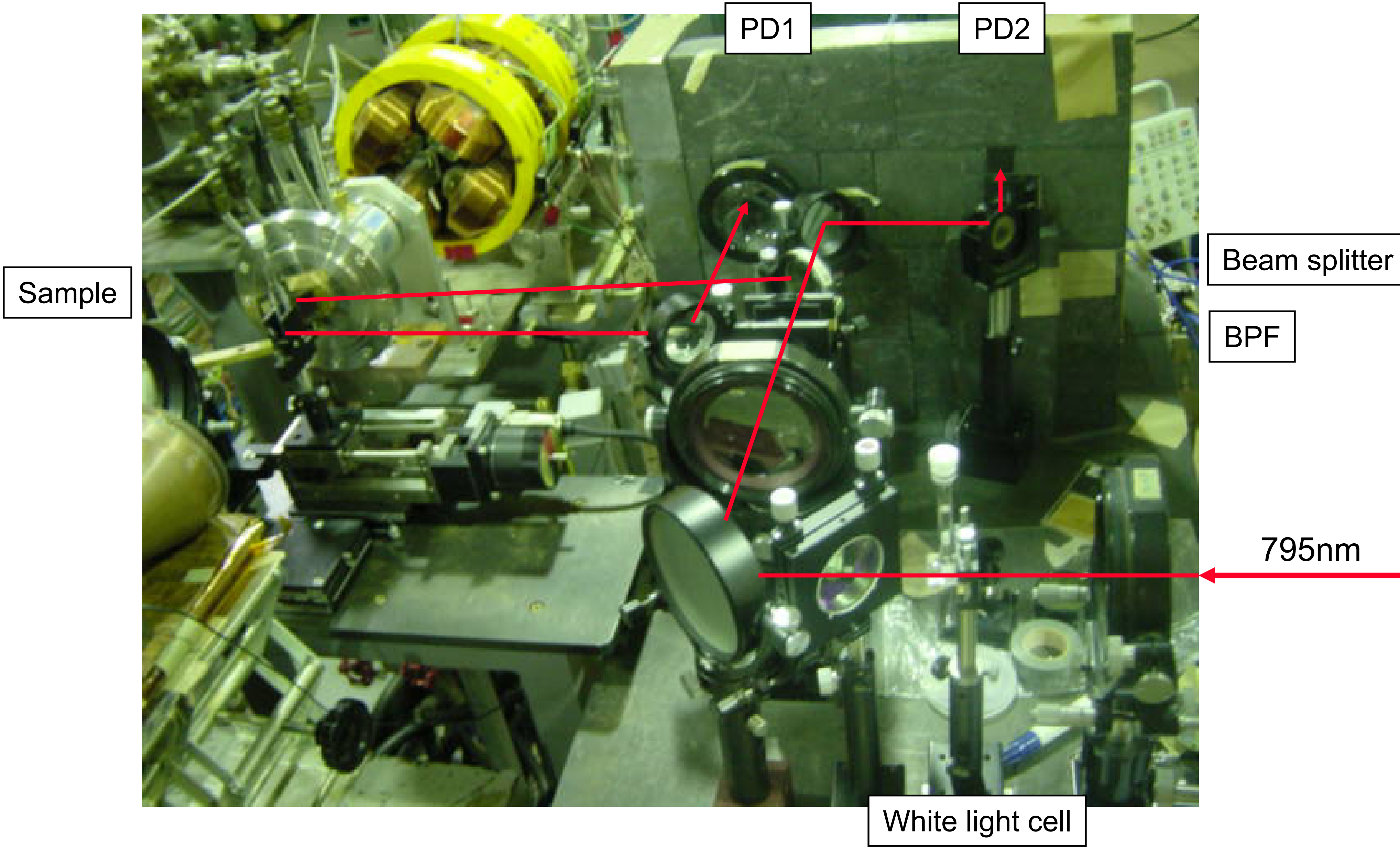
Measurement System

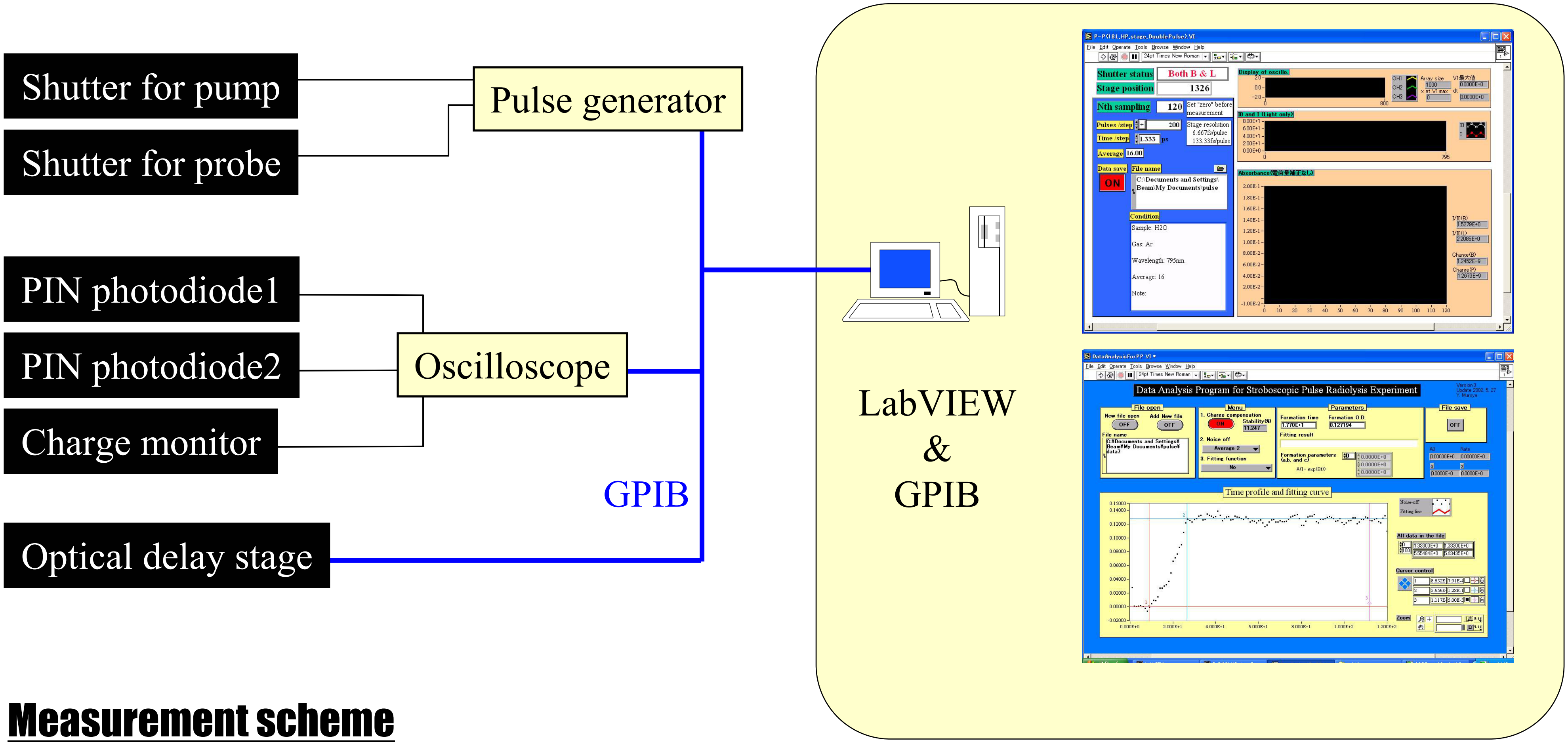


- Optical delay system
- Reference light for normalization of laser's fluctuation
- Elimination of noise by 2 shutters (beam on/off, laser on/off)

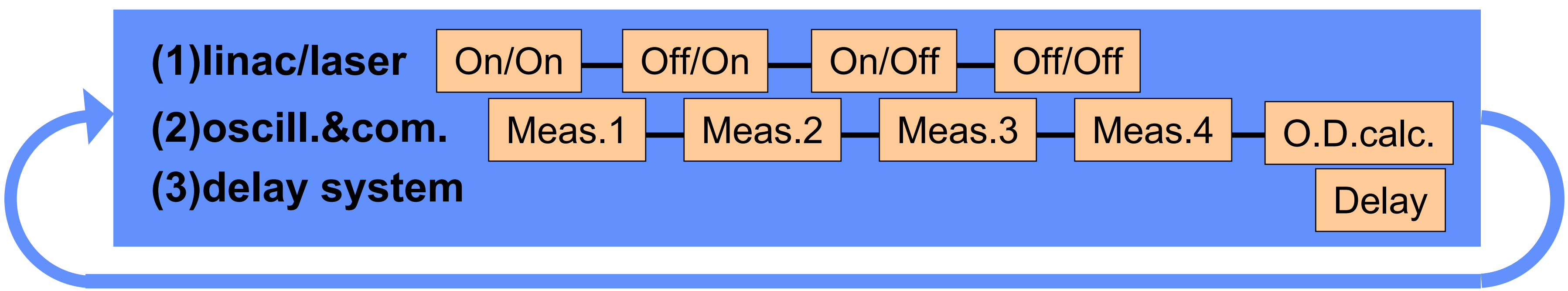
Measurement System



Data Acquisition System



Measurement scheme

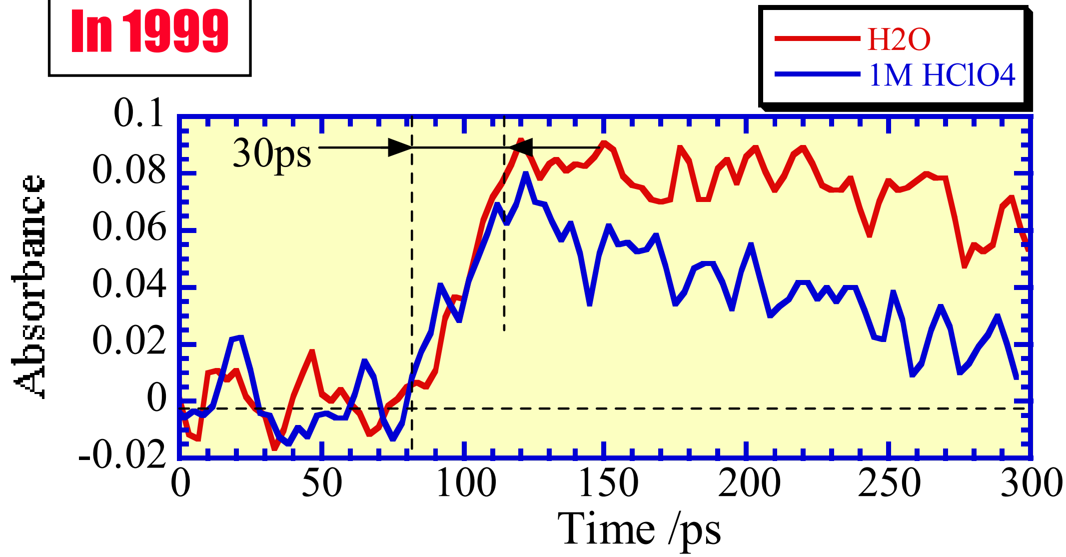


Preliminary Pulse Radiolysis

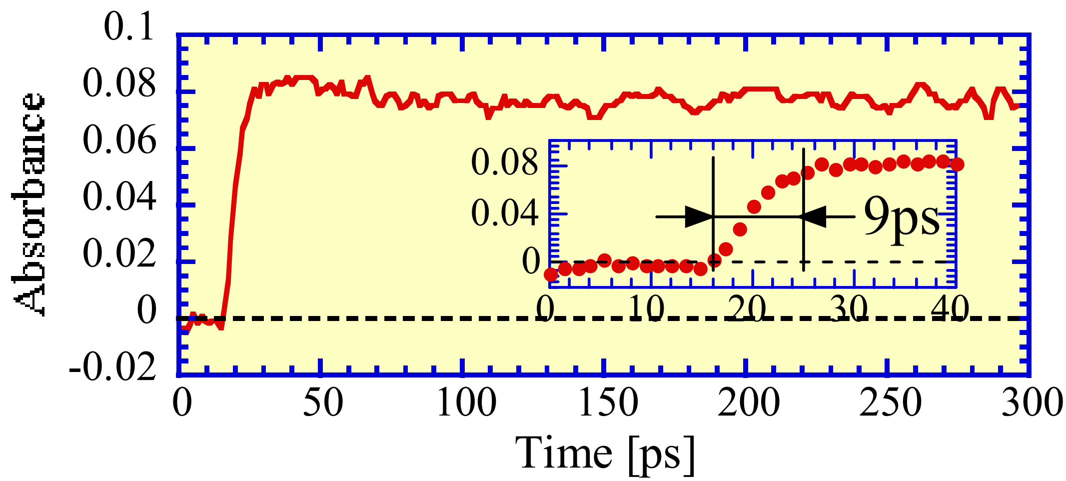
Condition

	H_2O&1M H^+	H_2O
l / mm	20 mm	5 mm
Charge Beam size Pulse width	0.8-1.0nC 4mm 7ps	0.8-1.0nC 4mm 3ps
Wavelength	795nm (Fundamental)	
Average	64	16
Time resol.	30ps	9ps

In 1999

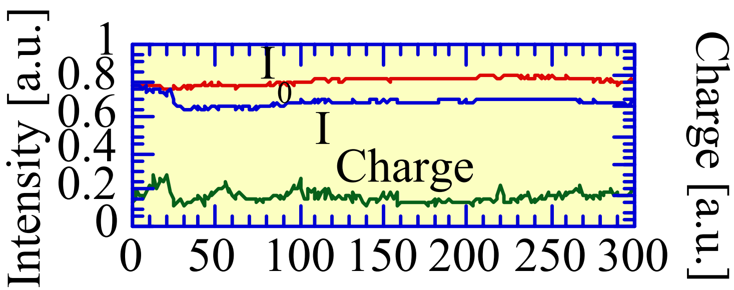


In 2002



Results

- O.D. still low



Improvement : dose increase & λ extend

Time resolution vs. dose

(1) 2~3ps : *pulse width (EB)*
(2) 100fs : *pulse width (laser)*
(3) <1ps : *synch.*
} **OK**
(4) 5ps /5mm : *Δt passing through H_2O*

→ Thinner cell & focused EB

Note: O.D. = $\varepsilon\, C\, l$
l↓ for better time resolution, but O.D.↓
then, C↑ for O.D.→

Introduction of white light continuum

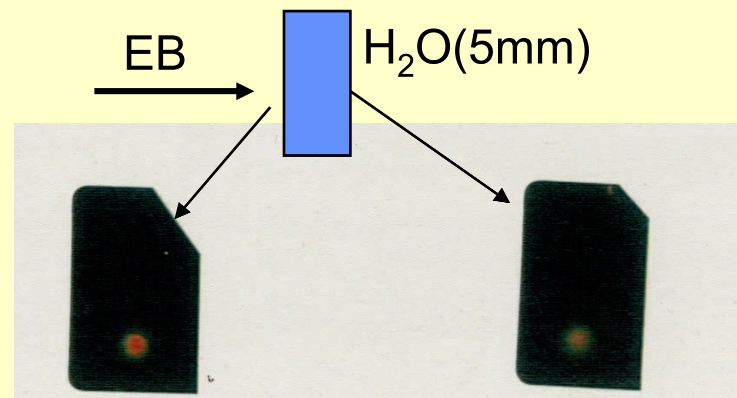
- 795nm → white
- Worse stability of intensity
- S/N↓ then average↑

	Previous	Current
Wavelength	795nm	400-1100nm
Average	16	64
Noise	~0.005 OD	~0.015 OD

Improvement

	Previous	Current
Charge	0.8-1.0nC	1.7-2.0nC
Beam size	4mm	3mm
Dose	13-15Gy	>40Gy/pulse
Pulse width	3ps	2ps

Estimation of dose by RadColor



- Accumulation 2000pulses
- Red region corresponds to 80-100kGy

Radiolysis of water measured at 700nm

- Time behaviors of e_{aq}^- at 700nm

Results

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

Good agreement

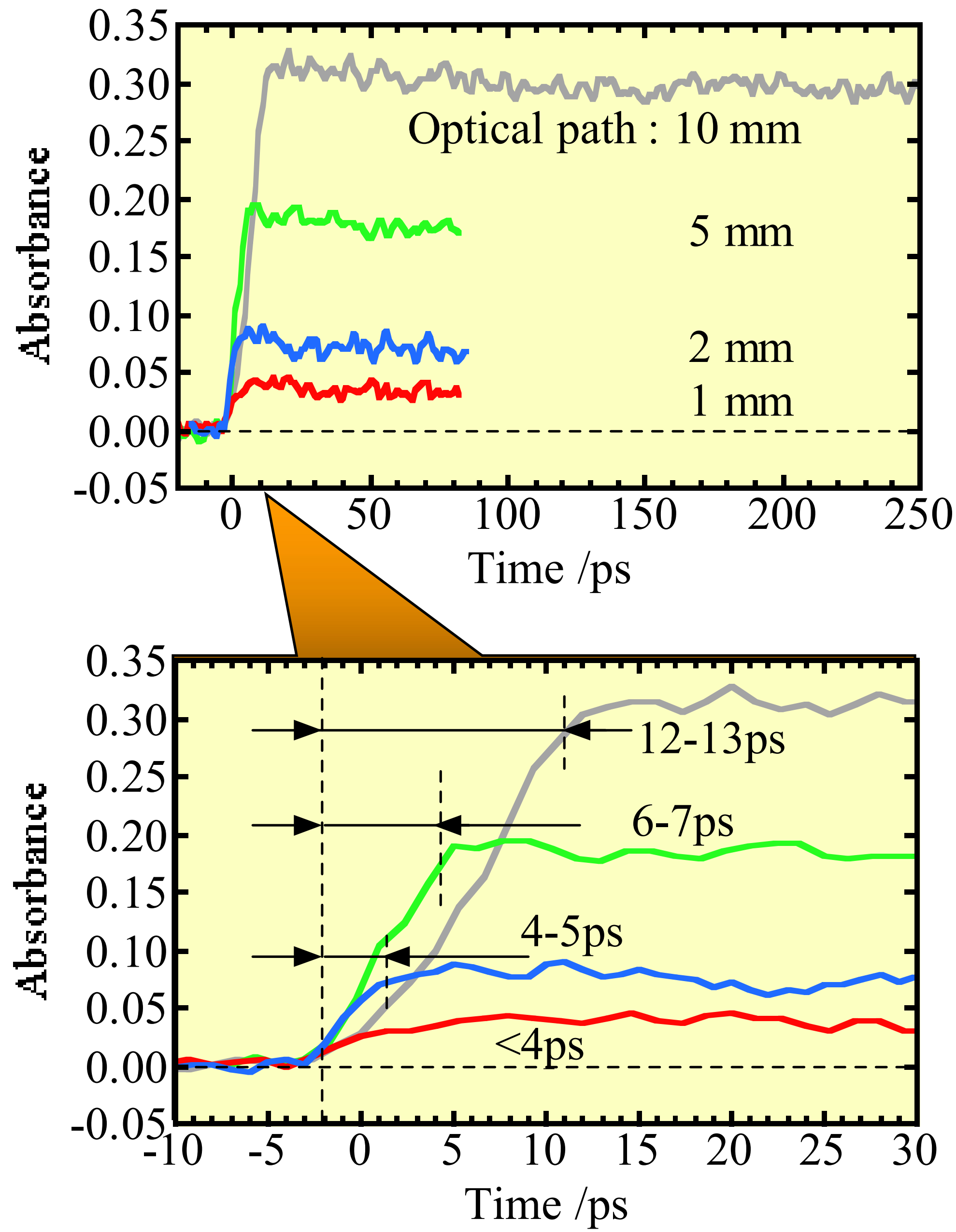
Time resol. /ps	12.2ps	7.2ps	5.2ps	3.2ps

Time resolution: δ_{total}

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

Dominant factor : δ_{diff}

due to refractive index n=1.33



G-value of the solvated electron

G [molecules/100eV]

$$nH_2O \rightsquigarrow e_{aq}^-, H_3O^+, H, OH, H_2, H_2O_2$$ ~100ns

$H_2O^+ + e^-$
$H_2O^* \rightarrow H_2O^+ + e^-$ ⇒ $e_{pre}^- \rightarrow e_{aq}^-$ < 1ps

Reported $G(e_{aq}^-)$

		SPR	KPR	Dose	Scav.	Sim.	G(time)	
1970	Tront						---	Kinetics only
1973	Tront	●		●			4.0(30ps)	
		●	●				4.0(30ps)	
1973	ANL		●	●			4.1(200ps)	Sub-ns KPR
1975	Tront	●			●			
			●		●		4.6(dry)	Dry electron
1976	ANL	●		● (1973)			4.6(100ps) 4.1(1ns)	Reconcilation 1973
1985	Hokkaido	●				●	4.8(30ps)	
1985 - 1996					●	●		
1996	NDRL & ANL	●	●				4.8(100ps)	Reconciliation 1976
1999	ANL	●	●				4.0 (time zero)	Fs laser Reconciliation
2000	Tokyo	●	●	●				

- Initial G : 4.0~4.8
- Primary G: 2.7

Which G is reliable ?

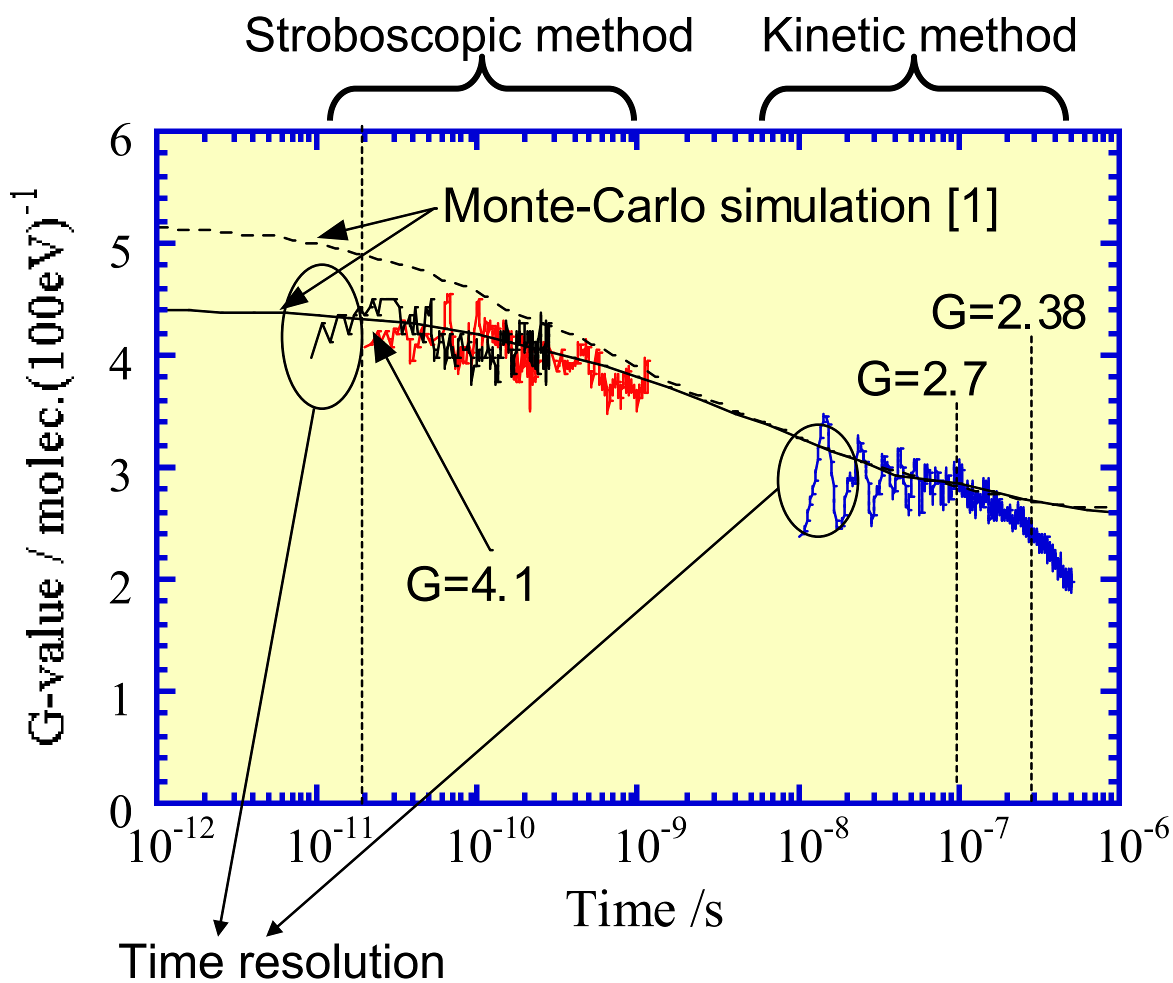
Application of RF-Gun Pulse Radiolysis

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

- Ps by SPR (795nm)
- Ns by KPR(He-Ne laser) (633nm)

Condition

Sample	H_2O
Gas	Ar
l / mm	18 mm
Charge Beam size Pulse width	0.8-1.0nC 4mm 3ps
Average	64



Note1 : O.D. already normalized by charge
Note2 : O.D. at 633nm normalized by ε
ε : 15500(633nm), 16800 (795nm)

$\boxed{G(20ps)=4.17\pm0.22}$

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

G of solvated electron in alcohols

	G	ε /$M^{-1}cm^{-1}$	τ_s	Ref.	D	η/cP	$\rho/10^{21}cm^{-3}$[1]
Methanol	**2.5** **1.6** **3.4** **3.1,3.0** **1.1**	15500(575nm) 10200(630nm) 17000(?) 10400(630nm)[7]	11 10.7[6]	[1] [3] [4] [2] [5]	32.6[2]	0.55[7]	14.8
Ethanol	**2.7** **1.6** **3.4** **2.8** **1.0**	12000(575nm) 9300(700nm) 15000(?) 9900(690nm)[7]	18 23[6]	[1] [3] [4] [2] [5]	24.3[2]	1.07[7]	10.2
1-propanol	**1.8** **2.0** **2.9,2.3** **1.0**	8400(575nm) 12800(700nm) 13000(?) 11000(640nm)[7]	24[1] 34[6]	[3] [4] [2] [5]	20.1[2]	1.92[7]	8
2-propanol	**2.3** **1.5** **2.8,1.8** **1.0**	8400(575nm) 14000(?) 13000(820nm)[7]	25	[1] [3] [2] [5]	18.3[2]	2.04[7]	6.5
1-butanol	**1.9** **2.3**	12000(635nm)[7]	30 39[6]	[1] [2]	17.1[2]	2.56[7]	3.8
1-octanol	**1.4**		45	[1]	10.3[2]	8.95[1] 7.36[7]	3.1
1-decanol	**2.0**	14000(650nm)[7]	51	[1]	7.8[2]	14.1[1] 11[7]	21.5

G of solvated electron in alcohols

	G	ε $/M^{-1}cm^{-1}$	τ_s	Ref.	D	η/cP	ρ/$10^{21}cm^{-3}$[1]
Ethylene Glycol	2.3 1.2	14000(580nm) 14000(?)	<5[1] 26	[4] [5]	37.7	19.9[1]	
Propylene Glycol (1.04)(1,2-PrD)		7500(570nm)[7]					
1,3-Propanediol (1.05)		6000(575nm)[7]					
Glycerol (1.26)(1,2,3-PrTri)		9700(530nm)[7]					

[1]G.A.Kenny-Wallace, C.D.Jonah, J.Phys.Chem., 86 (1982) 2572
[2]R.R.Hentz, G.A.Kenny-Wallace, J.Phys.Chem., 78 (1974) 514
[3]W.K.Wolff, J.W.Hunt, J.Phys.Chem., 77 (1973) 1350
[4]T.Sumiyoshi, M.Katayama, Bull.Chem.Soc.Jpn., 58 (1985) 3073
[5]M.J.Bronskill, J.W.Hunt, J.Chem.Phys., 53 (1970) 4201
[6]W.J.Chase, J.W.Hunt, J.Phys.Chem., 79 (1975) 2835
[7]C.Ferrandini, J.-P.Jay-Gerin, CRC press, (1991) 259

G of solvated electron in alcohols

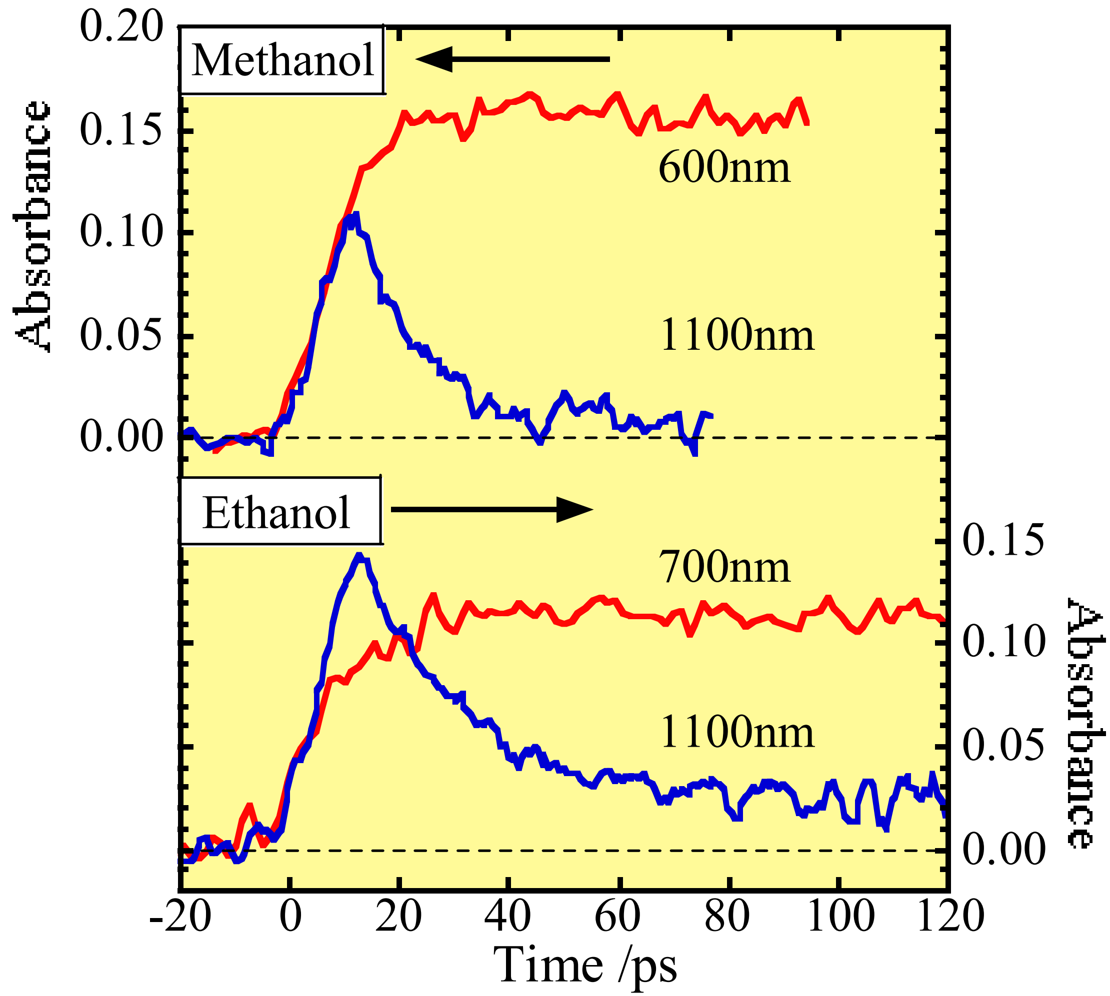
- Initial $G(e_{sol}^-)$ measured at VIS&IR

Condition

Sample	Methanol	Ethanol
Wavelength	600nm 1100nm	700nm 1100nm
l / mm	10 mm	
Average	64	

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

Results and discussion

Shorter τ
Larger dielectric constant→ large G

fs laser reported
-e_{sol}^- doesn't recover ~10%

↓

$e_{sol}^-(MeOH) > e_{sol}^-(EtOH) \sim e_{aq}^-$

↓

ε is correct?

Solvent (ρ /cm^3)	ε /$M^{-1}cm^{-1}$	Initial G	Initial Gε
H_2O (1.00)	18300 (700nm)	4.2	76800
Methanol (0.79)	10000 (600nm)	4.1	41000
Ethanol (0.79)	9900 (700nm)	3.6	35640
1-propanol (0.80)	12700 (700nm)	2.7	34300
2-propanol (0.79)	12000 (700nm)	2.3	27600
1-butanol (0.81)	11500 (700nm)	2.5	29000
1-decanol (0.84)	13500 (600nm)	2.5	33750
EG (1.1)	14000 (600nm)	2.8	39200
Propylene Glycol (1.04)(1,2-PrD)	7500 (570nm)	4.4	33000
1,3-Propanediol (1.05)	6000 (600nm)	6.1	36600
Glycerol (1.26)(1,2,3-PrTri)	8250 (600nm)	4.0	33000

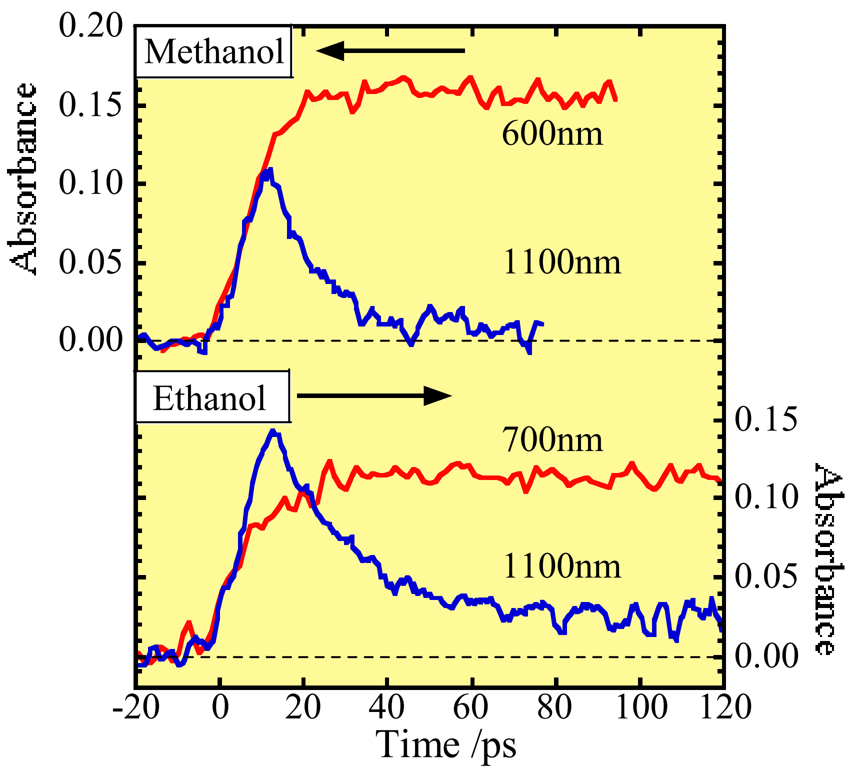
??

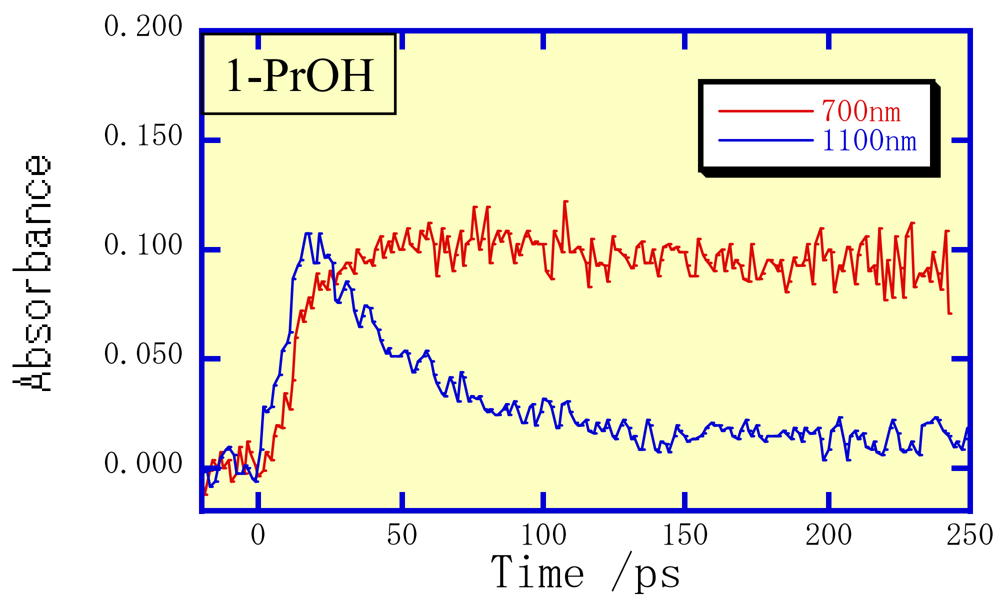
Necessity to measure
whole time region from ps to μs

Results and discussion

		MeOH	EtOH	PrOH	BuOH	DeOH
This work	τ (ps)@700nm or 600nm	9	11	9	10	15
	τ (ps)@1100nm	13	28	50	77	180
Report	τ_s (ps)	10	18	24	30	51
	τ (ps)@1300nm	10	22	32		

- Formation time is faster than previous reports
- Decay appreciates with previous reports



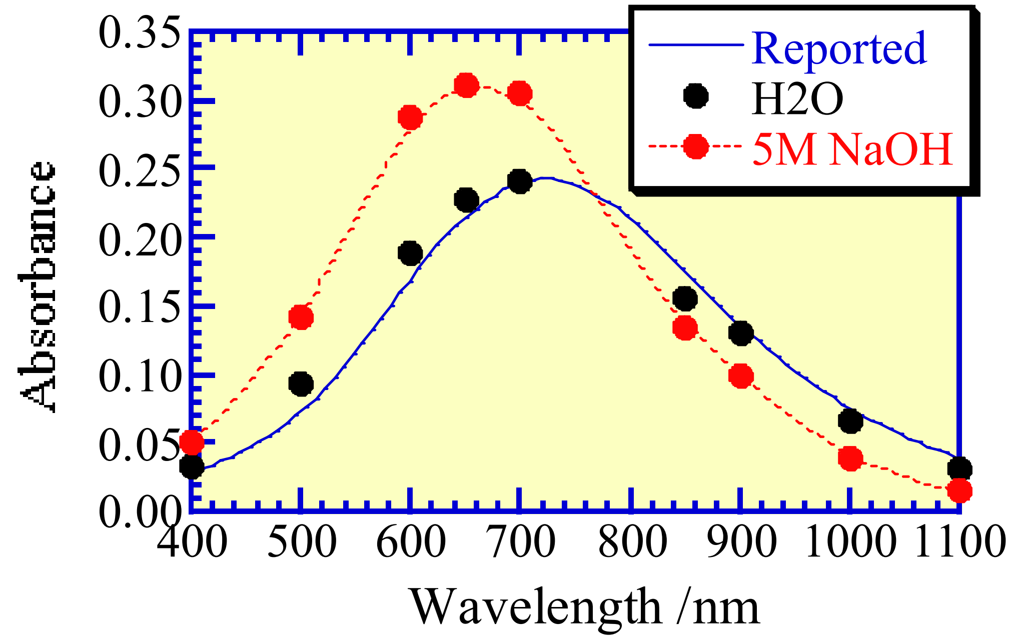


Radiolysis of water : spectrum

- $G(e_{aq}^-)$ measured from VIS to IR

Condition

	H_2O & 5M NaOH
l / mm	10 mm
Wavelength	400 – 1100 nm
Average	64



<700nm : O.D.(alkali) > O.D.(neat)
>700nm : O.D.(alkali) < O.D.(neat)

20% absorption increase
7% density increase → Increase of G

Summary

- Development of new pulse radiolysis system combined with laser photocathode rf-gun and fs white light continuum has been almost completed.

- <4ps time resolution was achieved.

- It has been started application of the system to clarify radiation-induced fast processes, i.e., G-value of e_{aq}^- , e_{sol}^- from several kinds of alcohol.