

# IR to visible photon conversion in rare-earth doped chalcogenide fibers for all-optical gas sensing

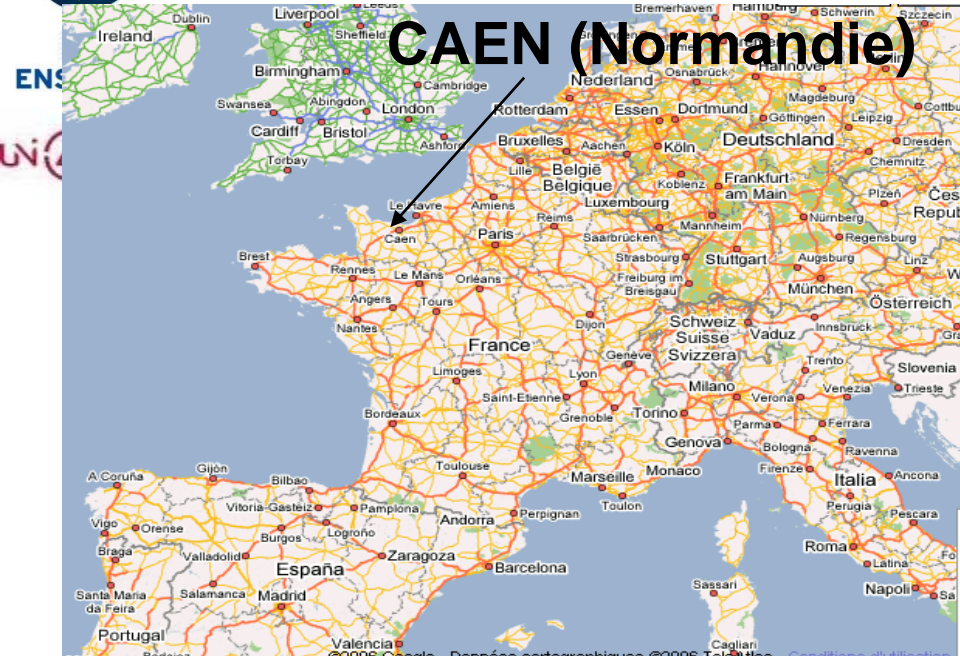
Florent Starecki<sup>1,2</sup>, A. Braud<sup>1</sup>, J.L. Doualan<sup>1</sup>, C. Boussard-Pledel<sup>2</sup>, V. Nazabal<sup>2</sup>, R. Moncorgé<sup>1</sup>, and P. Camy<sup>1</sup>

<sup>1</sup>CIMAP UMR 6252 CEA-CNRS-ENSICAen. Université de Caen. 14050 Caen Cedex 4. France

<sup>2</sup>Institut Sciences Chimiques de Rennes, UMR-CNRS 6226, F-35042 Rennes, France



CIMAP laboratory : ~ 100 persons 7 groups



Lasers and Materials for  
photonics and electronics

LIOA MIL NIMPH  
13 persons  
(Matériaux et Instrumentation Laser)

Ion-Matter interaction (heavy  
ions) and Defects

AMA MADIR SIMUL PM2E



<http://cimap.ensicaen.fr>



Group Matériaux et Instrumentation Laser (MIL)  
( 7 permanent + 4-5 PhD students/Post-docs)



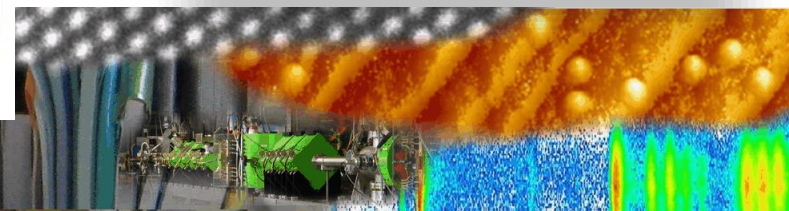
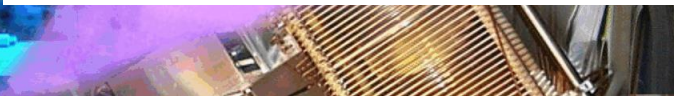
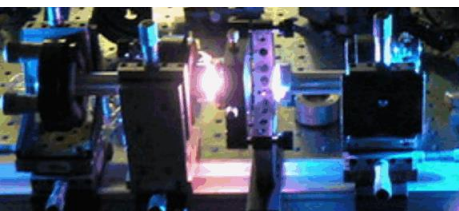
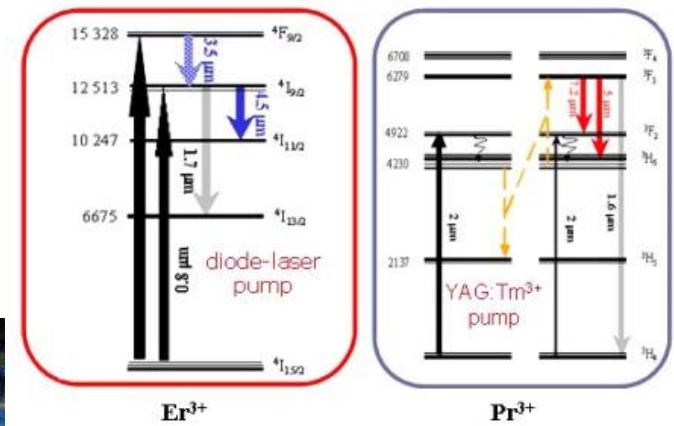
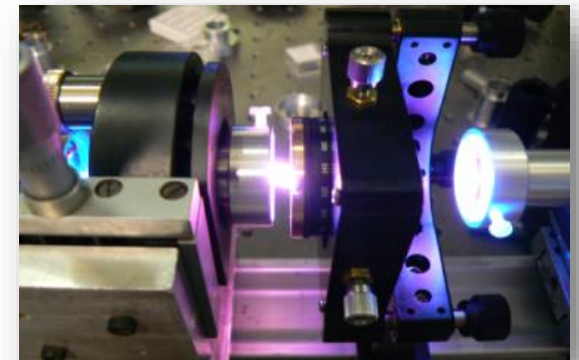
# Group Matériaux et Instrumentation Laser (MIL)

<http://cimap.ensicaen.fr/spip.php?rubrique65>

→ Crystal growth (low energy phonon crystals  
- Czochralski, Bridgman, LPE)

→ Spectroscopy of ions in solids and laser  
instrumentation in a wide spectral domain  
(nearUV→mid-IR)

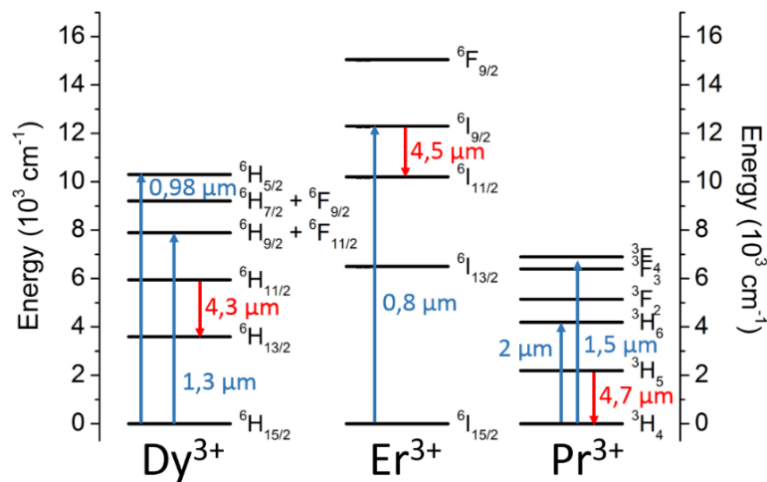
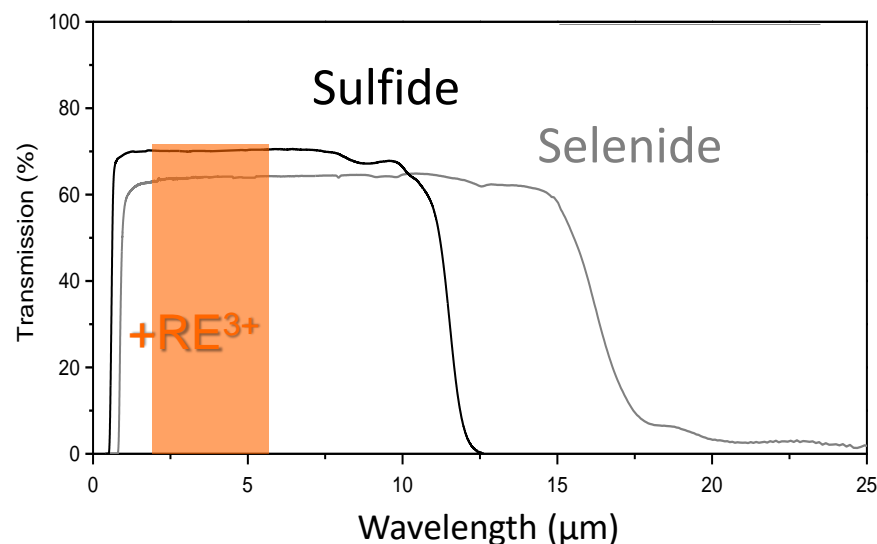
→ Prototype development (lasers and infrared  
gas detectors)



# Rare earth embedded in a chalcogenide glass

- Phonon energies, transparency and quantum efficiency

Glass matrix	Phonons energy (cm <sup>-1</sup> )
Silica (oxide)	~1100
Tellurite (oxide)	~750
Fluoride	400-600
Sulfide	350-450
Selenide/Chlorides	200-300
Tellurides/Bromides	100-200



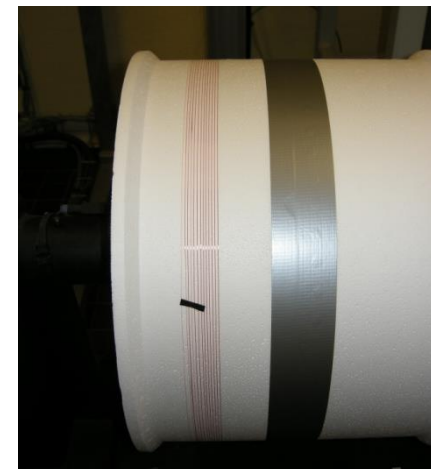
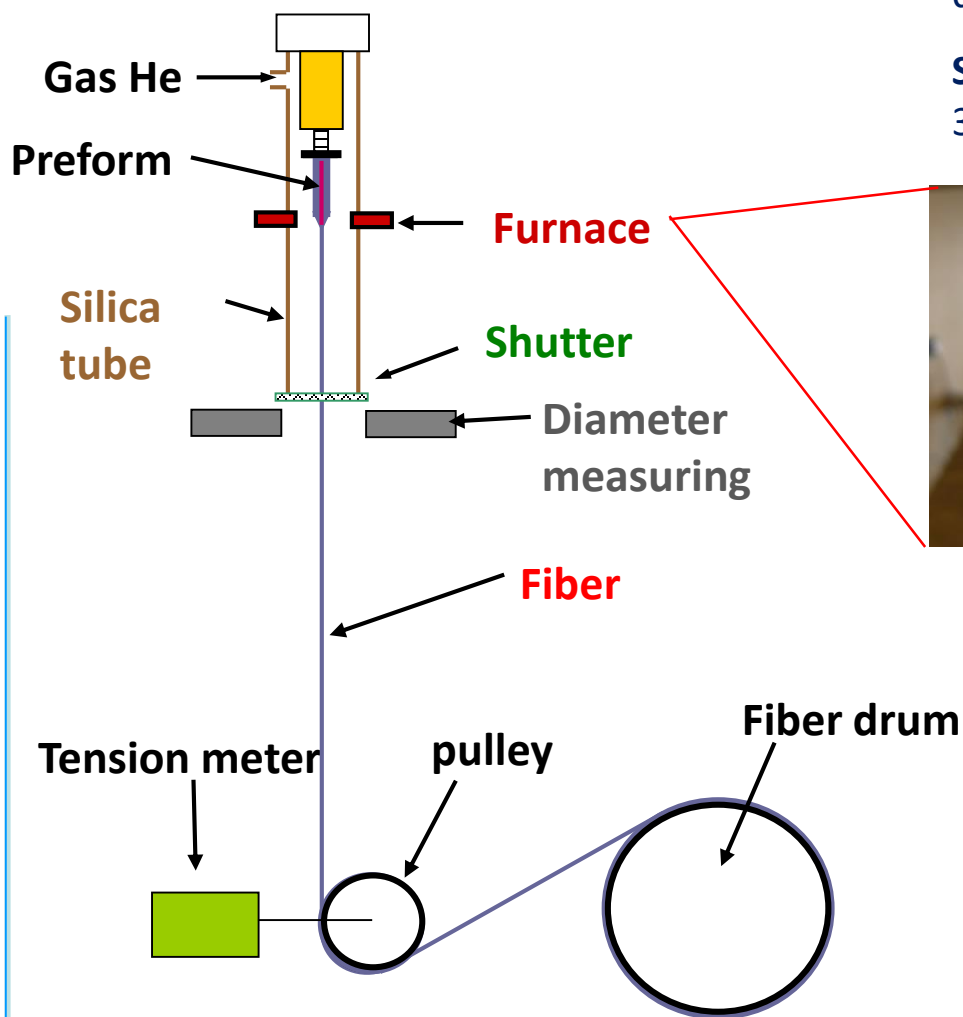
Matrix / Rare earth ion :

- Transparency for optical pumping
- Adapted phonon energies for an efficient mid-IR luminescence

# Fiber drawing

**Size of preform:** 10 cm length and 1cm diameter

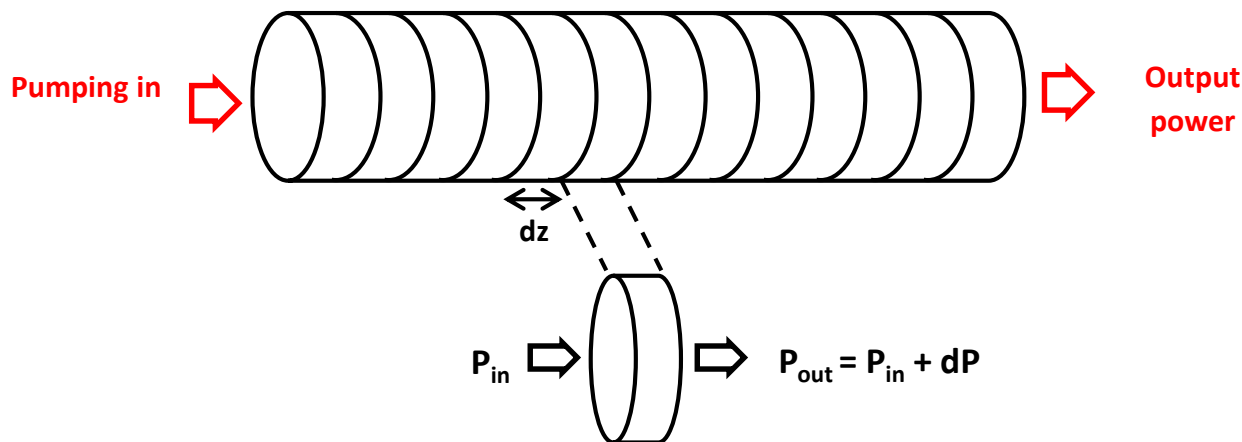
**Size of fiber:** several tens of meter for a 300  $\mu\text{m}$  diameter fiber



**Fibered rare earth doped mid-IR sources**

# Dy<sup>3+</sup>-doped mid-IR source : a model

- Simulation:
  - Simultaneous solving of population and propagation equations along the fiber



- Fluorescence guided contribution : solid angle considerations

$$\eta = \frac{\Omega}{4\pi} = \frac{2\pi(1 - \cos(\theta))}{4\pi}$$

solid angle  
 Isotropic emission basically

# Dy<sup>3+</sup>-doped mid-IR source : a model

## Population equations :

<sup>6</sup>H<sub>5/2</sub>+<sup>4</sup>F<sub>7/2</sub>

Pump absorption ←  $\sigma_p \cdot \phi_p(p) \cdot N_0 - \frac{N_4}{\tau_4} = 0$

<sup>6</sup>H<sub>9/2</sub>+<sup>4</sup>F<sub>11/2</sub>

$N_4 \cdot (A_{43}^R + A_4^{MP}) - \frac{N_3}{\tau_3} - W_{30} \cdot N_3 \cdot N_0 = 0$

<sup>6</sup>H<sub>11/2</sub>

$N_4 \cdot A_{42}^R + N_3 \cdot (A_{32}^R + A_3^{MP}) - \frac{N_2}{\tau_2} - W_{20} \cdot N_2 \cdot N_0 = 0$

<sup>6</sup>H<sub>13/2</sub>

$N_4 \cdot A_{41}^R + N_3 \cdot A_{31}^R + N_2 \cdot (A_{21}^R + A_2^{MP}) - \frac{N_1}{\tau_1} + 2 \cdot W_{30} \cdot N_3 \cdot N_0 + 2 \cdot W_{20} \cdot N_2 \cdot N_0 = 0$

$N_T = N_0 + N_1 + N_2 + N_3 + N_4$

Energy transfer

## Propagation equations :

Pump :

$$\frac{dP}{dz} = (-\sigma_p \cdot N_0 - \alpha_p) \cdot P$$

916 nm losses

Fluorescence :

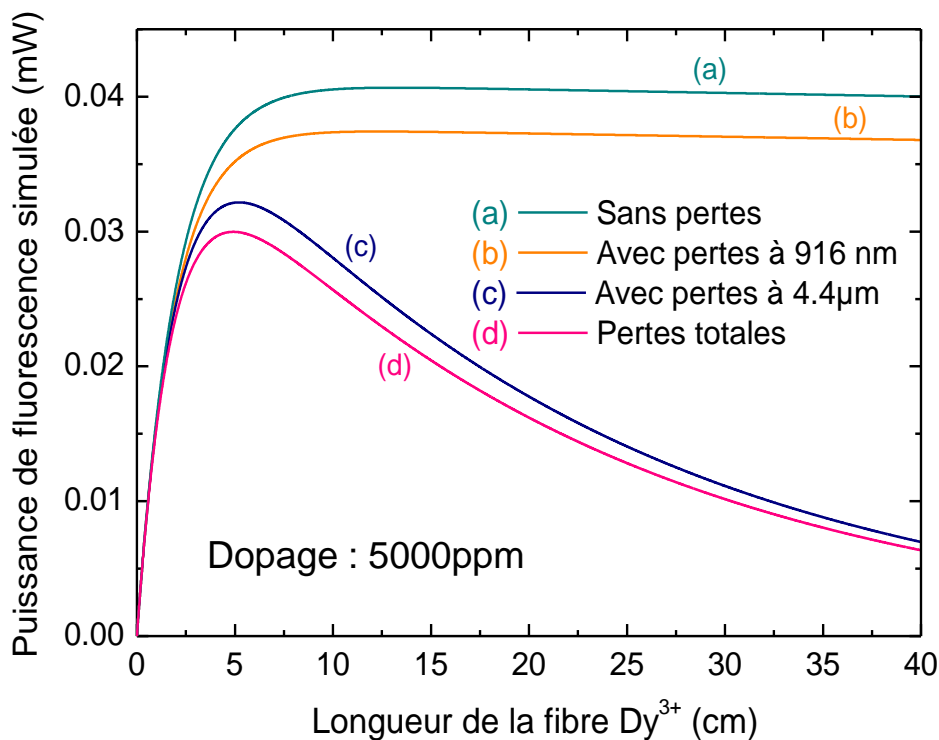
$$\frac{dP_{21}}{dz} = (\sigma_{21} \cdot N_2 - \sigma_{12} \cdot N_1 - \alpha_{p21}) \cdot P_{21} + A_{21}^R \cdot \eta \cdot h \cdot \nu_{21} \cdot S_f \cdot N_2$$

4.4μm losses

4.4μm spontaneous emission within the solid angle

# Dy<sup>3+</sup>-doped mid-IR source : a model

- Results : 4.4μm output power
  - Propagation losses influence :



(a) - increase of  $P_{IR}$  until full pump absorption (Beer-Lambert)

(b) - **916 nm losses (19 dB/m) : decrease of  $P_{IR}$**

(c) - **4.4μm losses (20 dB/m) : not compensated by Dy<sup>3+</sup> fluorescence → decrease of  $P_{IR}$**

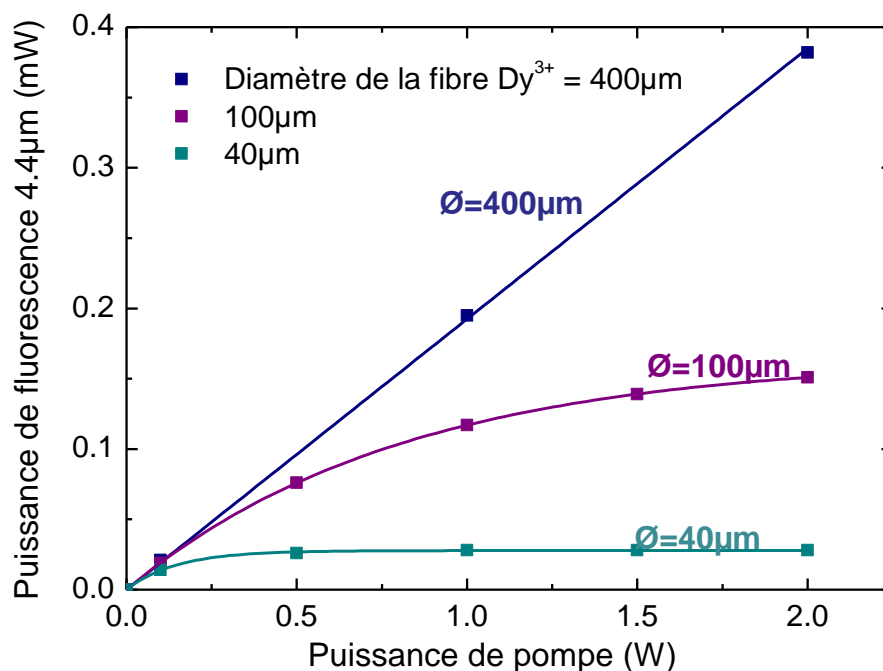
(d) - **All losses included**

## 4.4 μm losses dominance in the process

# Dy<sup>3+</sup>-doped mid-IR source : a model

## • Fiber diameter influence :

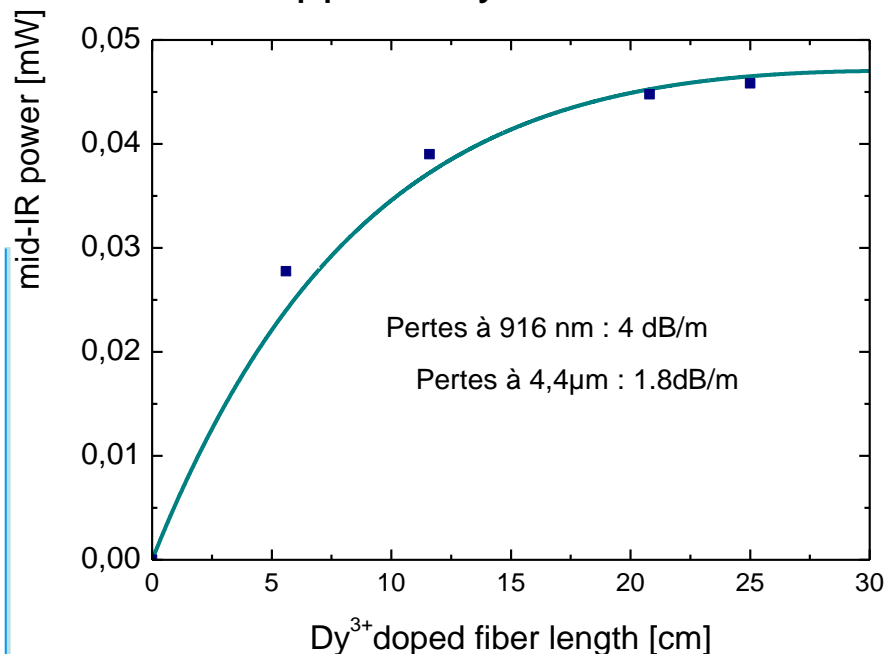
- $\varnothing_{\text{fibre}} = 400 \mu\text{m}$  : linear shift of  $P_{\text{IR}}$  with respect to  $P_{\text{pump}}$  → no ground state depletion
- $\varnothing_{\text{fibre}} = 40 \mu\text{m}$  : absorption saturation  
→  $P_{\text{IR}} \sim \text{cste} / P_{\text{pump}}$
- $\varnothing_{\text{fibre}} = 100 \mu\text{m}$  (mixed case) :
  - low pumping power → linear variation of  $P_{\text{IR}}$ ,
  - high pumping power → saturation



400 μm diameter fibers

# Dy<sup>3+</sup>-doped mid-IR source : experimental

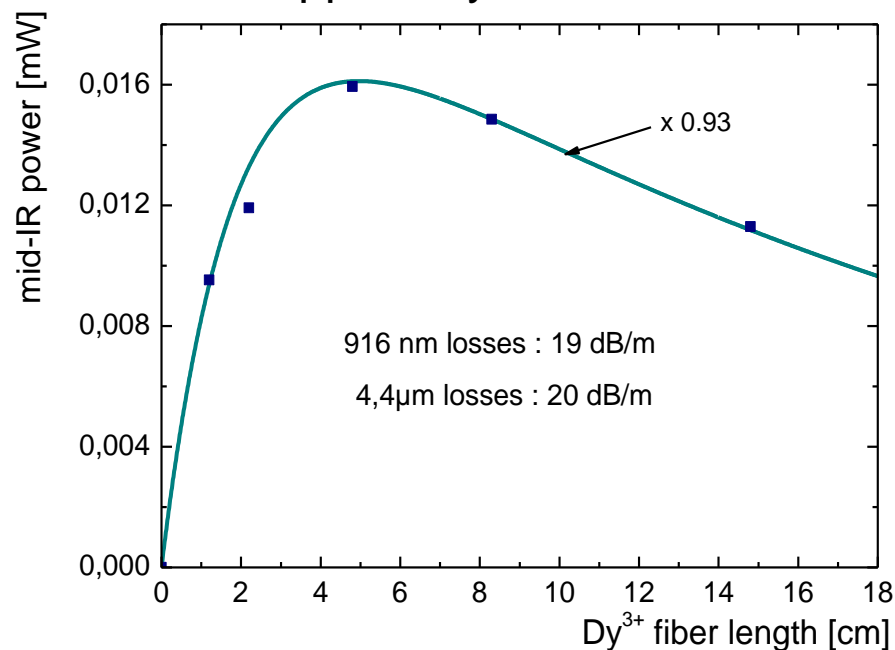
1000 ppm ; Dy<sup>3+</sup>GaGeSbS



1000 ppm fiber fluorescence stronger than the 5000 ppm case : losses and desactivated ions.

— Simulation  
■ Experimental

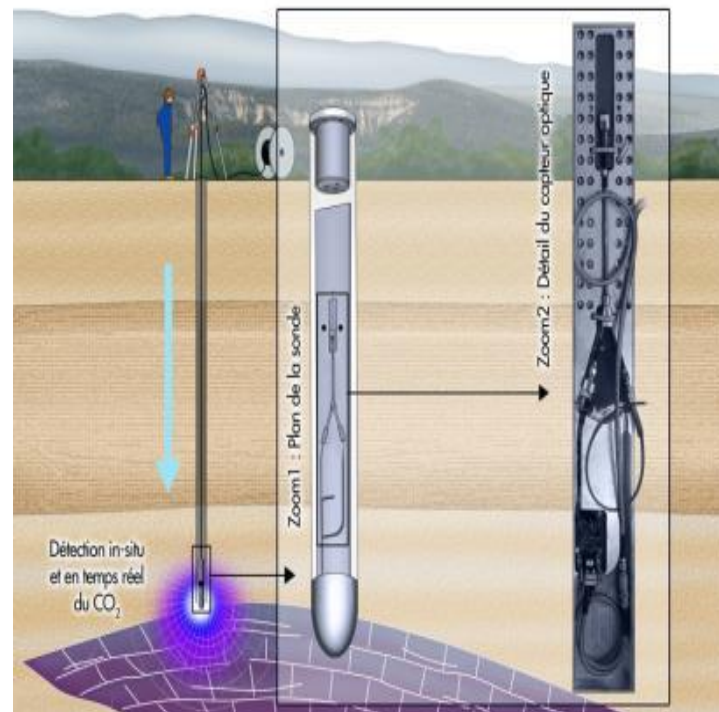
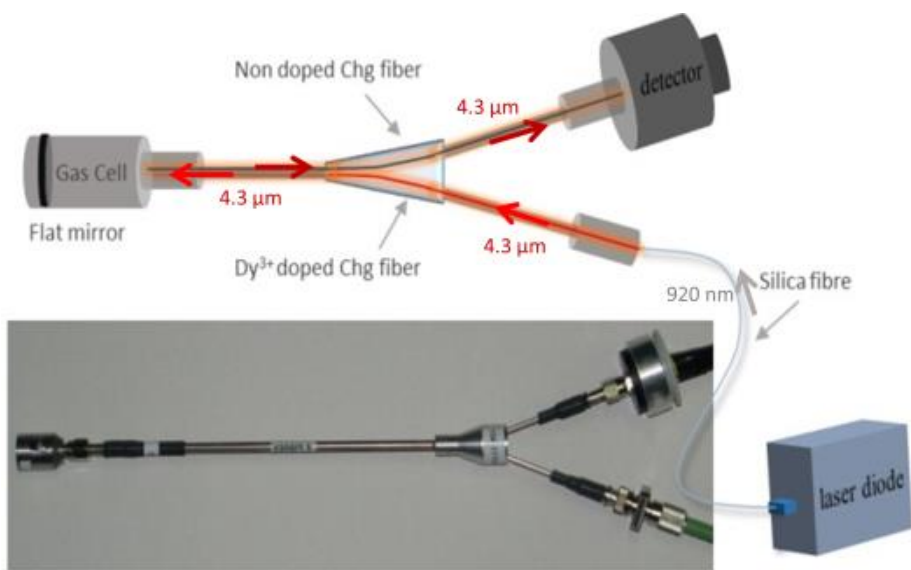
5000 ppm ; Dy<sup>3+</sup>GaGeSbS

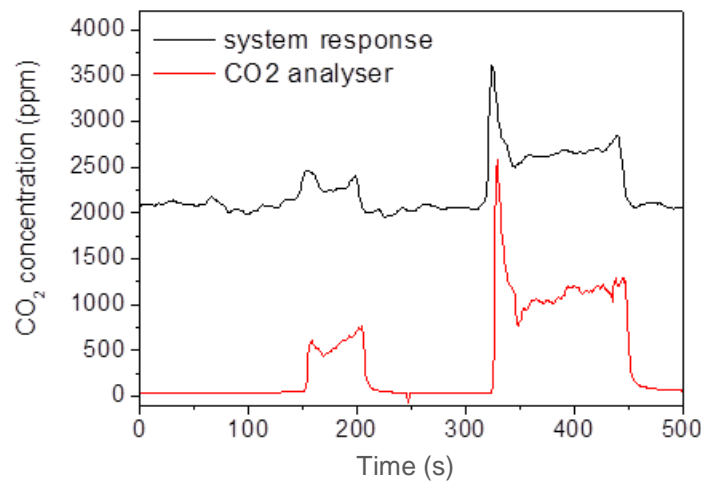
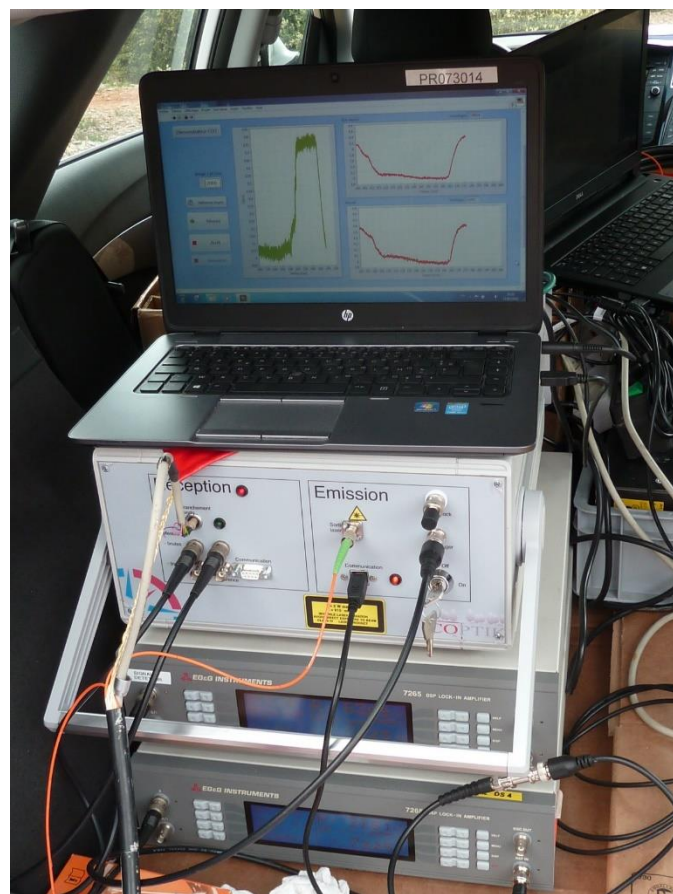


1000 ppm, 28 cm long, 400 μm diameter. Losses: 4 dB/m @916 nm and 1.8 dB/m @4.4μm

# Projet ADEME $\sqrt{\text{CO}_2}$ PTIK

- applications exemples
  - $\text{CO}_2$  leakage detection in gas pits





## Achievements to date:

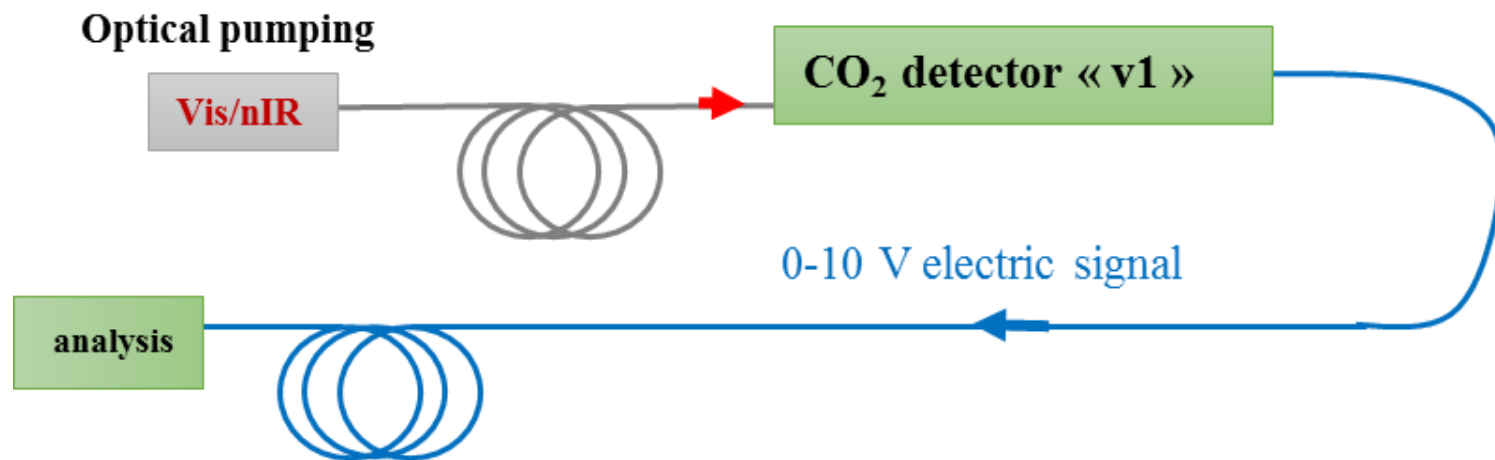
Detection by **fluorescence of Dy<sup>3+</sup>** in mid-IR around 100 m depth

Detection threshold of **few hundreds of ppm**



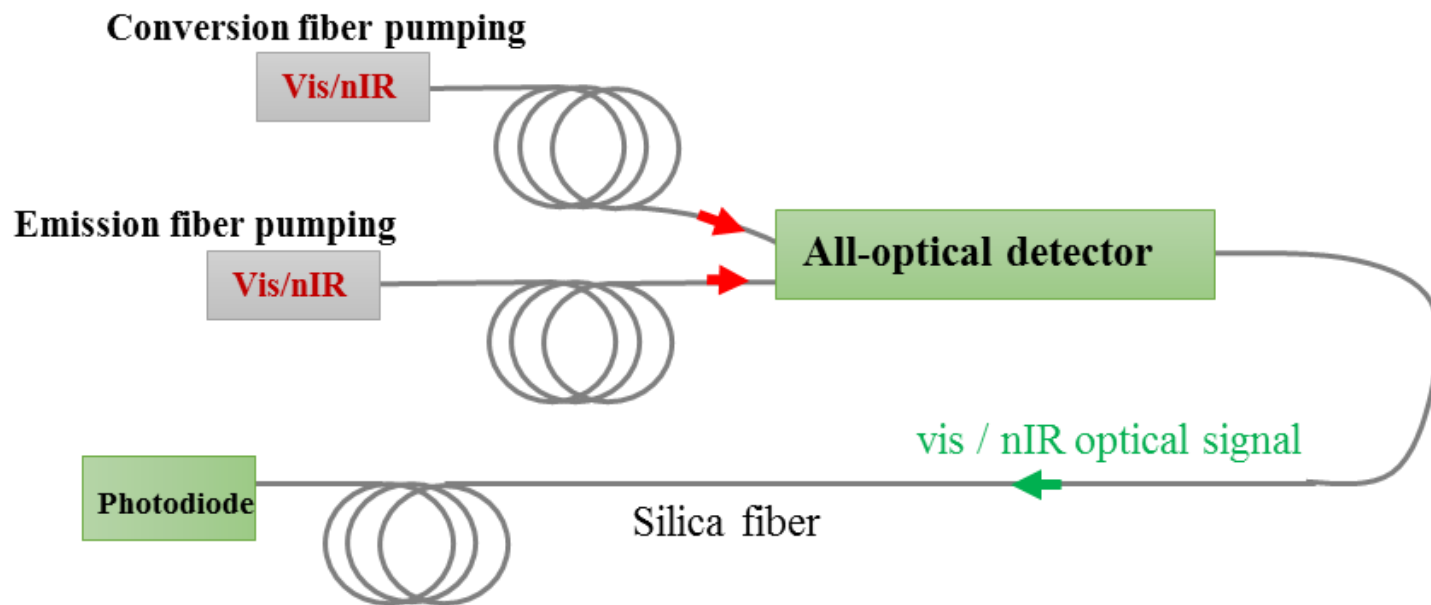
# All-optical detector

- Today : electronic parts remains in-situ



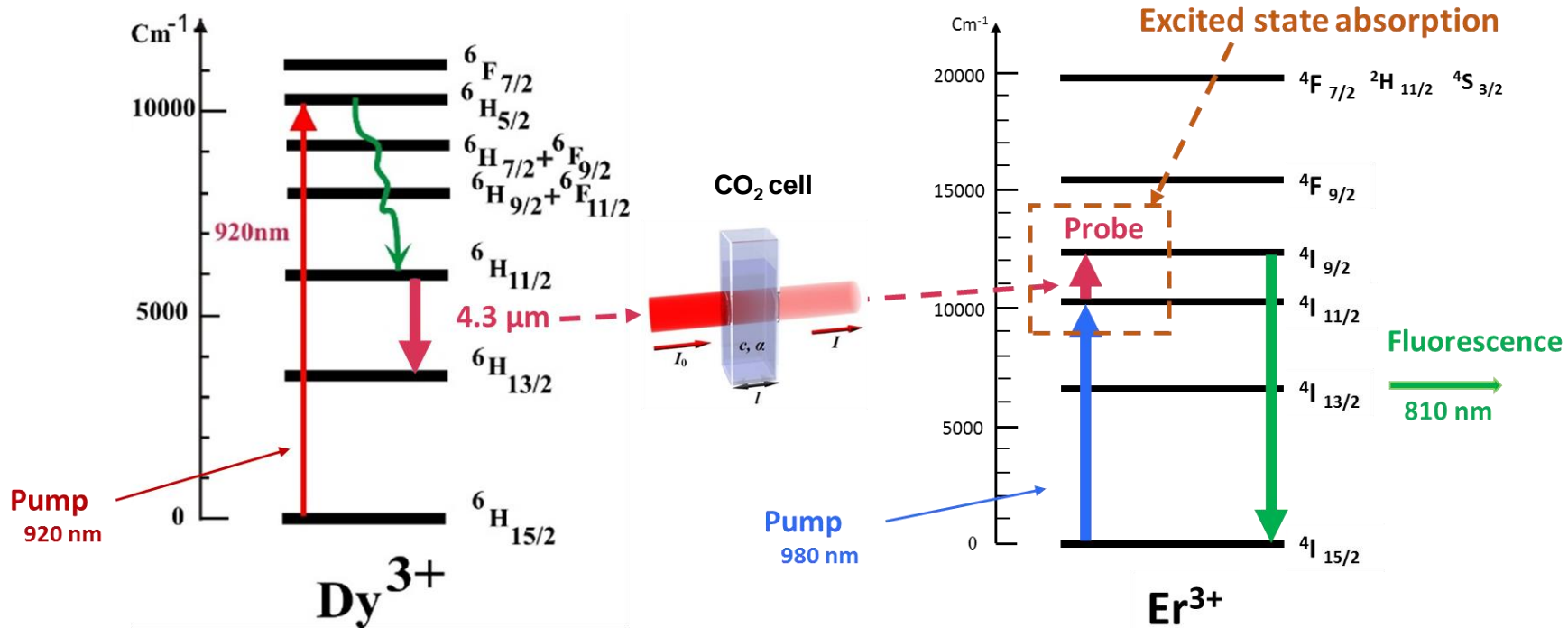
# All-optical detector

- Rare earth doped converter from m-IR to vis-nIR optical signal



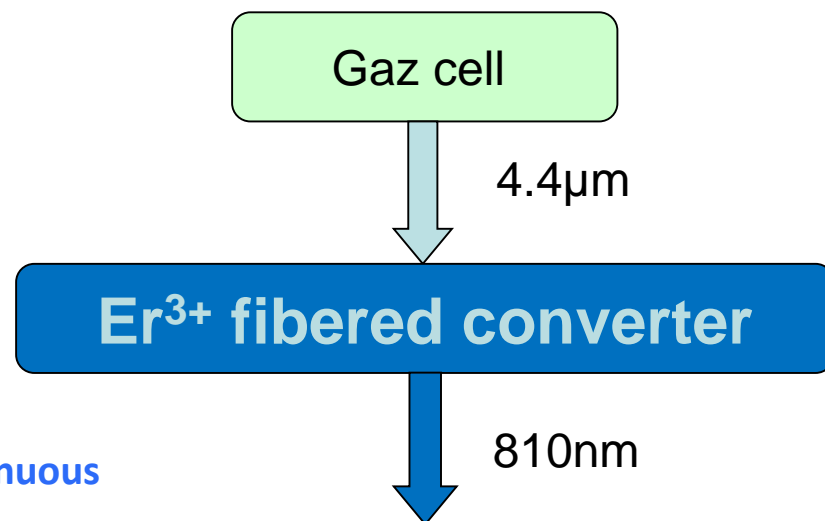
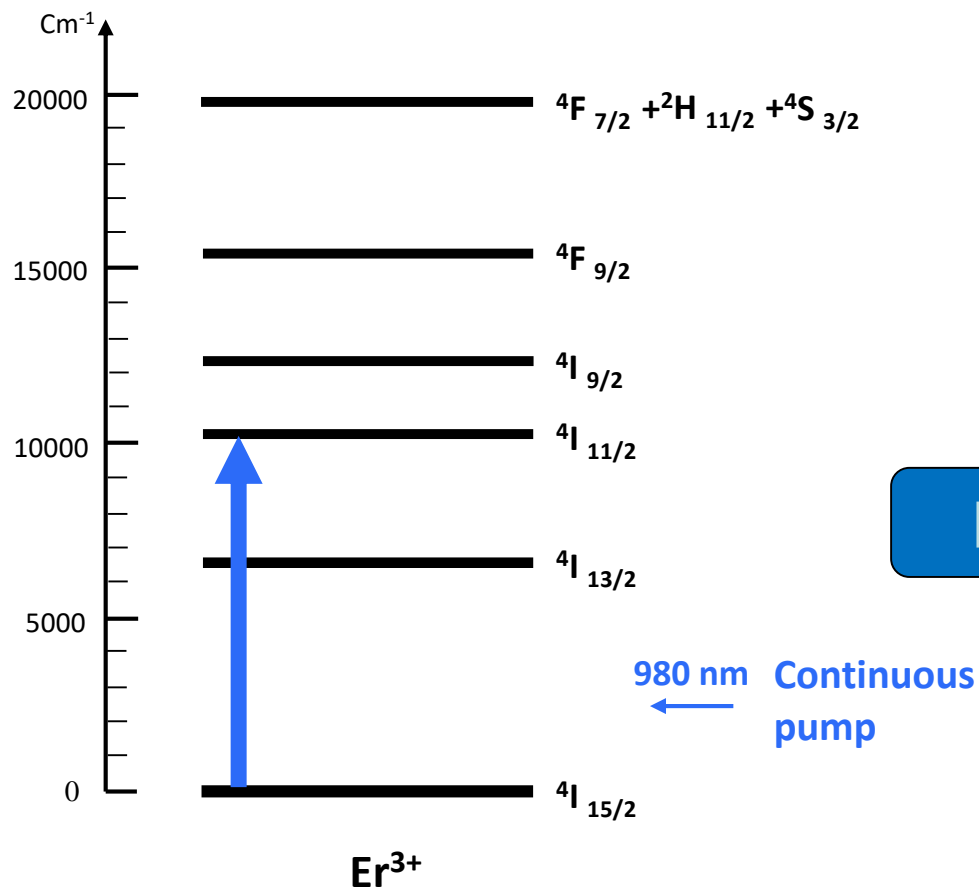
# AEE based energy conversion

- CO<sub>2</sub> case : 4,3  $\mu\text{m}$   $\rightarrow$  810 nm conversion
  - Using an Er<sup>3+</sup> excited state absorption



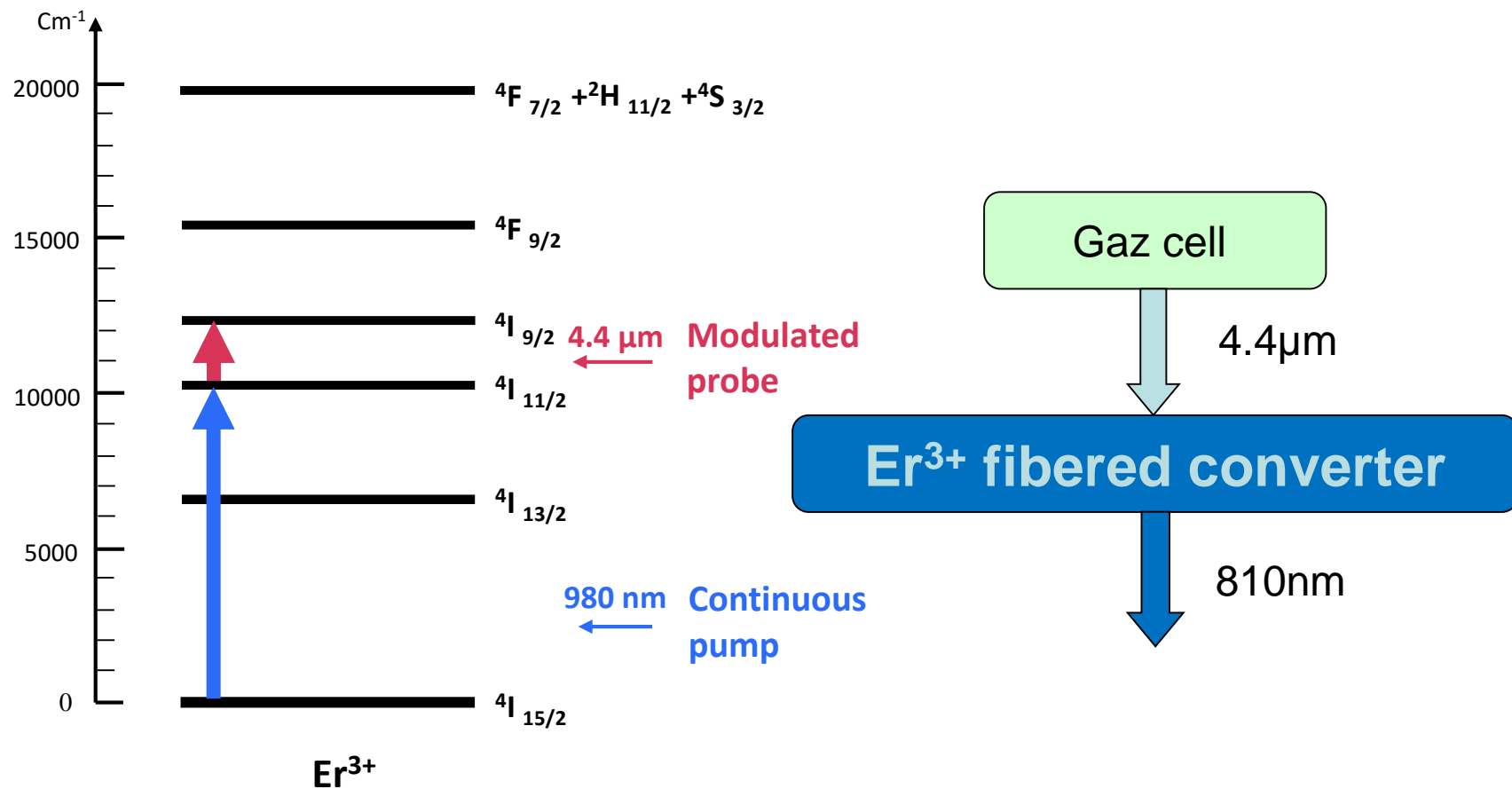
# AEE based energy conversion

- Erbium –  $\text{Er}^{3+}$  (from  $4.4\mu\text{m}$  to  $810\text{ nm}$ )



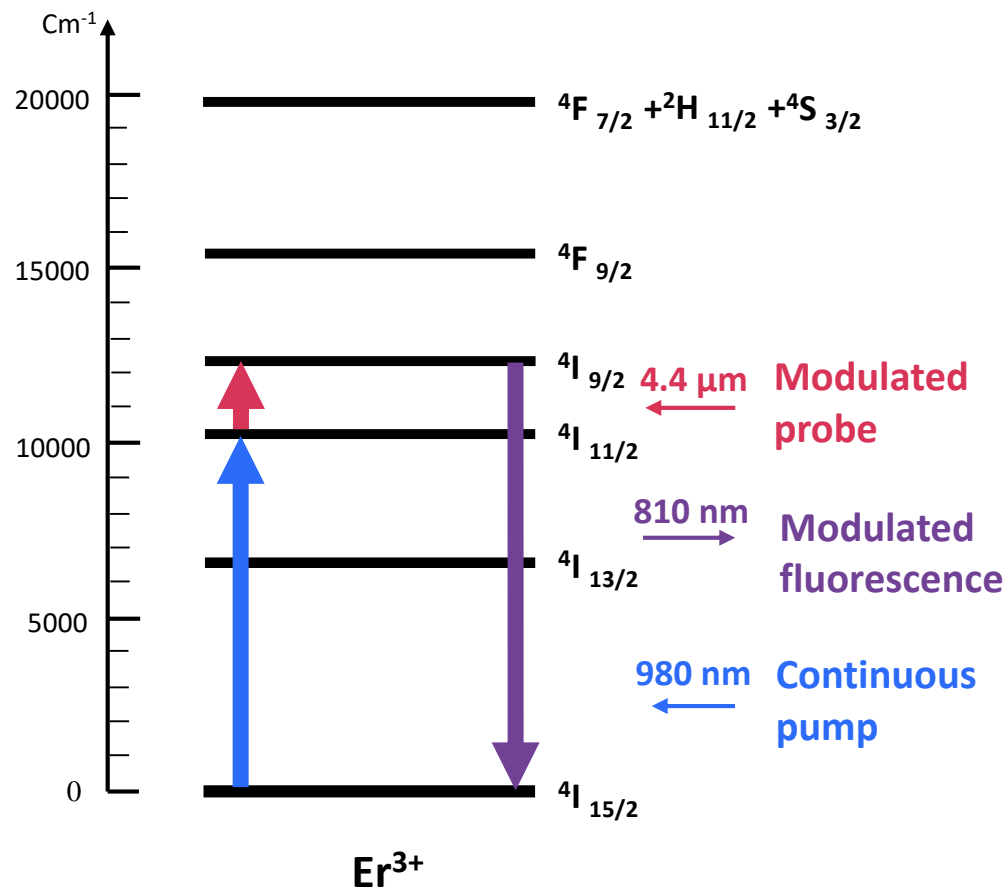
# AEE based energy conversion

- Erbium –  $\text{Er}^{3+}$  (from  $4.4\mu\text{m}$  to  $810\text{ nm}$ )



# AEE based energy conversion

- Erbium –  $\text{Er}^{3+}$  (from  $4.4\mu\text{m}$  to  $810\text{ nm}$ )

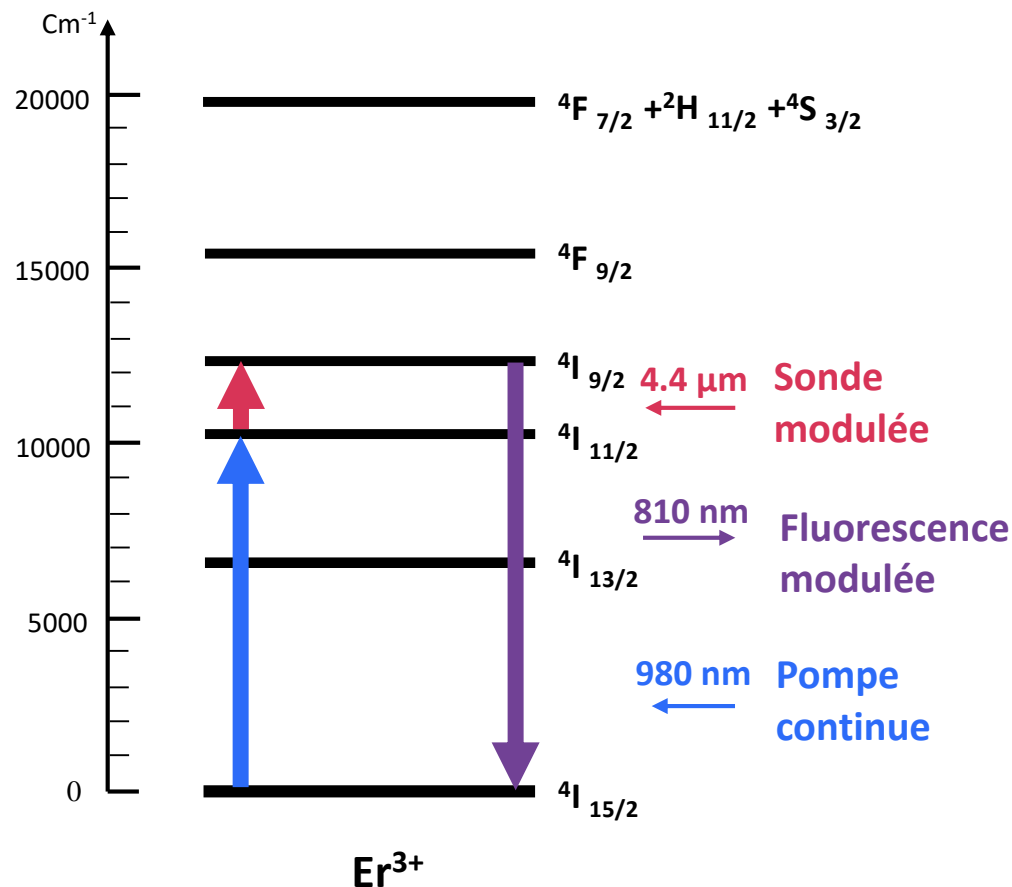


• quantum process:  
IR photon turned into nIR  
or visible photon

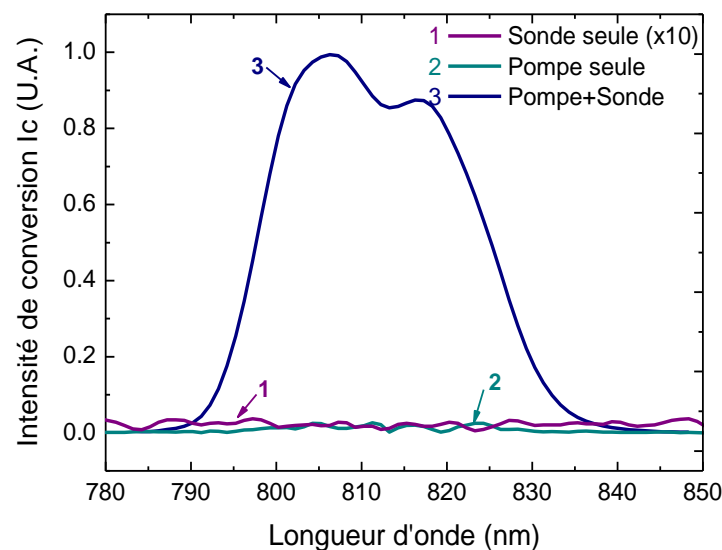
Excited stated absorption  
(ESA)

# AEE based energy conversion

- Erbium –  $\text{Er}^{3+}$  (from  $4.4\mu\text{m}$  to  $810\text{ nm}$ )



## Experimental proof





# 810 nm conversion in Er: GaGeSbS : a model

- Steady state population equations

○ Energy transfer

$${}^4S_{3/2} + {}^2H_{11/2} + {}^4F_{7/2} \quad -\frac{N_5}{\tau_5} + W_{22} \cdot N_2^2 - W_{50} \cdot N_5 \cdot N_0 = 0$$

$${}^4F_{9/2} \quad N_5 \cdot (A_{54}^R + A_5^{MP}) - \frac{N_4}{\tau_4} = 0$$

$${}^4I_{9/2} \quad N_4 \cdot (A_{43}^R + A_4^{MP}) + A_{53}^R \cdot N_5 - \frac{N_3}{\tau_3} + \sigma_{\text{esas}} \cdot \phi_s \cdot N_2 + W_{11} \cdot N_1^2 + W_{50} \cdot N_5 \cdot N_0 = 0$$

$${}^4I_{11/2} \quad N_3 \cdot (A_{32}^R + A_3^{MP}) + A_{42}^R \cdot N_4 + A_{52}^R \cdot N_5 - \frac{N_2}{\tau_2} + \sigma_p \cdot \phi_p \cdot N_0 - \sigma_{\text{esas}} \cdot \phi_s \cdot N_2 - 2 \cdot W_{22} \cdot N_2^2 = 0$$

$${}^4I_{13/2} \quad A_{21}^R \cdot N_2 + A_{31}^R \cdot N_3 + A_{41}^R \cdot N_4 + A_{51}^R \cdot N_5 - \frac{N_1}{\tau_1} - 2 \cdot W_{11} \cdot N_1^2 + W_{50} \cdot N_5 \cdot N_0 = 0$$

$$N_0 + N_1 + N_2 + N_3 + N_4 + N_5 = N_T$$



# 810 nm conversion in Er: GaGeSbS : a model

- Propagation equations

Pump (980nm):

$$\frac{dP}{dz} = (-\sigma_p \cdot N_0 - \alpha_p) P$$

982 nm losses

Probe (4.4μm) :

$$\frac{dP_s}{dz} = (-\sigma_{ESAS} \cdot N_2 - \alpha_{ps}) P_s$$

4.4μm losses

**Ic** (810nm converted) :

$$\frac{dP_{21}}{dz} = (\sigma_{21} \cdot N_2 - \sigma_{12} \cdot N_1 - \alpha_{p21}) P_{21} + A_{21}^R \cdot \eta \cdot h \cdot \nu_{21} \cdot S_f \cdot N_2$$

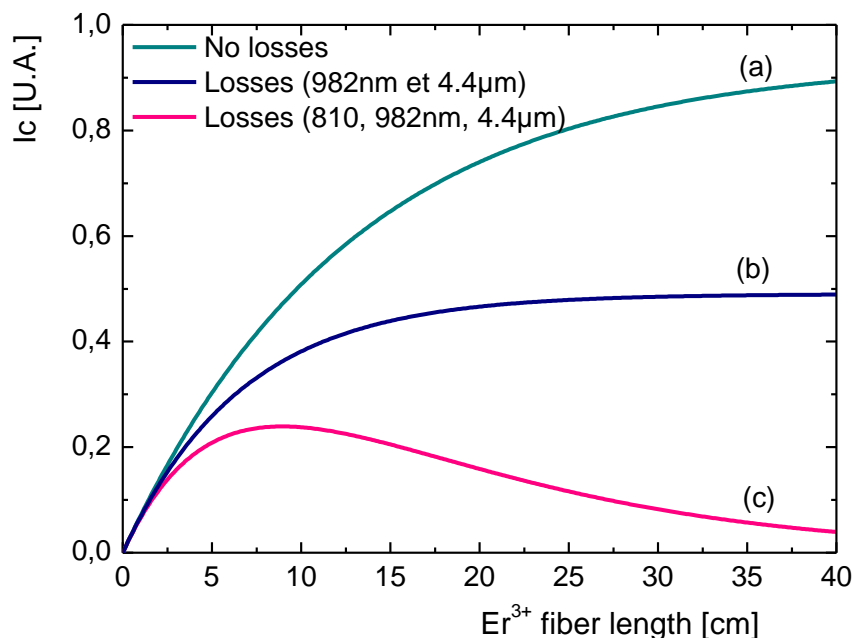
810 nm losses

810 nm spontaneous fluorescence emitted within the critical angle

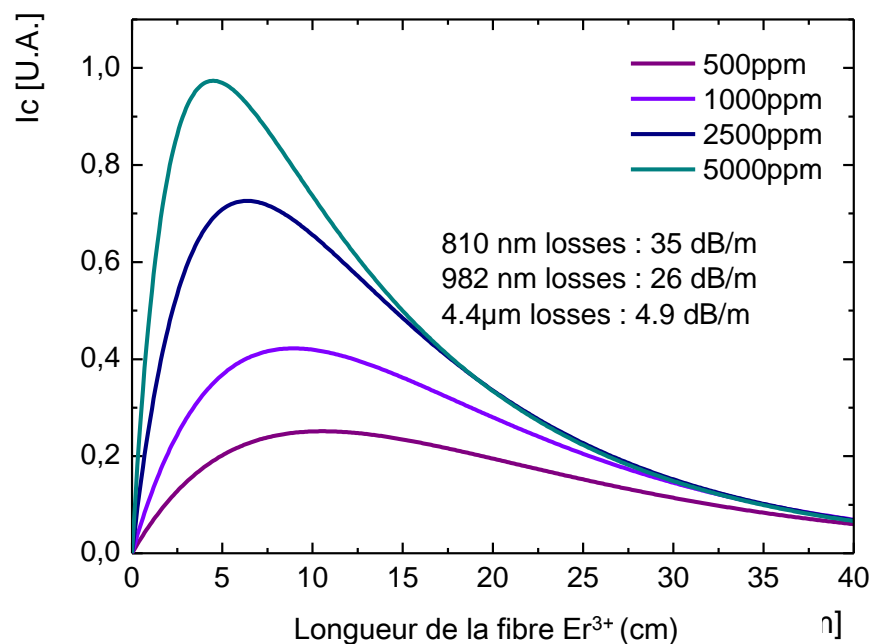
# 810 nm conversion in Er: GaGeSbS : a model

- 810nm converted intensity

Propagation losses influence



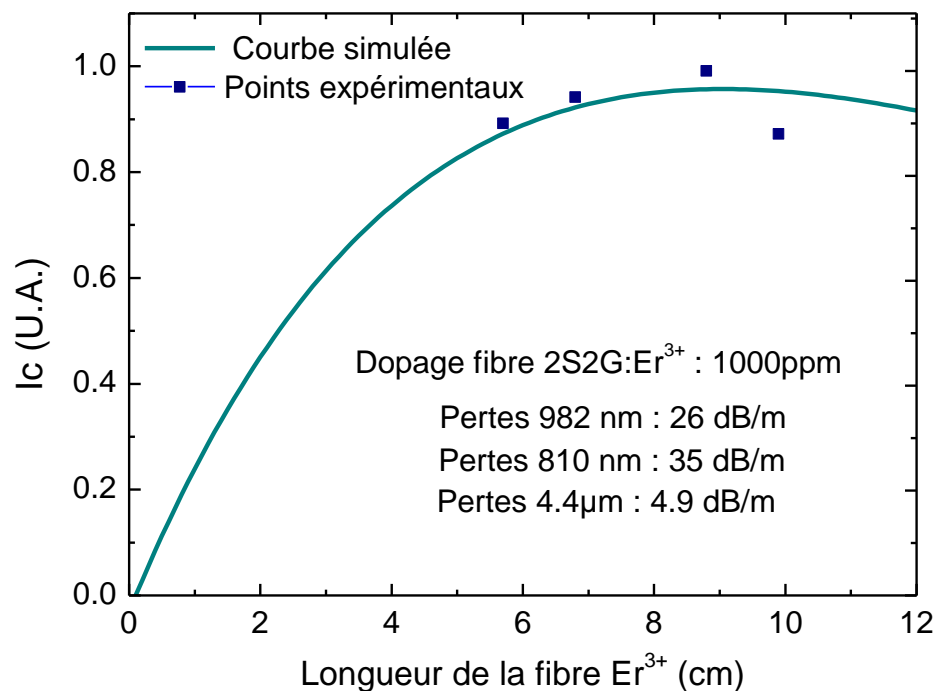
Er<sup>3+</sup> doping rate influence



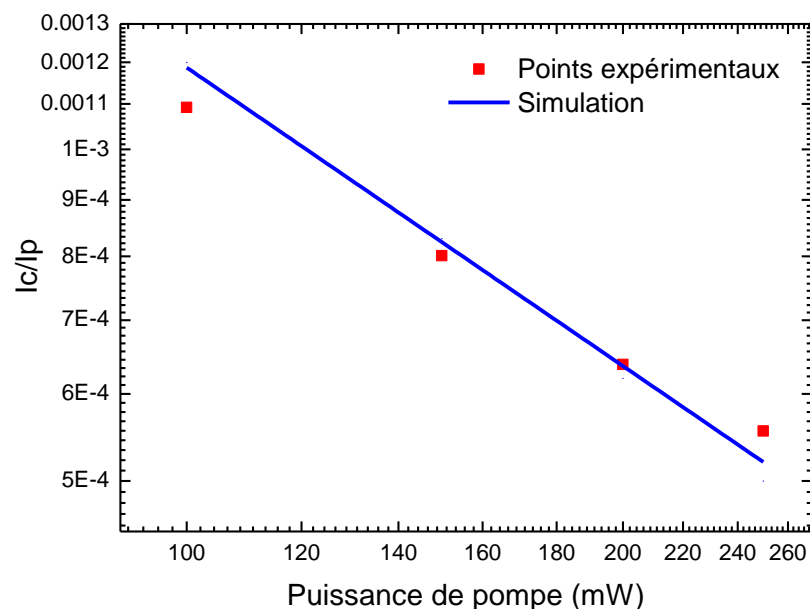
A good compromise: **2500ppm** doping rate, **6 cm** long corresponding to attenuation values of : **35 dB/m @810 nm, 26 dB/m @982 nm et 4.9 dB/m @4.4 µm**

# Simulation / experiments

- 1000ppm  $\text{Er}^{3+}$  GaGeSbS fiber ; 810 nm converted intensity



Signal to noise ratio as a function of the 980 nm pumping power





Thanks for your attention