Measurement of absolute absorption cross sections for HONO in the near infrared region by cw-CRDS technique coupled to laser photolysis

PhysicoChimie des Processus de Combustion et de l'Atmosphère PC2A

Université de Lille

Christa FITTSCHEN

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RÉGION NORD PAS DE CALAIS

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Introduction

Nitrous acid (HONO) is an important species in the atmosphere:

- HONO is a major precursor for OH radicals during the early morning in the atmosphere
- Major HONO sources are still missing : heterogeneous reaction of NO_2 on aerosols or reactions on the ground??
- HONO can be used as a precursor for OH radicals in laboratory studies by photolysing it at 351nm

→ Many reasons to be motivated for quantifying HONO

Goal :

- To determine absolute absorption cross sections of selected lines in the near infrared region in order to measure absolute HONO concentrations in future laboratory studies and maybe even in the atmosphere??

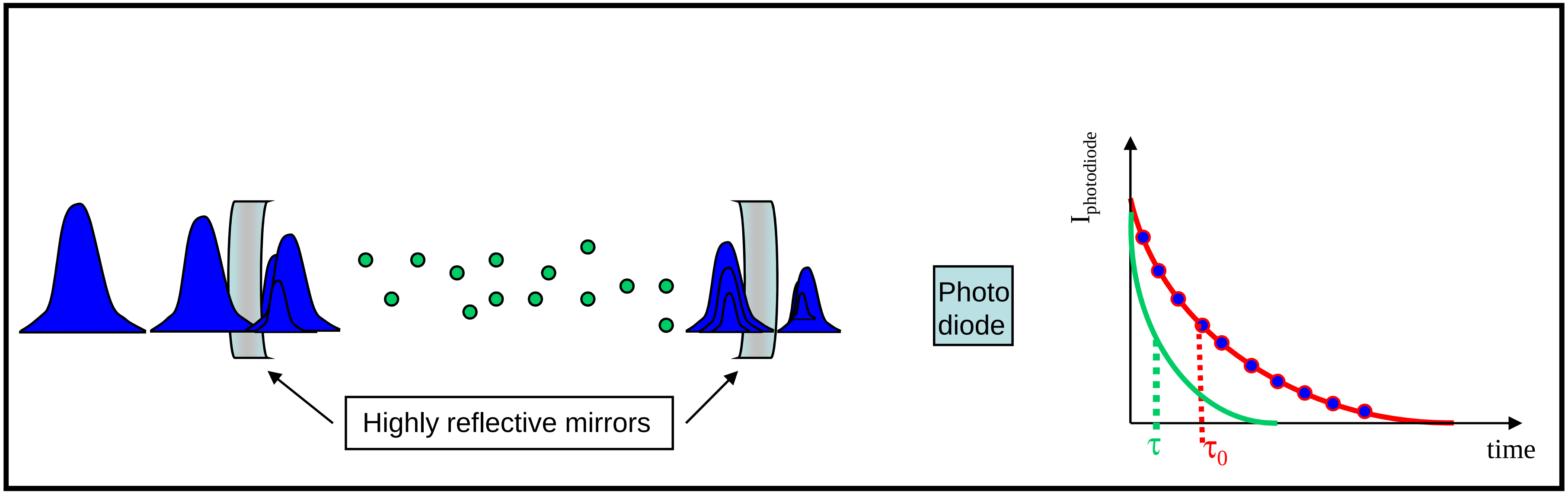
Problem:

- HONO is very instable → knowing its absolute concentration is very difficult

Solution:

- Cw-CRDS coupled to pulsed generation of HONO and calibrating its concentration against known absorption lines of HO_2

What is CRDS???



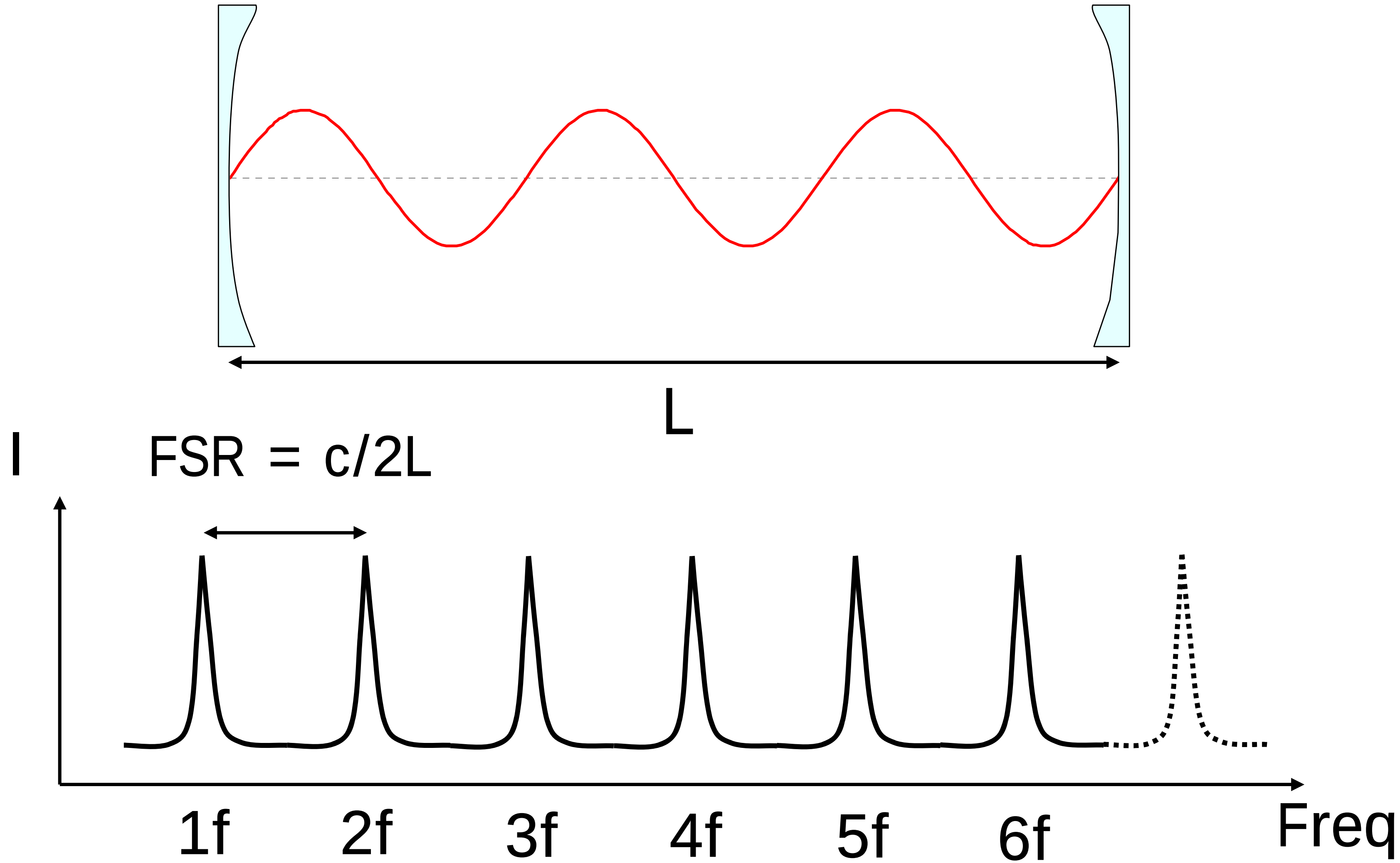
$$\tau_0 = \frac{L}{c\left(1 - R\right)}$$

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

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

Optical cavity has discrete modes

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



Differences between Pulsed and cw-CRDS

Pulsed CRDS

Source :

Pulsed laser (ns)

Larger bandwidth (>FSR)

cw - CRDS

Source :

Continuous laser (diode)

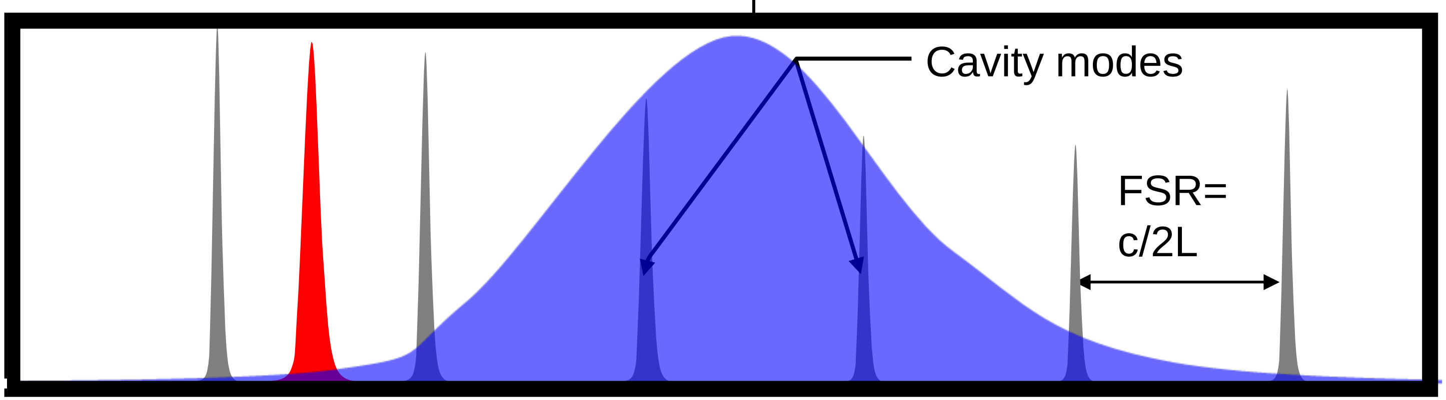
Smaller bandwidth (<<FSR)

Requirements :

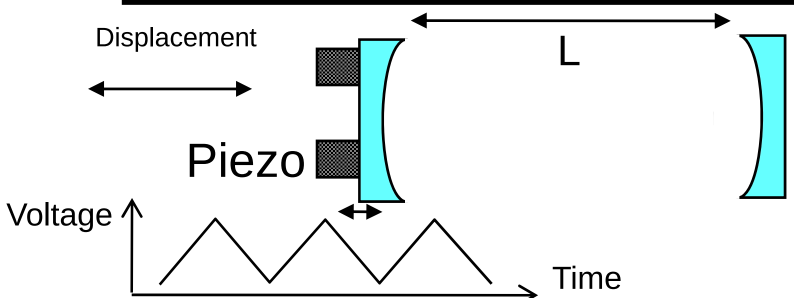
A switch to deviate the light (AOM)

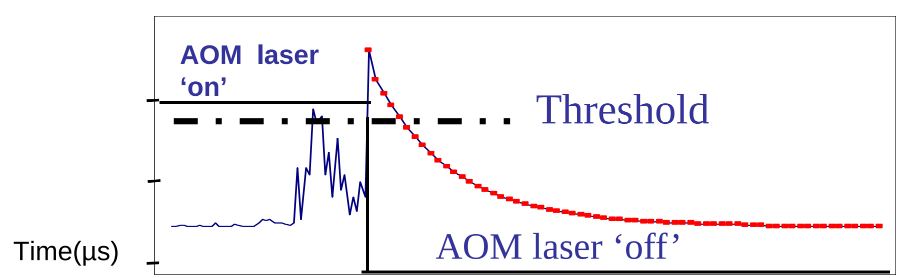
A system to change the cavity length or

Wavelength tuning

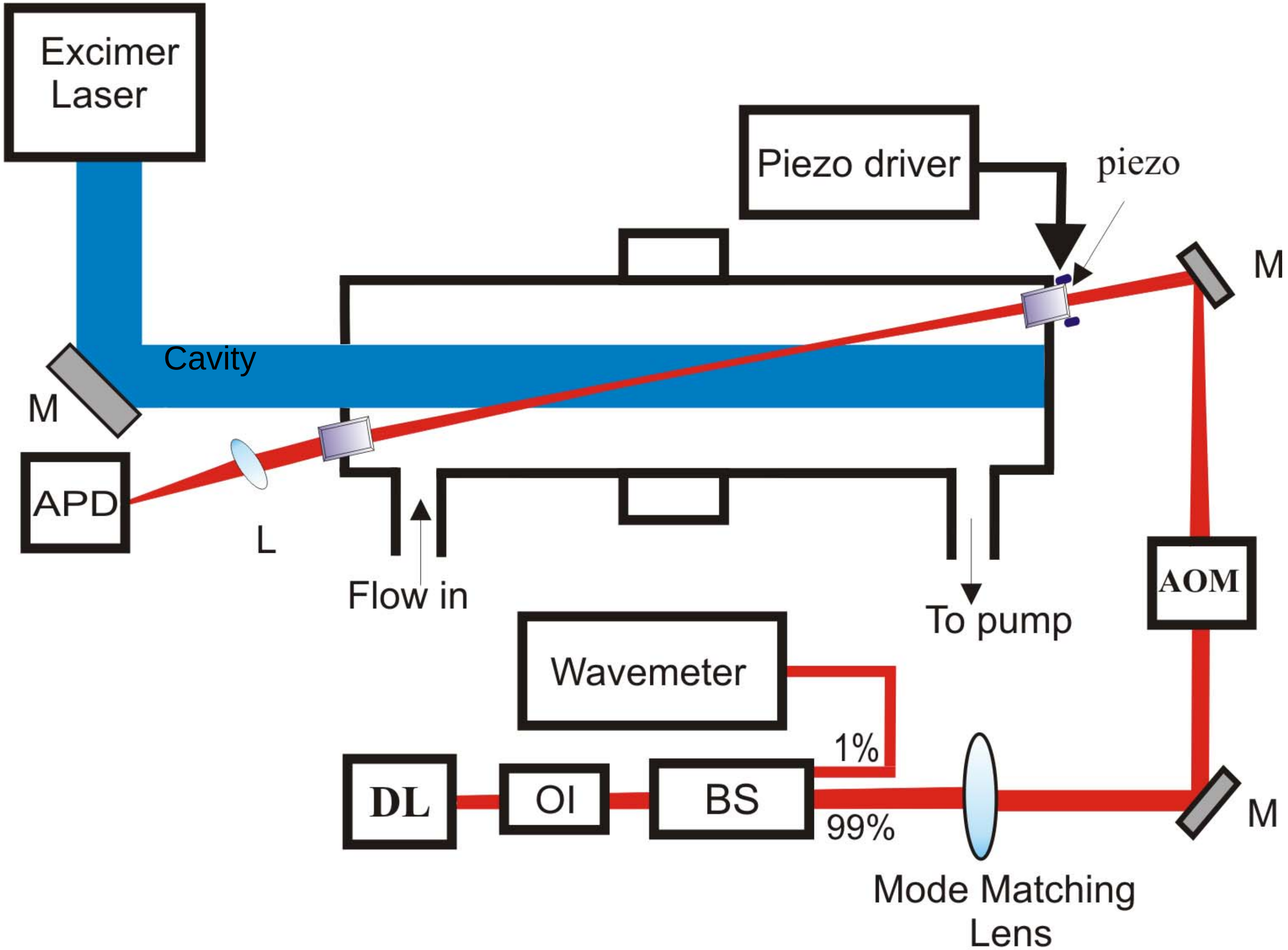


(FSR= Free Spectral Range)

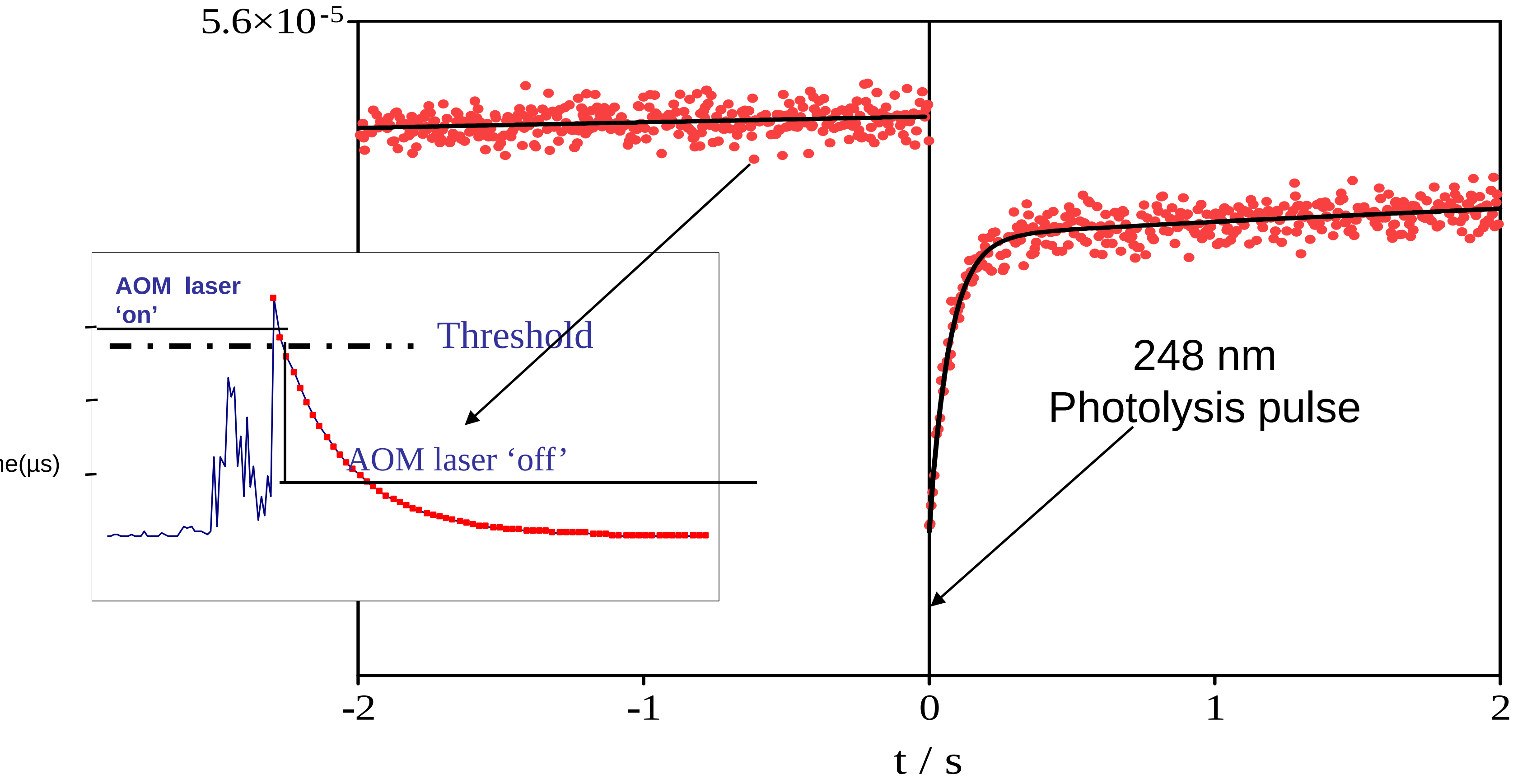




Schematic diagrams of the experimental system

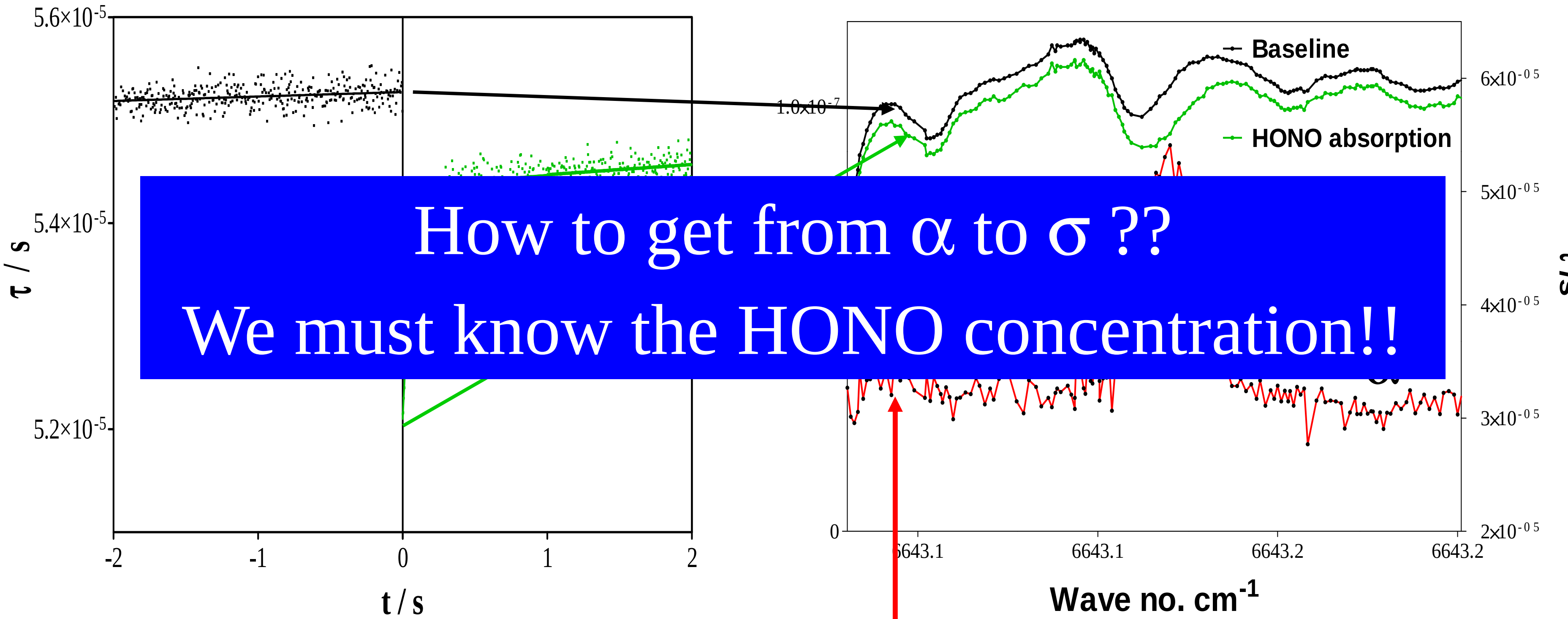


$$H_2O_2 + 248\ \text{nm} \rightarrow 2\ OH$$
$$OH + NO \rightarrow HONO$$



$$\alpha_{t=0} = [HONO] \times \sigma = \frac{R_L}{c}\left(\frac{1}{\tau_{t=0}} - \frac{1}{\tau_0}\right)$$

How to get the absorption spectrum?



How to get from α to σ ??

We must know the HONO concentration!!

Once a set ‘n’ ring-down events have occurred on one wavelength laser will be tuned to the next.

$$\alpha_{t=0} = [HONO] \times \sigma = \frac{R_L}{c}\left(\frac{1}{\tau_{t=0}} - \frac{1}{\tau_0}\right)$$

Calibration of the HONO concentration

$$H_2O_2 \xrightarrow{248\ nm} 2\ OH \qquad R_1$$

$$OH + H_2O_2 \longrightarrow HO_2 \qquad R_2$$

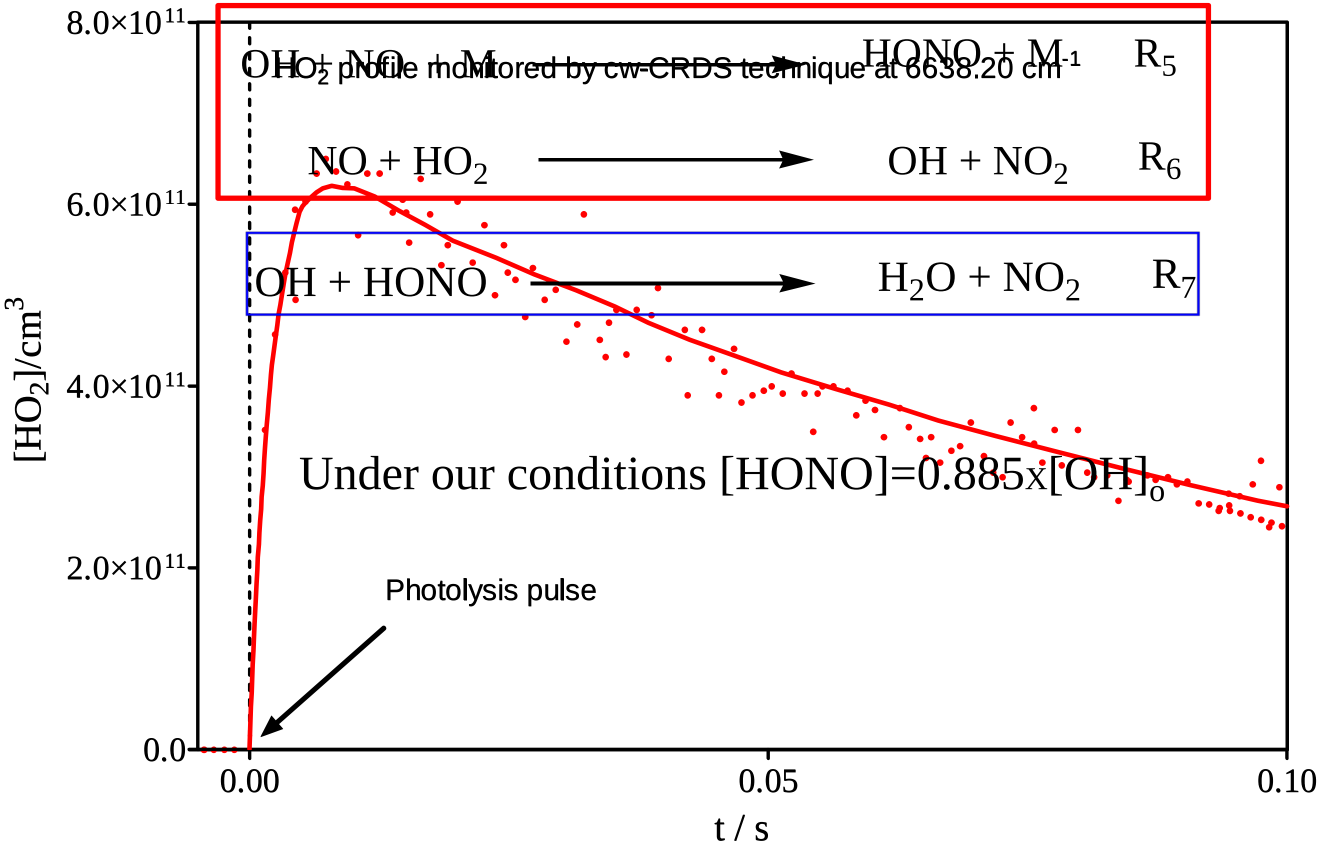
$$OH + HO_2 \longrightarrow H_2O + O_2 \qquad R_3$$

$$2\ HO_2 \longrightarrow H_2O_2 + O_2 \qquad R_4$$

$$OH + NO + M \longrightarrow HONO + M \qquad R_5$$

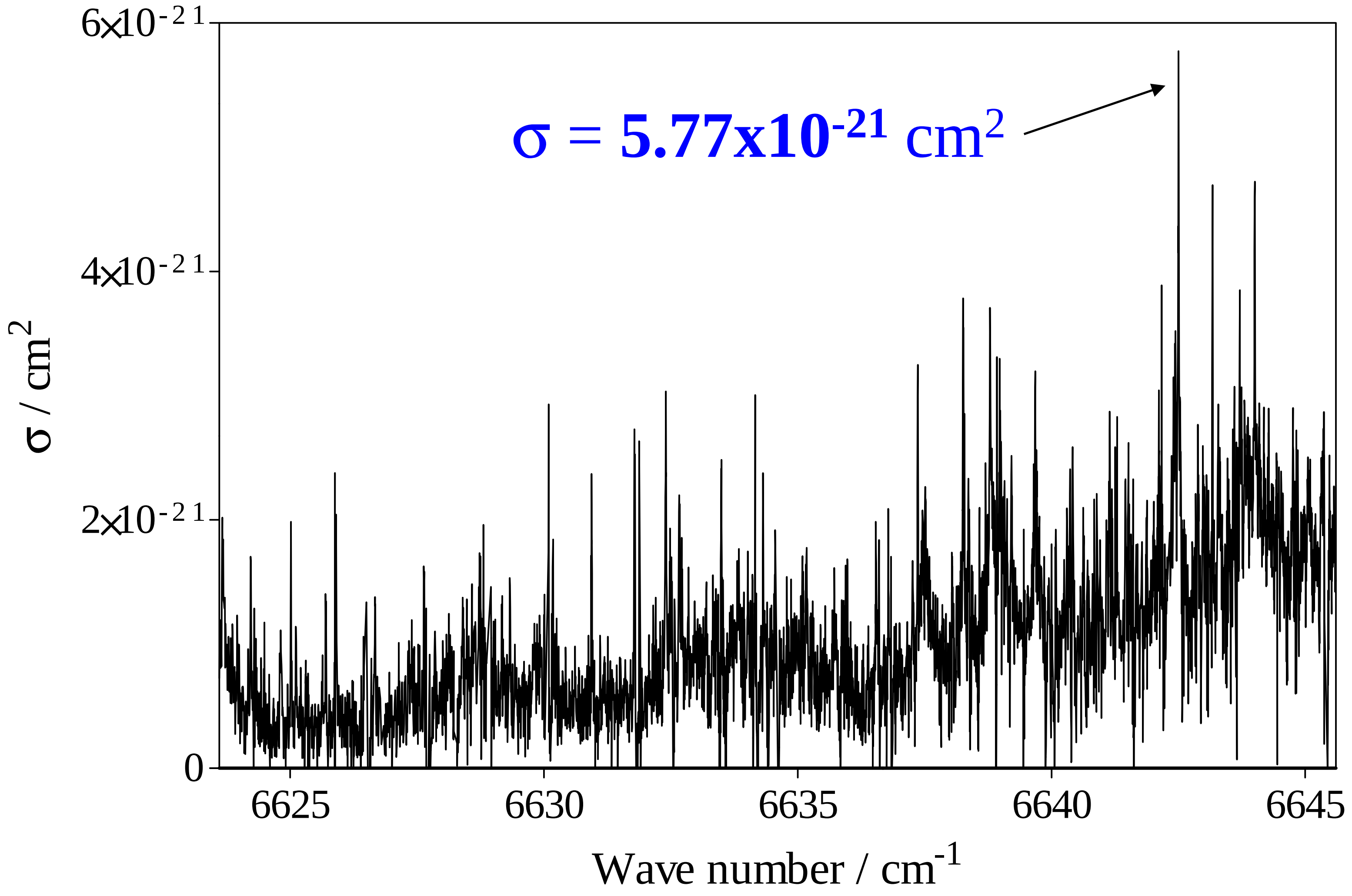
$$NO + HO_2 \longrightarrow OH + NO_2 \qquad R_6$$

$$OH + HONO \longrightarrow H_2O + NO_2 \qquad R_7$$

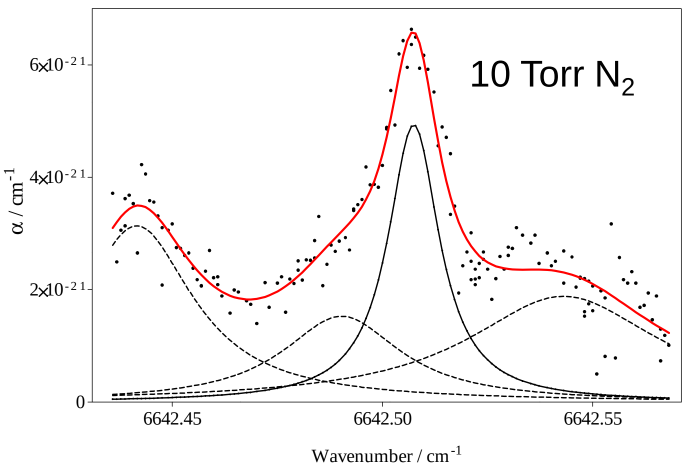


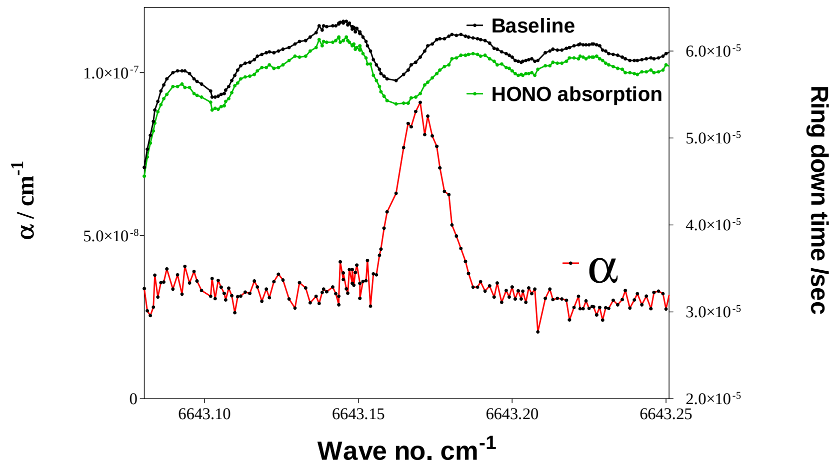
Under our conditions $[HONO]=0.885 \times [OH]_0$

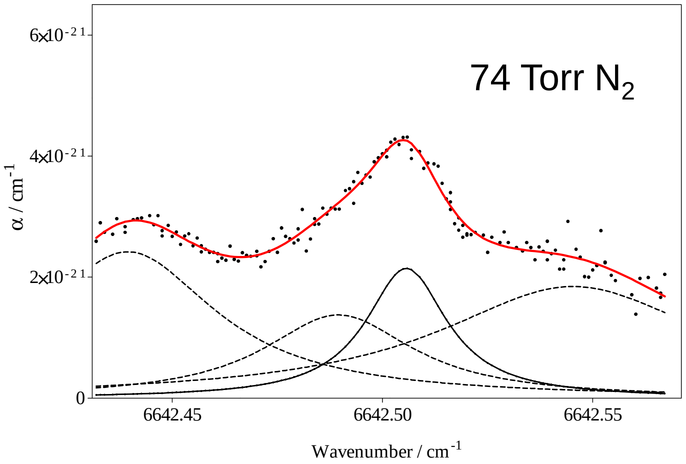
Full spectrum of HONO in 40 Torr He from 6623.5 -6645.5 cm^{-1}



Pressure broadening of HONO







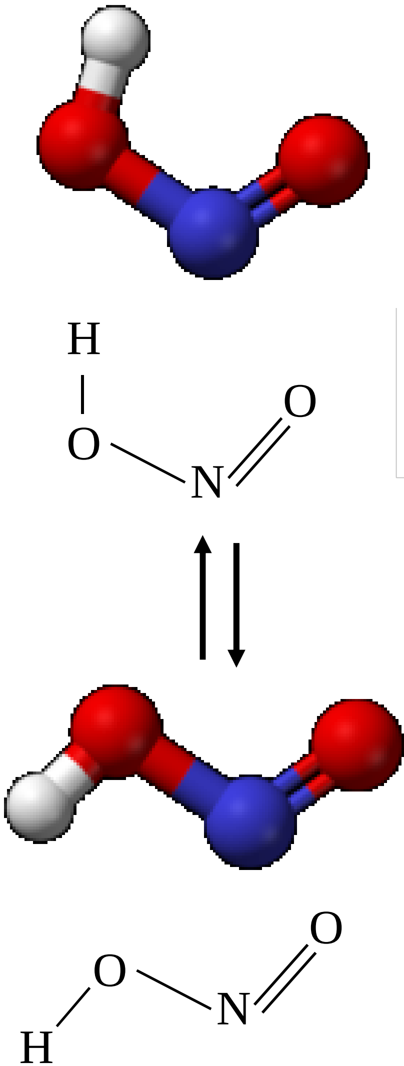
Pressure / Torr	He		N_2	
	$\sigma_{6642.51\ cm-1}$ / $10^{-21}cm^2$	$\sigma_{6642.46\ cm-1}$ / $10^{-21}cm^2$	$\sigma_{6642.51\ cm-1}$ / $10^{-21}cm^2$	$\sigma_{6642.46\ cm-1}$ / $10^{-21}cm^2$
10	7.0 ± 2.6	1.8 ± 1.0	6.6 ± 2.5	1.8 ± 1.0
40	5.8 ± 2.2	2.1 ± 1.1	5.1 ± 2.0	2.3 ± 1.2
74	4.6 ± 1.8	2.3 ± 1.2	4.3 ± 1.8	2.4 ± 1.2

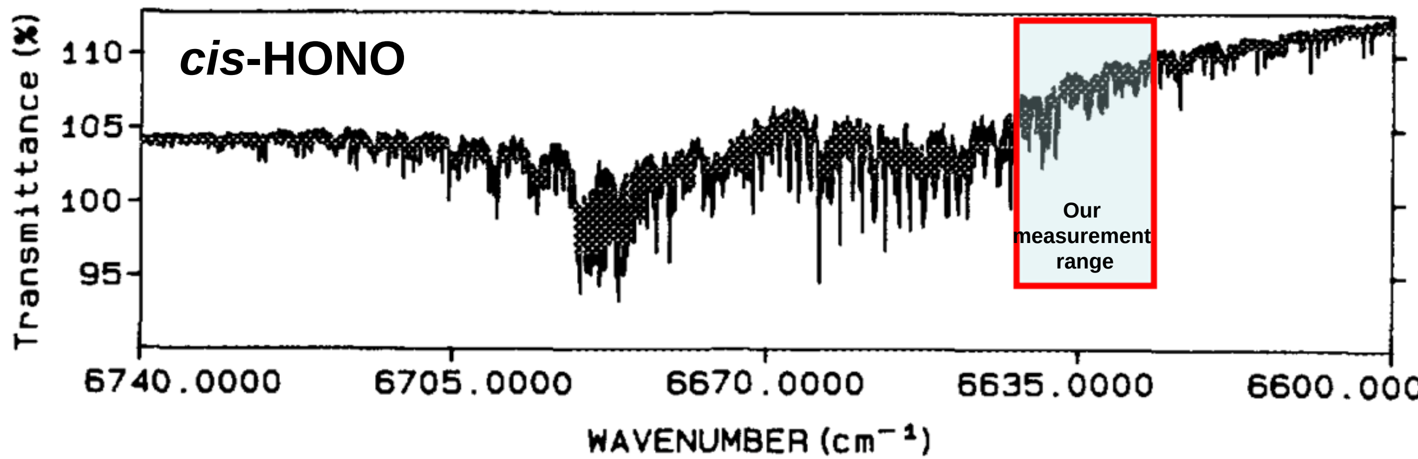
Conclusions

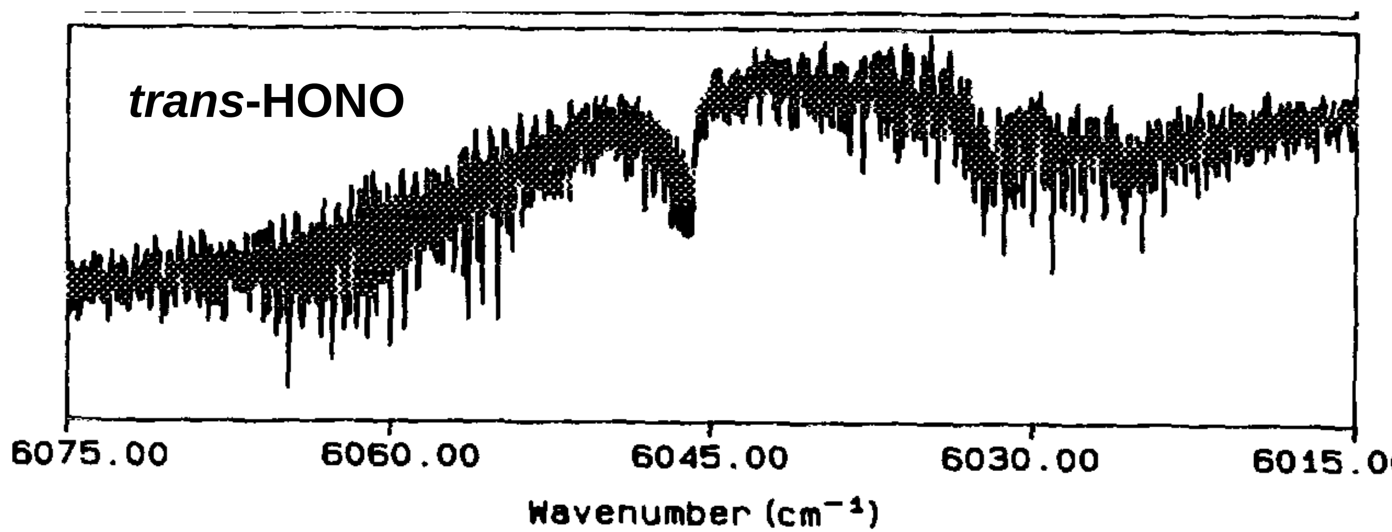
- Absorption spectrum of the HONO has been measured in the near infrared region (6623.6-6645.8 cm^{-1}) using cw-CRDS technique

- Absolute absorption cross-sections of the selected lines have been extracted from the measurement. Most intense line at 6642.5 cm^{-1} with σ = **4.3 x 10^{-21}** cm^2, gives a detection limit of **2.8 x 10^{10}** molecules/cm^3 at 74 Torr N_2

Conclusions







1.Guilmot J. M.; Godefroid M.; Herman M. *Journal of Molecular Spectroscopy* **1993**, *160*, 387-400.
2.Guilmot J. M.; Melen F.; Herman M. *Journal of Molecular Spectroscopy* **1993**, *160*, 401-410.

Thank you for your attention