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QUARTZ ENHANCED PHOTOACOUSIC SPECTROSCOPY WITH NEW ANTIMONIDE COMPOUNDS

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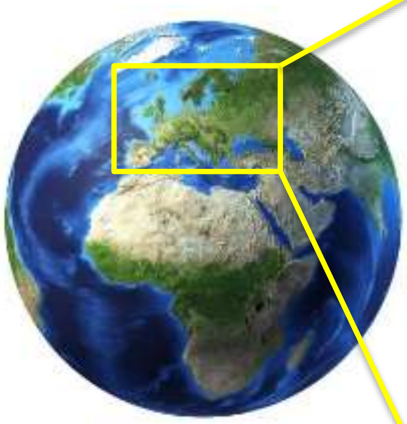

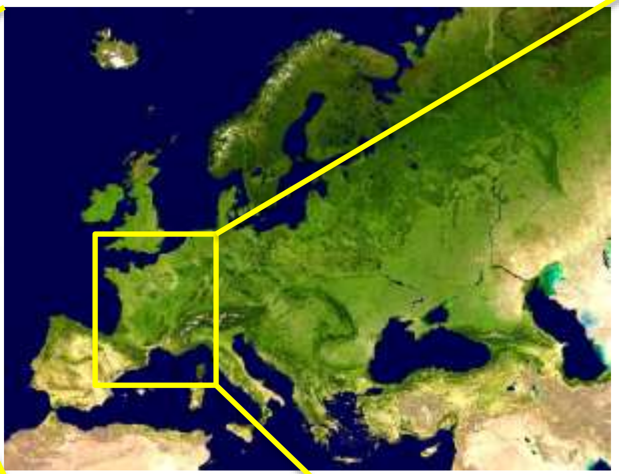

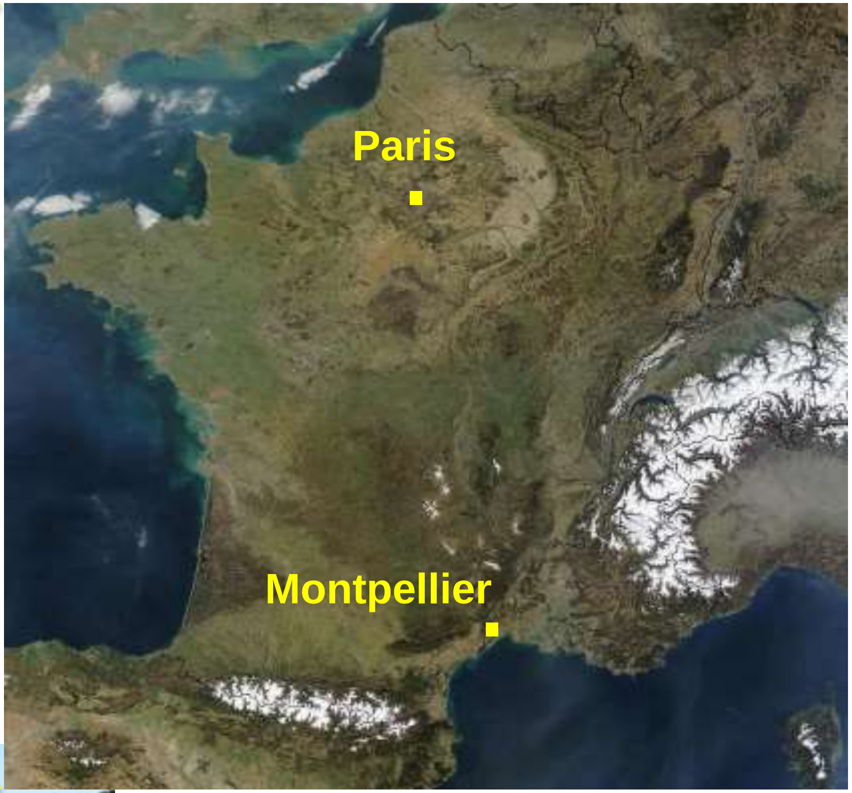

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34095 Montpellier CEDEX 5
France

Institut d'Electronique du Sud (IES)
UMR CNRS 5214

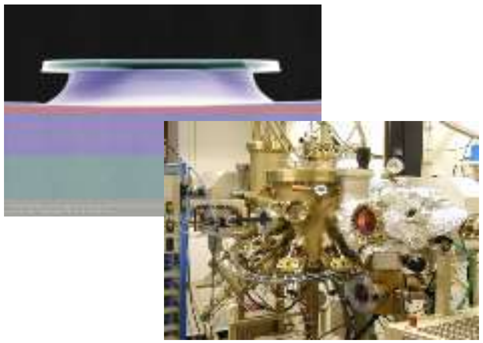
130 researchers:

- 64 Profs/associate prof
- 8 researchers CNRS
- 58 PhD students and post-doc

29 engineers, technicians, administrative

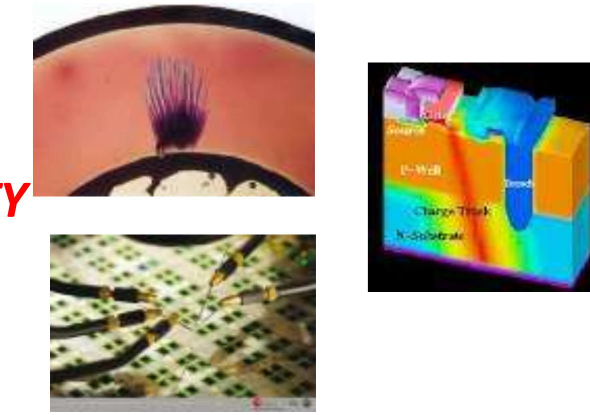
- 16 ITA CNRS
- 11 BIATOSS des Universités
- 2 BIATOSS Contractuels

Main skills / Expertise



INFRARED

RELIABILITY



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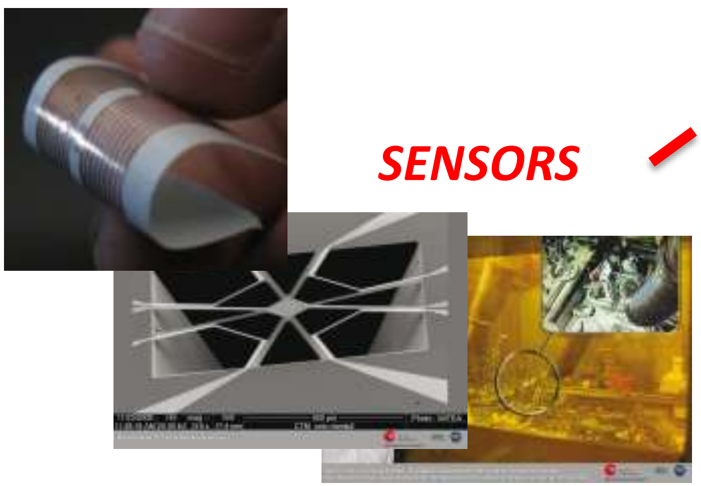
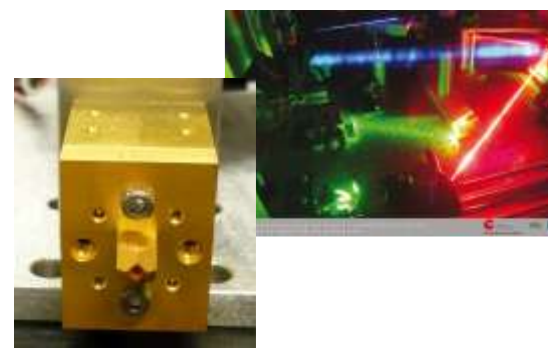
SENSORS



TéraHetz



IES (UMR CNRS-UM2 5214)

IES

Département 1	Département 2	Département 3
Sensors and Systems	**Waves and Photonics** nanoMIR group	**Reliability, Energy, Systems**

Groupe nanoMIR

nanostructures components for Mid-Infra-Red

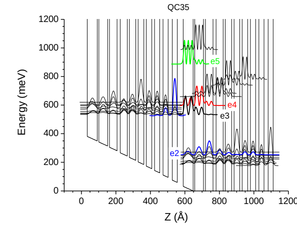
From materials… to prototypes
Spectral range : 2 to >20 µm

- **8 prof/ass prof** (1 on TDLS)
- **4 DR/CR**
- **5 engineers/technicians**
- **13 PhD students** (1 on TDLS) **+ 1 post-doc**

Sponsors: EC (ICT, FP6 & 7), ANR, DGA, Region, CNRS, ADEME, Industry, ..
EquipEx: EXTRA "EXcellence cenTRe on Antimonides" (2012-2019)

Ressources of nanomir group

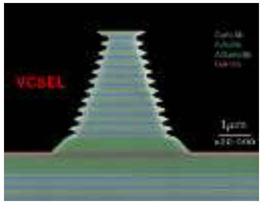
- **Design/modelisation** of structures

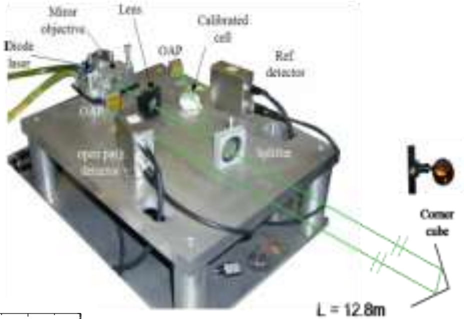


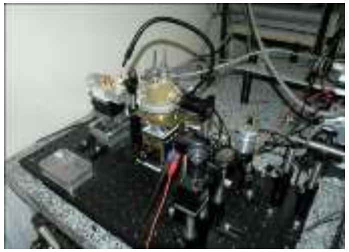
- **2 MBE reactors** dedicated to antimonides *(Riber 11 cellules ; Varian 8 cellules)*

- **Caracterisation benchs,** for materials and compounds :
  - PL/transmission with temperature
  - P – I, I – V, λ – I, spectral response
  - photo-voltage surface spectroscopie

- Devices **processing**

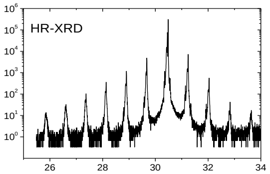




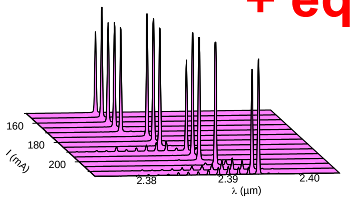


- Gas detection **setups**

- **Common Services (UM2)** for:
  - Caracterisations : X Rays, AFM, EFM,…
  - Devices processing



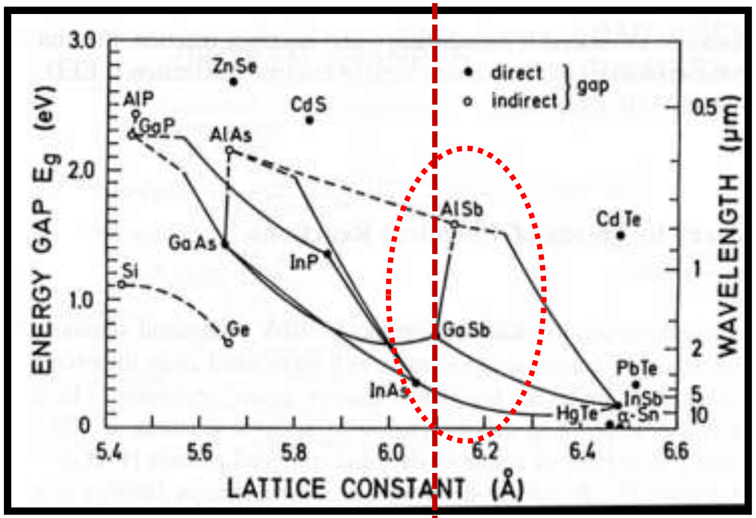
+ équipex EXTRA

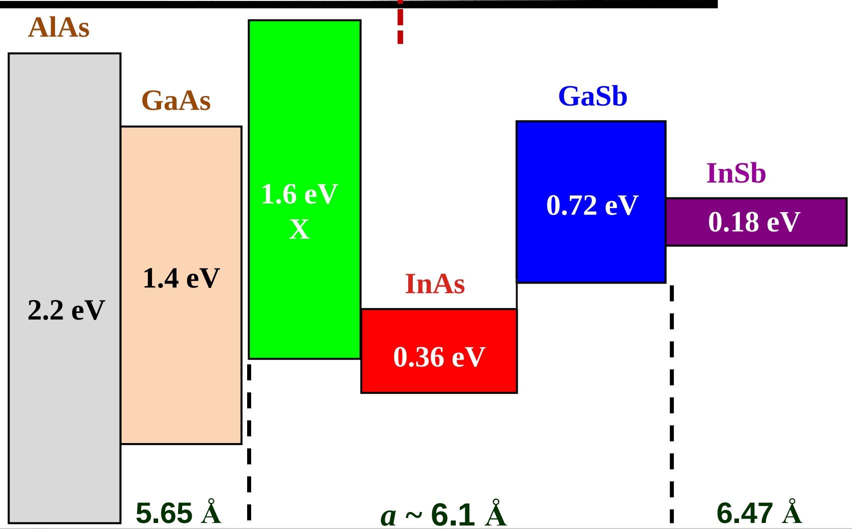


- **Single frequency Antimonide compounds in the infrared**
  - **Materials/spectral ranges**
  - **QW structures**
  - **QCL structures**
- **Applications**
  - **Collaborations**
  - **QEPAS sensing**
  - **Perspectives**
- **Conclusion**

Antimonide compounds

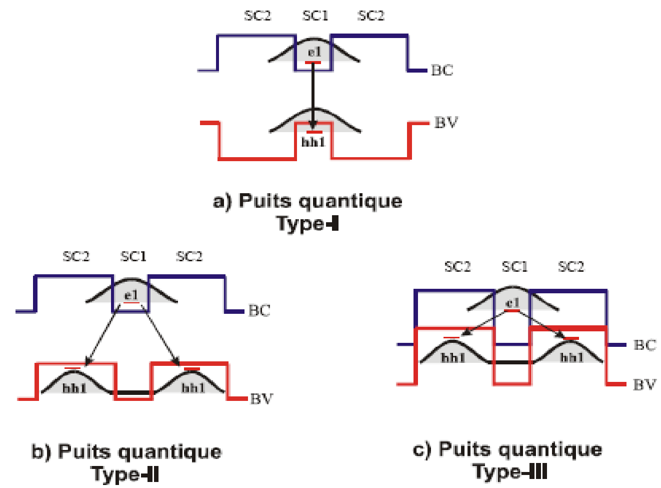
« 6.1 Å semiconductors »: GaSb, InAs, AlSb, InSb and alloys
AlGaAsSb, GaInAsSb, AlGaInAsSb… quasi-lattice matched on GaSb





0.15 eV < Bandgap < 2 eV

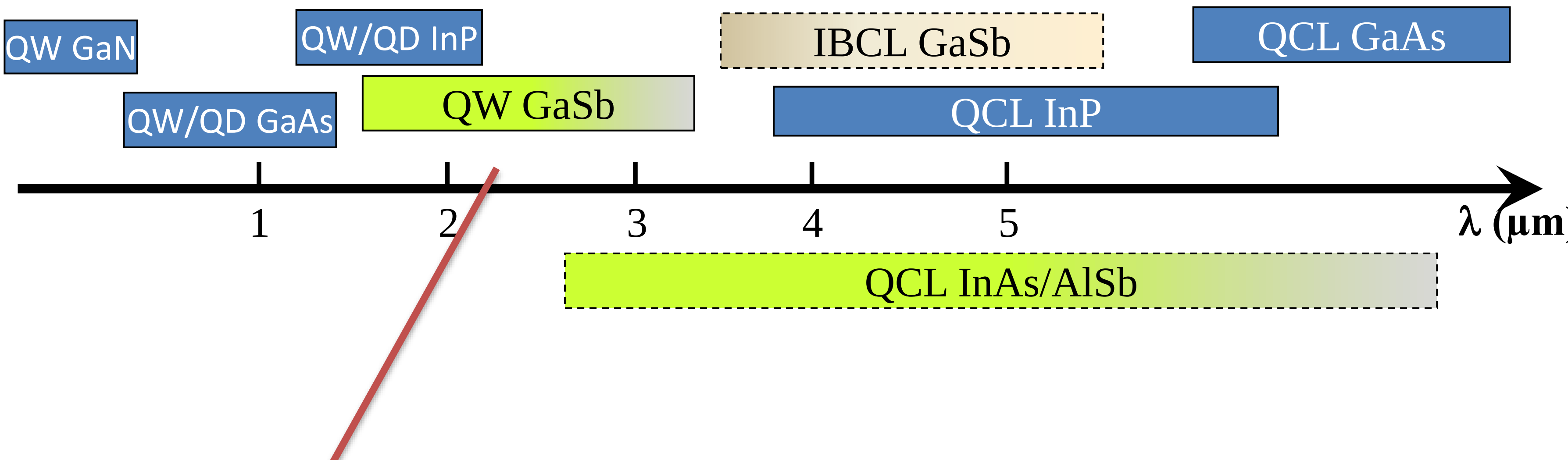
Sb-technology :
- **Small gaps,**
- **Type I to Type III alignements,**



- **low masses,**
- **high mobilities,**
- **Flexible : many alloys**

Inter-bands or intra-bands

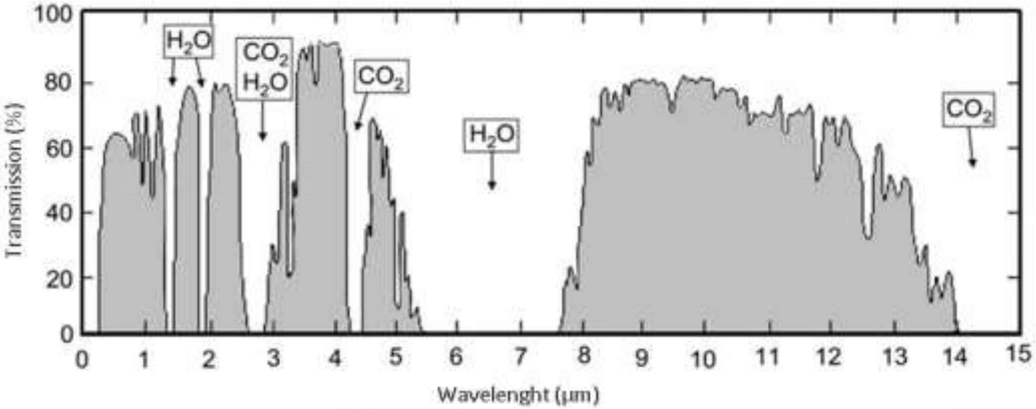
Antimonide compounds

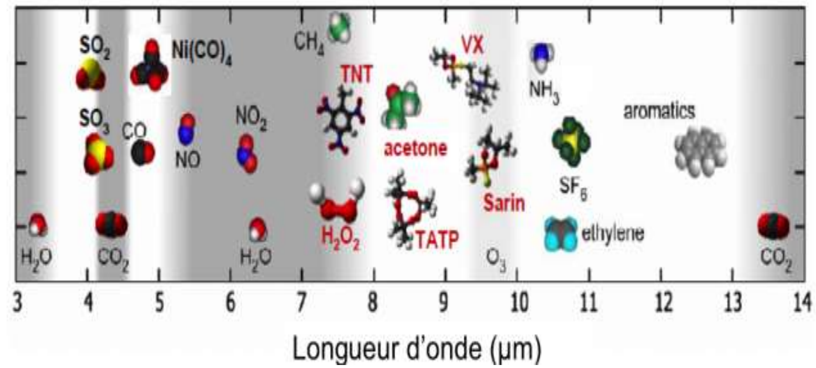


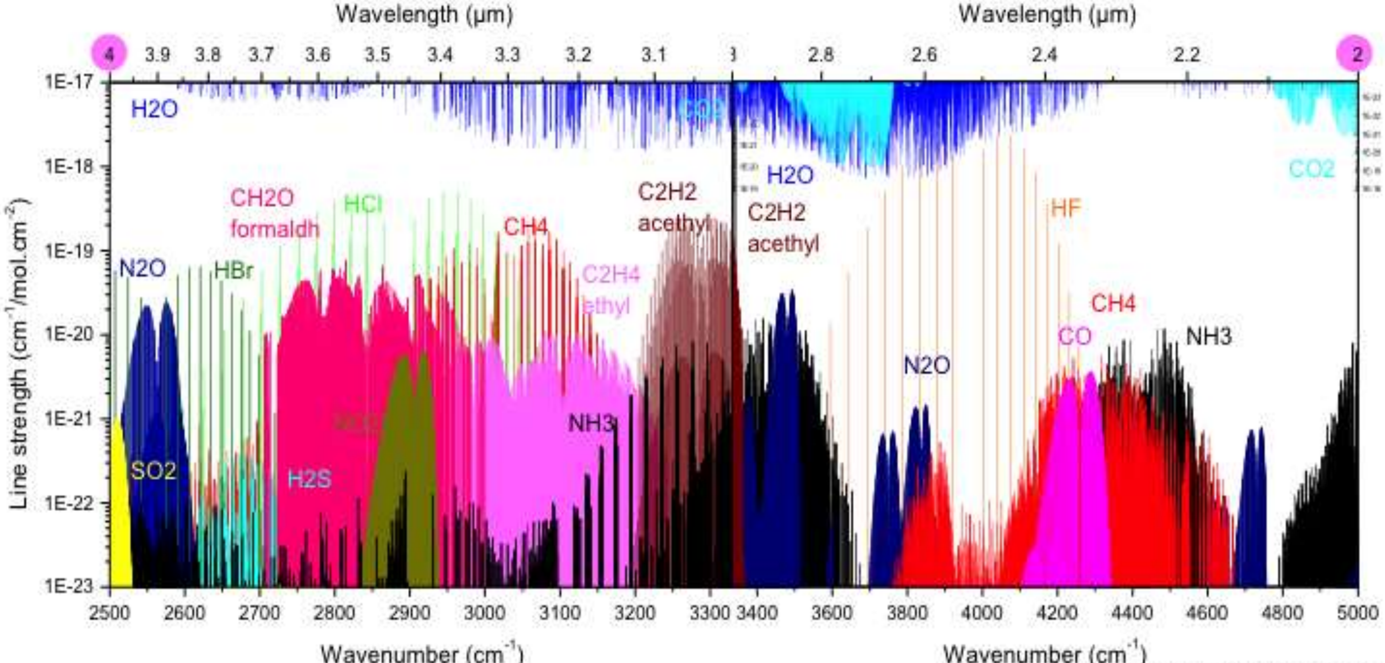
Mature
RT, CW,
Atmospheric transmission window,
cheap detectors

GaSb, AlSb, InAs, InSb + alloys:
AlGaAsSb, GaInAsSb, AlGaInAsSb …

Infrared spectral range





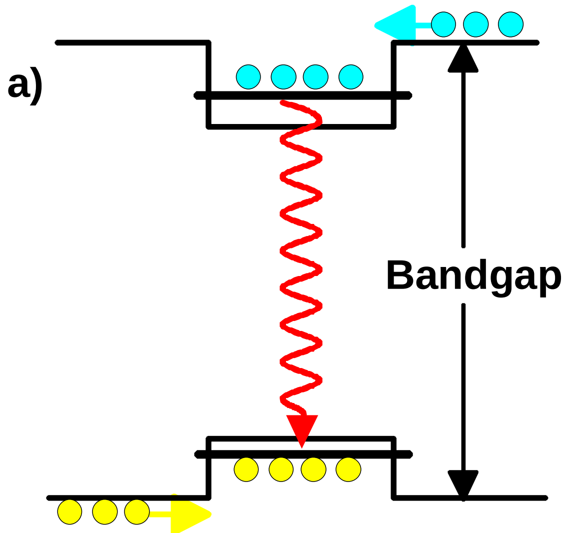


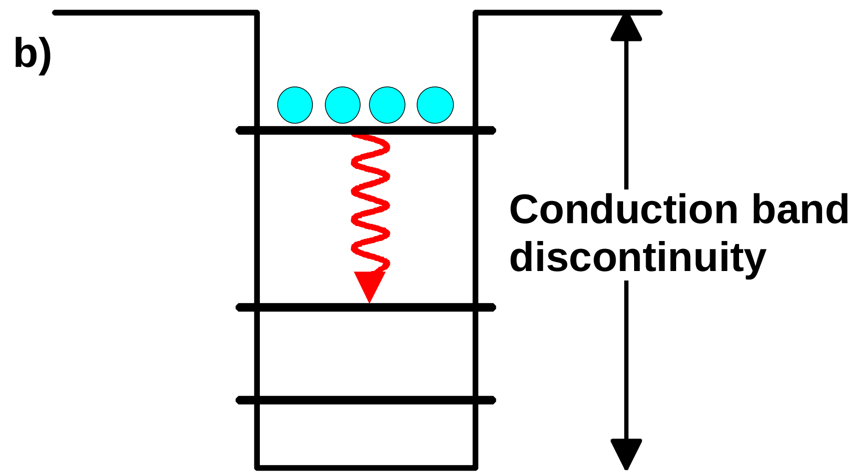
HITRAN database

Mid-IR

- Transparence windows of the atmosphere
- Strong absorption lines of many “interesting” gases

Antimonide compounds





Inter-bands
Transitions
(type I)

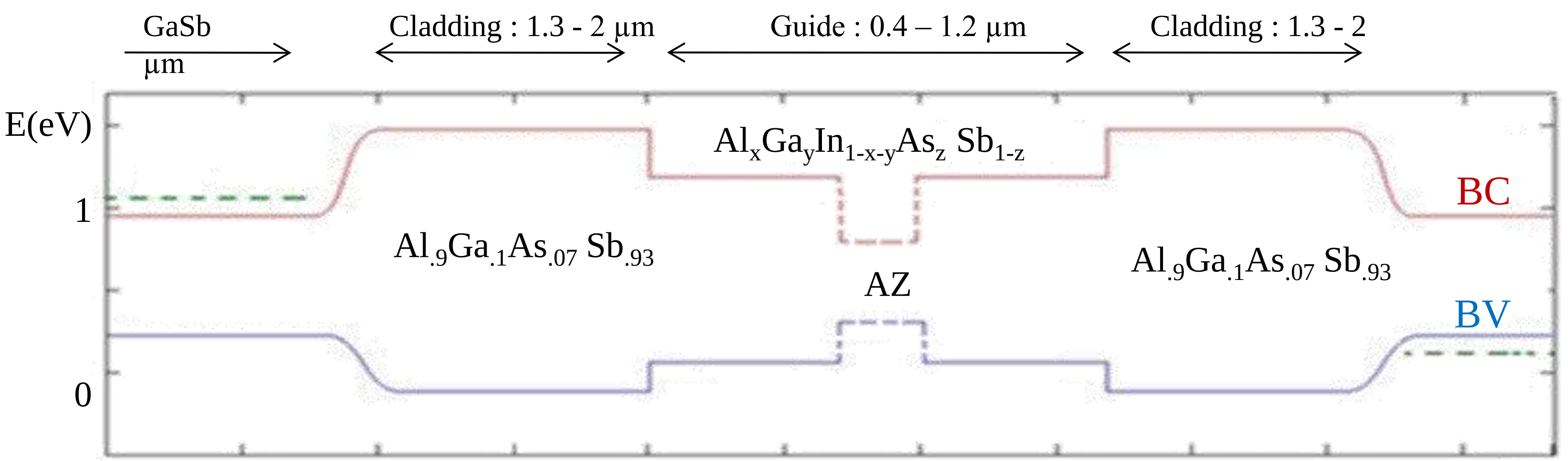
Small gaps
for **diodes** lasers

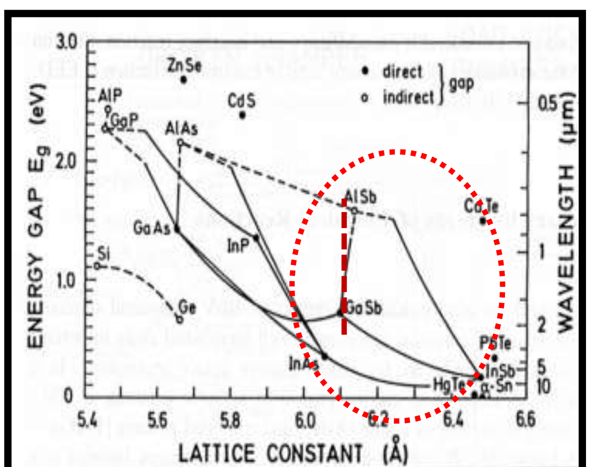
Inter-sub-bands
(intra bands)
Transitions

Large Offsets
for **cascade** lasers

Diodes lasers GaInAsSb/AlGaAsSb (EELs)

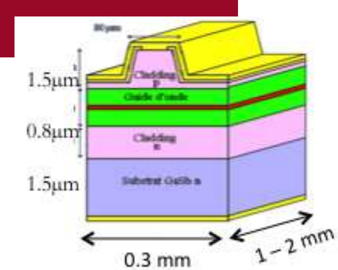
The basic device in the GaSb technology: typical band-structure design



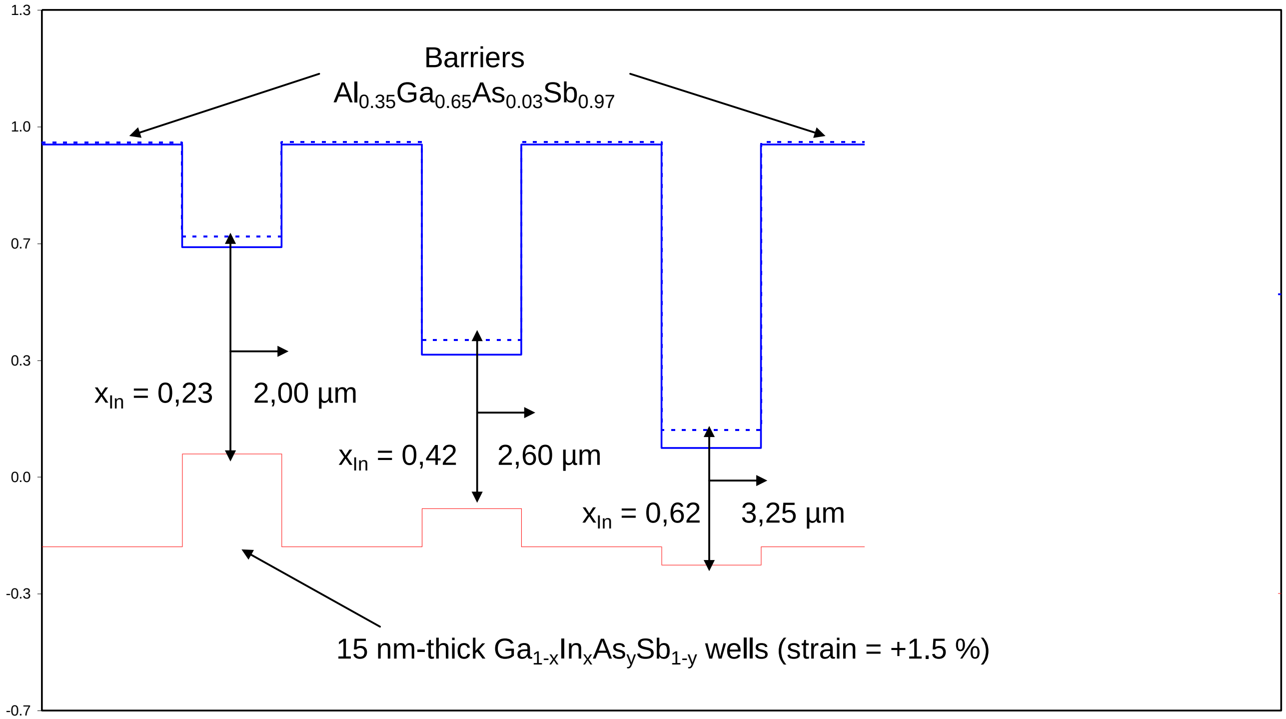


Lattice-matched $Al_{0.9}Ga_{0.1}As_{0.08}Sb_{0.92}$ cladding layers

Strained (ε ~1.5 – 2%) GaInAsSb quantum wells



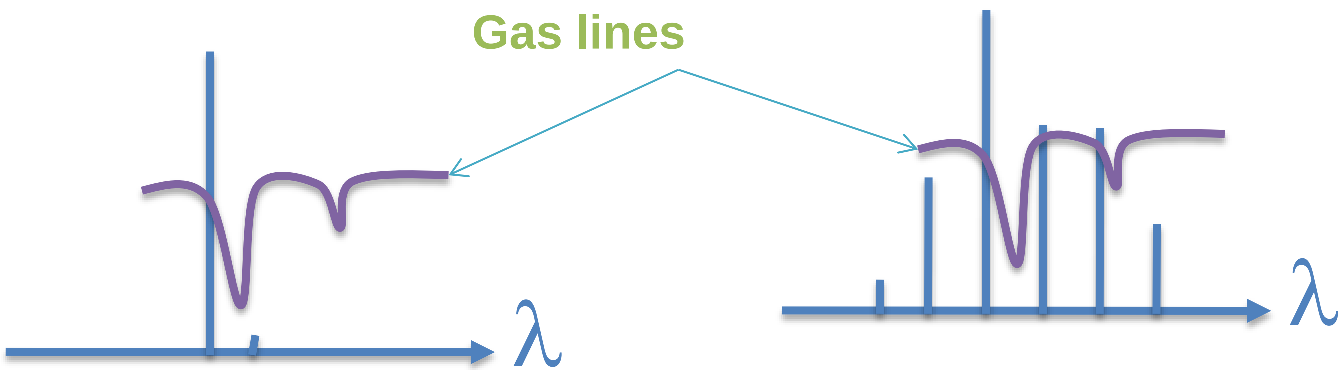
Diodes lasers GaInAsSb/AlGaAsSb (EELs)



2 µm < λ < 3 µm: GaInAsSb / AlGaAsSb (quaternary materials)

Diodes lasers GaInAsSb/AlGaAsSb (EELs)

Single frequency devices ?



SMSR = 25

SMSR = 5

1 line detected

2 lines detected at the same time
=
Tricky signal processing

FP semiconductor lasers are not perfect sources !

- strong divergence
- multimode emission

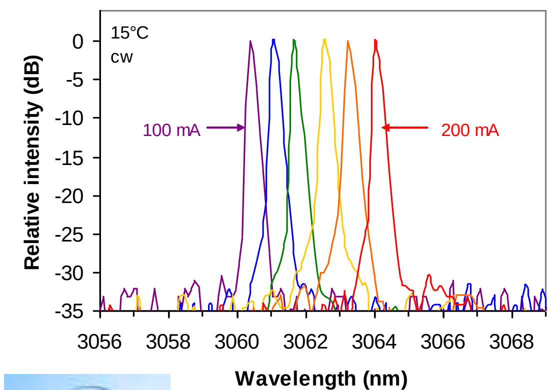
→ need frequency filtering

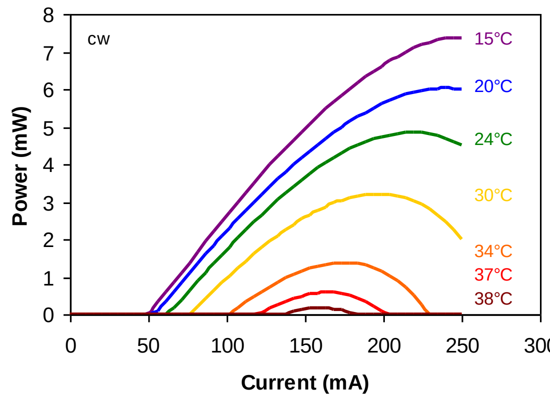
Solut

- •External cavities – grating coupling
- •Multi-sections lasers - DBR
- •Coupled cavities (C3 lasers)
- •DFB

Diodes lasers GaInAsSb/AlGaAsSb (EELs)

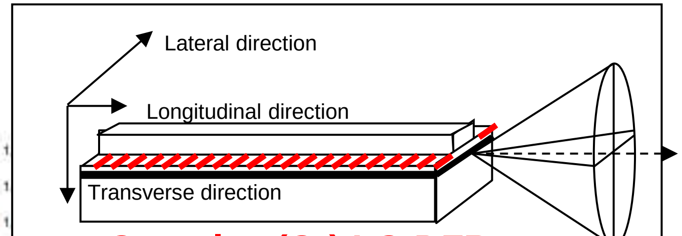
QW - DFB lasers



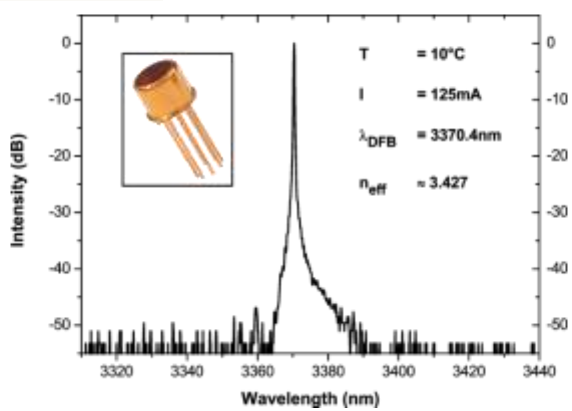


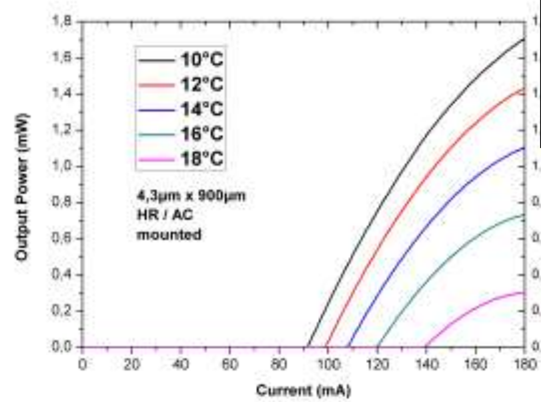
SMSR = 34 dB
Tuning range = 3.7 nm
CW operation up to 38°C
I_{th} = 54 mA @ 20°C
P_{max} = 6 mW

*Belahsène et al., IEEE PTL **22**, 1084 (2010)*



Complex (Cr) LC-DFB





SMSR > 35 dB
Tuning range = 2.5 nm
CW operation up to 38°C
I_{th} = 90/140 mA @ 10°C/20°C
P_{max} = 1.7 mW à 10°C

*Naehle et al., Electron. Lett., **47**, 46 (2011)*

LC DFB → index coupled DFB

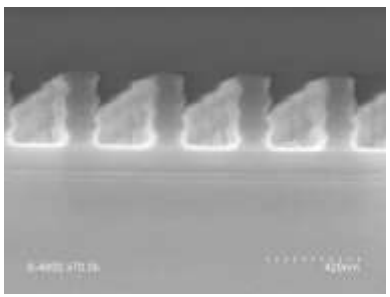
*Perspectives : ANR NexCILAS : **index-coupled DFB***

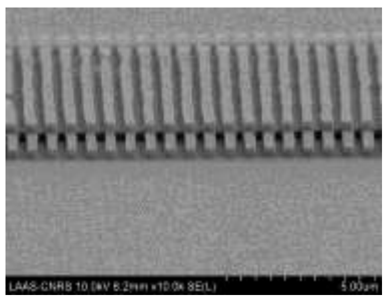
DFB orders 1 (low losses) to 4 (easier to process)

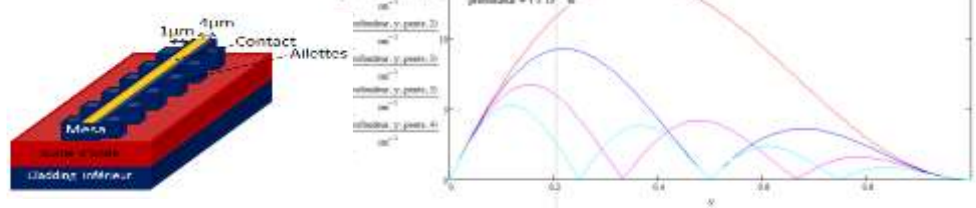
Alternative technology to complex-LC-DFB : **index coupling** → better performances

2 explored ways :

→ **Sidewall corrugation**

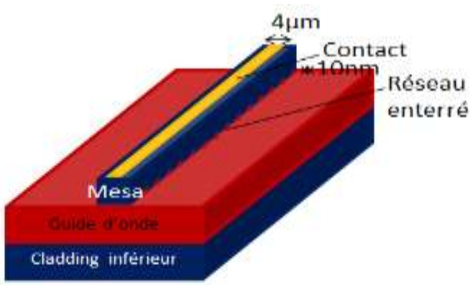


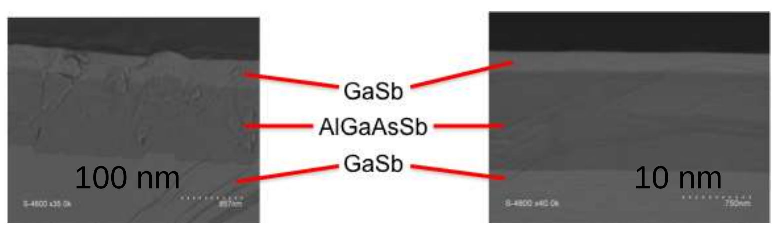




Kim C. S. et al., APL95 231103 (2009)

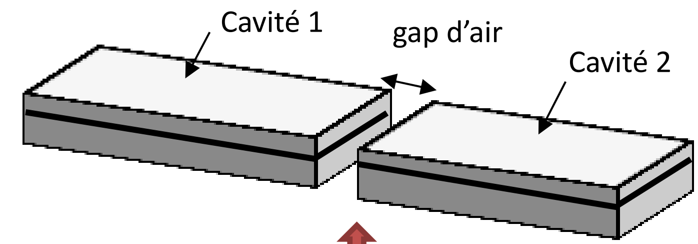
→ structure **regrowth** : corrugation on the ridge





Diodes lasers GaInAsSb/AlGaAsSb (EELs)

EEL PhC-coupled cavities lasers



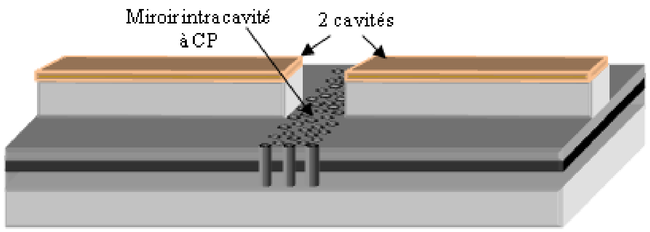
C3 lasers

- Cleaved Coupled cavities with air gap
- Mecanic Instability

≠

Projet ANR CRISPI (2007-2010) : C2-PhC
Coupled cavities lasers with photonic cristals

- no clivage
- Controle of the intra-cavity reflectivity



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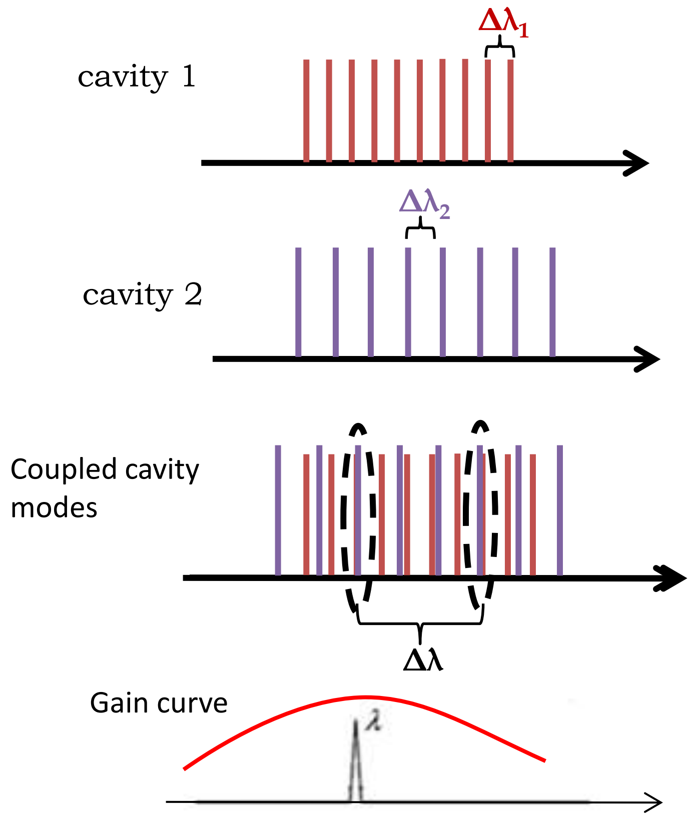
LAAS-CNRS
CRISPI

photonic CRIStal Lasers for infrared SPectroscopy
ANR-07-BLAN-0326-01

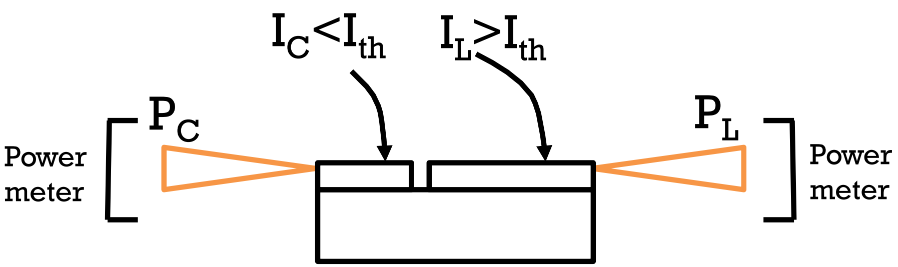


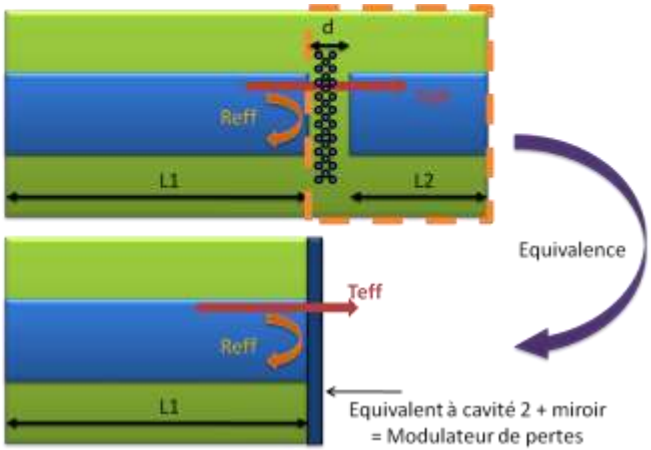
G.P Agrawal, N.K Dutta, 1986.

EEL PhC-coupled cavities lasers

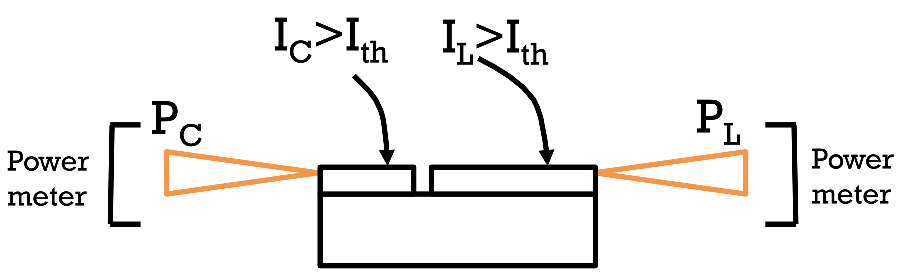
Very high tuning potential : gain curve + longitudinal modes
70 nm 4 nm

active-passive Configuration : Passive cavity = losses modulator





active-active Configuration **:**

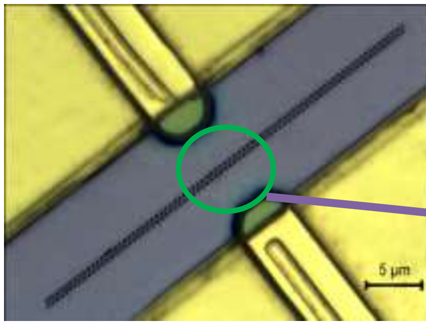


Diodes lasers GaInAsSb/AlGaAsSb (EELs)

EEL PhC-coupled cavities lasers

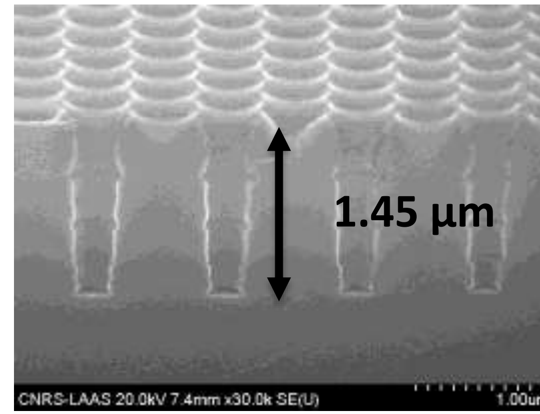
Collaboration LAAS, **ANR CRISPI project**

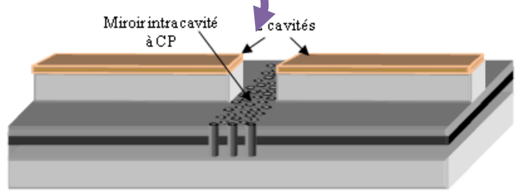
SMSR ~25 dB @ 2.60 µm

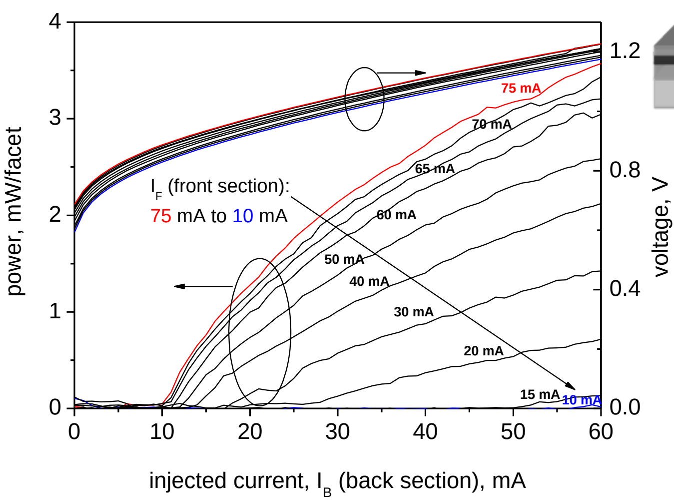


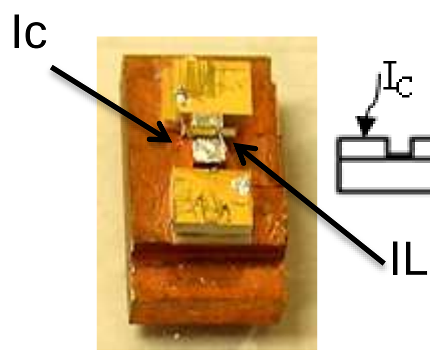
LAAS-CNRS

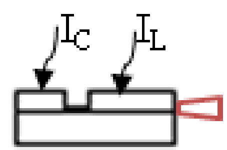
Moumdji et al., Electron. Lett. 45 (2009) 1119

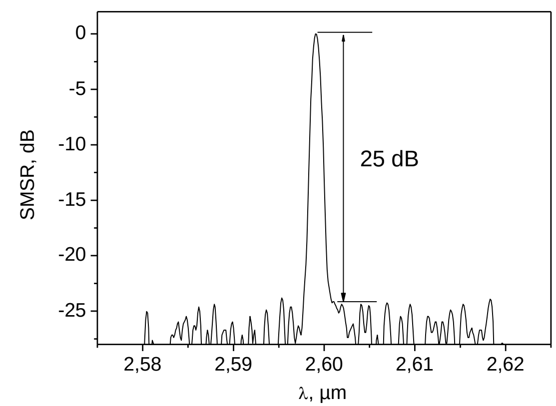










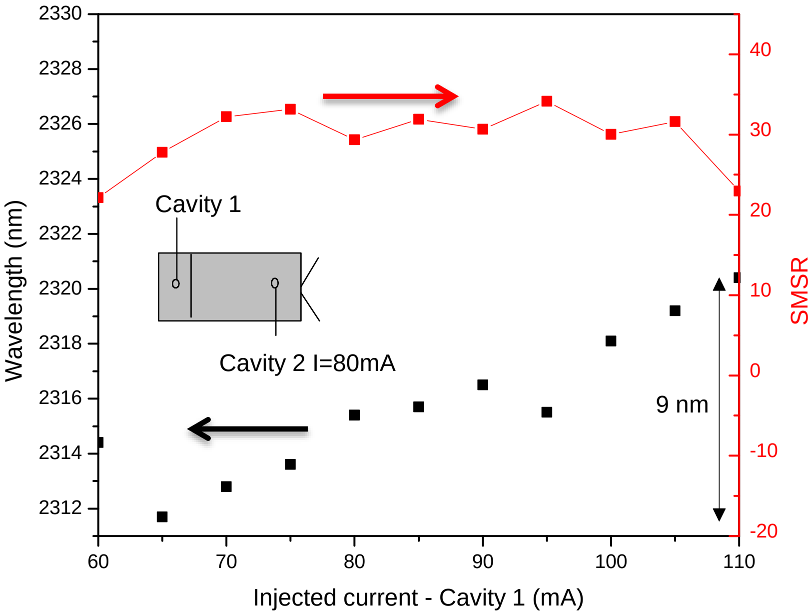


M. Jahjah, S. Moumdji, Electron Lett. 4 (5) pp 277 (2012)

Diodes lasers GaInAsSb/AlGaAsSb (EELs)

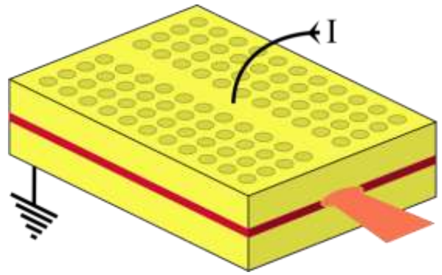
EEL PhC-coupled cavities lasers

Perspectives : MIDAS project : Multiplexed infrared diodes for absorption spectroscopy (P2N 2011)

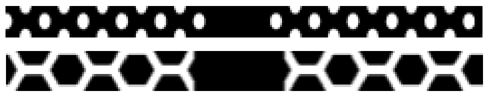


- High SMSR
- good tuning properties
- A tricky process

- **First All-CP Sb-based Lasers**
- Based on CRISPIS progresses

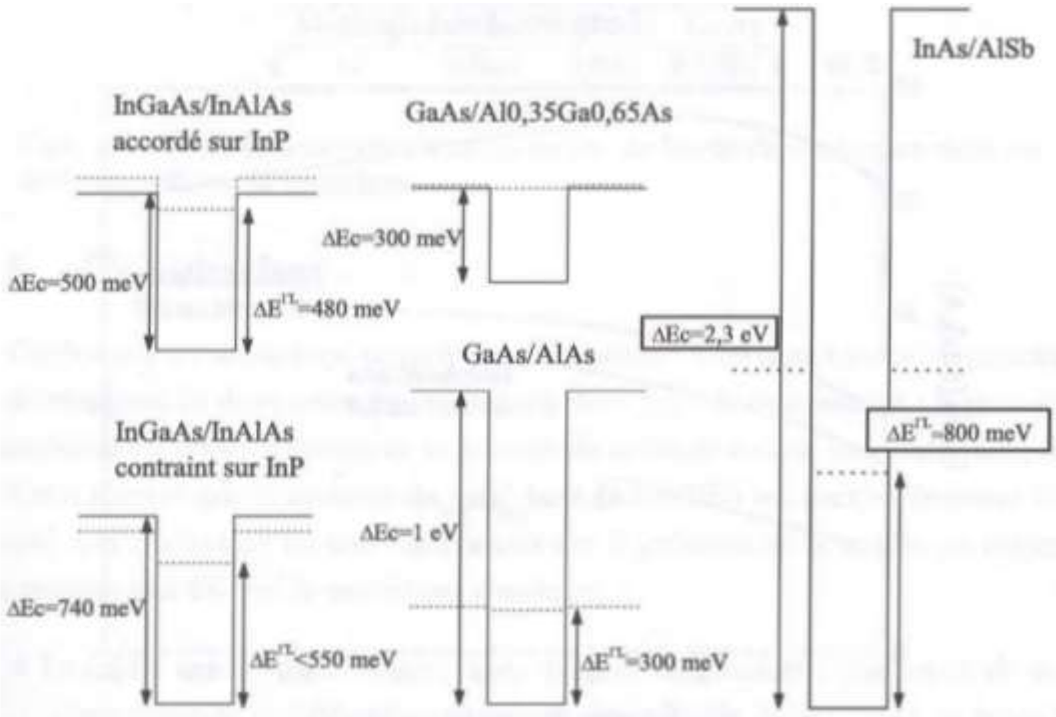


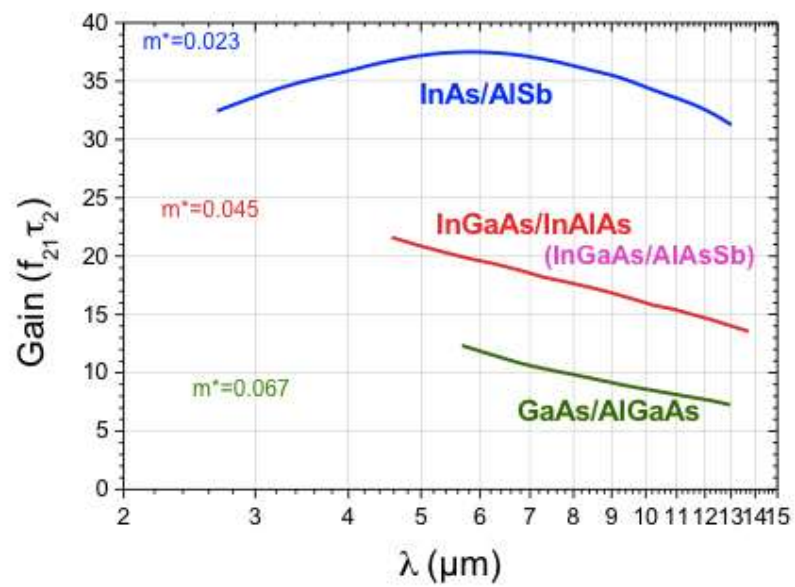
- Structures W3 or W5 : larger guides easier
- Theoretical studies
  - Active region thickness,
  - shape of CP,
  - nb of patterns



Quantum cascade lasers InAs/AlSb (QCLs)

Band offsets in III-V semiconductor technologies





InAs/AlSb system best suited for short wavelength QCLs

Key parameters : $\Delta E_c = 2.3$ eV

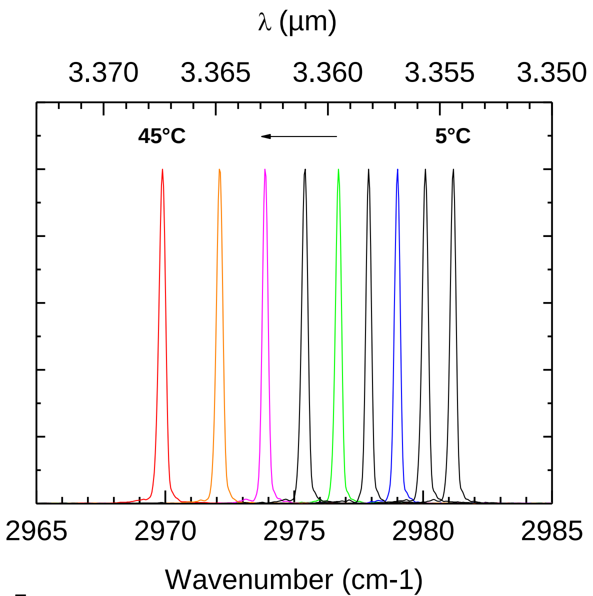
$m^* = 0.023$

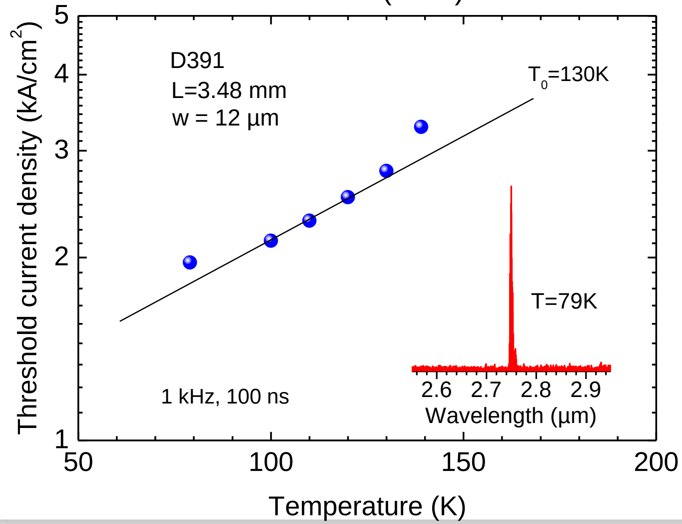
$\Delta L = 0.8$ eV

- **High gain**
- **Short wavelength**

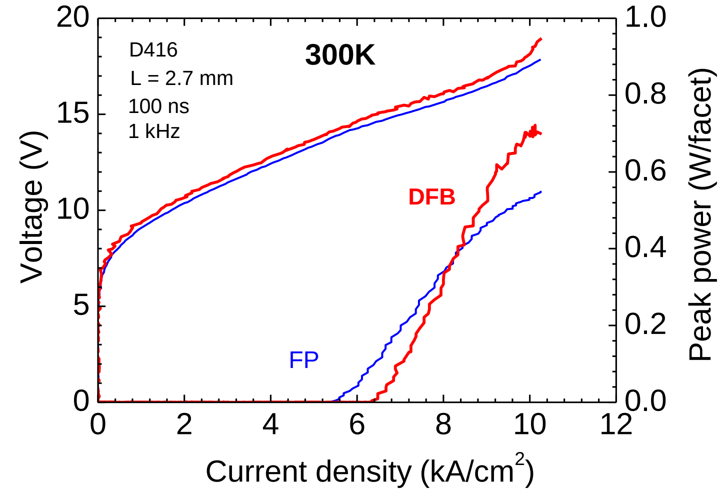
Quantum cascade lasers InAs/AlSb (QCLs)

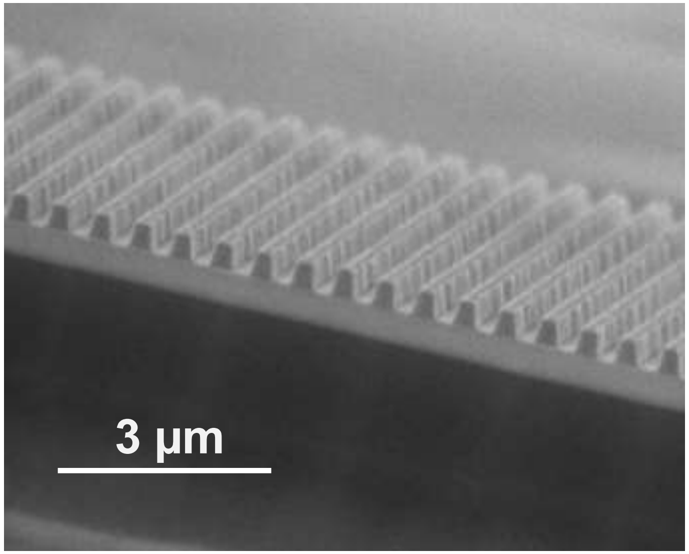
Short wavelength InAs/AlSb QCLs



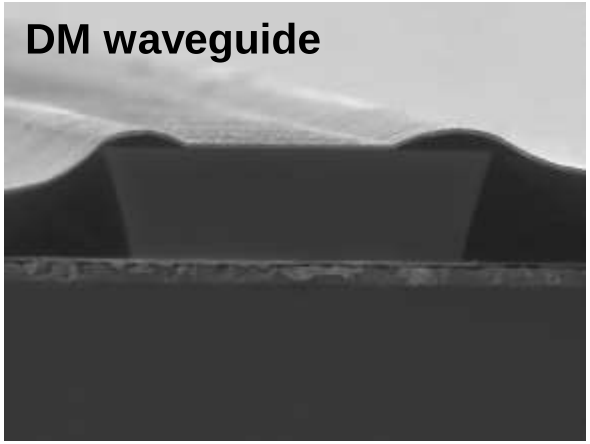


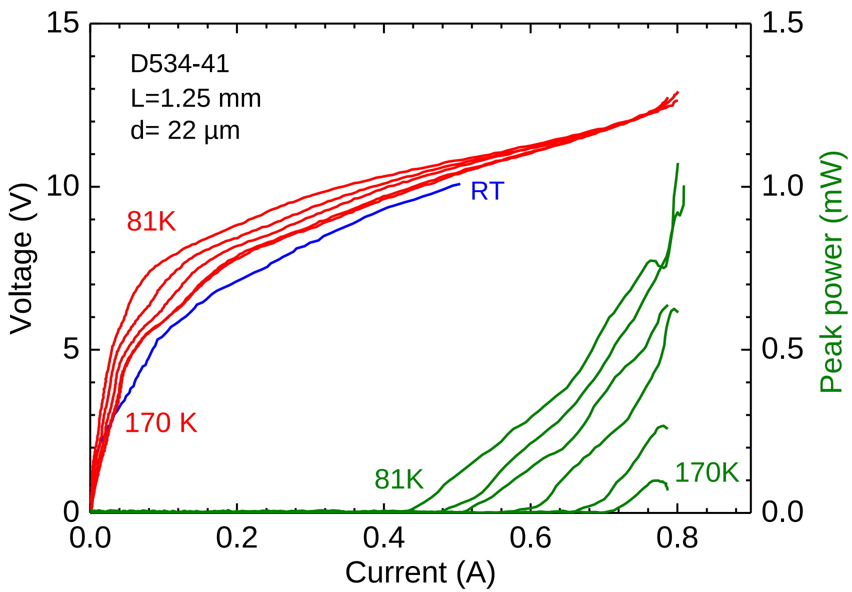
Cathabard, O., Electron. Lett. ***45*** *(2009) 1028-1030*
O. Cathabard, Appl. Phys. Lett. ***96*** *(2010) 141110*



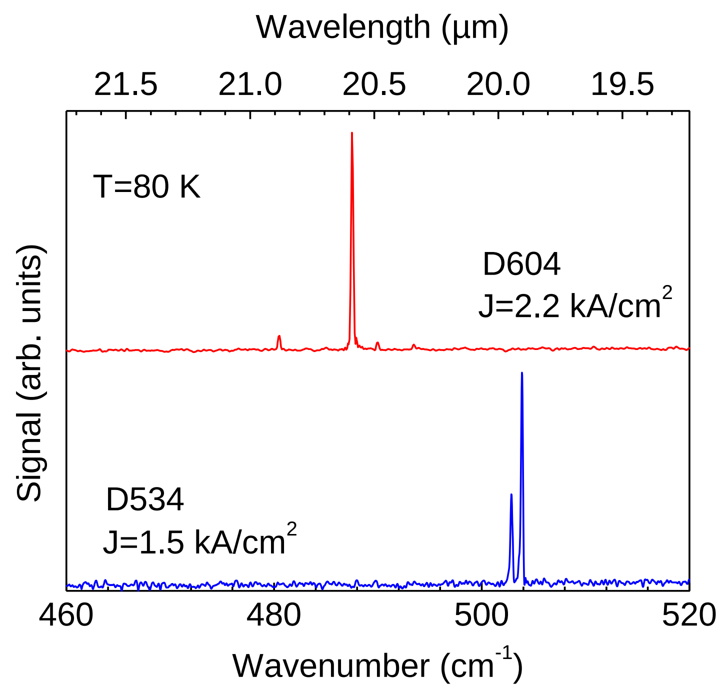


Quantum cascade lasers InAs/AlSb (QCLs)





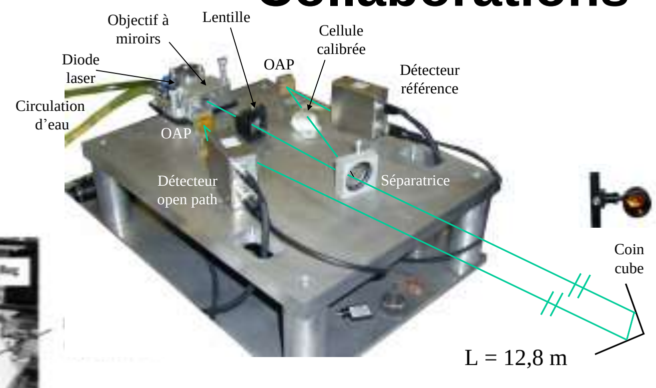
InAs/AlSb QCLs emitting near 20 µm



- **Single frequency Antimonide compounds in the infrared**
  - **Materials/spectral ranges**
  - **QW structures**
  - **QCL structures**
- **Applications**
  - **Collaborations**
  - **QEPAS sensing**
  - **Perspectives**
- **Conclusion**

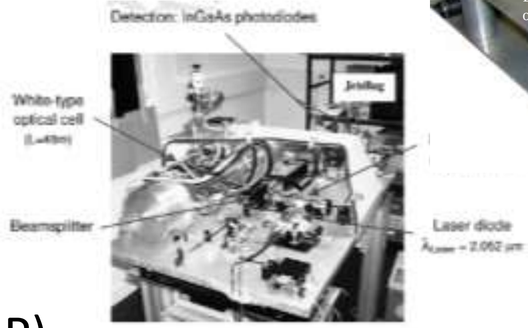
Applications

Collaborations



- Open path/multipass WMS demonstrator (IES)

  Vicet, et al. Spectrochimica Acta A, Vol 58a (11), pp2405-2412, 2002

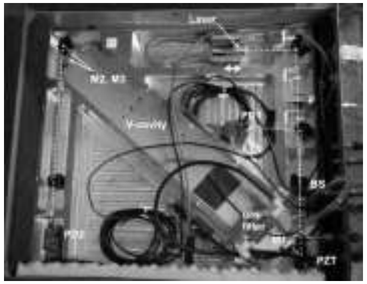


- Direct detection (SA)

  V. Zeninari,.Infrared Physics and Technology, 45, 2004

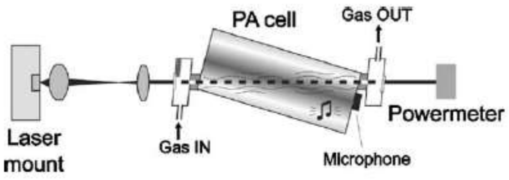
- Cavity ring down spectroscopy (LSP)

  *Kassi, S . Opt. Express **14** (2006) 11442–11452*



- Photoacoustic spectroscopy (EPFL)

  S.Schilt, Spectrochimica Acta A, 60,2004.



- Mirage detection (IPEIN)

  Hamdi A., J. of Physics : Conference Series 214, 2010

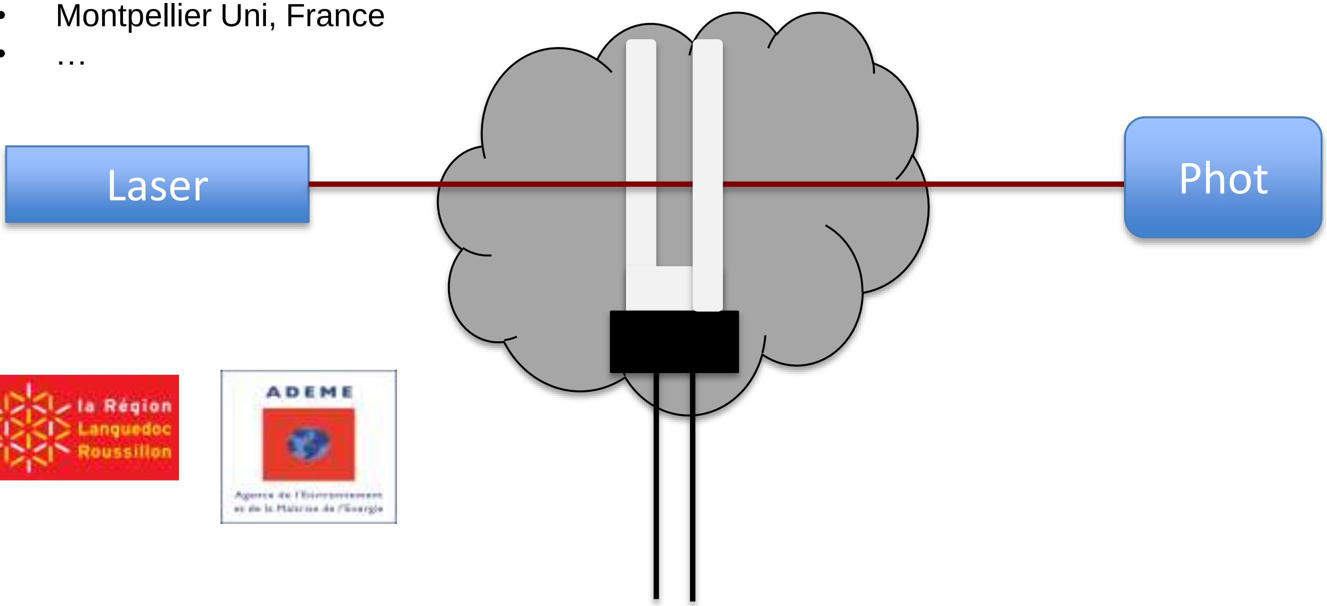
Applications : QEPAS sensing

Basics

- Rice Uni, USA
- LPCA, France
- Politechnico Bari, Italy,
- Laser application centre, Goslar, Germany
- Inst Spectroscopy, Russia
- Univ Heifei, China
- Montpellier Uni, France
- …

** A. A. Kosterev, Opt. lett. **27**, No. 21 (2002)*

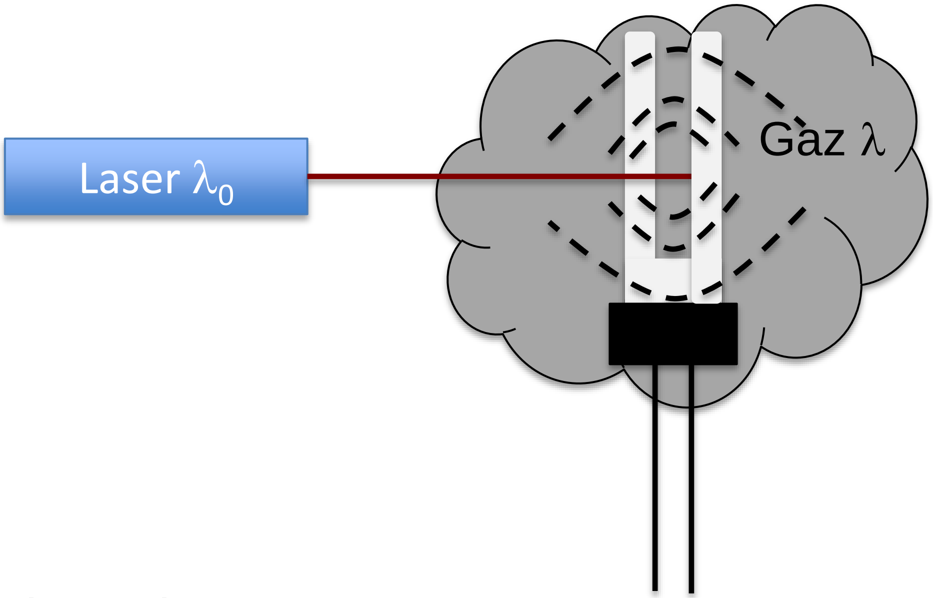
(uncaped) QTF =
Quartz Tuning fork



- Photoacoustic detection without resonnant cell
- Very high quality factor of the QTF
- « Universal » detector : adapted to each source wavelength

Applications : QEPAS sensing

Basics



f_0 QTF = 32,7 kHz
Laser Modulation : f_0 ($f_0/2$ si $2f$)
if $\lambda_0 = \lambda$ → absorption
if $\lambda_0 \neq \lambda$ → no absorption

Absorption → T ↗, P ↗
Sound wave generation→ Piezo signal S

QEPAS Signal Amplitude

$$S = k.\frac{\alpha.P.Q}{f_0}$$

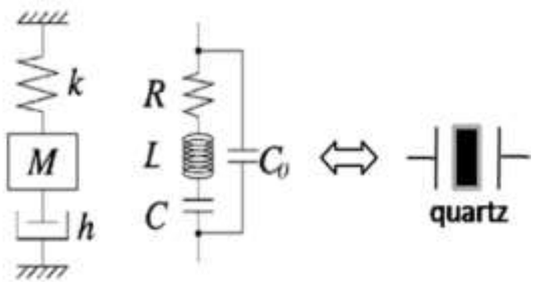
Commercial QTF, Q from 10^4 to 10^6 (vacuum)

K: constant
α: absorption coef (cm^{-1})
P: optical power (mW)
Q: QTF quality factor
f_0: QTF resonnant frequency (Hz)

Applications : QEPAS sensing

Q factor

Butterworth-Van Dyke RLC model

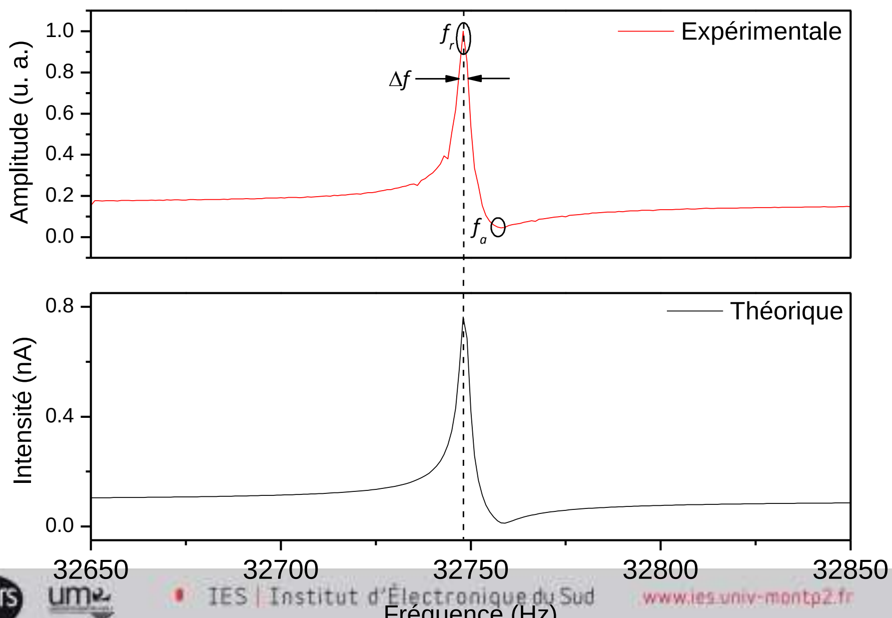


R→ Losses
L→ Mass
C→ Stiffness
C_0→ electrodes

Resonance frequency $f_r = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$

Quality factor $Q = \frac{1}{R}\sqrt{\frac{L}{C}}$

Anti-resonance frequency $f_a = \frac{1}{2\pi}\sqrt{\frac{1}{LC_{éq}}}$



f_r=32748 Hz f_a=32758 Hz

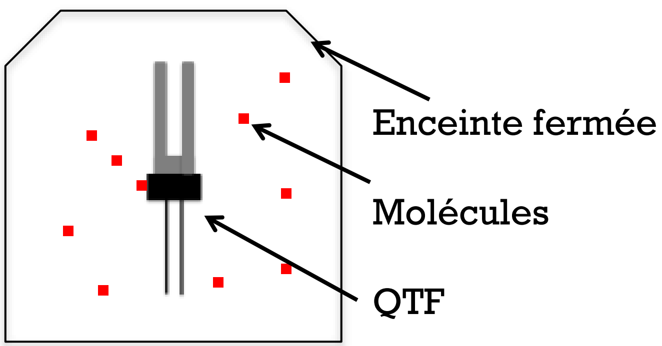
Δf=1.64 Hz $Q=f_r/\Delta f=2.10^4$

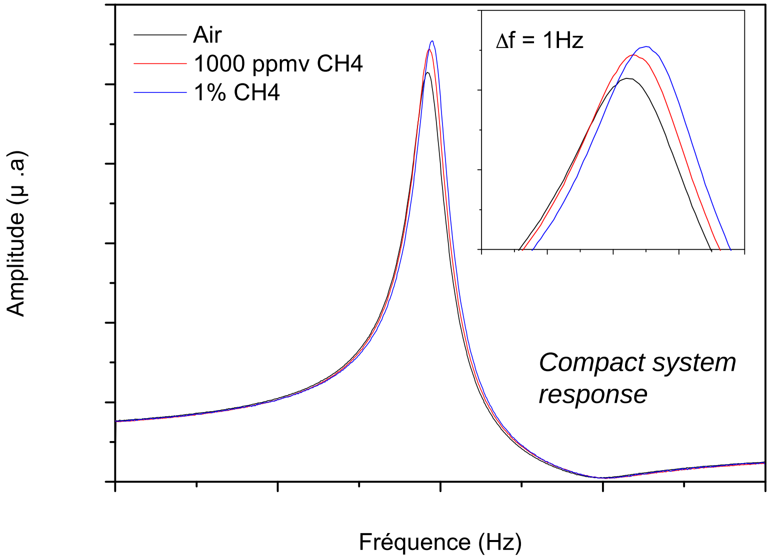
Simulation QTF
R= 180 KΩ,
L= 11718 H,
C= 2 fF,
C_0= 3.3 pF

Applications : QEPAS sensing

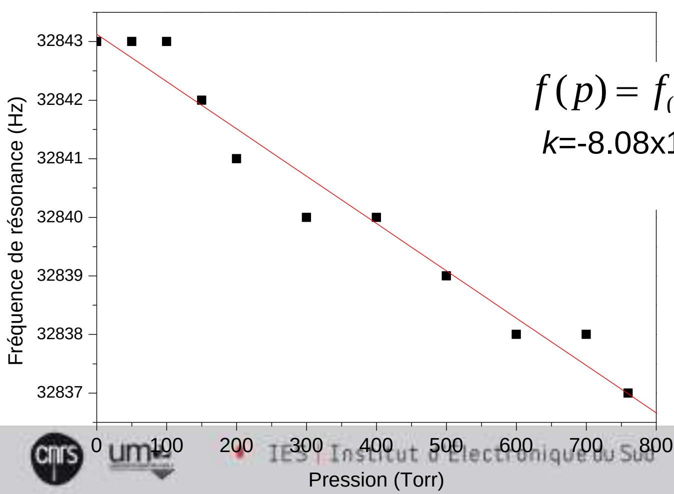
QTF response

The QTF response depends **on gas**



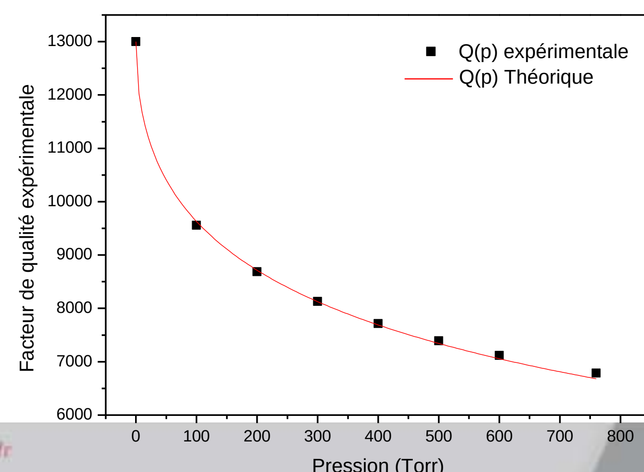


The QTF response depends **on pressure**



$$f(p) = f_{(P=0)} + kp$$

k=-8.08x10^{-3} Hz/Torr

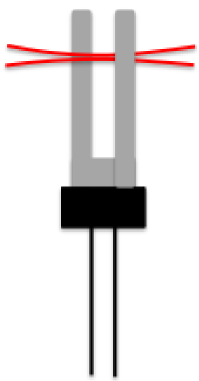


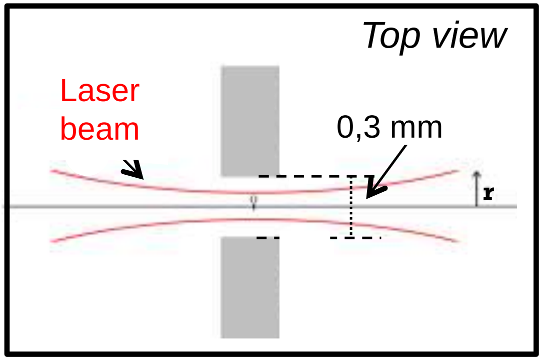
$$Q(P) = \frac{Q_{(P=0)}}{1 + Q_{(P=0)}.aP^b}$$

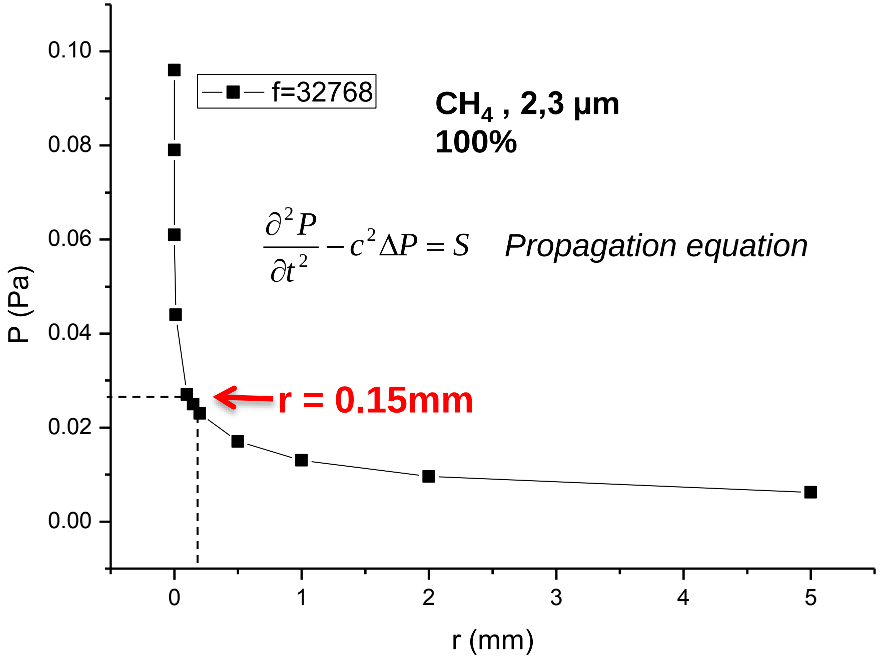
a=2.82x10^{-6}

b=0.49

Modelisations







$$\frac{\partial^2 P}{\partial t^2} - c^2 \Delta P = S$$ *Propagation equation*

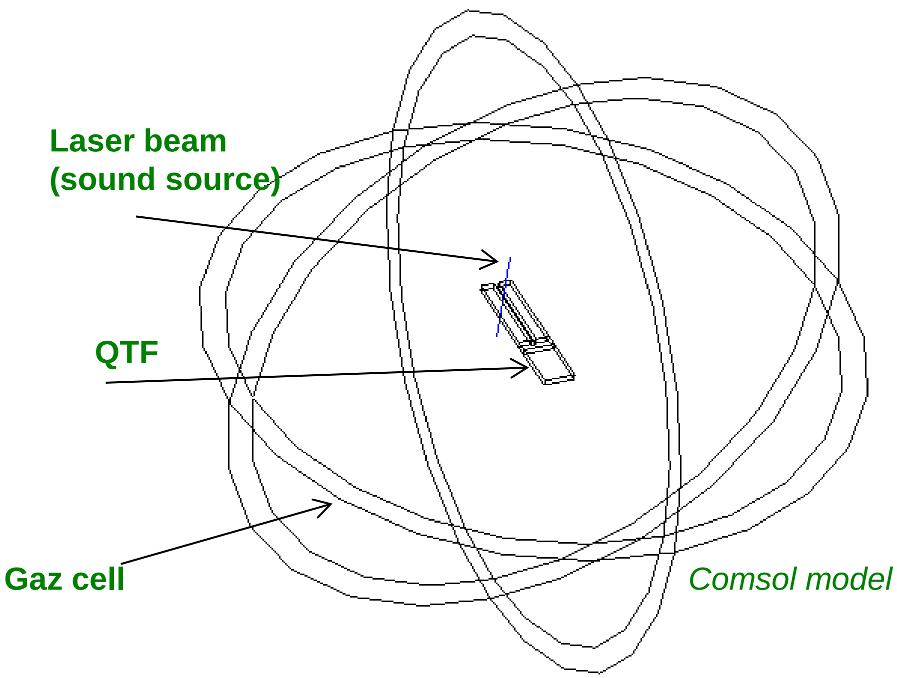
N. Petra, et Al.: Appl. Phys. B 94, 673-680 (2009)

$$P(r,t) = A\left[J_0\left(\frac{\omega . r}{c}\right).\cos \omega t + Y_0\left(\frac{\omega . r}{c}\right).\sin \omega t \right]$$ *Solution*

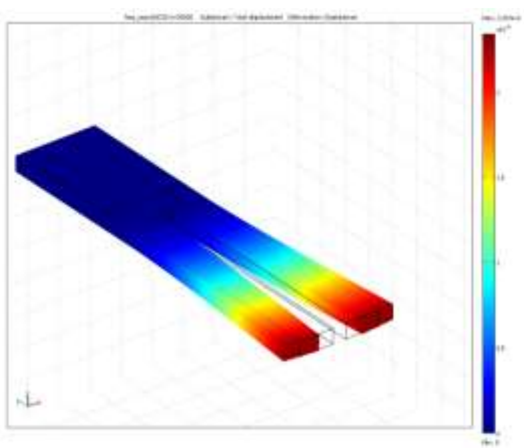
$$A = (\gamma - 1).\omega.\kappa_{eff} \cdot \frac{W_L}{8.c^2}$$ *Pressure amplitude*

Pressure amplitude → acoustic wave ***intensity*** *for a given distance of the source*

Modelisations

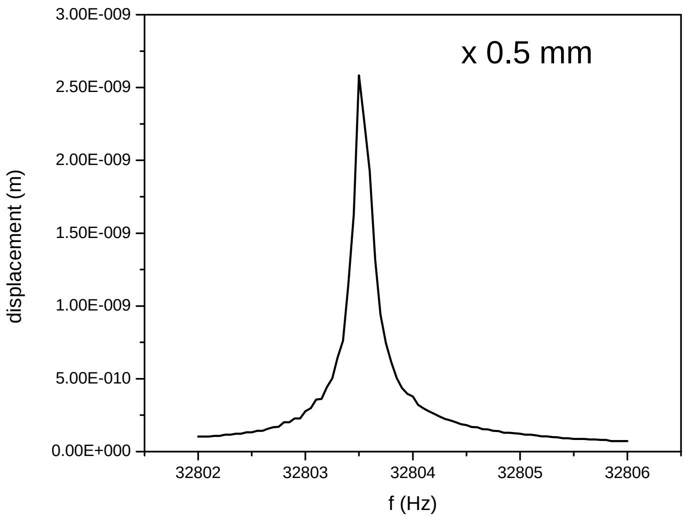


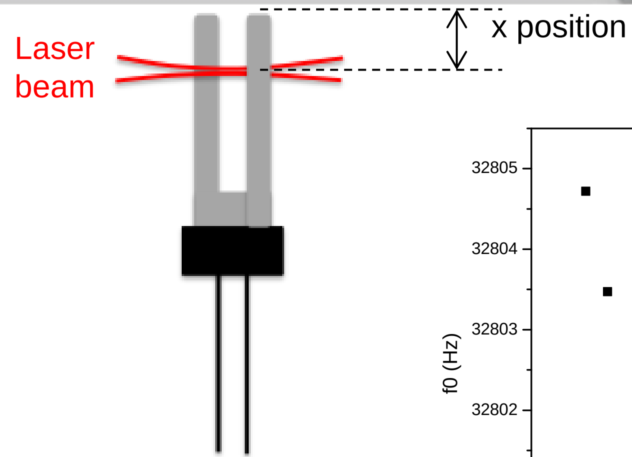
- Sound source = line or point
- Frequency study → evaluation of f_0, Q
- Gas and pressure can be changed
- Piezoelectric study : evaluation of displacement and surface charges

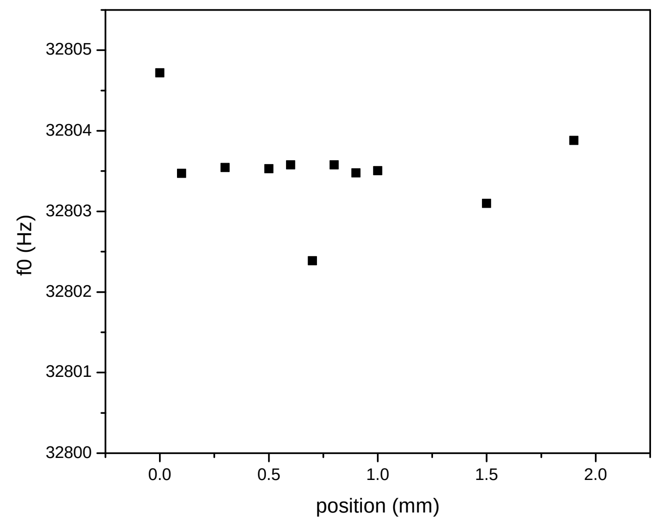


Applications : QEPAS sensing

Modelisations





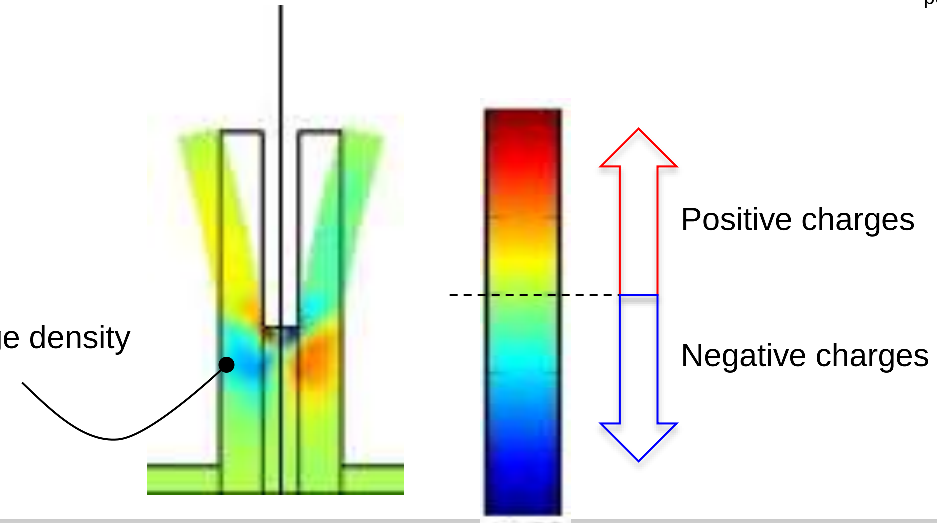


Resulting current

$$I_{out} = 2\pi f_0 \iint \rho_s \, dA$$

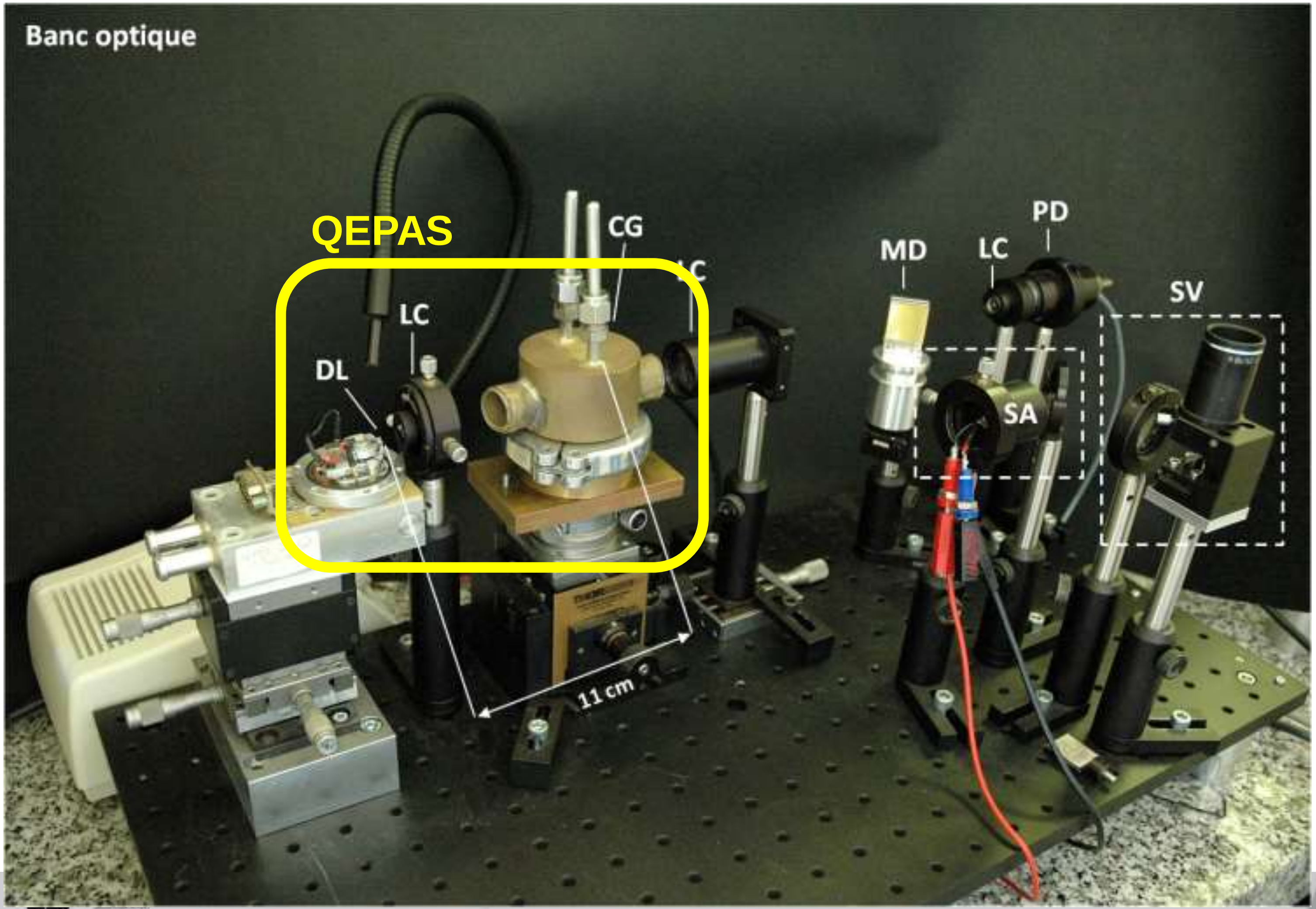
Resonant frequency

Surface charge density



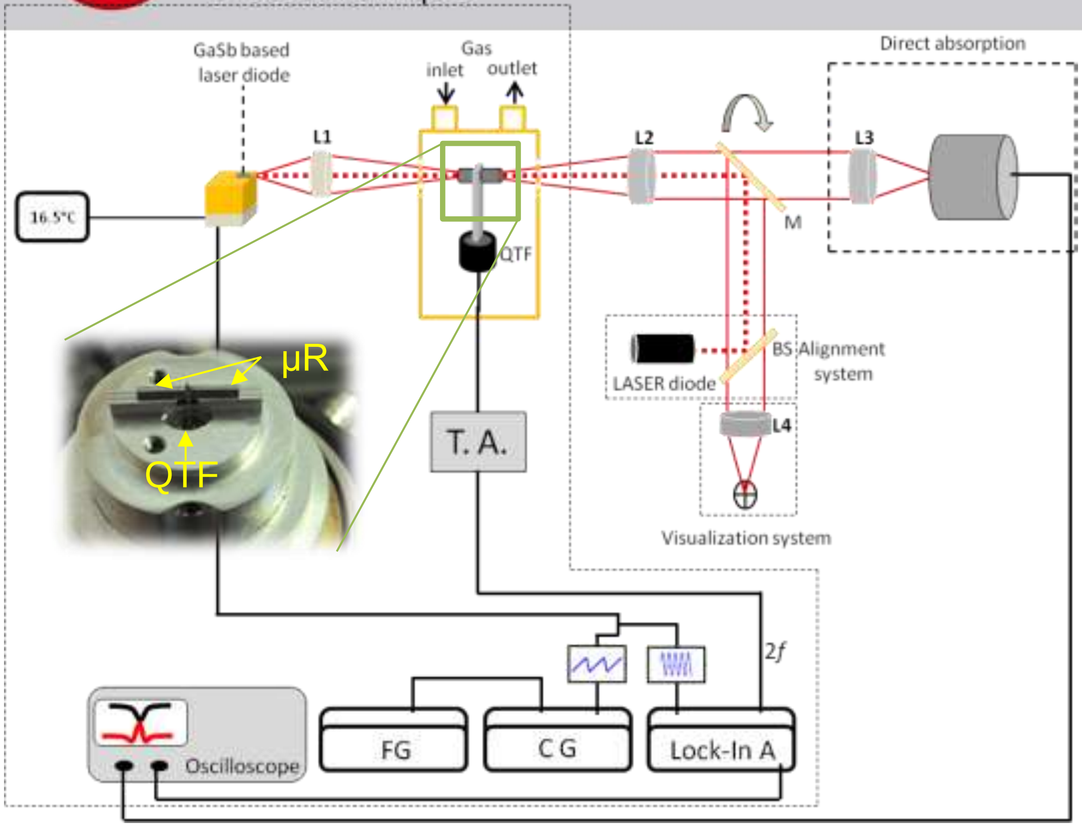
Ex: $I_{(0,7mm)} = 10.4$ nA

Results on CH_4 sensing

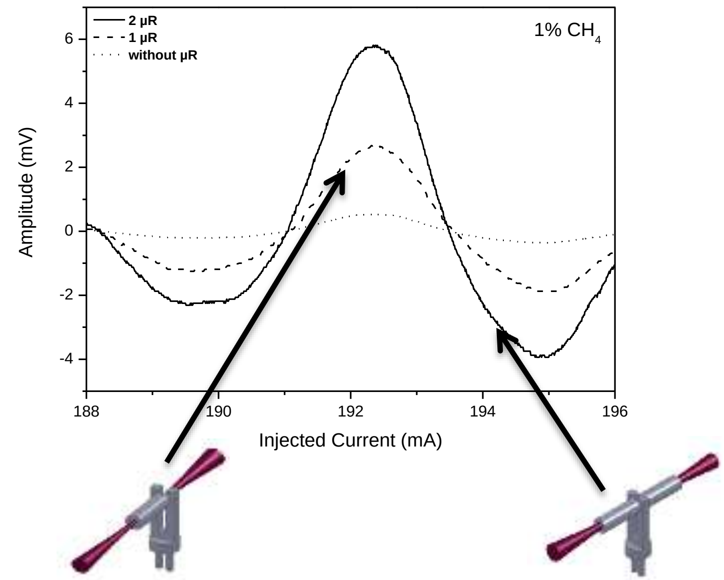


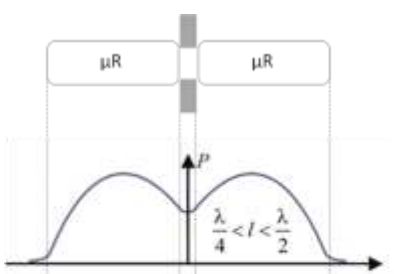
- DL: Laser Diode
- LC: Lens
- CG: Gas cell
- MD: Flat miroir
- PD: PhotoDiode
- SA: Alignement system
- SV: Visualisation system

Applications : QEPAS sensing



Results on CH_4 sensing





P: pression de l'onde acoustique

λs : sound wavelength depending on gas
λs = 0.88x10^{-2} m @ f = 32.768 kHz

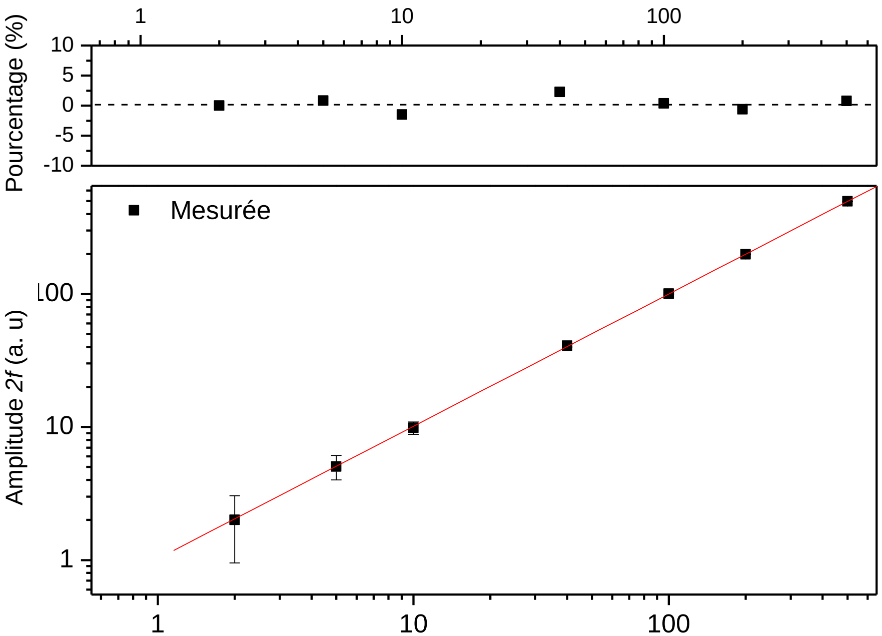
Dimensions :
l=4.4 mm, Dl=0.5 mm
→ λs/2 (fondamental mode)

« on-beam » µR configuration :

- Lower Q
- But higher acoustic interaction
- → 10x gain

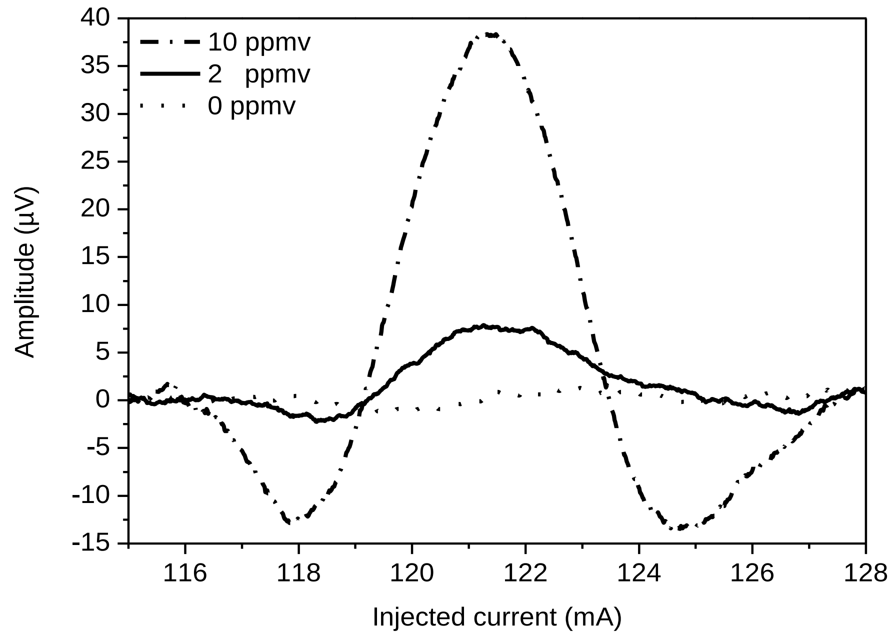
Results on CH_4 sensing

FP Laser 2.3 µm



M. Jahjah, Applied Phys B.106 (2) 483-489, 2012

C2 phC Laser 2.3 µm



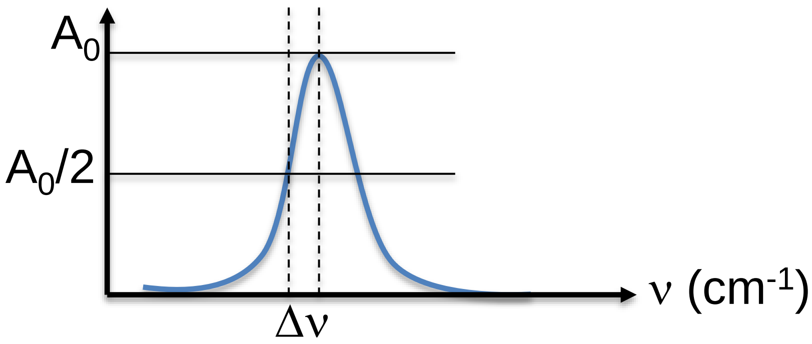
S=1.398x10^{-21} cm^{-1}/mol.cm^{-2} ; σ=4242.1807 cm^{-1}

M. Jahjah, Electron Lett. 4 (5) pp 277 (2012)

Detection limit : 400 ppbv CH_4 (1σ)

Applications : QEPAS sensing

Results on CH_4 sensing

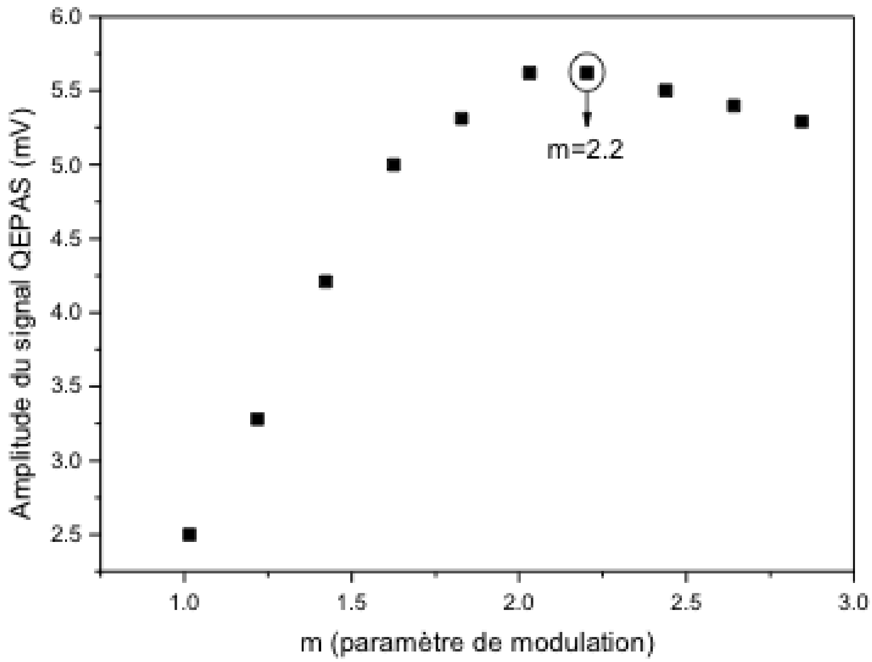


$\Delta\nu$ = half width at half maximum (cm^{-1})
Δ = modulation amplitude
Δ = **m**.$\Delta\nu$, **m = modulation parameter**

*J. Reid and D. Labrie: "Second-Harmonic Detection with Tunable Diode Lasers - Comparison of Experiment and Theory", Appl. Phys. B **26**, 203-210 (1981)*

Theoretical optimum : m = 2,2

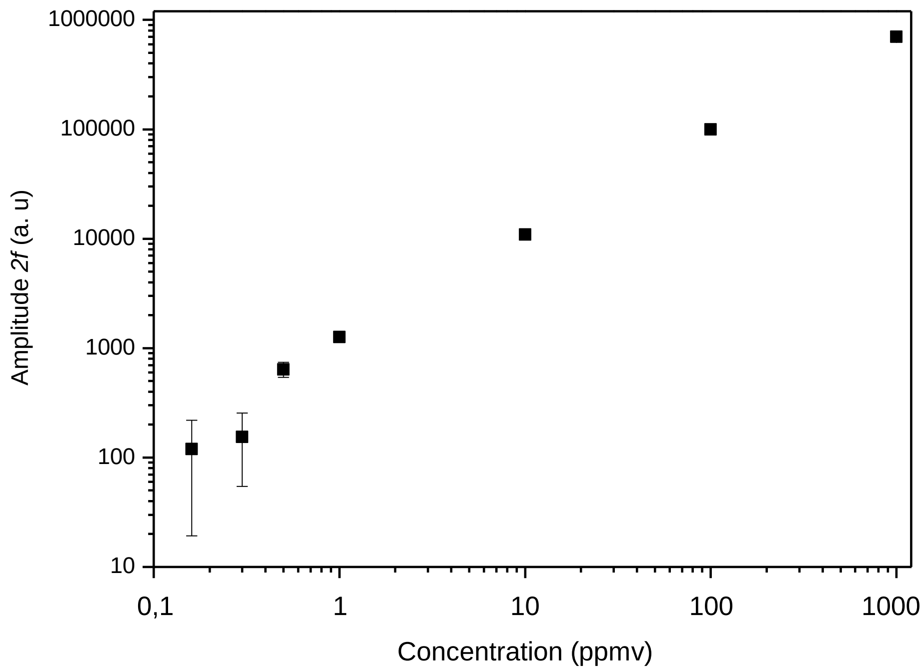
C2 Ph C Laser
$2\Delta\nu$ = 5,06 Ghz (P_{atm})
σ = 4242,1807 cm^{-1}
S = $1{,}398.10^{-21}$ $cm^{-1}/mol.cm^{-2}$
Measurement for 1% CH_4



Applications : QEPAS sensing

Results on CH_4 sensing

DFB Laser 3.3 µm



σ_1=2958.23 cm^{-1} ; $\mathbf{S_1}$=6.28x10^{-20} cm^{-1}/molecule.cm^{-2}

Jahjah, *Optics Lett. 37 (14) 15 july 2012*

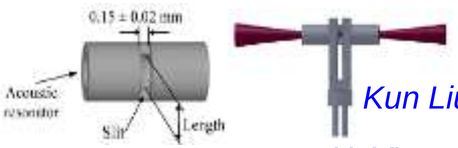
Detection limit: 100 ppbv CH_4 (1σ)

α_{min} = 1.92x10^{-8} cm^{-1}

Tc = 1s

How to improve ?

→ Increase the laser power : QCL ??
→ Focus on stronger lines
→ Improve optical design, positions µR



Kun Liu Opt. LETT. 34, 10 (2009)

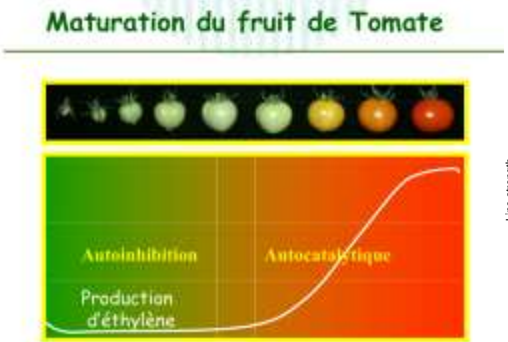
H. Yi · Appl Phys B, online 3 april 2012

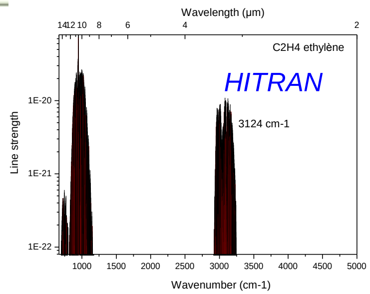
→ Electronics (TA, lockin, compensation RAM…)

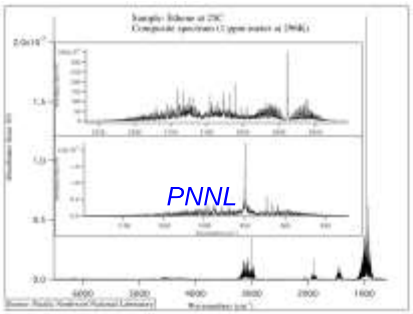
→ Allan variance
→ multigaz

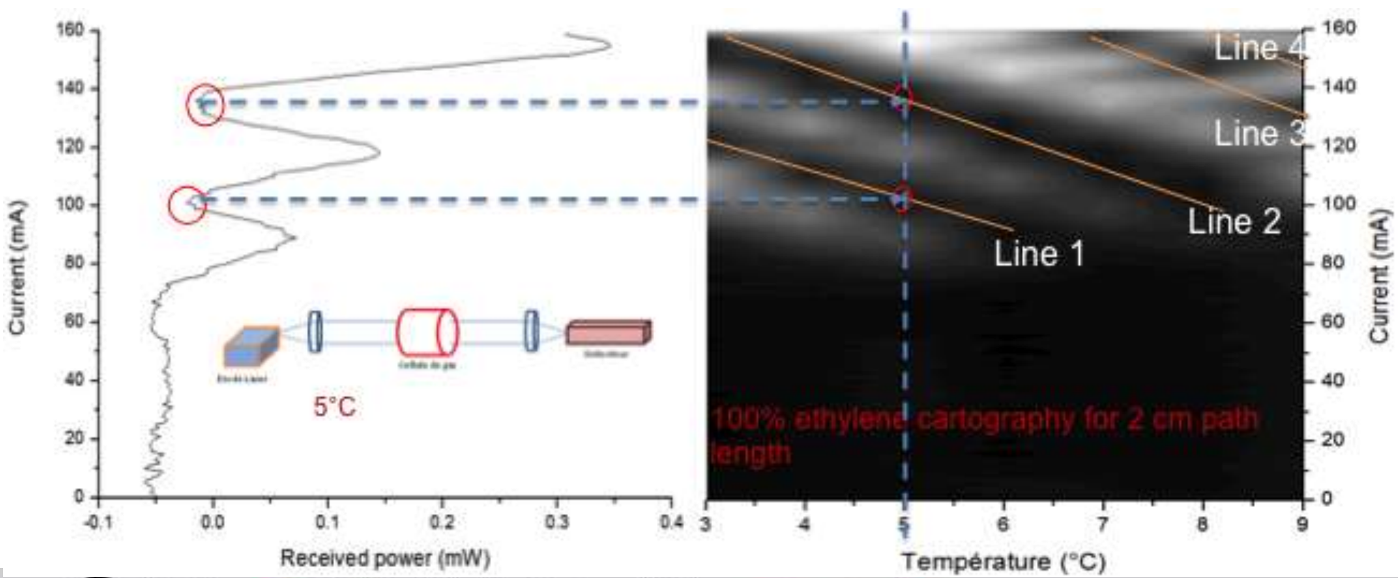
Perspectives : applications

Ethylene measurements (Labex NUMEV – LSTM)









Laboratory optical bench

- Ethylene detection with laser diode at **3.325 µm**
- **Growth at IES & process at Nanoplus**

	Wavenumber (cm^{-1})	Line strength ($cm^{-1}/mol\ cm^{-2}$)
1	3008.581	5.97×10^{-21}
2	3007.524	8.94×10^{-21}
3	3006.818	2.95×10^{-21}
4	3006.753	4.76×10^{-21}

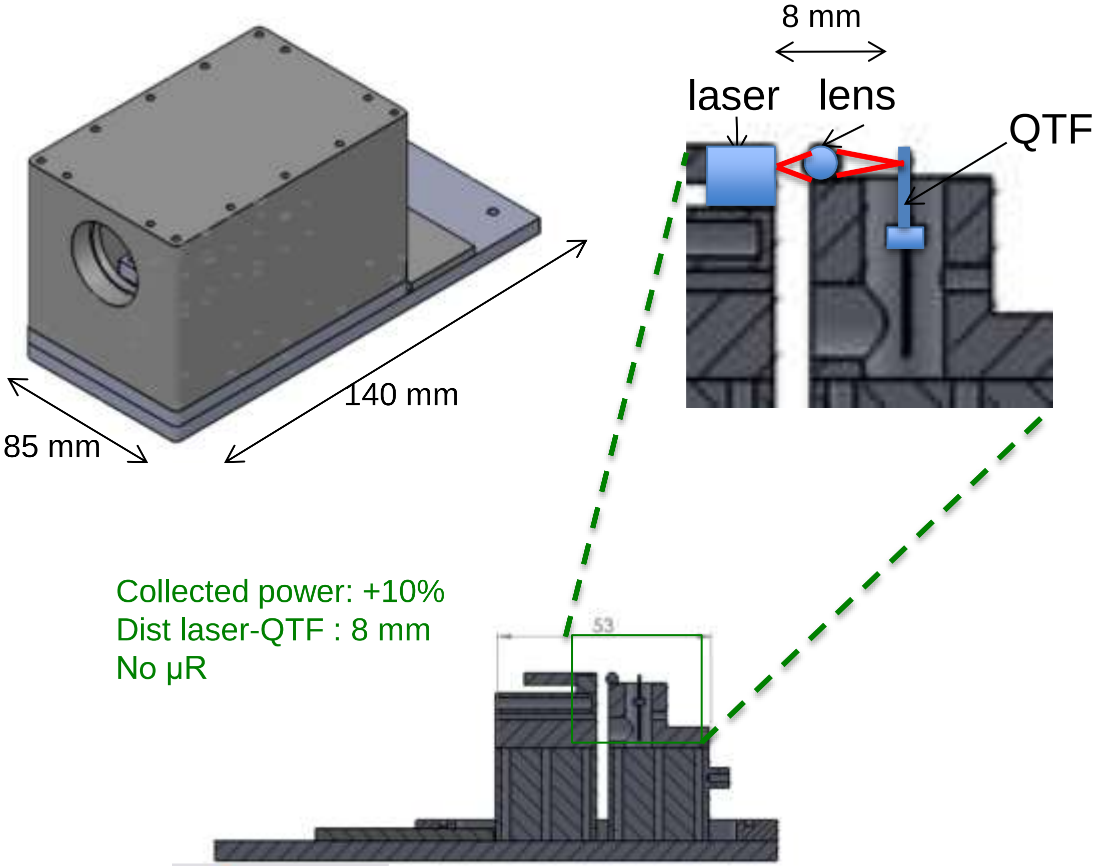
- **First results, high concentrations ok, waiting for calibrated mixtures**
- **Improvement ? → IES QC Laser @ 10.5 µm**

Perspectives : applications

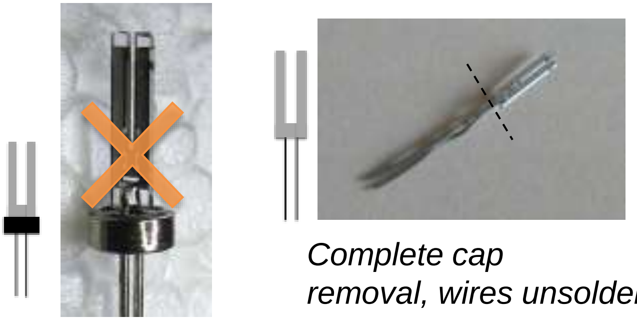
- **Compact system**: in situ measurements inside/outside
  - High CH_4 emission: waste treatment(ADEME), lagoons(INRA)
  - climat controlled sites for tests : ECOTRON, INRA
  - automobile industry(JRC-ISPRA)
  - Formaldehyde ?

Perspectives : compact system

*ANR NexCILAS : * Next generation of Compact Infrared Laser based Sensor for environmental monitoring (Blanc inter 2011)*

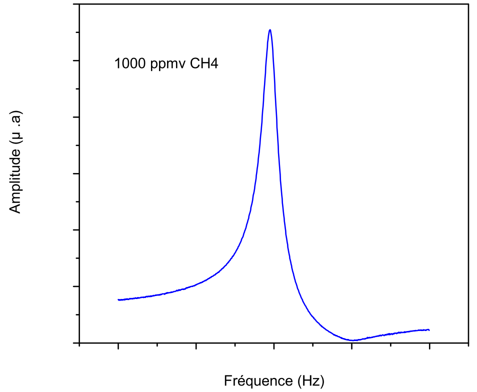


Collected power: +10%
Dist laser-QTF : 8 mm
No µR



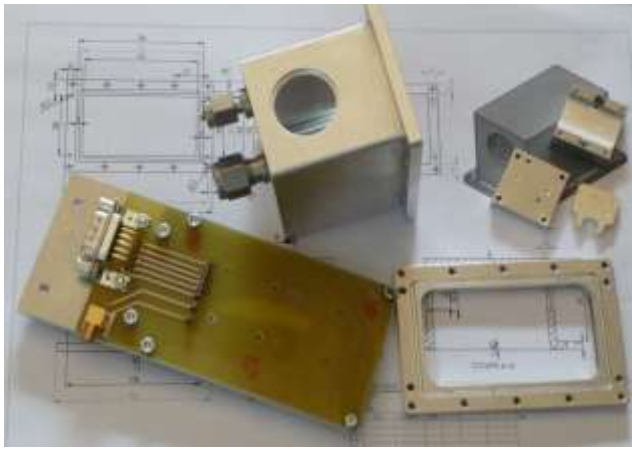
Complete cap removal, wires unsoldered

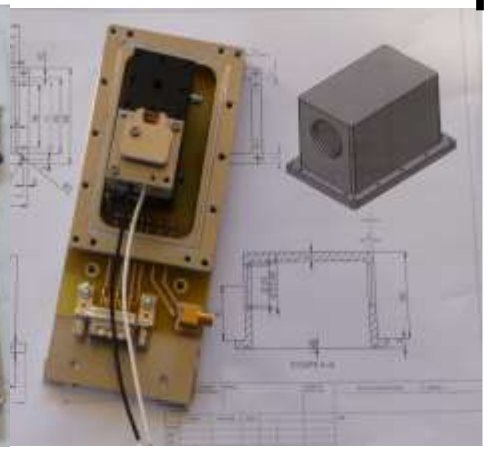
Isolated mount → decrease noise

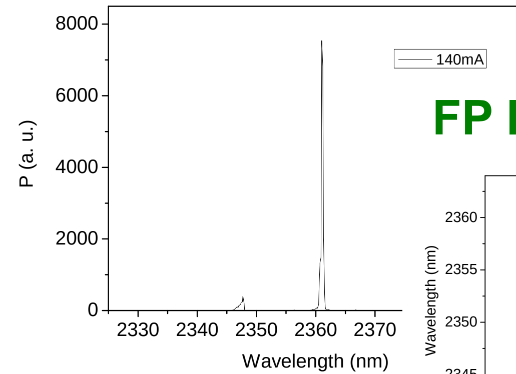


Applications : QEPAS sensing

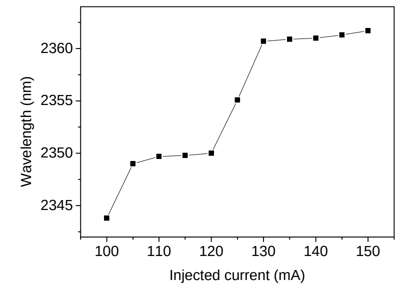
Perspectives : compact system

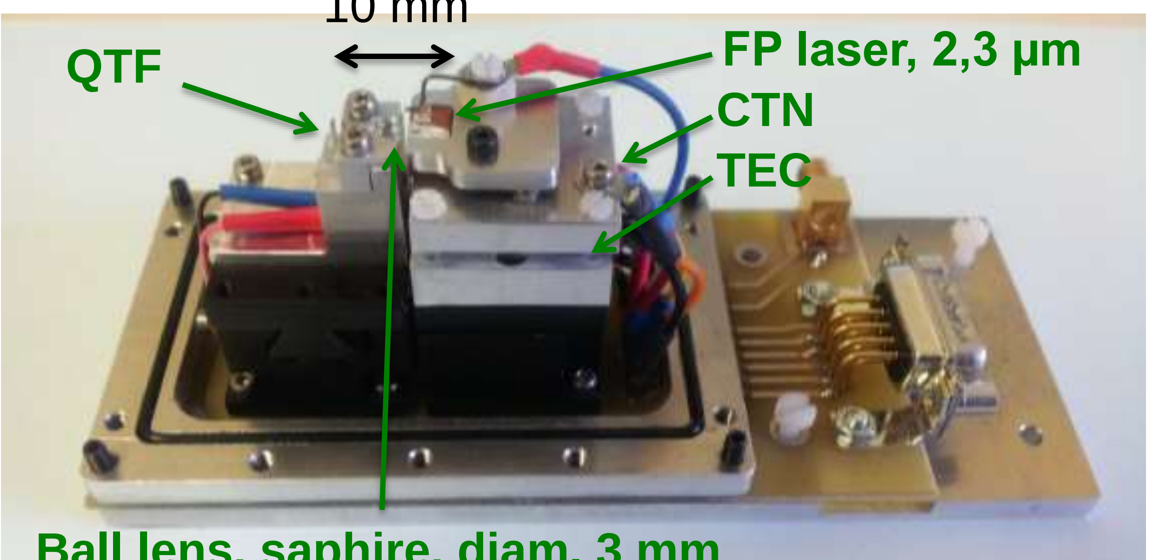


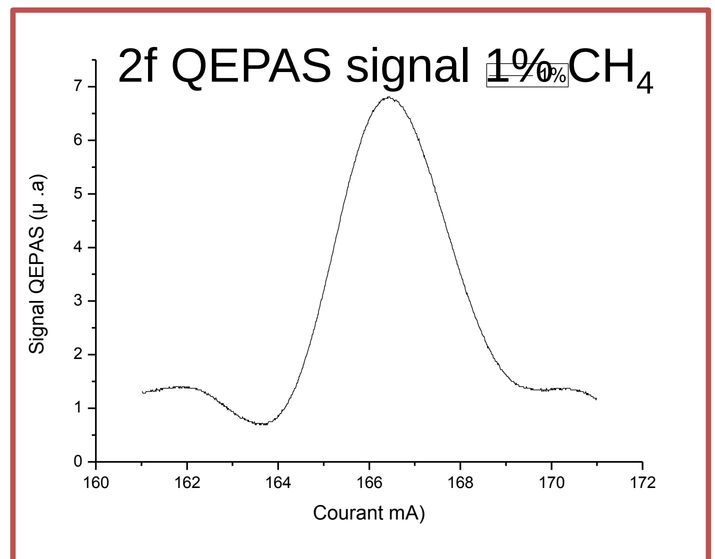




FP laser, 2,3 µm



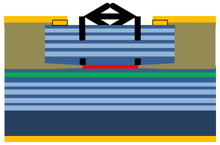




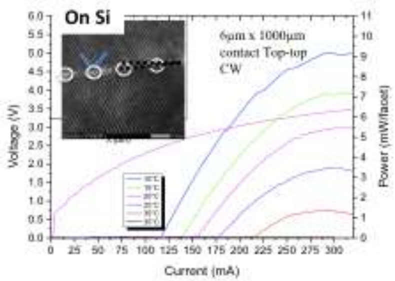
Conclusion

- **Antimonide compounds**
  - **A complex but versatile material system**
  - **Many progresses in MBE growth during the past 10 years**

- **Many compounds :**
  - **lasers Diodes 2 – 3 µm: mature**
  - **Strong work on *:* QCLs, V(E)CSELs and III-V silicon integration**



- **Applications : miniaturisation towards lab-on-chip ?**



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- Philippe CHRISTOL [Pr]
- Arnaud GARNACHE [CR]
- Pierre GRECH [IE1 CNRS]
- Grégoire NARCY [IE2 CNRS]
- Jean-Philippe PEREZ [MC]
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Fundings/collaborations

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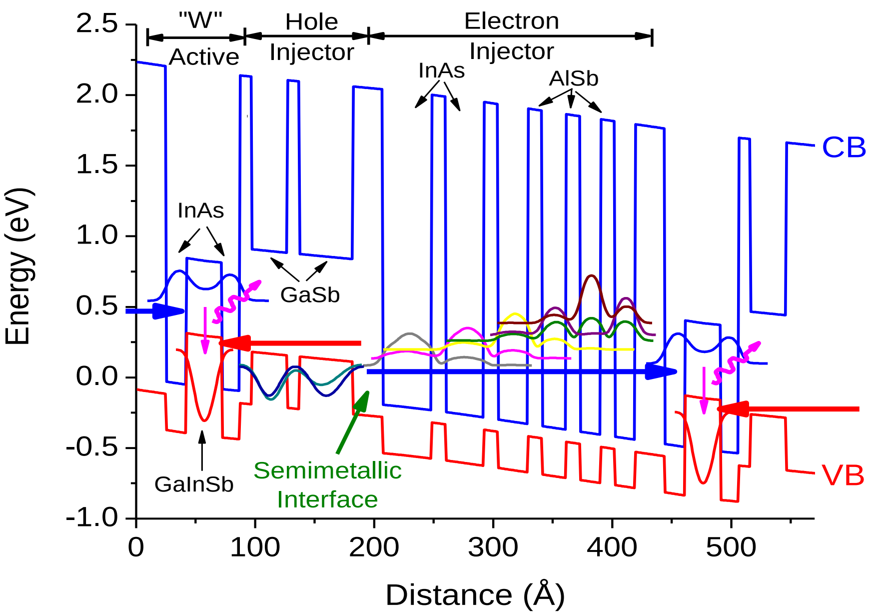
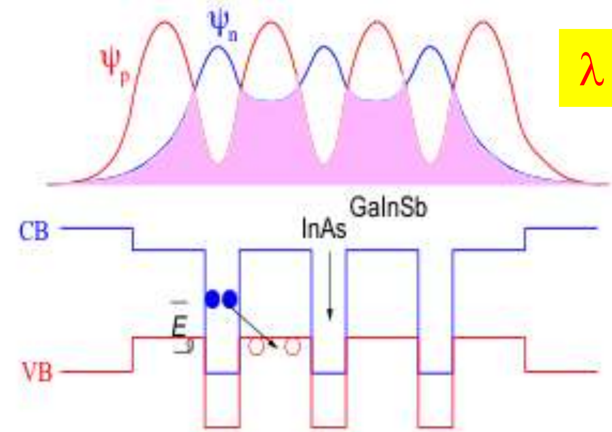
Antimonide Interband cascade lasers (ICLs) (NRL, USA)



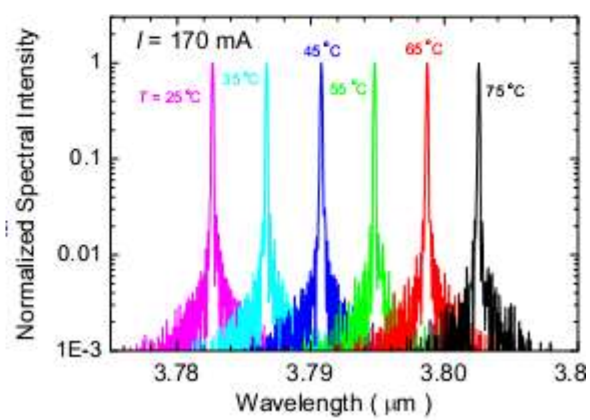
*Vurgaftman et al., NJP **11**, 125015 (2009)*
Vurgaftman et al., Nature Com. 2, 585 (2011)
Meyer et al., Photonics West 2013



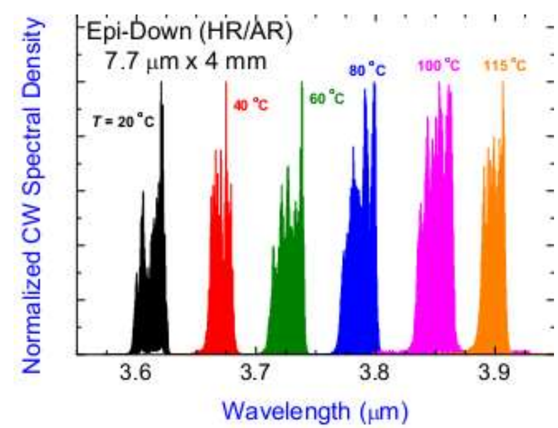
λ > 3.6 µm

Disadvantage:
(1) Spatially indirect (but high gain for thin QWs)
(2) 3D Density-of-States

Advantages:
(1) Excellent electrical confinement
(2) Access to much longer λ



DFB



High power

Can also be cited : uni Wurtzburg (poster B16) + nanoplus