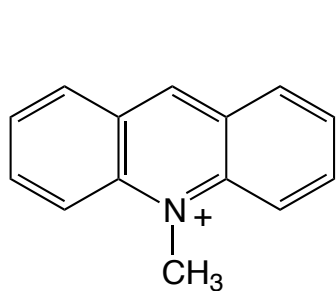
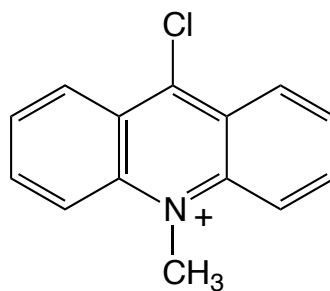


## 7.3 Examples of homogeneous and nano-heterogeneous systems

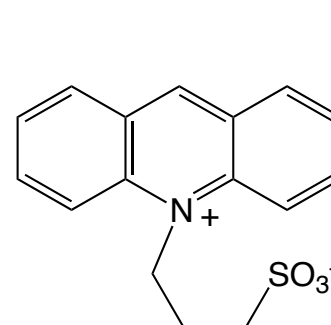
### A. Photo-oxidation of aromatic hydrocarbons by acridinium dyes



MA<sup>+</sup>

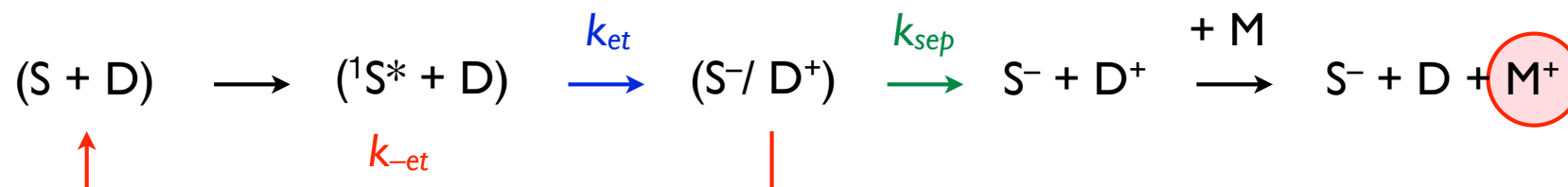


CMA<sup>+</sup>



APS<sup>0</sup>

Dye	$\tau$ [ns]	$\Phi_f$	$\phi(S/S^-)$ [V/ SHE]	$\Delta E_{0,0}$ [eV]
10-methyl-acridinium (MA <sup>+</sup> )	42	0.71	- 0.184	2.66
9-chloro, 10-methyl-acridinium (CMA <sup>+</sup> )	40	0.68	- 0.027	2.71
10-acridinium-3-propylsulfonate (APS <sup>0</sup> )	36	0.65	- 0.350	2.74



## Photo-oxidation of aromatic hydrocarbons by acridinium dyes

The quantum yield  $\Phi_{M^+}$  for the production of the radical cation monitor  $M^+$  is measured by ns laser transient absorption spectroscopy (laser flash photolysis). The reaction  $D^+ + M \rightarrow D + M^+$  being quantitative,  $\Phi_{M^+}$  can be expressed by:

$$\Phi_{M^+} = \Phi_{et} \cdot \Phi_{sep} = \frac{k_{et}}{\sum k_i} \cdot \frac{k_{sep}}{k_{sep} + k_{-et}}$$

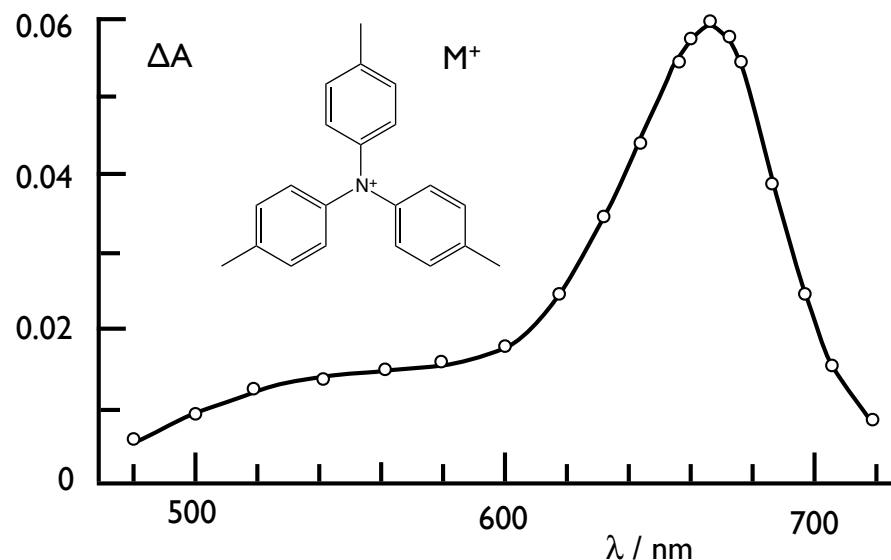
where  $\Phi_{et}$  is the quantum yield of the forward electron transfer process, and  $\Phi_{sep}$  the yield of the separation of the ion pair ( $S^-/D^+$ ).

The value of  $\Phi_{et}$  is accessible experimentally by applying Stern-Volmer's method. The rate constant for back electron transfer  $k_{-et}$  can then be simply estimated from the relationship:

$$k_{-et} = k_{sep} \cdot \left( \frac{\Phi_{et}}{\Phi_{M^+}} - 1 \right)$$

The separation rate constant  $k_{sep}$  was measured separately and was found to be independent of the donor D :

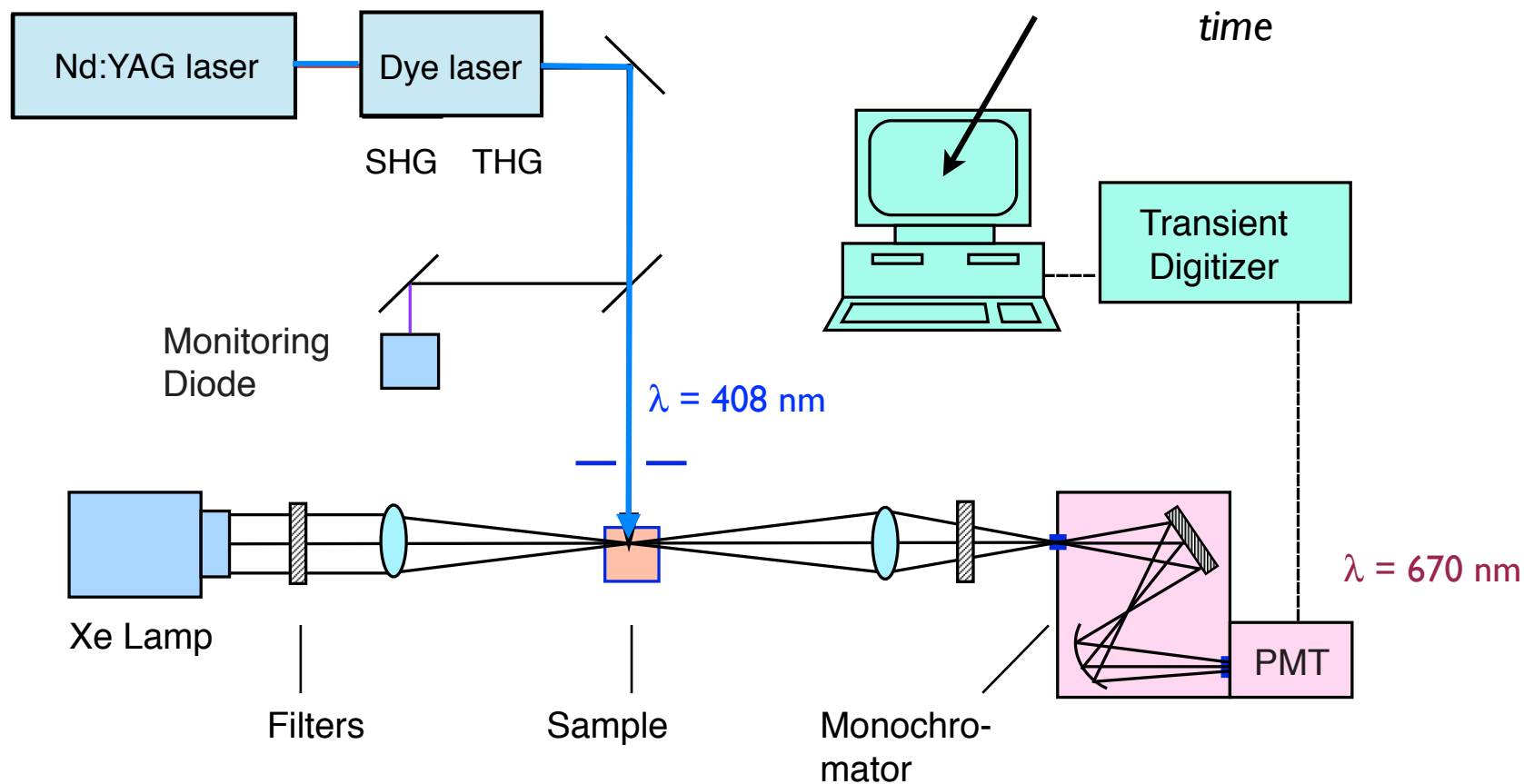
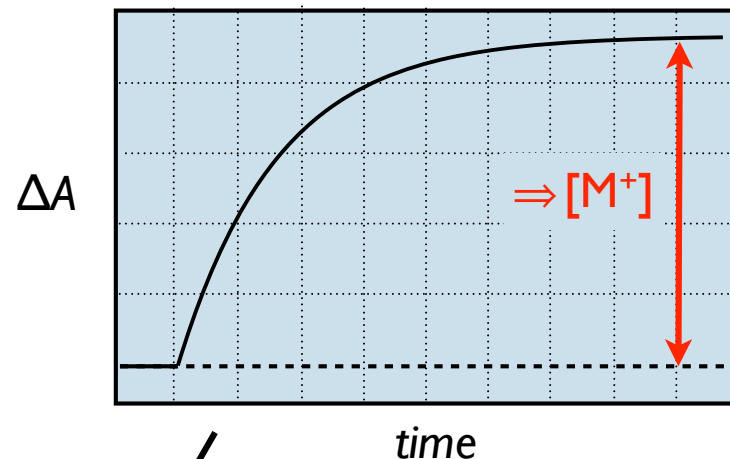
$$k_{sep} = 2.5 \cdot 10^9 \text{ s}^{-1}$$



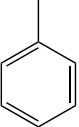
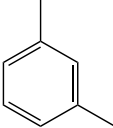
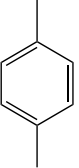
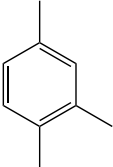
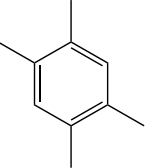
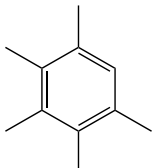
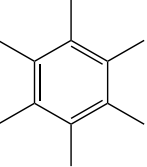
Transient absorption spectrum of tri-*p*-tolylamine radical cation obtained upon ns pulsed laser irradiation of 10-methyl acridinium perchlorate  $5 \cdot 10^{-5}$  M, *m*-xylene  $5 \cdot 10^{-2}$  M, and tri-*p*-tolylamine  $5 \cdot 10^{-4}$  M in degassed acetonitrile. Wavelengths for dye excitation and  $M^+$  monitoring were  $\lambda_{exc} = 408$  nm and  $\lambda_{obs} = 670$  nm, respectively.

# Photo-oxidation of aromatic hydrocarbons by acridinium dyes

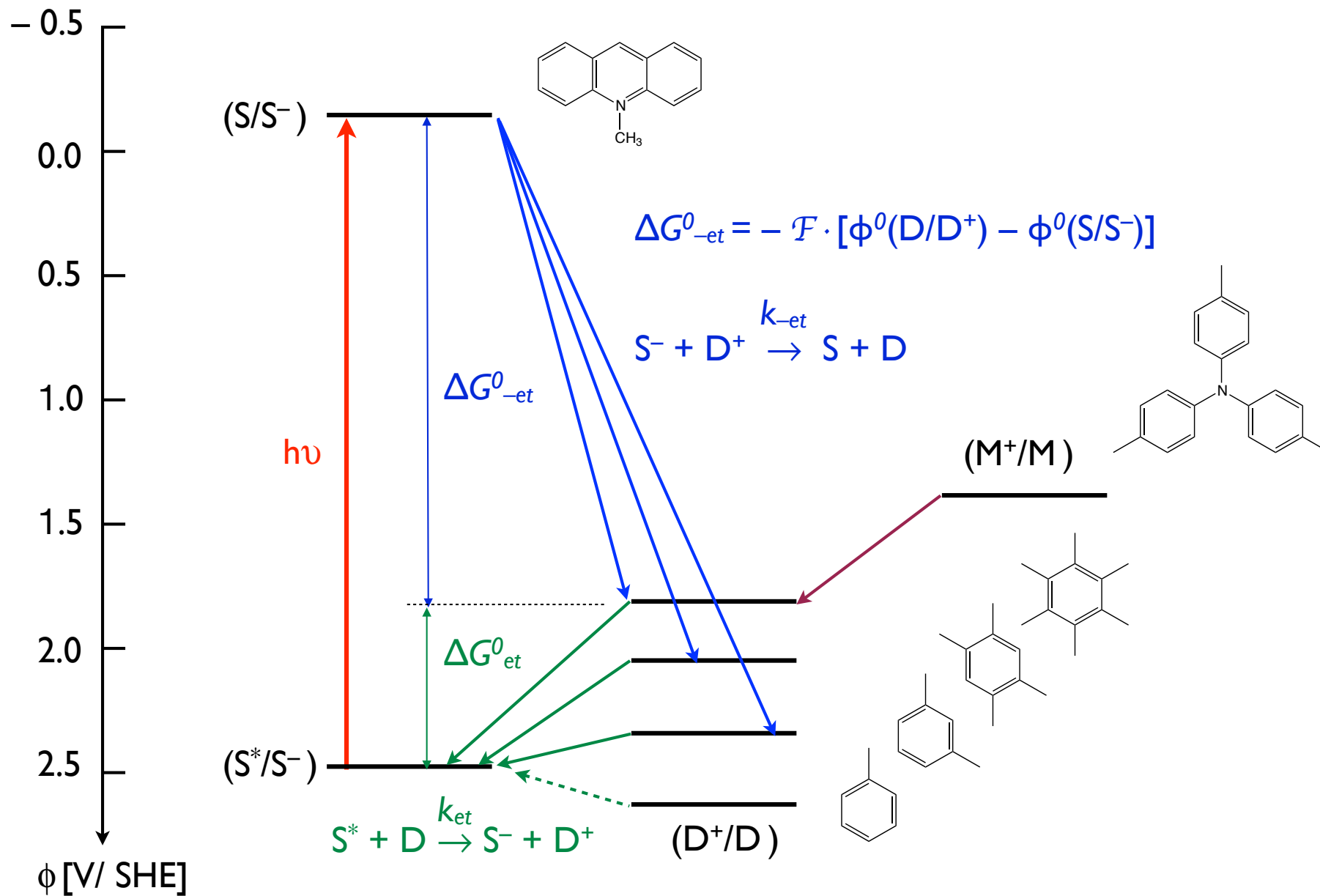
## Ns laser flash photolysis



## Photo-oxydation of aromatic hydrocarbons by acridinium dyes

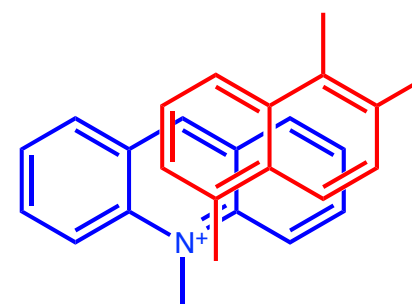
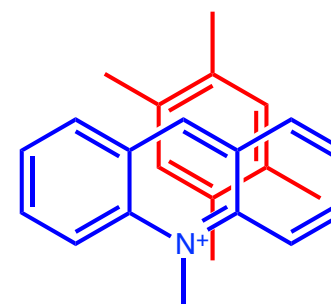
Donor	$\phi(D^+/D)$ [V/ SHE]	$-\Delta G^0_{-et}$ [eV]		
		MA <sup>+</sup>	CMA <sup>+</sup>	APS <sup>0</sup>
	2.64	2.82	2.67	2.99
	2.40	2.58	2.43	2.75
	2.30	2.48	2.33	2.65
	2.16	2.34	2.19	2.51
	2.05	2.23	2.08	2.40
	1.98	2.16	2.01	2.33
	1.86	2.04	1.89	2.21

# Photo-oxidation of aromatic hydrocarbons by acridinium dyes

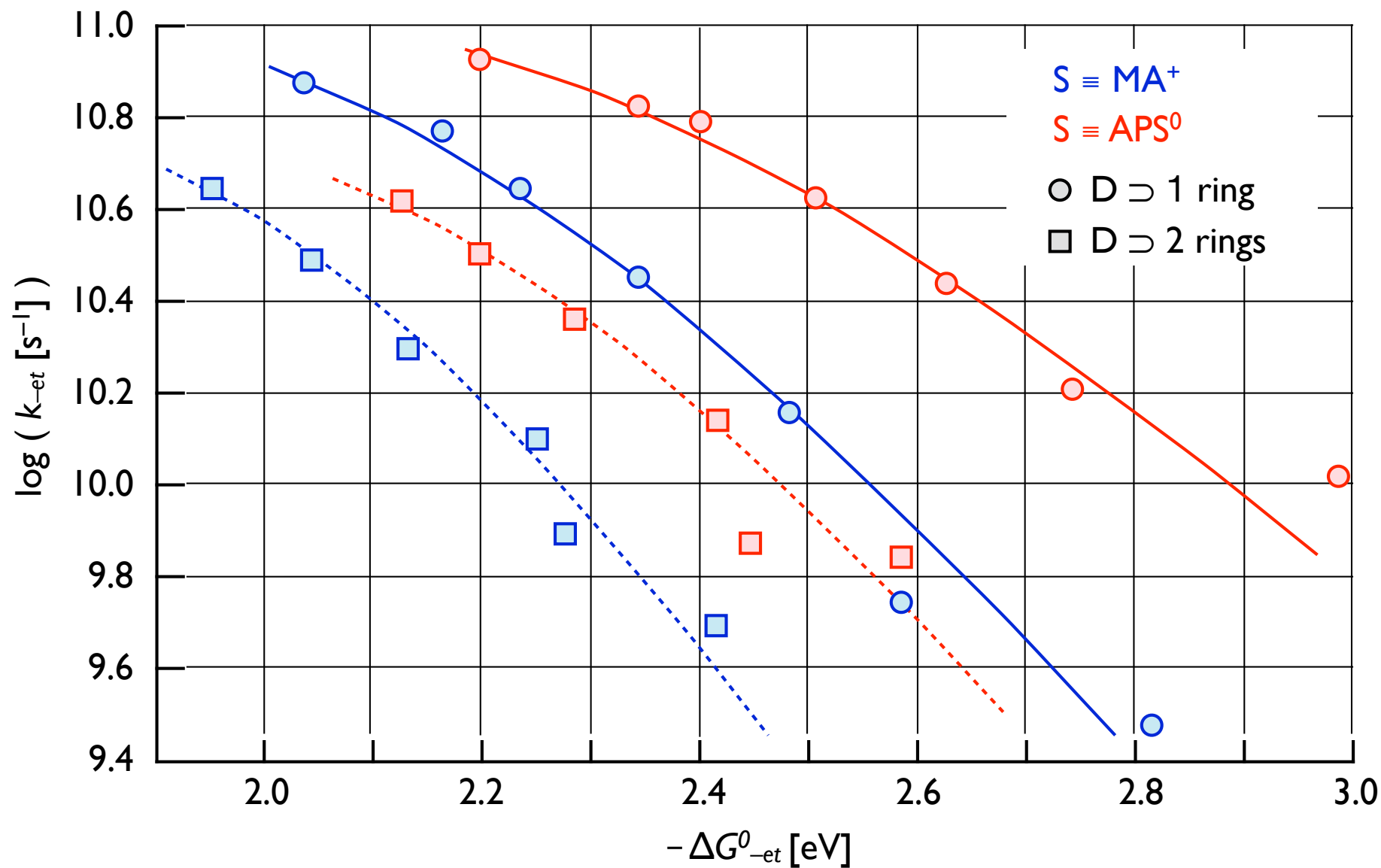


## Photo-oxidation of aromatic hydrocarbons by acridinium dyes

Donor	$-\Delta G^0_{-et}$ [eV]	$\Phi_{et} / \Phi_{M^+}$	$\log ( k_{-et} [s^{-1}] )$
Toluene	2.82	0.487	9.47
m-xylene	2.58	0.339	9.74
p-xylene	2.48	0.158	10.17
1,2,4-trimethylbenzene	2.34	0.092	10.44
Durene	2.23	0.061	10.63
Pentamethylbenzene	2.16	0.044	10.78
Hexamethylbenzene	2.04	0.037	10.86
Biphenyl	2.41	0.363	9.69
Diphenylacetylene	2.27	0.277	9.86
Naphthalene	2.25	0.175	10.12
2-methylnaphthalene	2.13	0.125	10.29
2,6-dimethylnaphthalene	2.04	0.082	10.50
2,3,5-trimethylnaphthalene	1.95	0.061	10.63



## Photo-oxidation of aromatic hydrocarbons by acridinium dyes



## Photo-oxydation of aromatic hydrocarbons by acridinium dyes

### Non-linear fitting of the parameters of Marcus-Dogonadze's equation

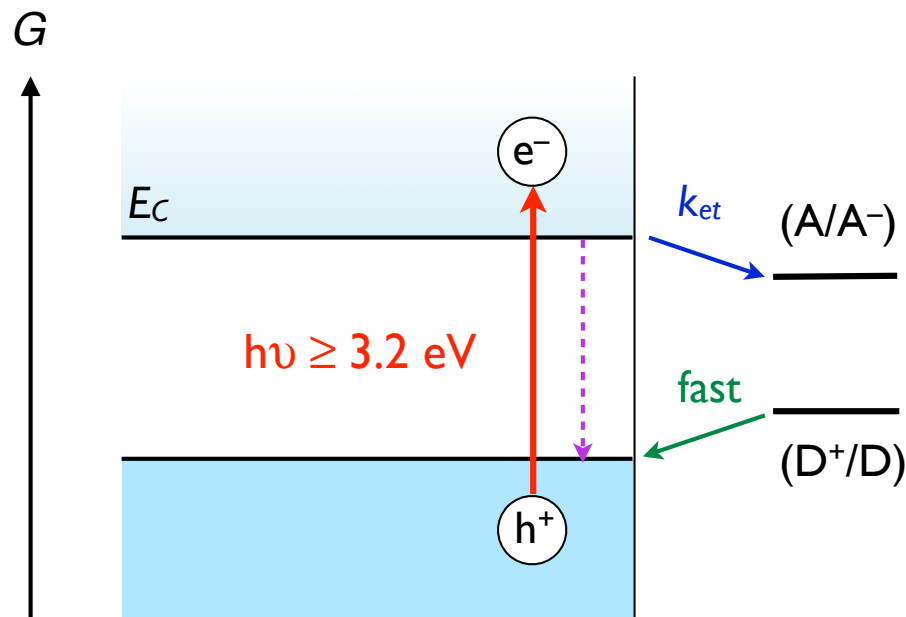
$$k_{et} = |H_{DA}|^2 \cdot \frac{1}{\sqrt{2\pi \cdot \lambda_{out} \cdot k_B T}} \cdot \exp\left(\frac{-\lambda_{in}}{h\nu}\right) \cdot \sum_{n=0}^{\infty} \frac{\left(\frac{\lambda_{in}}{h\nu}\right)^n}{n!} \cdot \exp\left[\frac{-\left(\Delta G_r^0 + n h\nu + \lambda_{out}\right)^2}{4 \lambda_{out} \cdot k_B T}\right]$$

The vibrational frequency  $\nu$  is set to  $\bar{\nu} = \text{constant} = 1500 \text{ cm}^{-1}$

S	MA <sup>+</sup>		APS <sup>0</sup>	
D	1 ring	2 rings	1 ring	2 rings
$ H_{DA} ^2 \text{ [cm}^{-1}\text{]}$	24.0	21.5	25.0	21.5
$\lambda_{out} \text{ [eV]}$	1.6	1.4	1.6	1.4
$\lambda_{in} \text{ [eV]}$	0.20	0.20	0.45	0.45



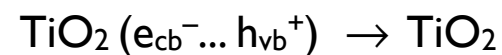
## B. Light-induced heterogeneous ET from the conduction band of TiO<sub>2</sub> to an acceptor in solution



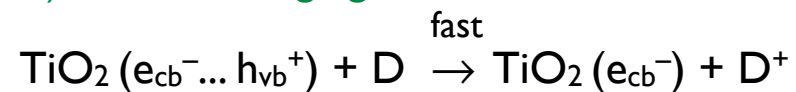
### 1) Intrinsic absorption of light



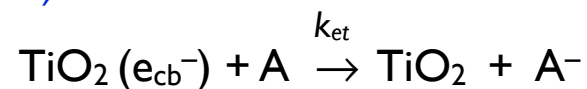
### 2) Electron-hole recombination



### 3) Hole scavenging



### 4) Interfacial electron transfer



### Dependence of $\Delta G^0_{\text{et}}$ upon the solution pH

$$E_{F,n}^* \approx E_C = -\mathcal{F} \cdot [\phi_C (\text{pH}=0) - 0.059 \text{ V} \cdot \text{pH}]$$

where :  $\phi_C (\text{pH}=0) \approx -0.210 \text{ V} / \text{SHE}$

$$\Delta G^0_{\text{et}} = -\mathcal{F} \cdot \phi^0 (\text{A/A}^-) - E_{F,n}^*$$

$$\Delta G^0_{\text{et}} \approx -\mathcal{F} \cdot [\phi^0 (\text{A/A}^-) - \phi_C (\text{pH}=0) + 0.059 \text{ V} (\text{pH})]$$

experimental variable

# Light-induced interfacial electron transfer

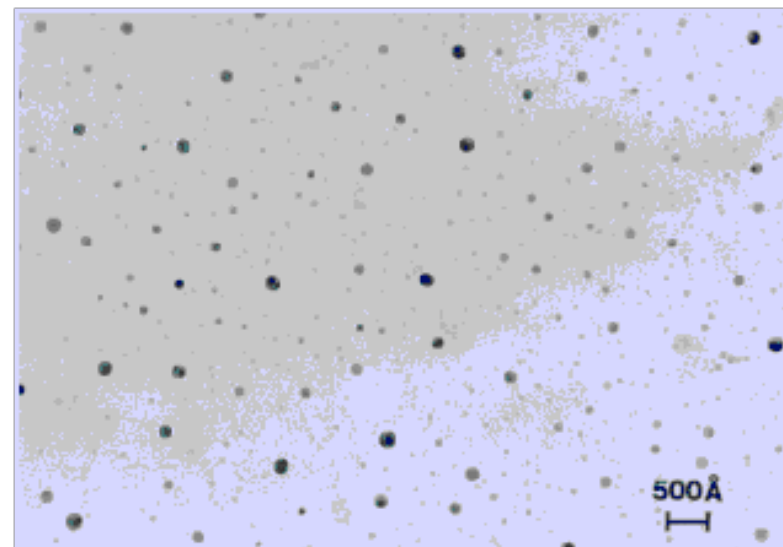
## Aqueous suspension of TiO<sub>2</sub> nanoparticles

Particle radius ~ 5-10 nm

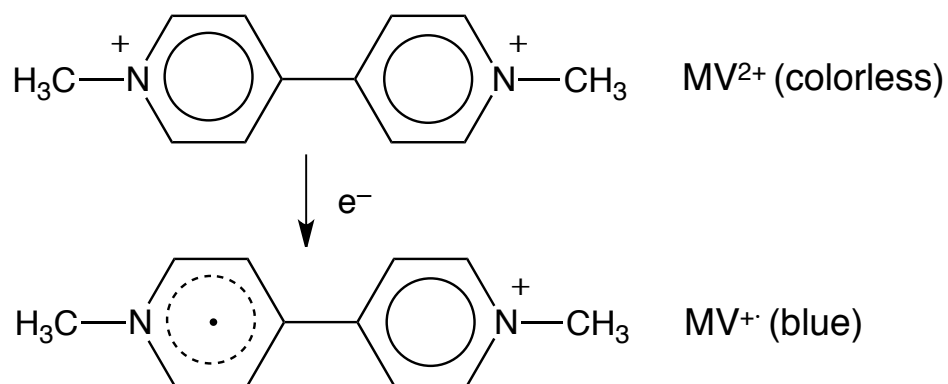
⇒ weak Rayleigh scattering

⇒ transparent colloid

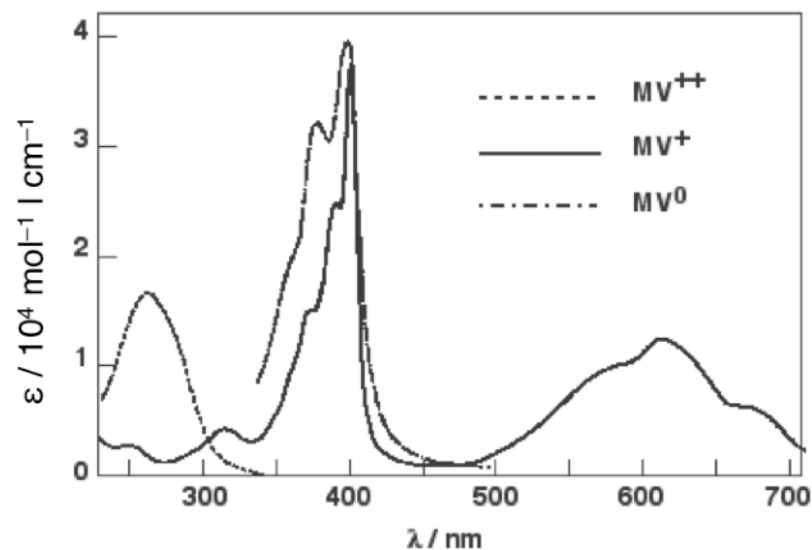
⇒ allows for the application of ns laser transient absorption spectroscopy technique to monitor ET kinetics



## Electron acceptor A

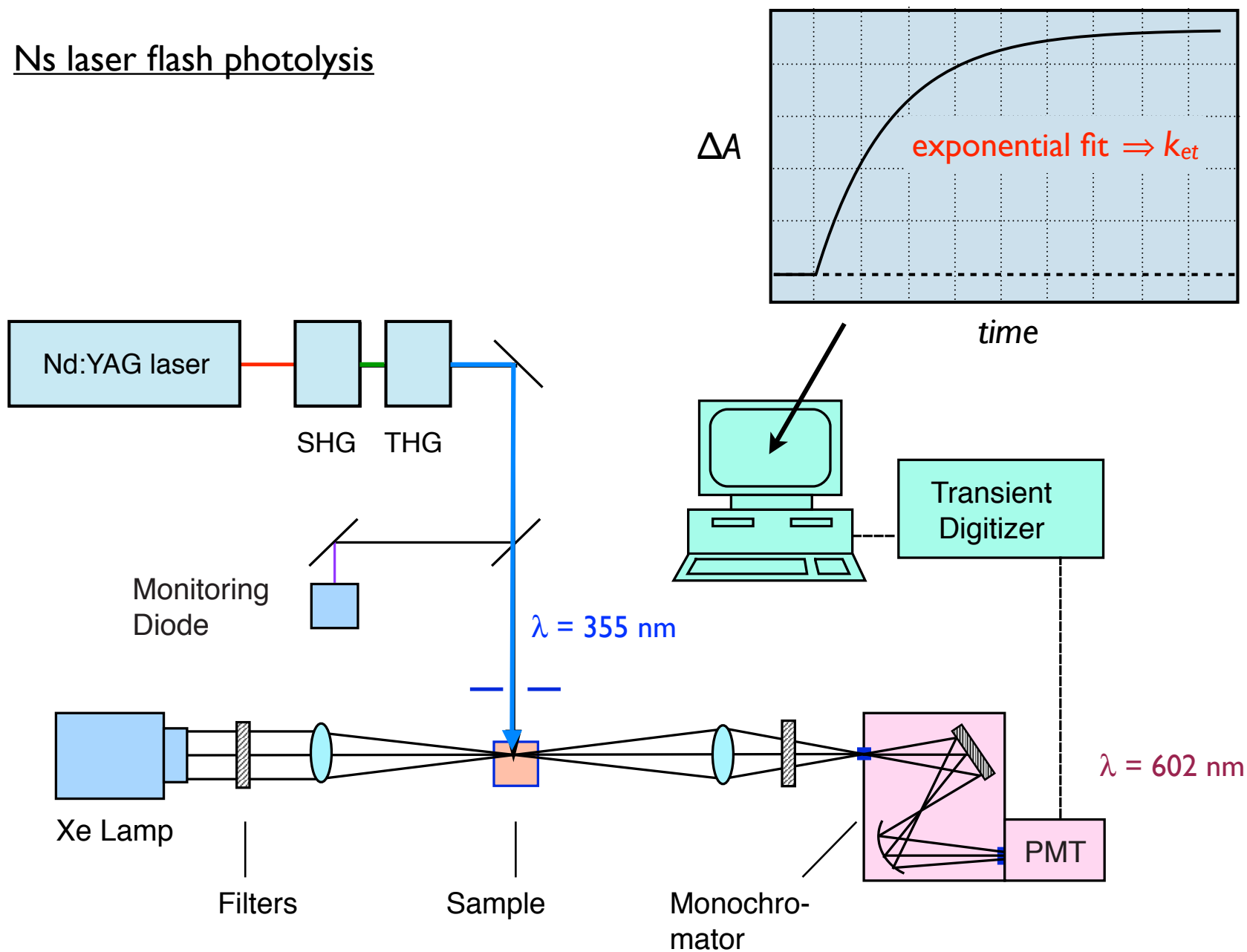


$$\phi^0 (MV^{2+}/MV^{+}) = -0.446 \text{ V / SHE}$$

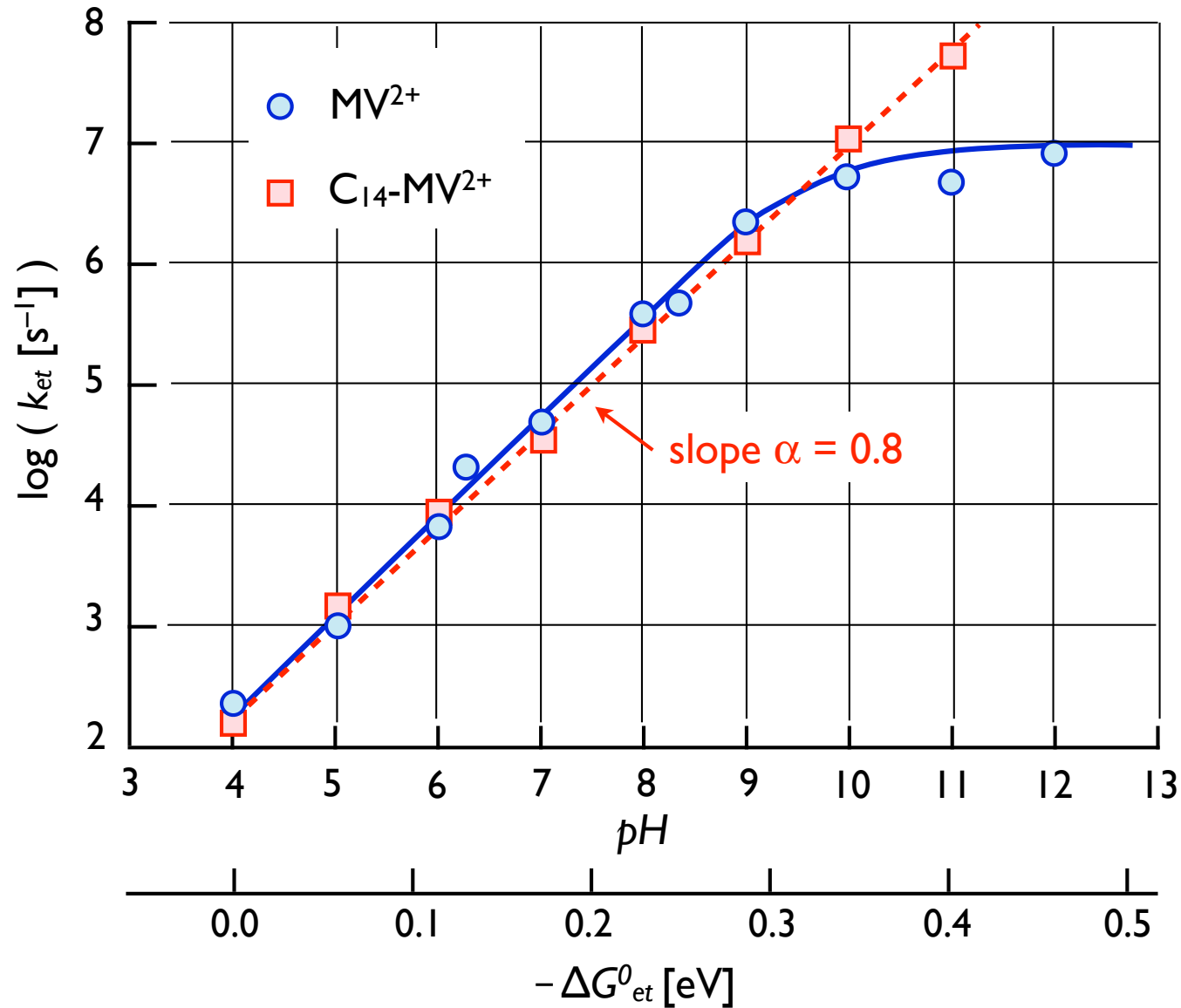


# Light-induced interfacial electron transfer

## Ns laser flash photolysis



## Light-induced interfacial electron transfer



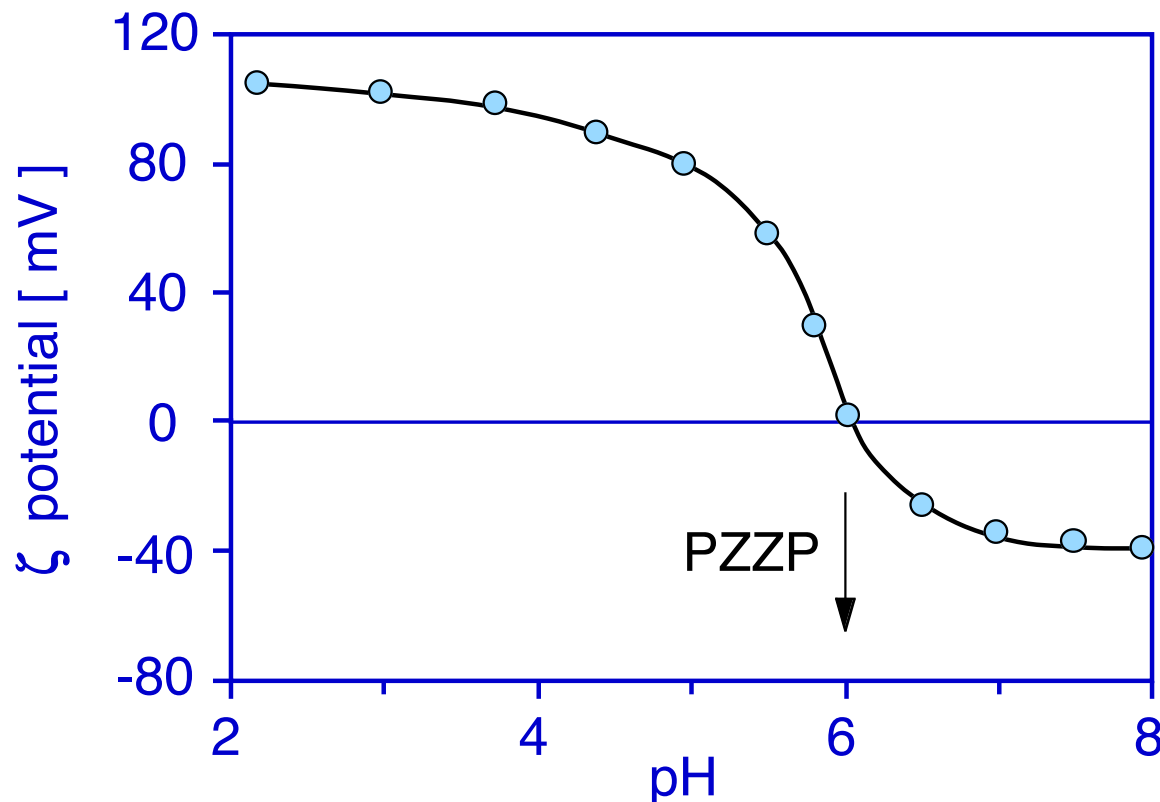
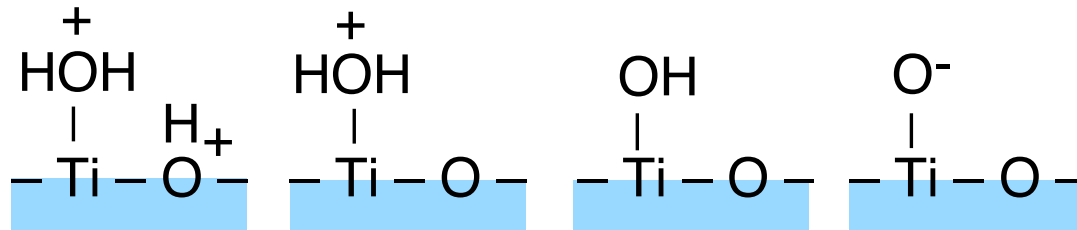
$$[MV^{2+}]_0 = 10^{-3} \text{ M}$$

Tafel equation:

$$\ln i = \ln i_0 + \frac{\alpha \cdot F \cdot \eta}{RT}$$

$$\ln \left( \frac{k_{et}}{k_{et}^0} \right) = \alpha \cdot \frac{-\Delta G_{et}^0}{RT}$$

## Light-induced interfacial electron transfer

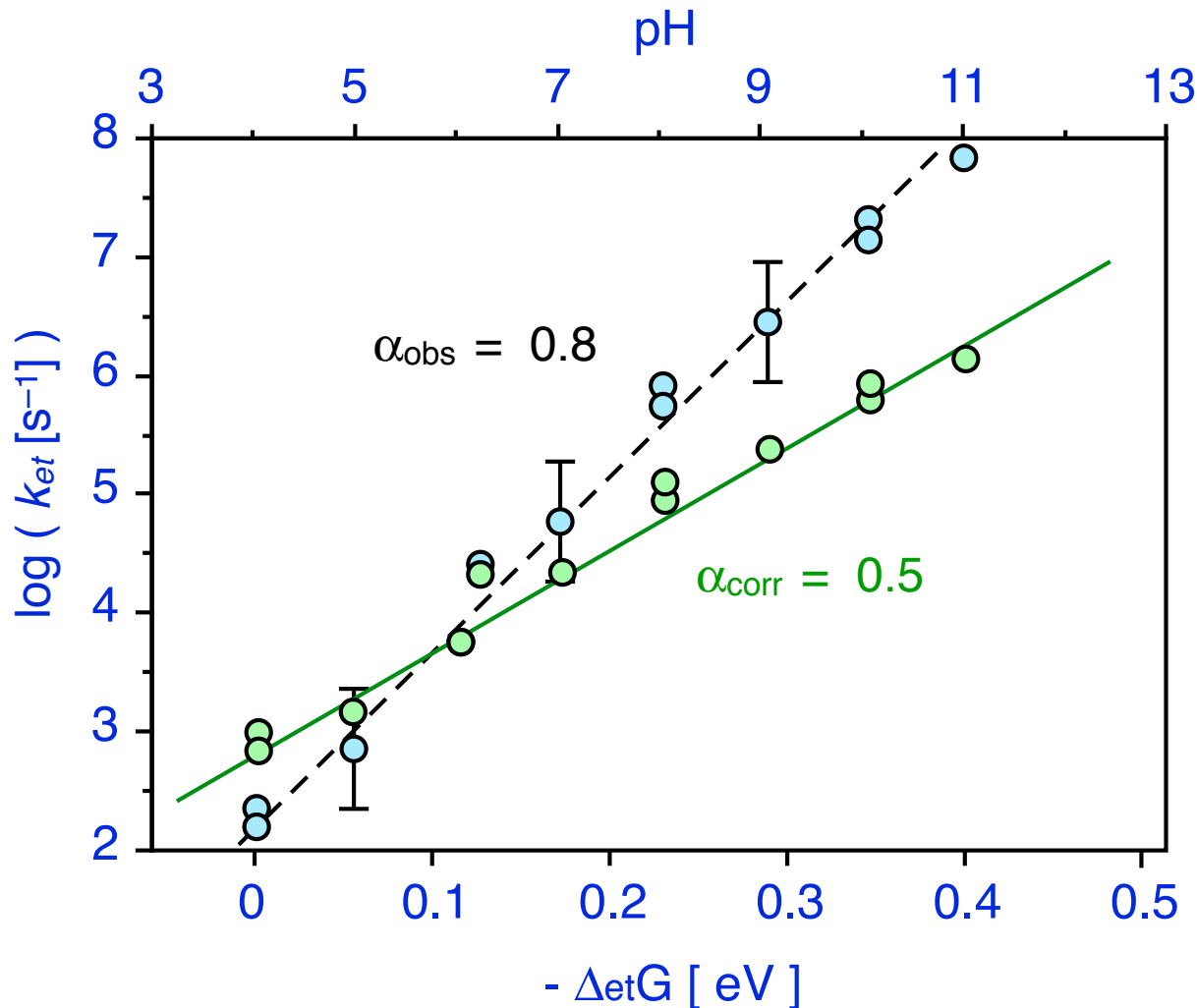


The surface of titanium dioxide is amphoteric. In acidic medium, terminal  $\text{-OH}$  groups, as well as oxygen bridges are protonated, yielding a positive surface charge. In alkaline medium, terminal hydroxyl groups are deprotonated, resulting in a negative surface charge. An isoelectric point, corresponding to a neutral surface, is found typically for  $pH = 6$ .

The zeta-potential of colloidal particles can be easily measured as a function of  $pH$  by use of electrophoresis technique.

## Light-induced interfacial electron transfer

Results displayed on page 51 are well fitted by Tafel linear equation with a slope  $\alpha = 0.8$ . The latter value ( $\alpha \neq 0.5$ ) is not compatible with the assumption of a kinetically symmetric activated complex and thus with the classical Marcus theory.



Experimental results can be corrected for electrostatic interactions between the solid oxide charged surface and the acceptor cations in solution by using a semi-empirical function:

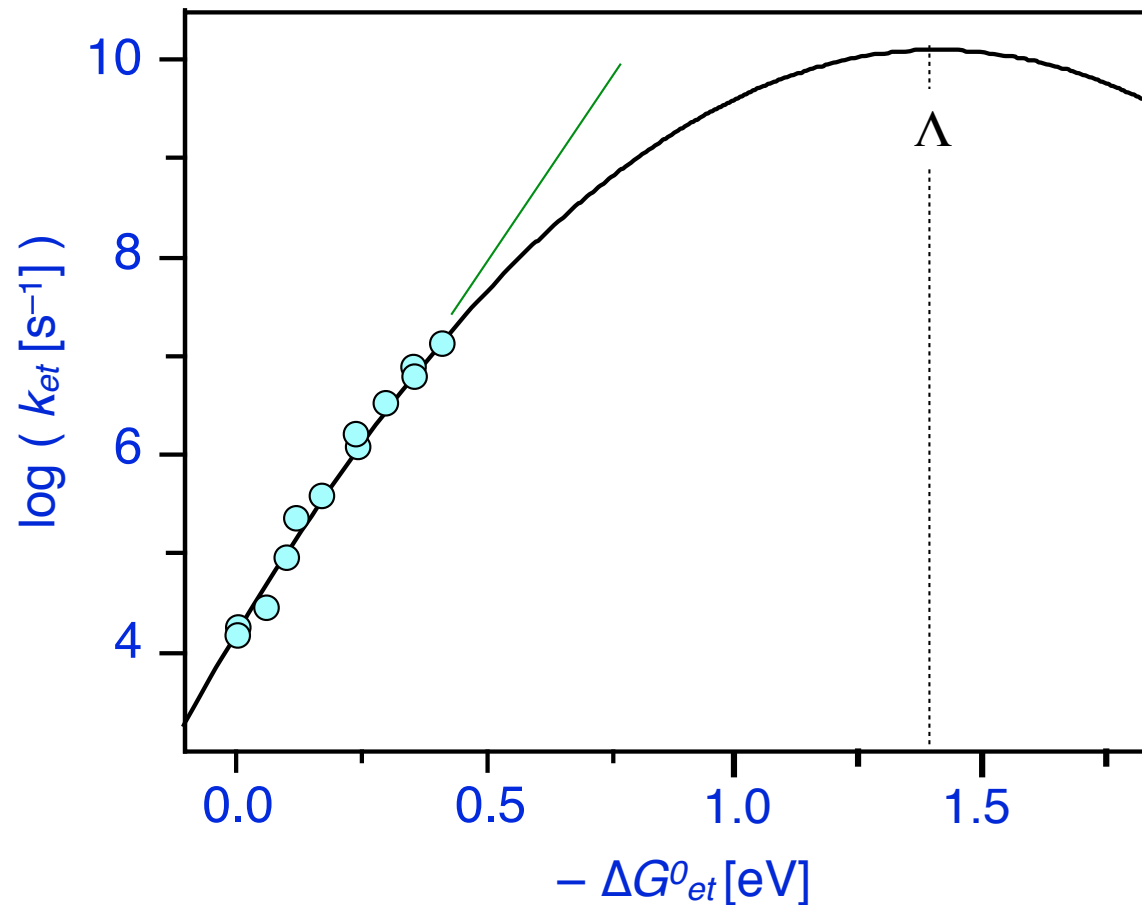
$$\alpha_{corr} = \alpha_{obs} - \frac{\gamma}{\sqrt{\mu}}$$

in which  $\gamma$  is an adjustment factor and  $\mu$  is the ionic strength of the liquid medium.

## Light-induced interfacial electron transfer

Non-linear fitting of the parameters of Marcus classical relation applied to diabatic ET

$$k_{et} = |H_{DA}|^2 \cdot \frac{\sqrt{\pi}}{\hbar \cdot \sqrt{k_B T \cdot \Lambda}} \cdot \exp\left(-\frac{(\Lambda + \Delta G_{et}^0)^2}{4\Lambda \cdot k_B T}\right)$$



$$|H_{DA}|^2 = 7.6 \text{ cm}^{-1}$$

$$\Lambda = 1.4 \text{ eV}$$