Combining cw- CRDS and LIF with Laser Photolysis : Kinetic and Spectroscopic Studies of HOx radical reactions

PhysicoChimie des Processus de Combustion et de l'Atmosphère PC2A

Université de Lille

Christa FITTSCHEN

RÉGION NORD PAS DE CALAIS

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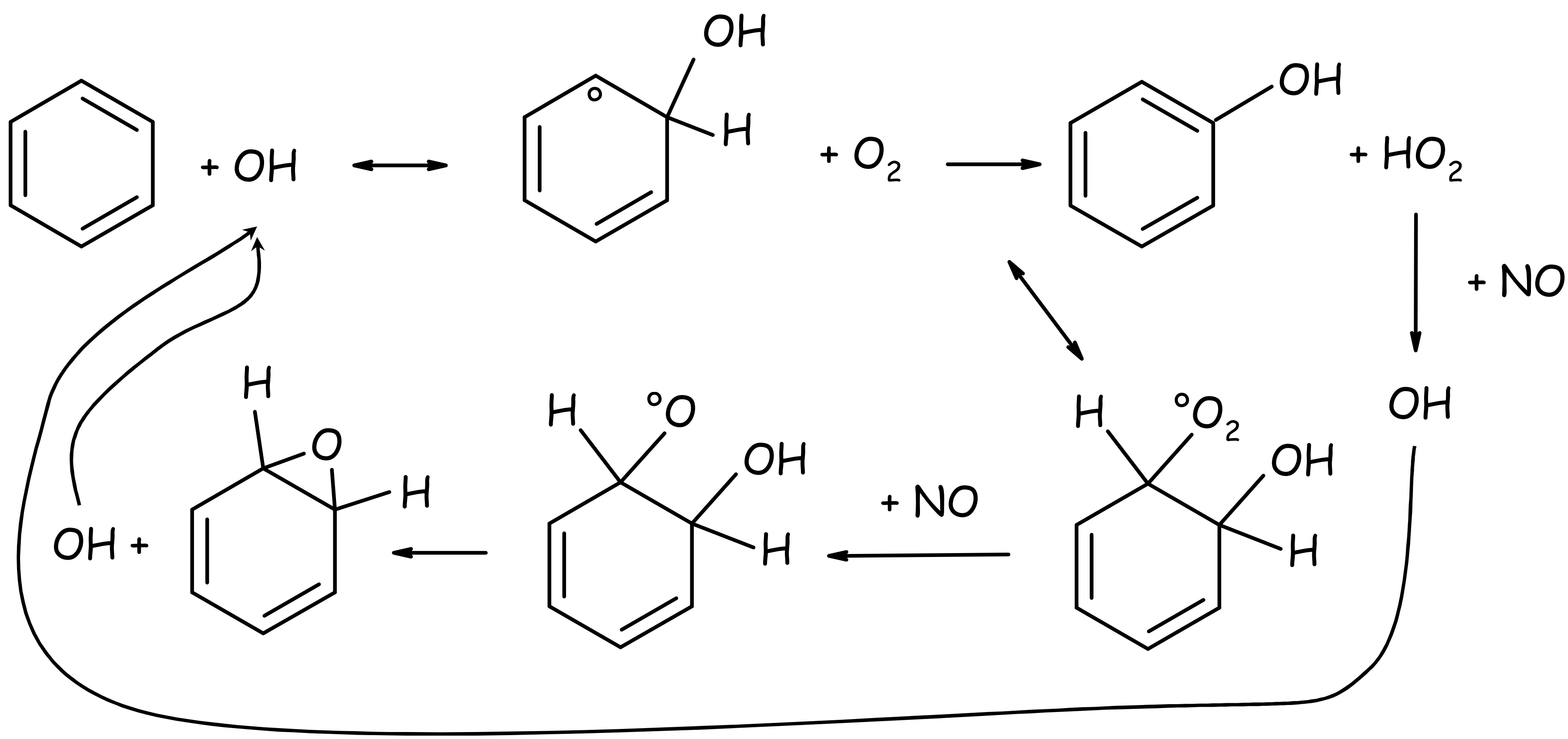
Université Lille1 Sciences et Technologies

Why detecting OH and HO_2 simultaneously?



What you want is a simultaneous quantitative detection of OH and HO_2

- OH sensitive and selective by LIF, but not absolute
- And HO_2???

Detection of HO_2

Non-optical methods:

- ESR spectroscopy has been applied, but is time-consuming
- CIMS

Optical methods:

- HO_2 unfortunately does non fluoresce
- Many studies have been done by UV-absorption spectroscopy
    - good sensitivity
    - bad selectivity (large, unstructured absorption band)
- OH vibration in IR region (around 3, 7 et 10 µm) have line spectrum
    - good selectivity, good sensitivity
    - strong pressure broadening, demanding experiment
- Overtone of ν_1 OH vibration is in the telecom region : 1.5µm!!

Exploiting the near IR around 1.5 µm to study the HO_2 radical

Overtone spectroscopy means small absorption coefficients

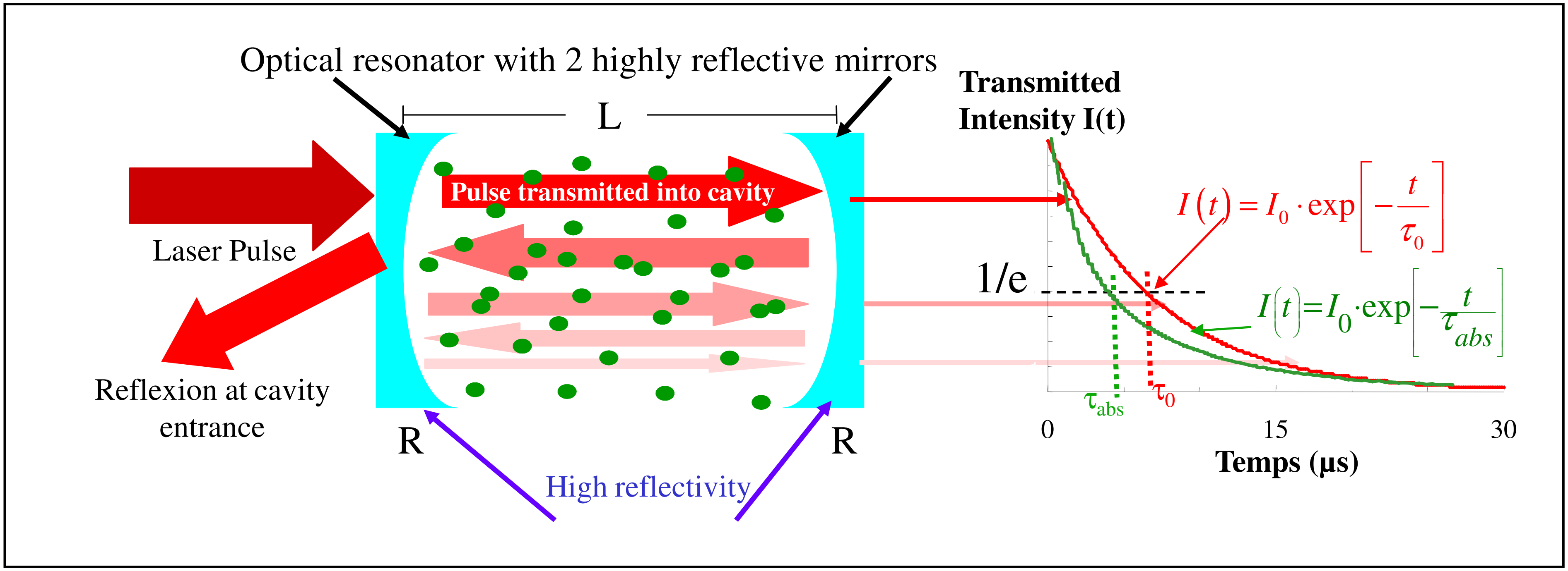
⇒ A sensitive detection technique is needed:

Wavelength modulation spectroscopy has been used mainly by S. Sander, C. Taatjes, K. Tonokura:

- complex experimental set-up,
- not an absolute technique

Other solution: CRDS!!!!!!!!!!!

What is CRDS ?



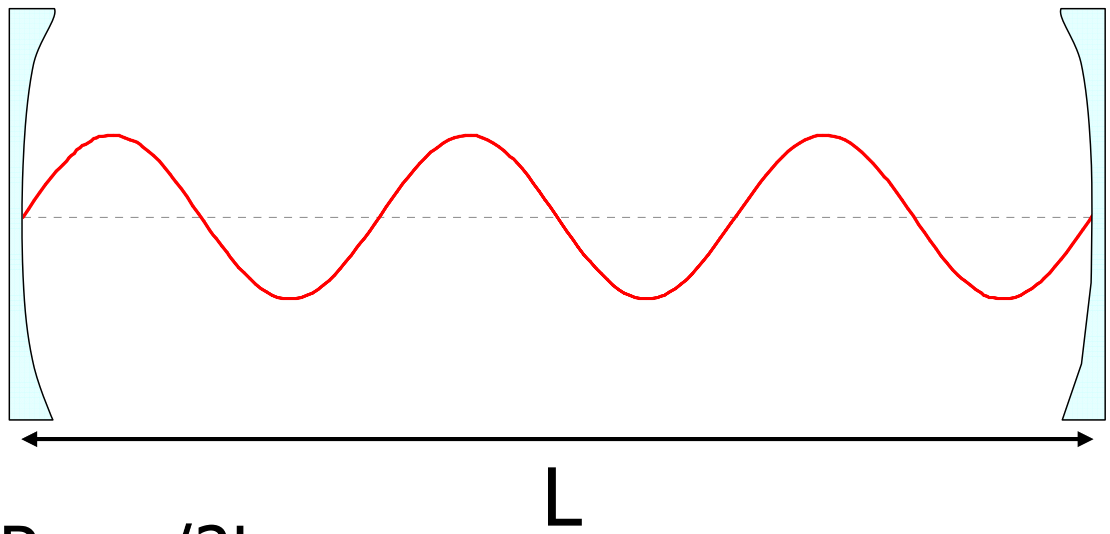
$$\tau_0 = \frac{L}{c\,(1-R)}$$

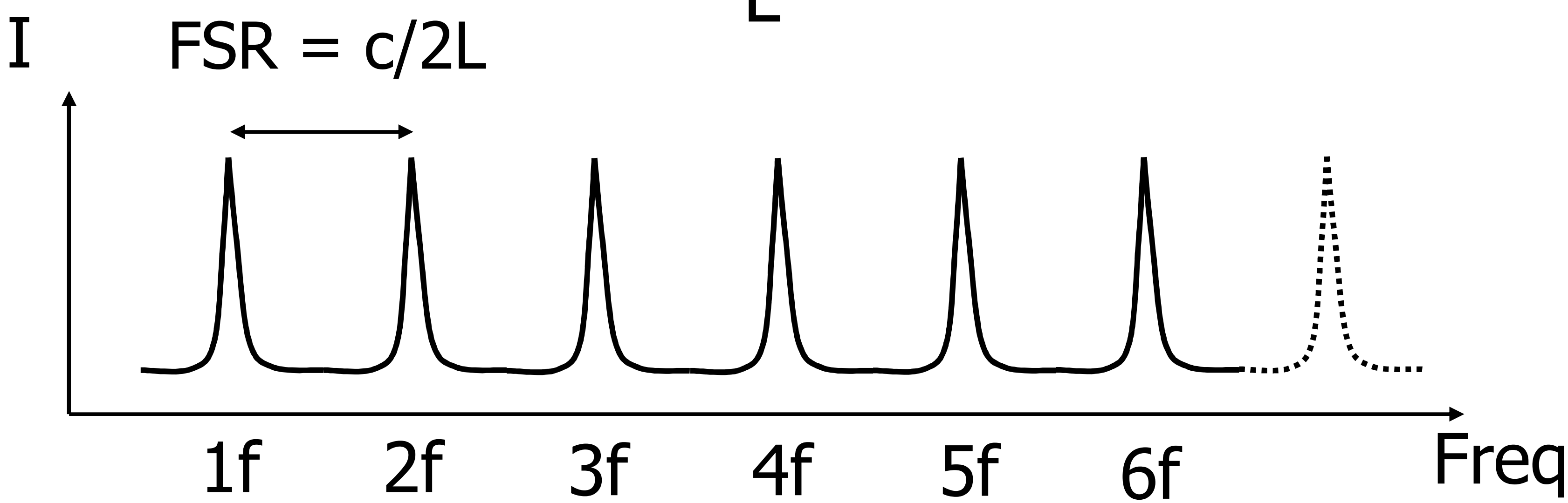
$$\tau_{abs} = \frac{L}{c\{(1-R)+[abs]\sigma_{abs}L\}}$$

$$[abs]\,\sigma_{abs} = \frac{1}{c}\left(\frac{1}{\tau_{abs}} - \frac{1}{\tau_0}\right)$$

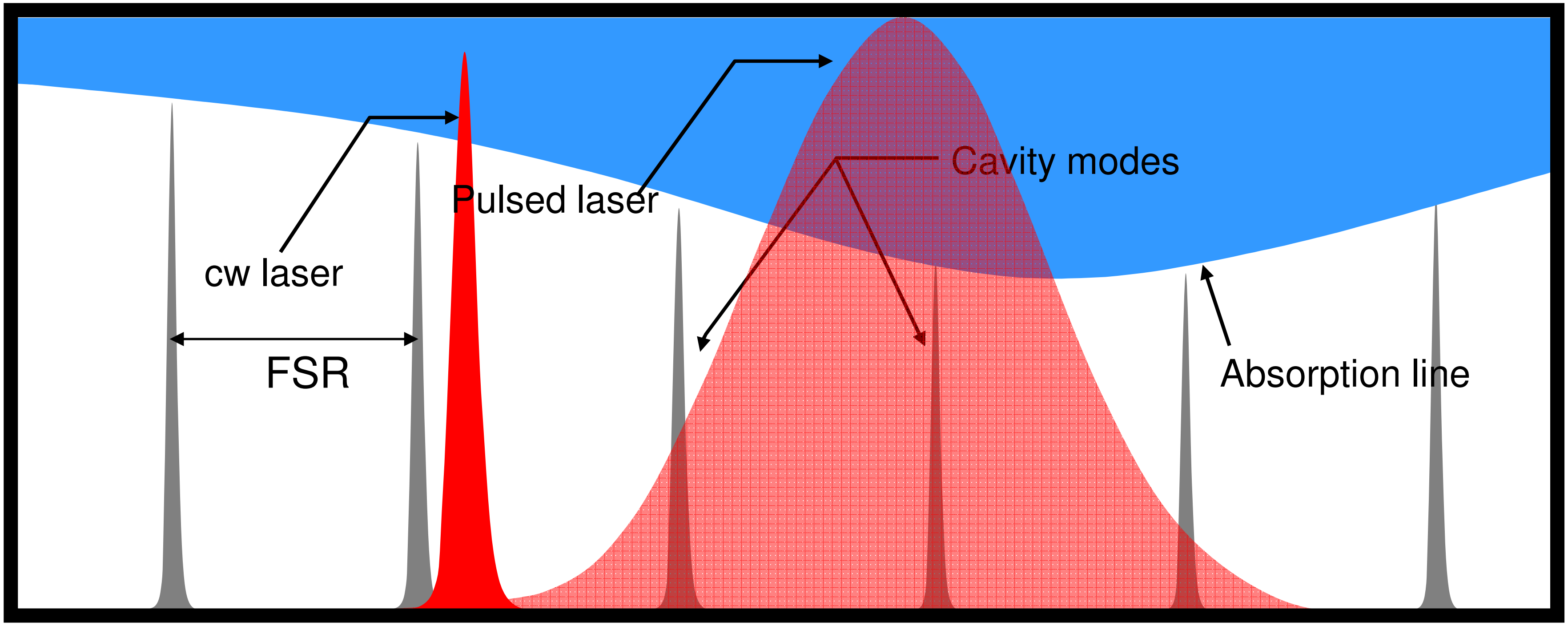
Optical cavity has discrete modes

For efficient injection L must be $n \times \lambda / 2$





Spectrale line width



→ Width of pulsed laser ~ some GHz

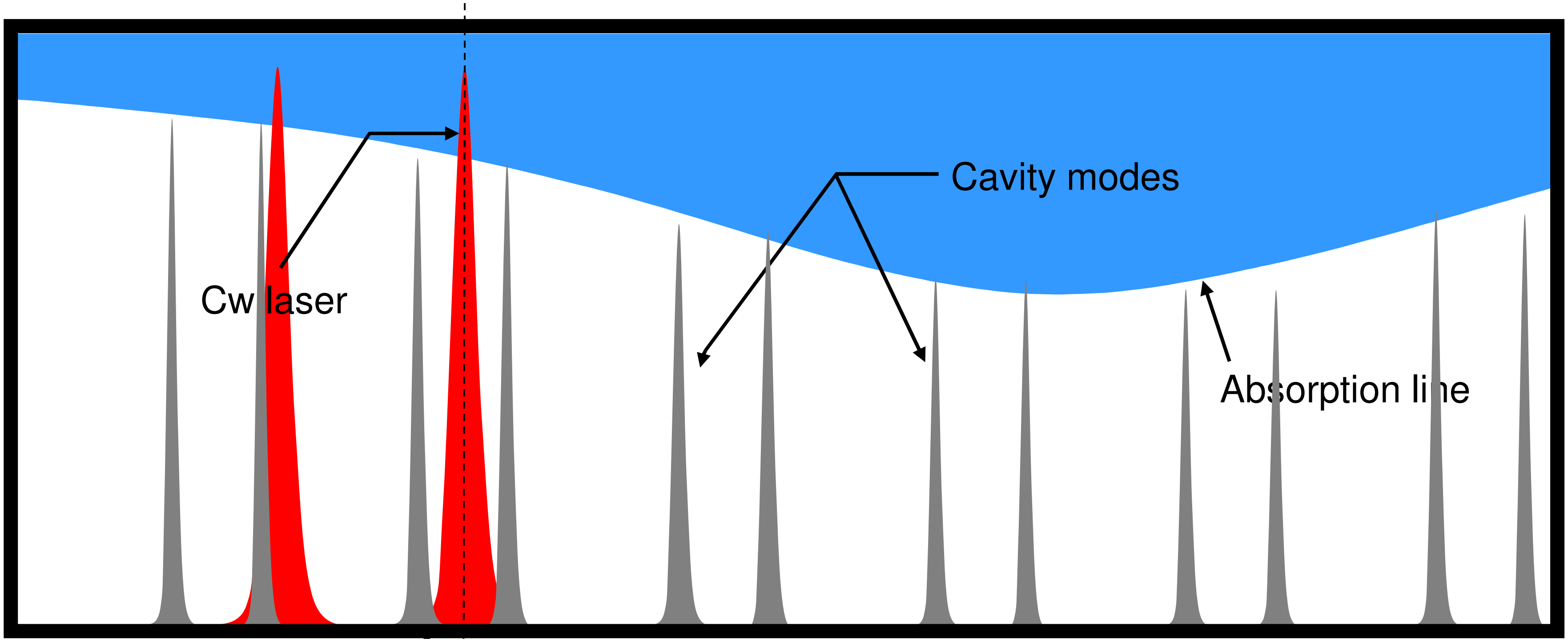
→ Doppler FWHM HO_2 : 0.4 GHz (T_{amb})

→ Free spectrale range ~ 200 MHz

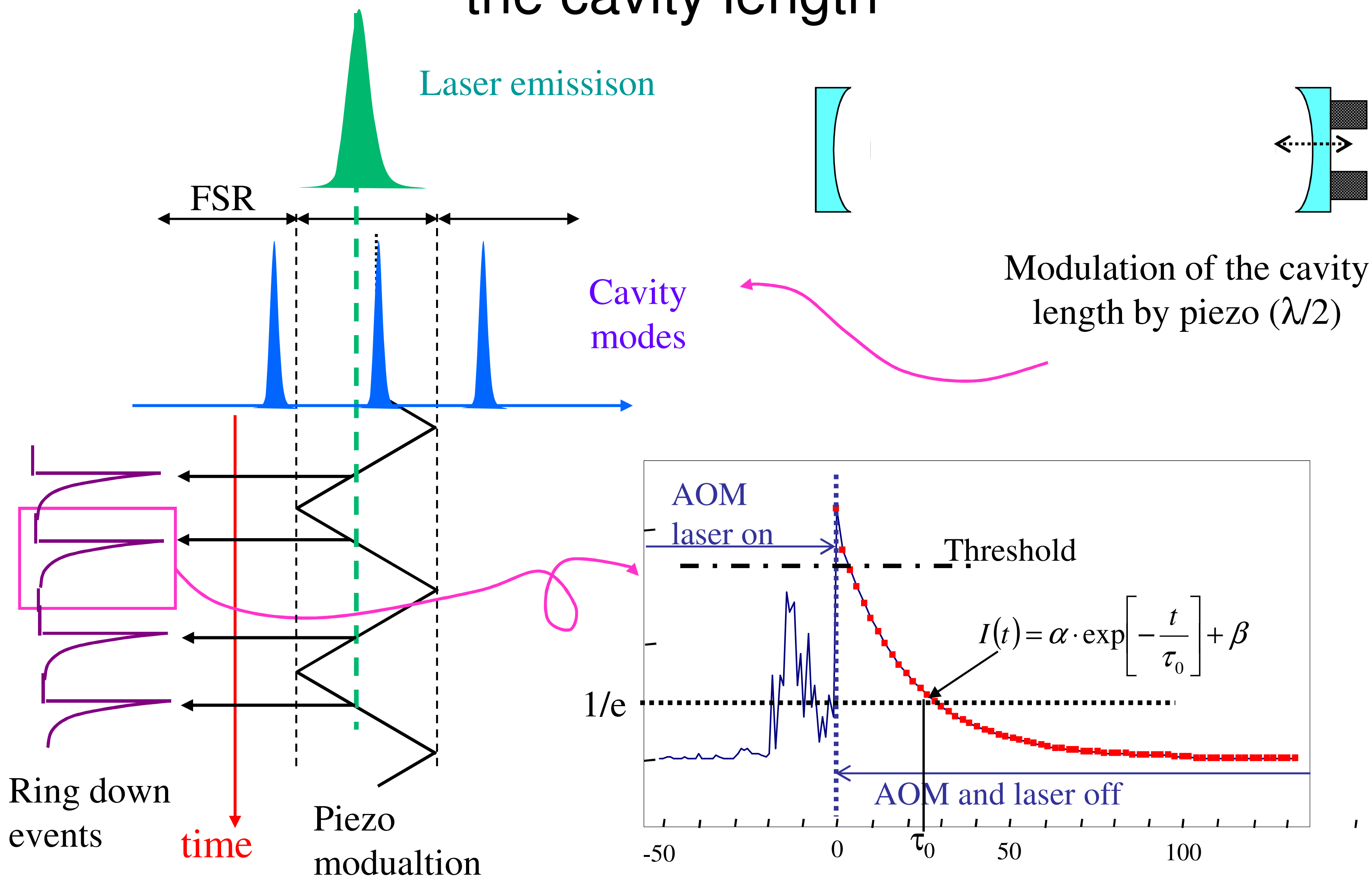
→ Width of cw laser ~ 2 MHz

→ Width of cavity modes: some 10 kHz

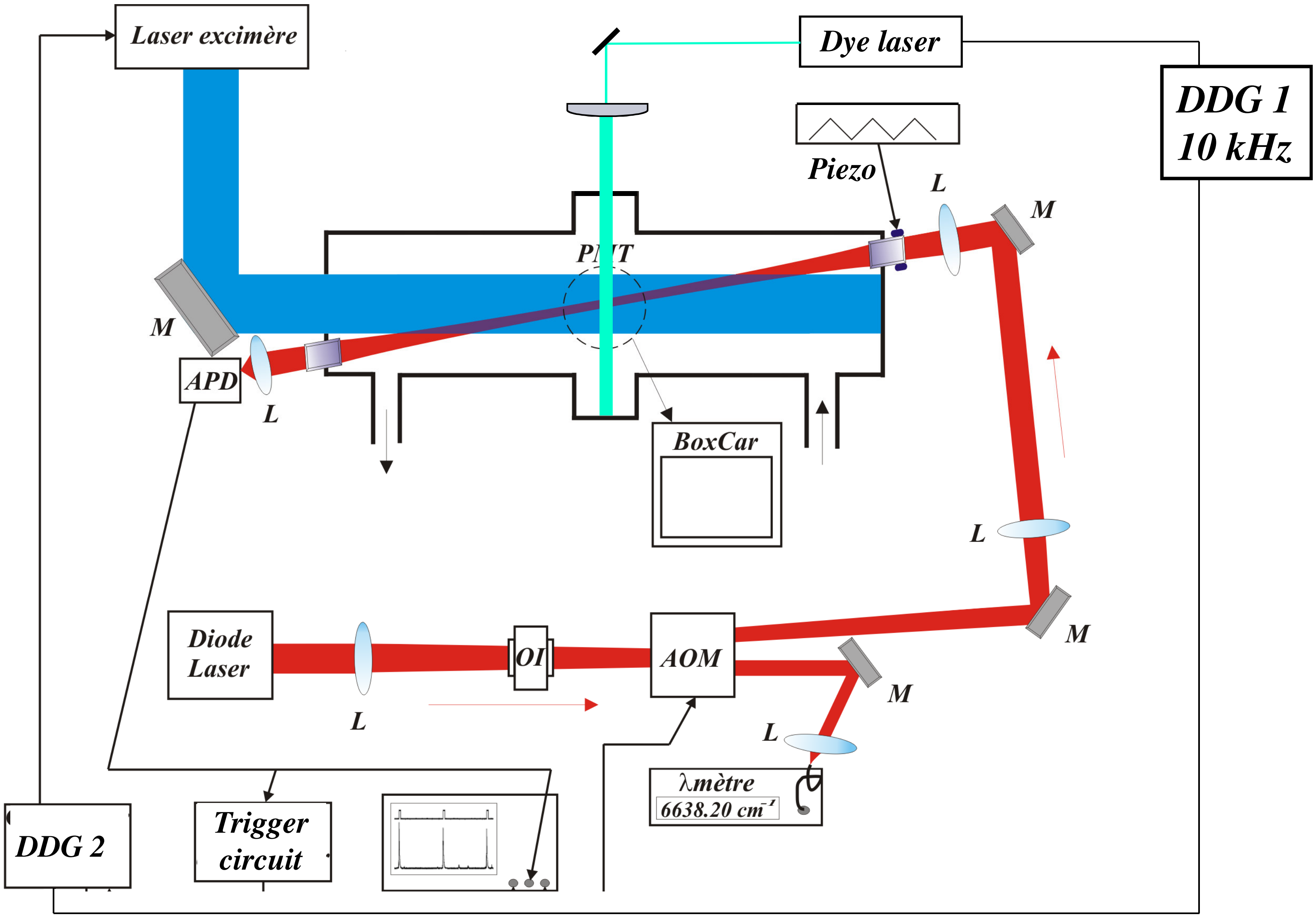
Light injection by resonance



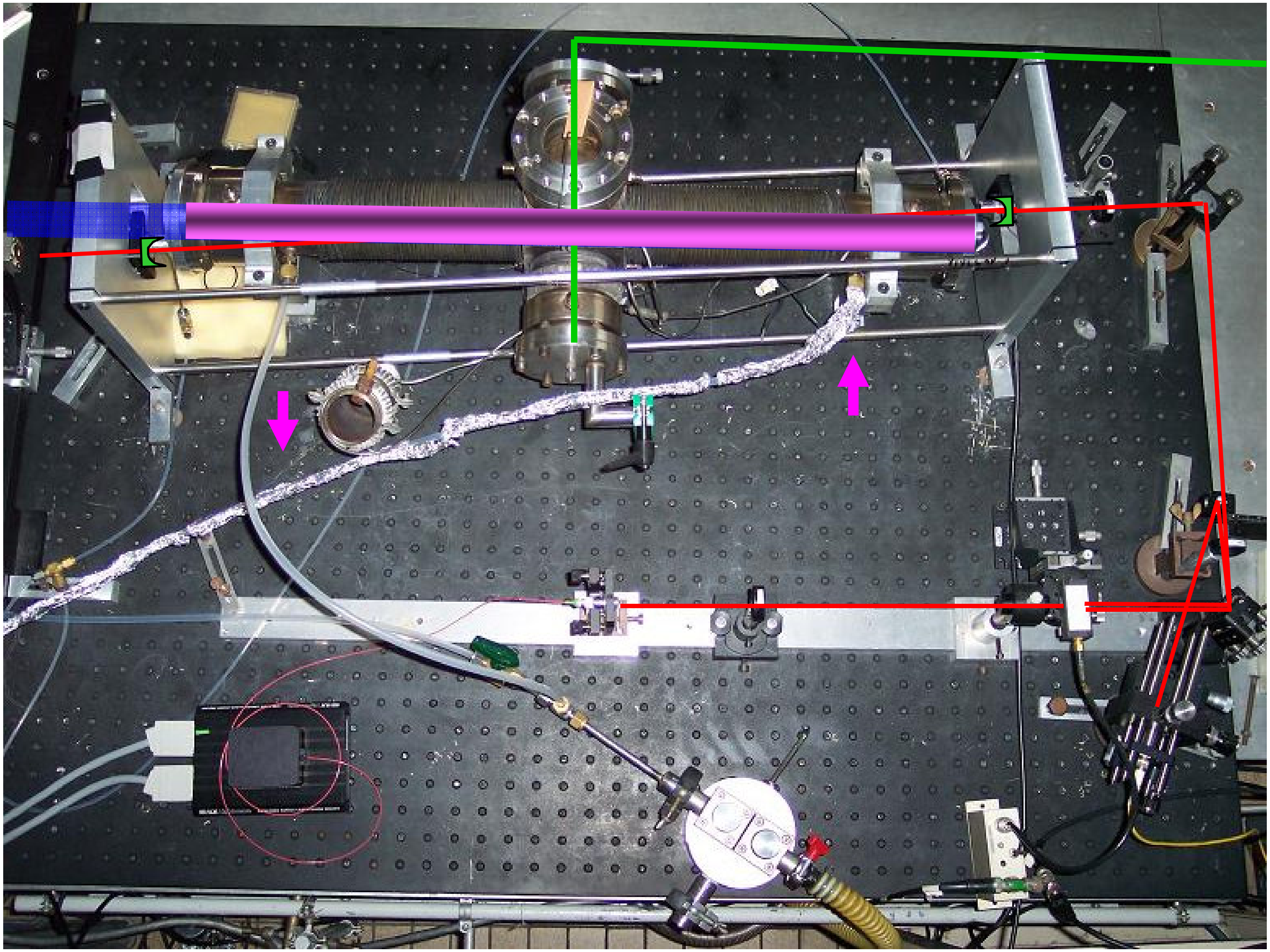
Solution 2: Move around the modes by modulating the cavity length



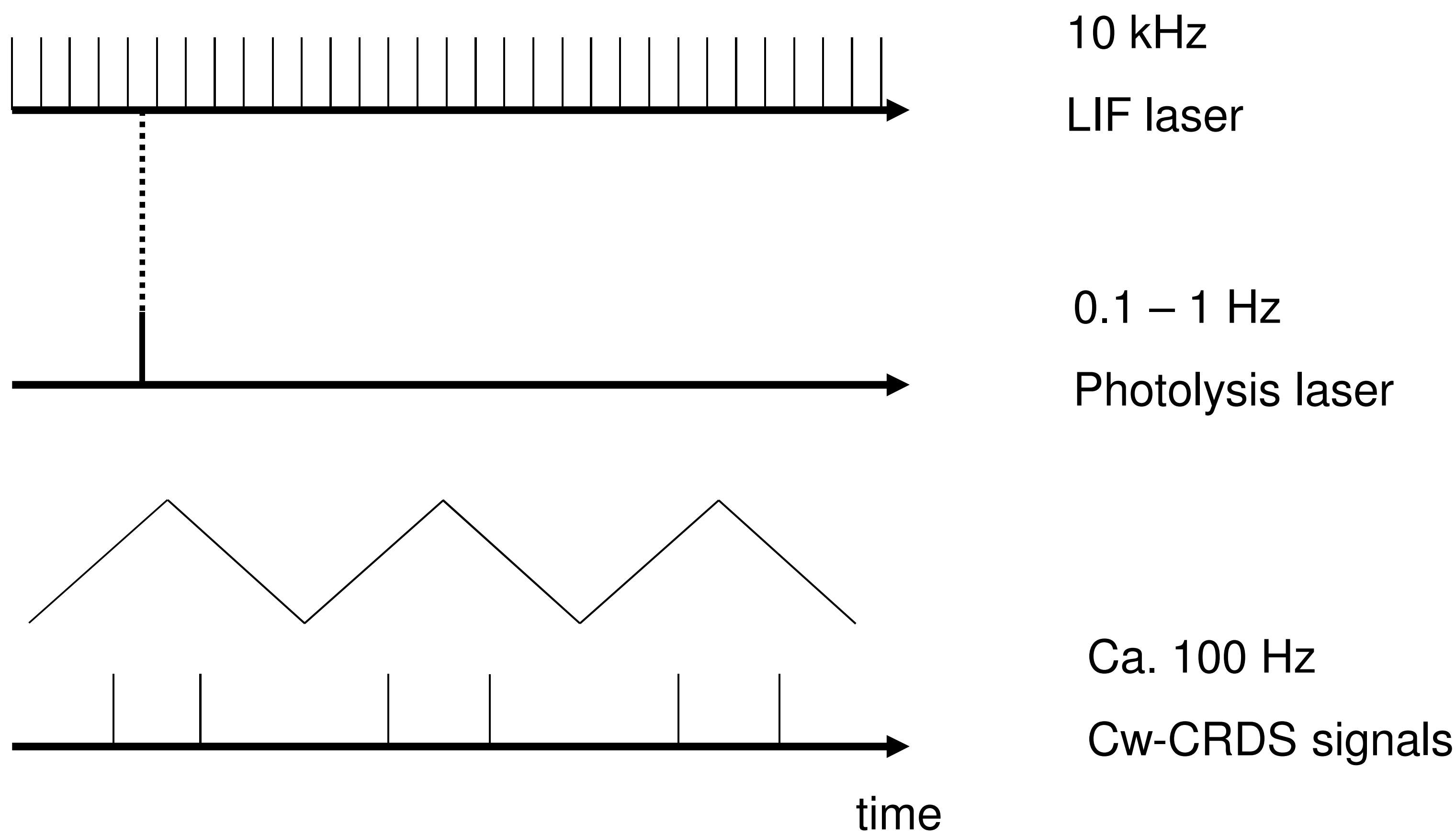
Experimental set-up



Laser Photolysis – cw-CRDS – LIF



Synchronization of LIF and cw-CRDS



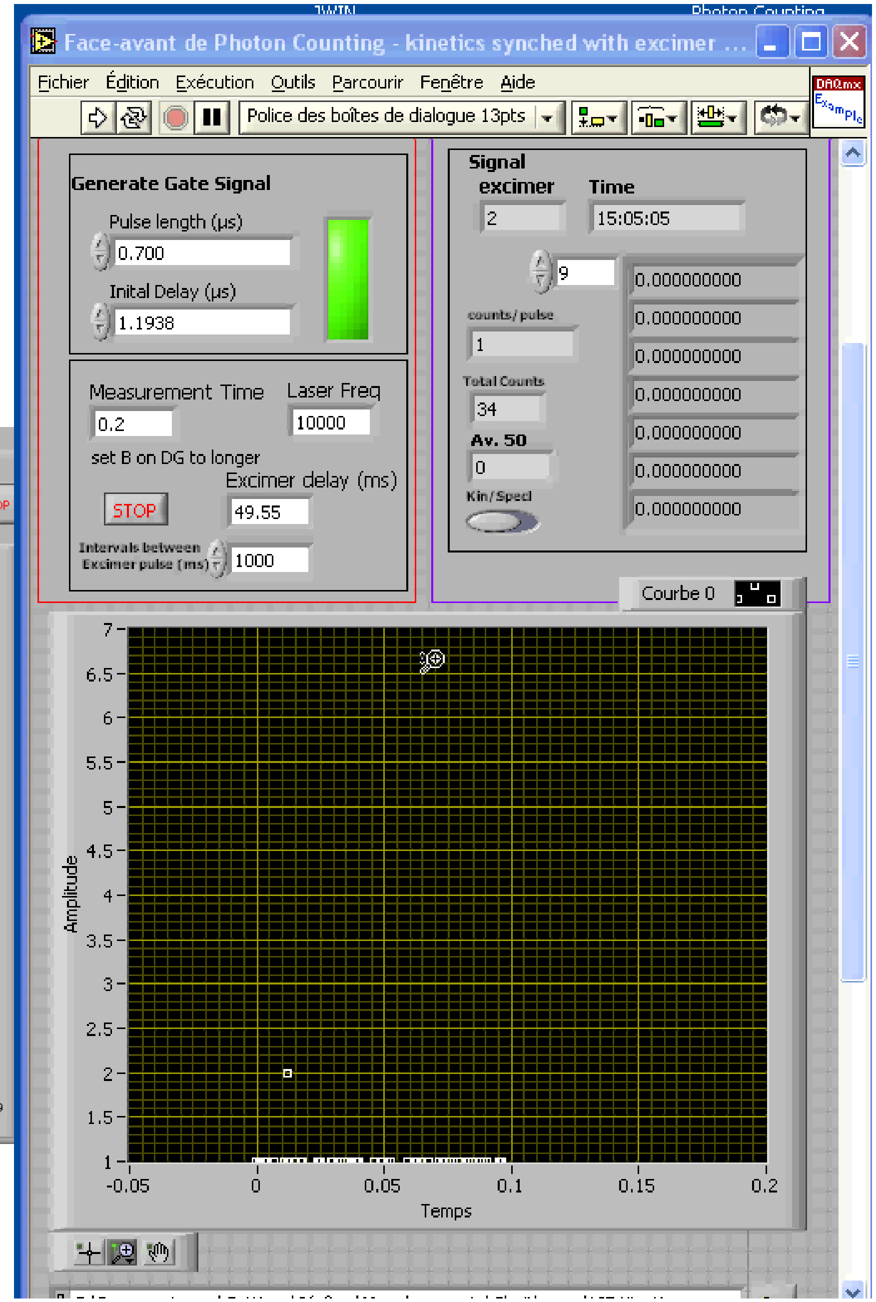
Typical signals

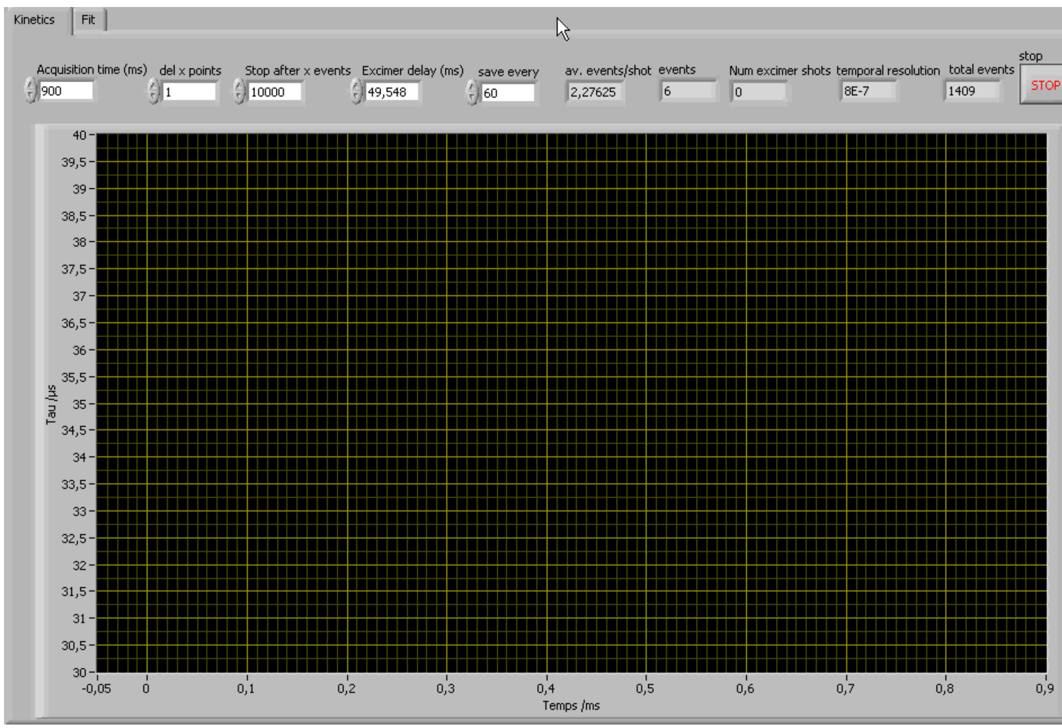
H_2O_2 Photolysis at 248 nm

$[OH]_0 = 1.0\times10^{12}\ cm^{-3}$

$[H_2O_2]_0 = 7\times10^{11}\ cm^{-3}$

OH



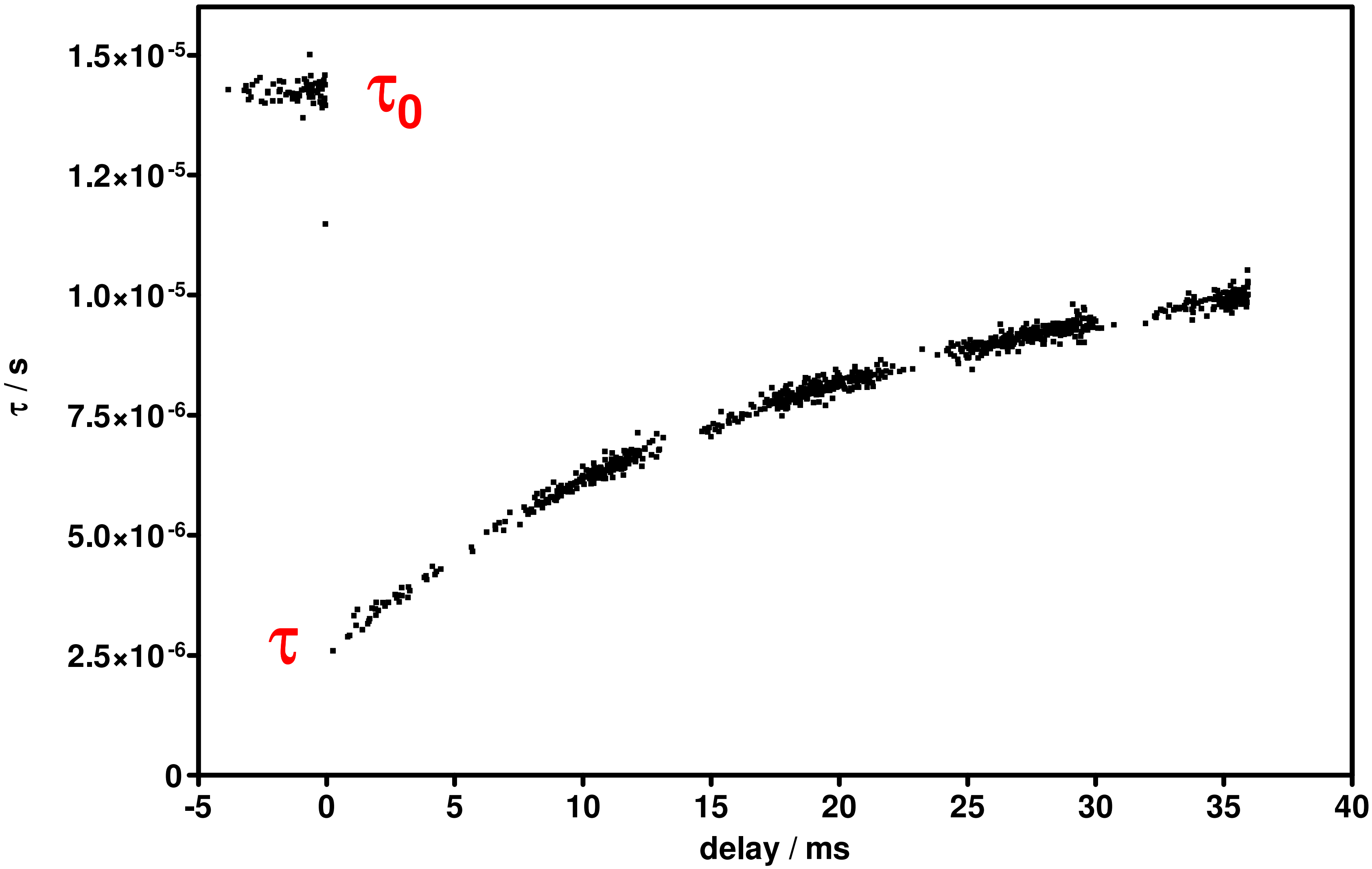


HO_2

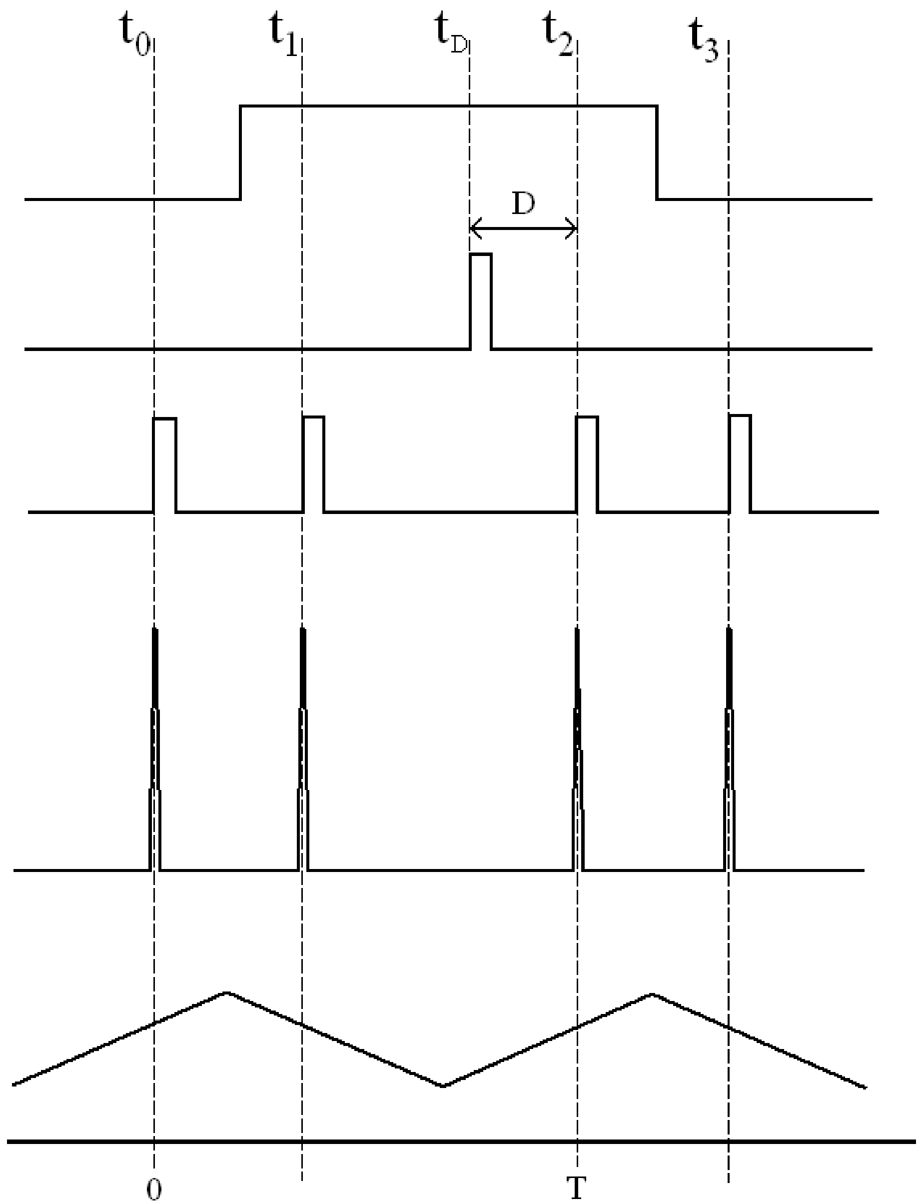
First Applications:

- Near IR-absorption spectrum of HO_2
- Calibration of OH fluorescence signal
- HO_2 yield in 248nm excitation of C_6H_6
- HO_2 yield in the oxidation of SO_2

Measurement of HO_2 absorption spectrum



Timing of different signals



Acquisition window of oscilloscope

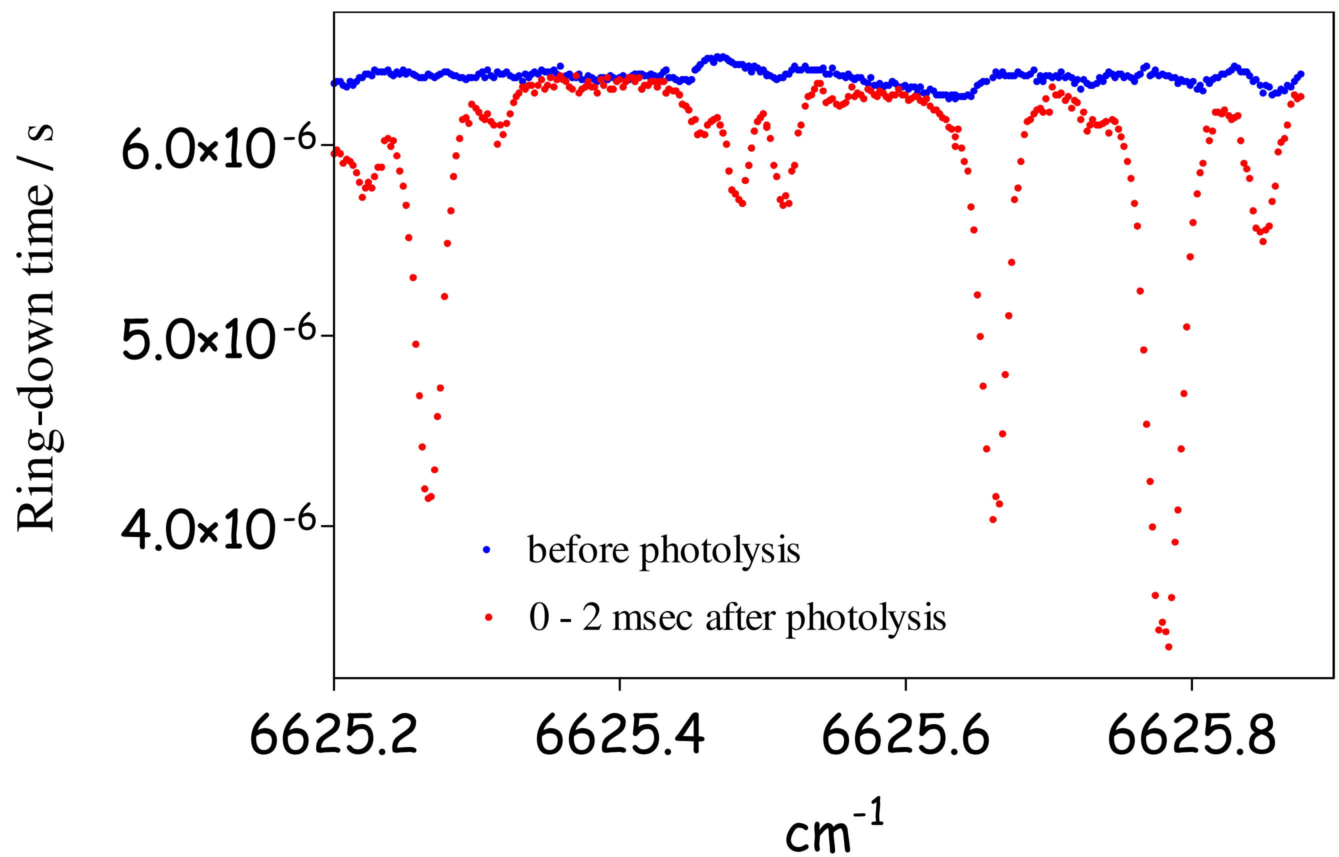
Signal send to trigger Excimer laser

Signal send to the AOM

Signal transmitted by the cavity

Modulation of the cavity length

Absorption of HO_2 around 6625 cm^{-1}

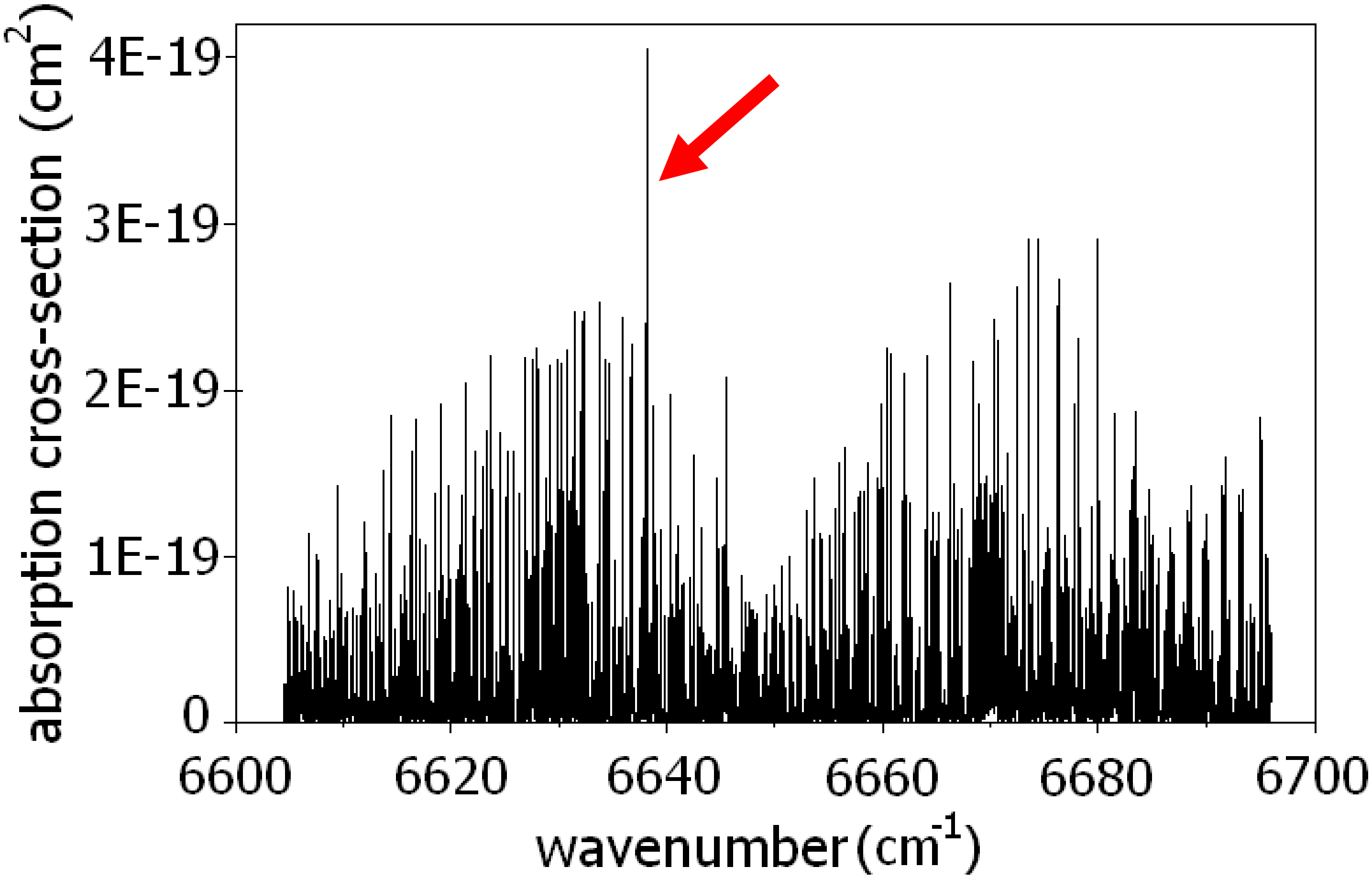


$$\alpha = [HO_2] \times \sigma = \frac{L_c}{L_A \times c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

If you know σ, you know $[HO_2]$

If you know $[HO_2]$, you know σ

HO_2 spectrum between 6600 and 6700 cm^{-1}



Absorption line at 6638.20 cm^{-1} is used for kinetic measurements

First Applications:

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- HO_2 yield in the oxidation of SO_2

Calibration of OH signal

- Photolysis of H_2O_2 at 248 nm and simultaneous observation of the OH and HO_2 profiles

- cw-CRDS gives absolute HO_2 concentrations

- OH signals from LIF will than be brought to an absolute scale

HO_2 concentration – time profile

$H_2O_2 + h\nu_{248nm} \rightarrow OH + OH$

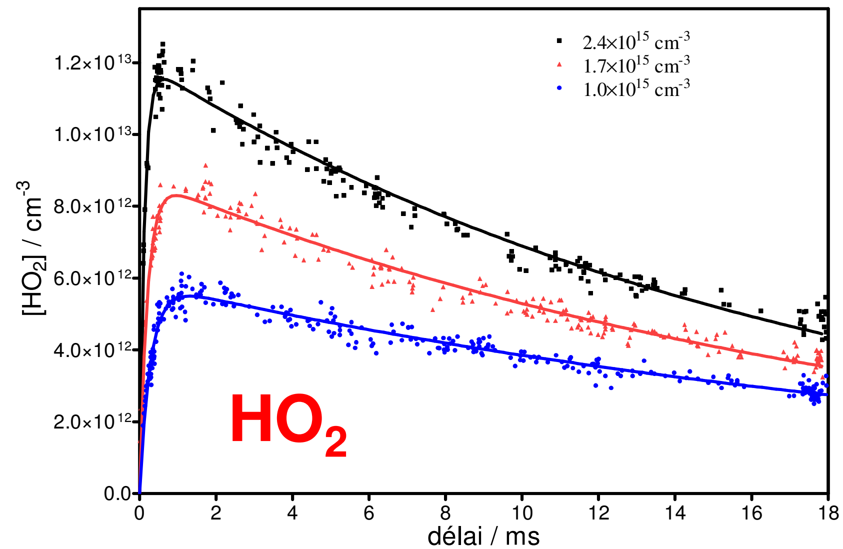
$OH + H_2O_2 \rightarrow H_2O + HO_2$

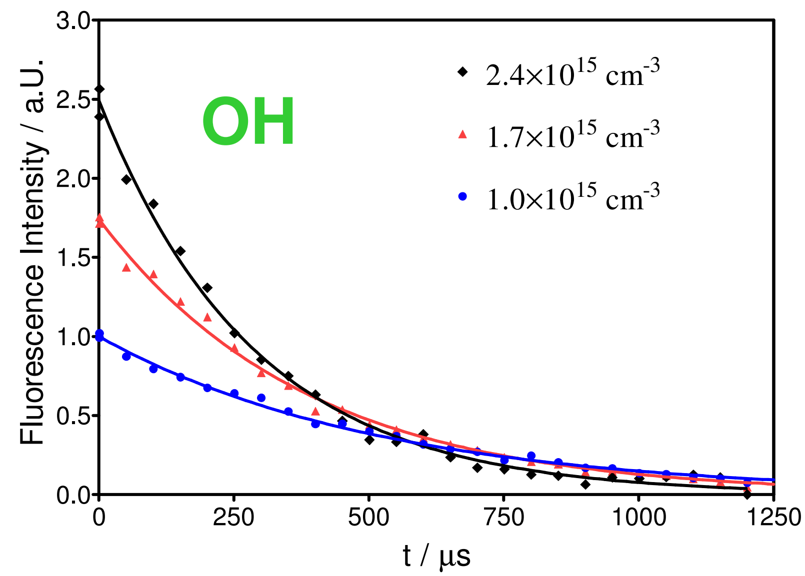
$OH + HO_2 \rightarrow H_2O + O_2$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$HO_2 \rightarrow$ Diffusion

Only valid if Φ_{OH} for H_2O_2 photolysis is 2!!!!





First Applications:

- Near IR-absorption spectrum of HO_2
- Calibration of OH fluorescence signal
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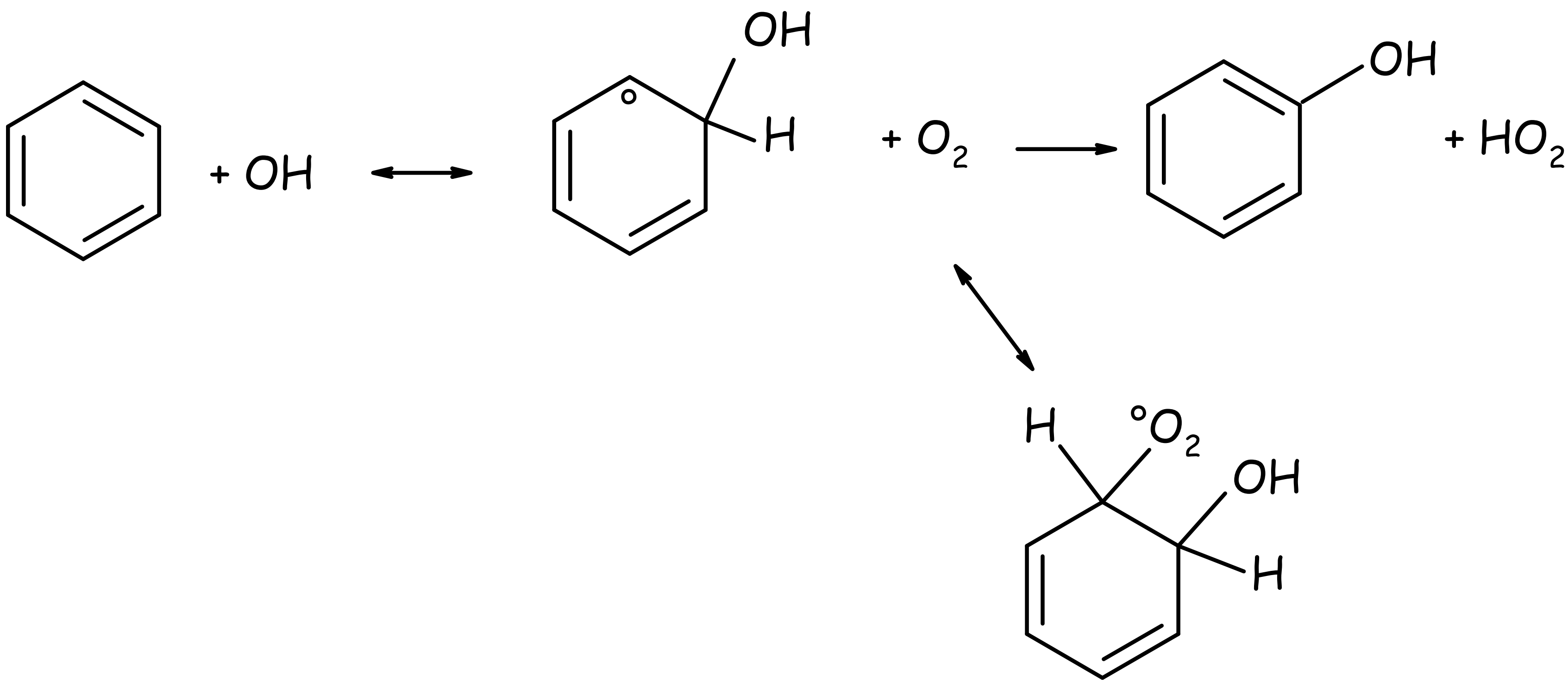
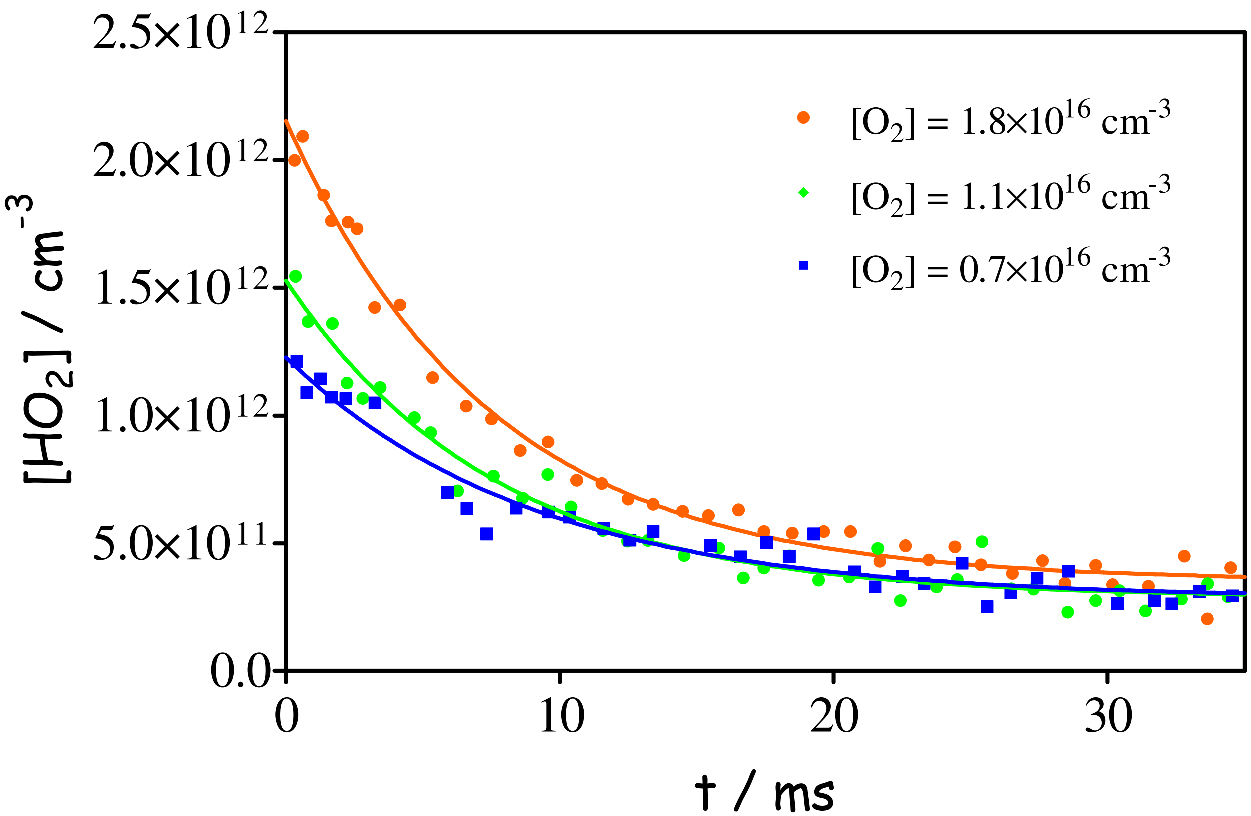
- HO_2 yield in the oxidation of SO_2

Ready to have a look at how many HO_2 radicals are formed how fast in the oxydation of benzene!!



Surprise!! HO_2 is formed **without OH** in the system $C_6H_6 + O_2 + h\nu_{248nm}$!!!!



$[C_6H_6] = 4.5\times10^{15}$ cm^{-3}

$E_{248nm} = 14$ mJ cm^{-2}

p = 50 Torr He

- HO_2 build-up always “immediate”, even at lowest $[O_2]$ → H + O_2 is much too slow
- Initial HO_2 concentration is linear with C_6H_6 concentration
- No further $[HO_2]$ increase above $[O_2] \approx 3 \times10^{16}$ cm^{-3}

Possible mechanism:

$C_6H_6 + h\nu_{248nm} \rightarrow C_6H_6^*$

$C_6H_6^* \rightarrow C_6H_6 + h\nu$ $k_{fluo,\ ISC}$

$C_6H_6^* + O_2 \rightarrow C_6H_6 + O_2^*$ $k_{quenching}$

$C_6H_6^* + O_2 \rightarrow C_6H_5 + HO_2$ $k_{reaction}$

$$\varphi_{reaction} = 0.15$$

First Applications:

- Near IR-absorption spectrum of HO_2
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- HO_2 yield in the oxidation of SO_2

HO_2 yield in the oxidation of SO_2

-H_2SO_4 is important in atmospheric nucleation mechanism

- Recent laboratory show that “in-situ” H_2SO_4 is more efficient than “old” H_2SO_4

- Question is, if the currently accepted mechanism

$$SO_2 + OH \rightarrow HOSO_2 \quad (1)$$

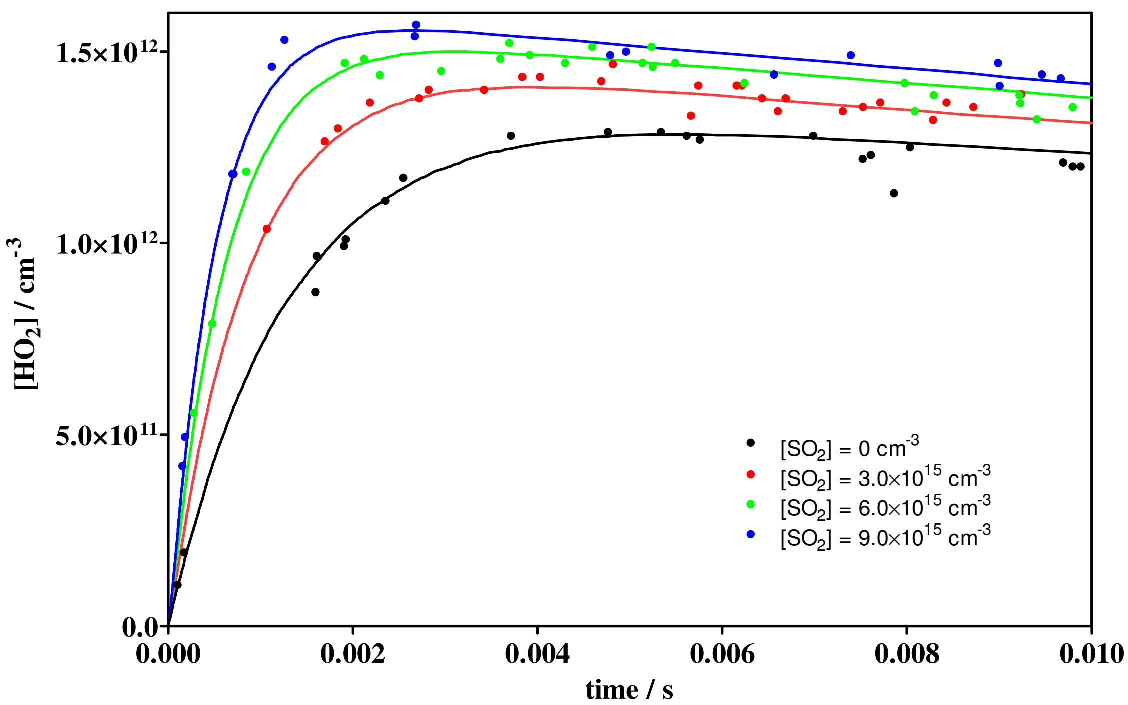
$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \quad (2)$$

$$SO_3 + 2\ H_2O \rightarrow H_2SO_4 + H_2O \quad (3)$$

of SO_2 oxidation is reliable.

We have tried to clarify step (1) and (2) by measuring HO_2-yield.

HO_2 profiles



$OH + H_2O_2 \rightarrow HO_2 + H_2O$

$2\ HO_2 \rightarrow H_2O_2 + O_2$

$OH + HO_2 \rightarrow O_2 + H_2O$

$OH + SO_2 \rightarrow HSO_3$

$HSO_3 + O_2 \rightarrow HO_2 + SO_3$??

$[H_2O_2] = 3.3\times10^{12}\ cm^{-3}$

$[OH]_0 = 1.8\times10^{12}\ cm^{-3}$

Full line describe model with 100% HO_2 yield

Conclusion

• Absolute absorption coefficients of HO_2 have been measured in the wavelength range 6600 – 6700 cm^{-1}

J. Thiebaud; S. Crunaire; C. Fittschen; J. Phys. Chem. A (2007)

• Quantum yields in the 248nm photolysis of H_2O_2 have been measured

J. Thiebaud, A. Aluculesei, C. Fittschen, J. Chem. Phys., 126, 186101 (2007)

• HO_2 radicals have been detected upon 248 nm irradiation of C_6H_6 / O_2 mixtures

A. Aluculesei, A.Tomas, C. Schoemaecker, C.Fittschen, Applied Physics B: Lasers and Optics 92, 379-385 (2008)

•HO_2 yield in the SO_2 oxidation has been measured

•Air broadening coefficients have been measured

N. Ibrahim, J. Thiebaud, J. Orphal, C. Fittschen, J. Mol. Spec, 242, 64 (2007)

Thanks to my coworkers:

Jérôme Thiebaud
Coralie Schoemaecker
Alex Parker
Chaithanya Jain

Thank you for your attention!

First Applications:

- Near IR-absorption spectrum of HO_2
- Calibration of OH fluorescence signal
- OH yield in the 248nm photolysis of H_2O_2
- HO_2 yield in 248nm excitation of C_6H_6
- HO_2 yield in the oxidation of SO_2

Photolysis of H_2O_2 at 248 nm

3 possible pathways at 248 nm

$H_2O_2 + h\nu$	$\rightarrow HO + HO$	(1)	$\lambda_{threshold}$ = 557 nm
	$\rightarrow H_2O + O(^1D)$	(2)	$\lambda_{threshold}$ = 359 nm
	$\rightarrow H + HO_2$	(3)	$\lambda_{threshold}$ = 324 nm

Contradictions for the quantum yields from 2 studies

Ravishankara et.al. : Φ_1=2.09 ± 0.36
Schiffmann et al. : Φ_1=1.58 ± 0.23

HO_2 formation mechanism

	$H_2O_2 + h\nu \rightarrow OH + OH$	Φ_1
	$H_2O_2 + h\nu \rightarrow H_2O + O(^1D)$	Φ_2
Formation	$H_2O_2 + h\nu \rightarrow H + HO_2$	Φ_3
	$OH + H_2O_2 \rightarrow H_2O + HO_2$	
	$H + H_2O_2 \rightarrow H_2 + HO_2$	
	$O(^1D) + H_2O_2 / H_2O \rightarrow \rightarrow HO_2$	
Consumption	$OH + HO_2 \rightarrow H_2O + O_2$	
	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	
	$HO_2 \rightarrow$ Diffusion	

HO_2 formation mechanism

Formation

$H_2O_2 + h\nu \rightarrow OH + OH$ — Φ_1

$H_2O_2 + h\nu \rightarrow H_2O + O(^1D)$ — Φ_2

$\mathbf{H_2O_2 + h\nu \rightarrow H + HO_2}$ — Φ_3

$OH + H_2O_2 \rightarrow H_2O + HO_2$

$H + H_2O_2 \rightarrow H_2 + HO_2$

$O(^1D) + H_2O_2 / H_2O \rightarrow \rightarrow$ ~~HO_2~~

Consumption

$OH + HO_2 \rightarrow H_2O + O_2$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

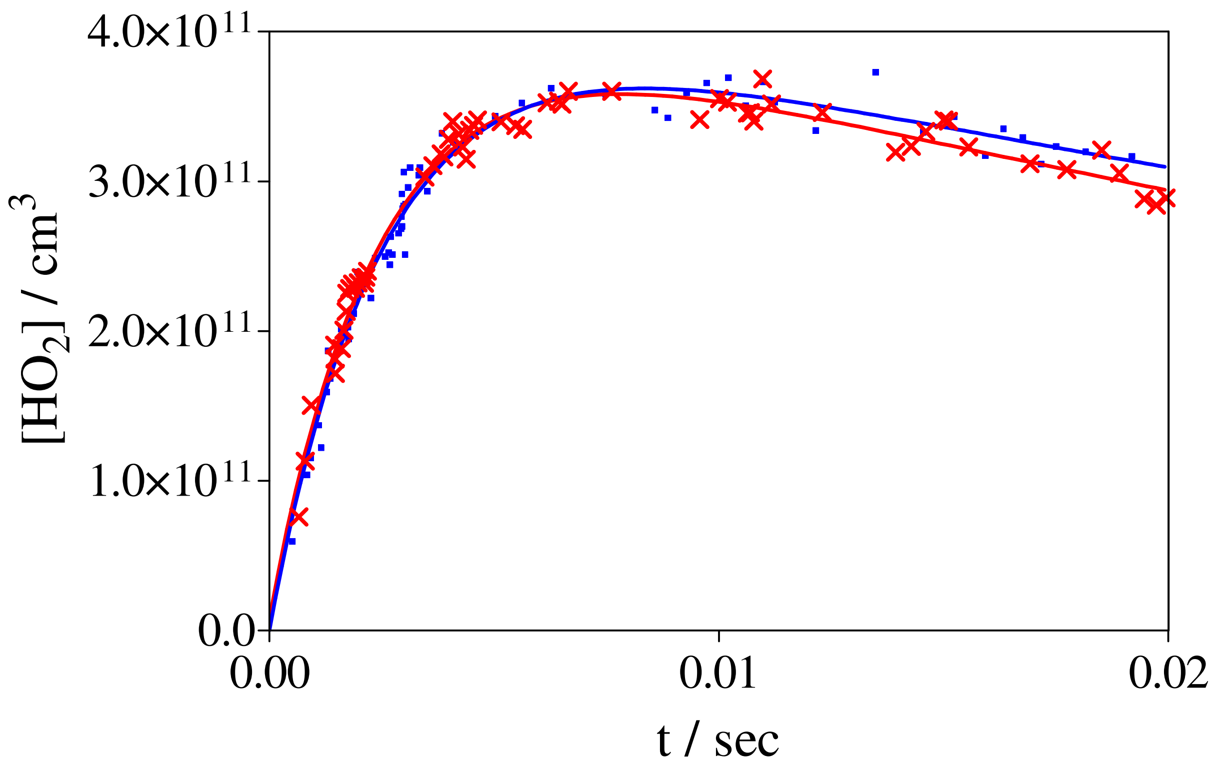
$HO_2 \rightarrow$ Diffusion

In the presence of O_2:

$H + O_2 \rightarrow HO_2$ — Φ_3

$O(^1D) + O_2 \rightarrow O_3$ — Φ_2

HO_2 concentration-time profile



Red : 25 Torr He

Blue : 15 Torr He

10 Torr O_2

Fitting of the signals leads to $\Phi_2 < 0.02$ and $\Phi_3 < 0.01$

Good agreement with Ravishankara et al.

Possible mechanism:

$C_6H_6^* \rightarrow C_6H_6 + h\nu$ $\quad k_{fluo}$

$C_6H_6^* + O_2 \rightarrow C_6H_6 + O_2^*$ $\quad k_{quenching}$

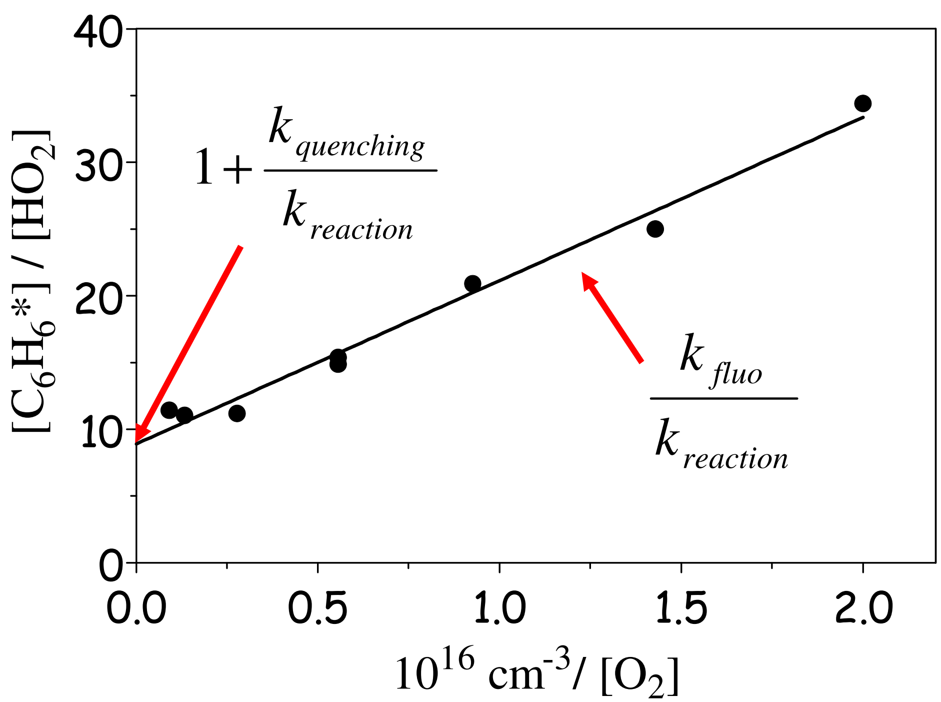
$C_6H_6^* + O_2 \rightarrow C_6H_5 + HO_2$ $\quad k_{reaction}$

$$\frac{[HO_2]}{[C_6H_6^*]} = \frac{k_{reaction} \times [O_2]}{k_{fluo} + k_{quenching} \times [O_2] + k_{reaction} \times [O_2]}$$

$$\frac{[C_6H_6^*]}{[HO_2]} = 1 + \frac{k_{fluo} + k_{quenching} \times [O_2]}{k_{reaction} \times [O_2]}$$

$$\rightarrow \frac{k_{fluo}}{k_{reaction} \times [O_2]} \qquad [O_2] \rightarrow 0$$

$$\rightarrow 1 + \frac{k_{quenching}}{k_{reaction}} \qquad [O_2] \rightarrow \infty$$



$k_{quenching}$ from literature:

2.5×10^{-10} cm^3s^{-1}

Intercept

$k_{quenching} = 2.22 \times 10^{-10}$ cm^3s^{-1}

$k_{reaction} = 2.8 \times 10^{-11}$ cm^3s^{-1}

Slope

$k_{fluo} = 3.6 \times 10^6$ s^{-1}

τ_{fluo} = 190 nsec

$\tau_{fluo, literature}$ = 80 nsec

$\varphi_{HO_2} = 0.13$

Direct measurement: $\varphi = 0.2$

$$C_6H_6 + O_2 + h\nu_{248nm} \rightarrow HO_2$$

Is not important in atmospheric conditions,

BUT :

248 nm photolysis of H_2O_2 has been used in earlier studies as precursor for OH radicals!!

Question:

How many HO_2 (and phenyl) radicals are formed from the C_6H_6 photolysis compared to OH radicals from H_2O_2 photolysis??

- Calculation from quantum yield :

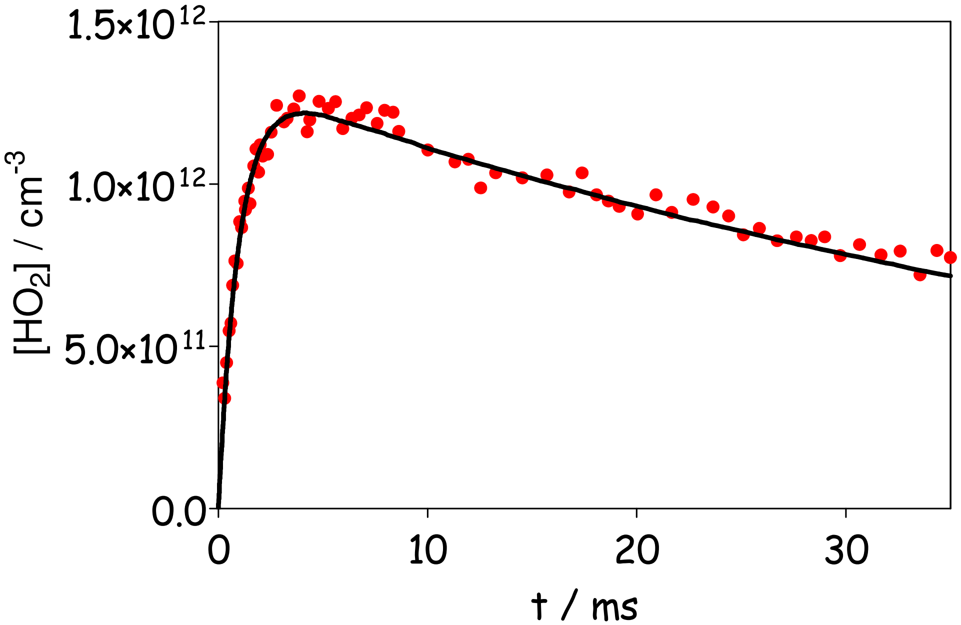
$\varphi_{HO_2} = 0.17$ $\varphi_{OH} = 2$

$\sigma_{C_6H_6} = 3\times10^{-19}cm^2$ $\sigma_{H_2O_2} = 3\times10^{-19}cm^2$

→ $[HO_2] = [C_6H_5] = 0.25 \times [OH]$

- Problem: Uncertainty is high, because you need $\sigma_{C_6H_6}$, $\sigma_{H_2O_2}$, σ_{HO_2} and E_{248nm}

- Other possibility: Direct measurement



$H_2O_2 + h\nu_{248nm} \rightarrow 2\ OH$

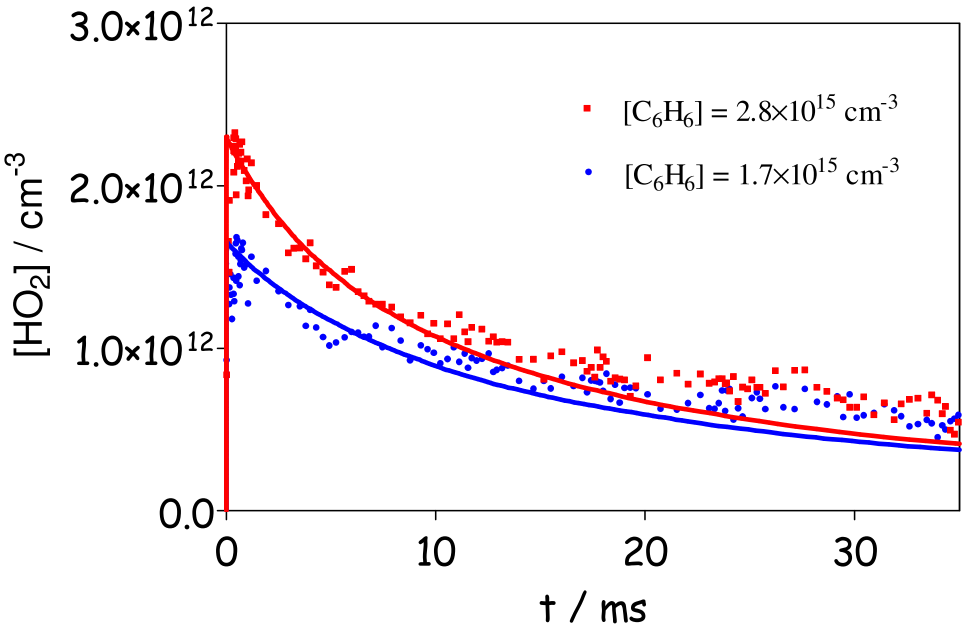
$H_2O_2 + OH \rightarrow H_2O + HO_2$

$HO_2 + OH \rightarrow H_2O + O_2$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Simulation with known k leads to

[OH] formed per $[H_2O_2]$



C_6H_6 / O_2 photolysed under the same conditions leads to:

$[HO_2]$ formed per $[C_6H_6]$

Comparing both ratios:

$[HO_2] = [C_6H_5] = 0.25 \times [OH]$

Knowledge of HO_2 absorption coefficient in the near IR region

• First detection of the absorption feature in near IR by Hunziker and Wendt in 1974, line strength estimated by comparison with UV absorption

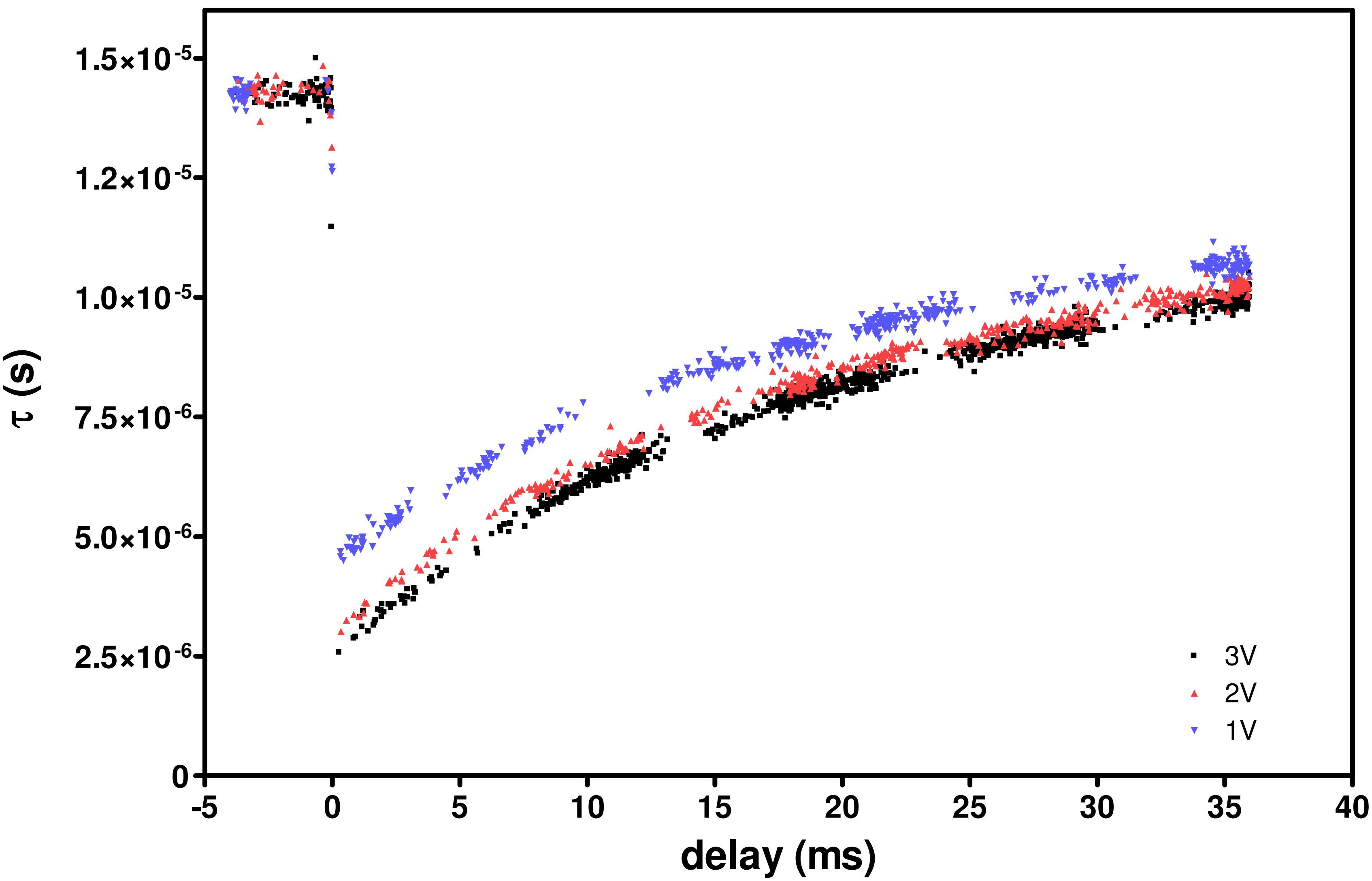
• Johnson *et.al.* published in 1991 line strengths of 23 lines between 1508 and 1510 nm, obtained by wavelength modulation spectroscopy and calibrated by UV absorption

• C. Taatjes *et.al.* published in a footnote line strength for one line at 1509.25 nm, obtained by wavelength modulation spectroscopy, without information on calibration procedure

• Christensen *et.al.* estimated line strength of one intense line at 1506.4 nm by comparing with the line strength obtained by Johnson *et.al.*

→ not so much is known ....

How to extract σ from the kinetics?



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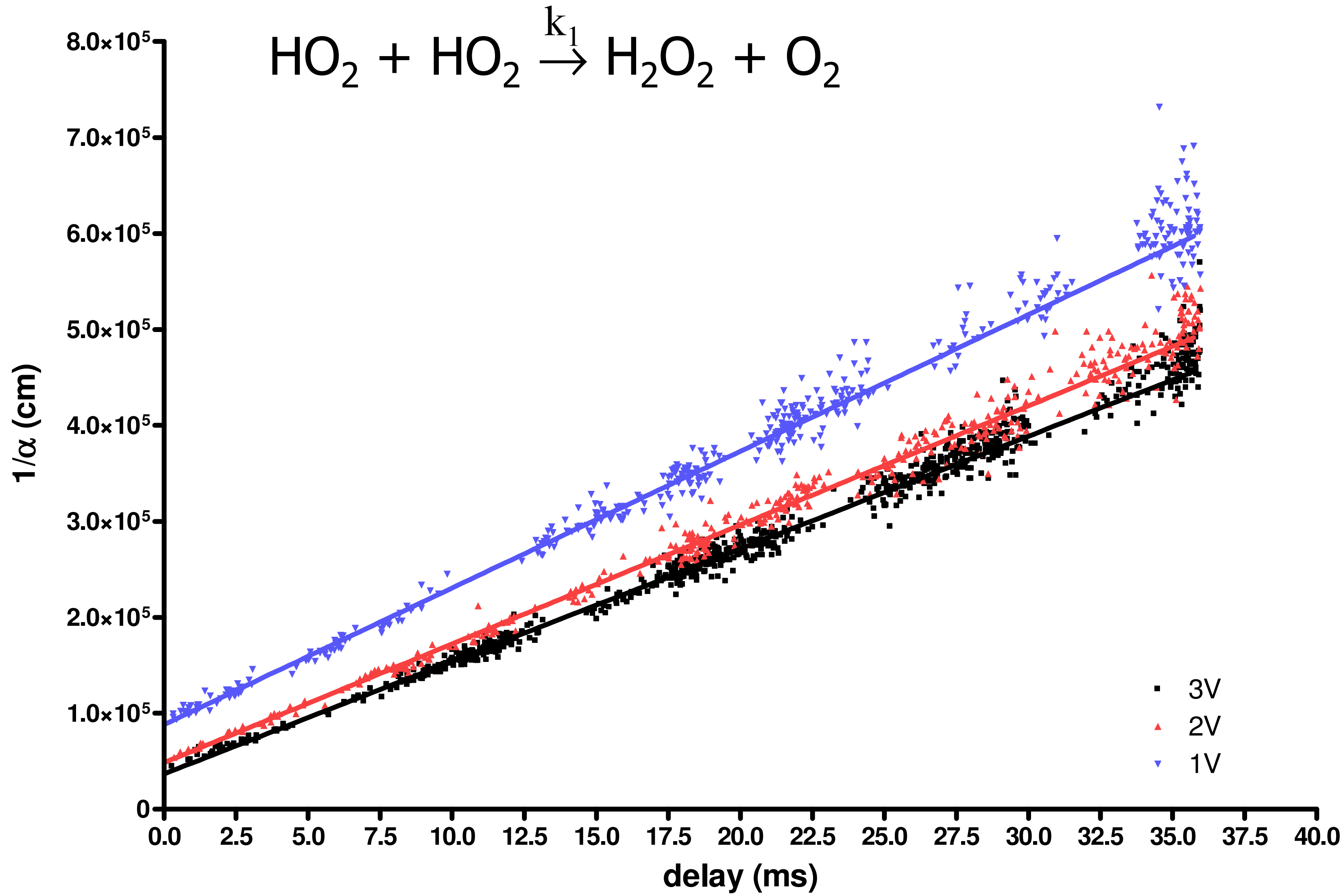

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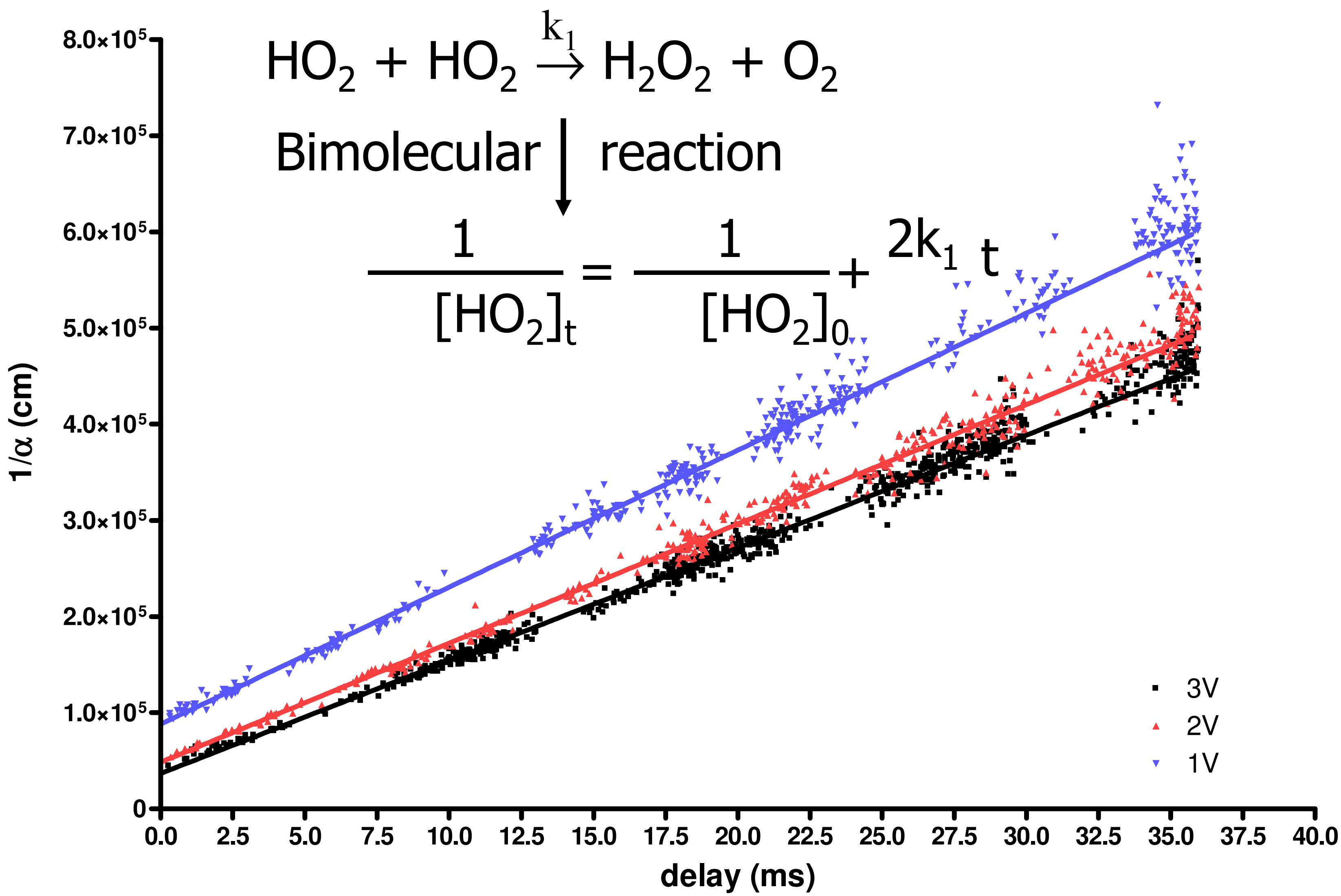
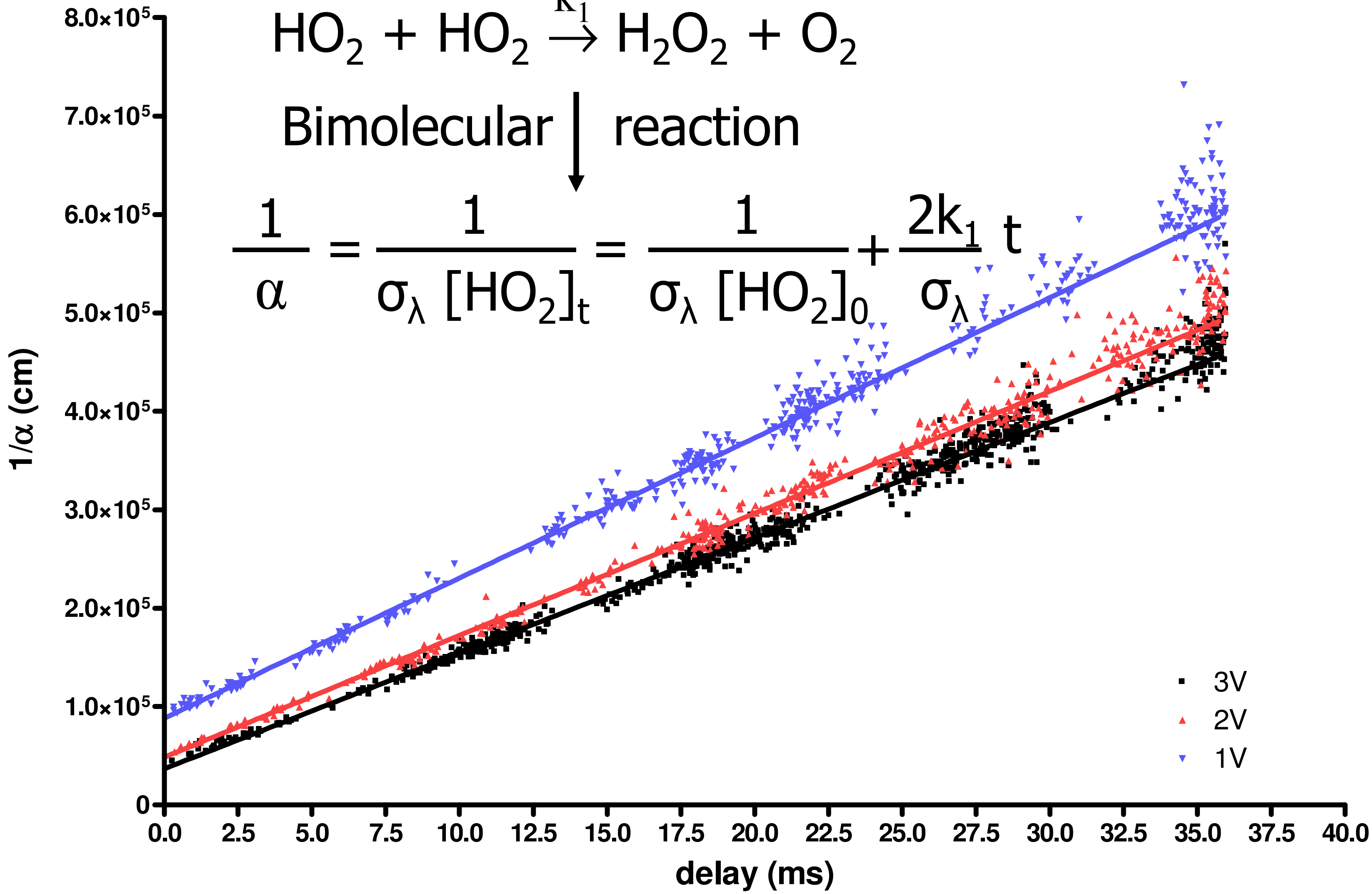


How to extract σ from the kinetics?

$$HO_2 + HO_2 \xrightarrow{k_1} H_2O_2 + O_2$$

Bimolecular reaction

$$\frac{1}{\alpha} = \frac{1}{\sigma_\lambda [HO_2]_t} = \frac{1}{\sigma_\lambda [HO_2]_0} + \frac{2k_1}{\sigma_\lambda} t$$



Real life is a little more complicated due to diffusion…