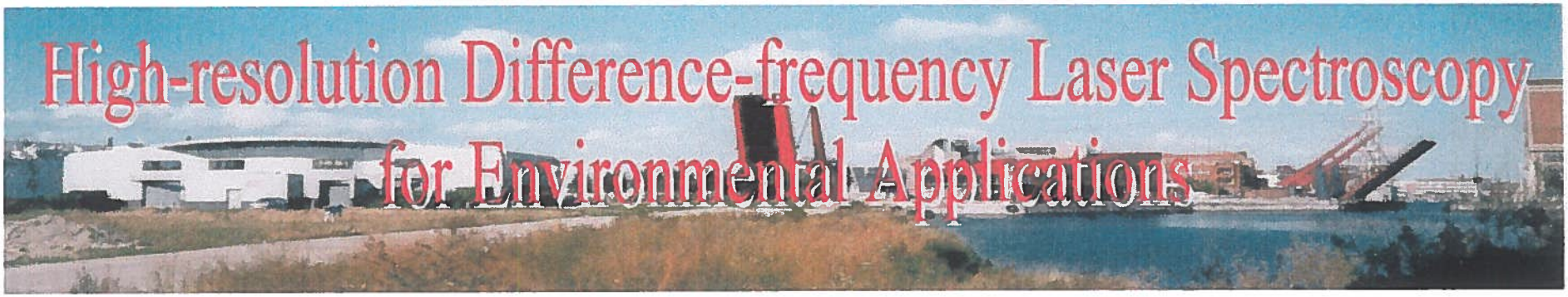

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Frank Tittel, Rice University, USA

Paul Davies, University of Cambridge, UK

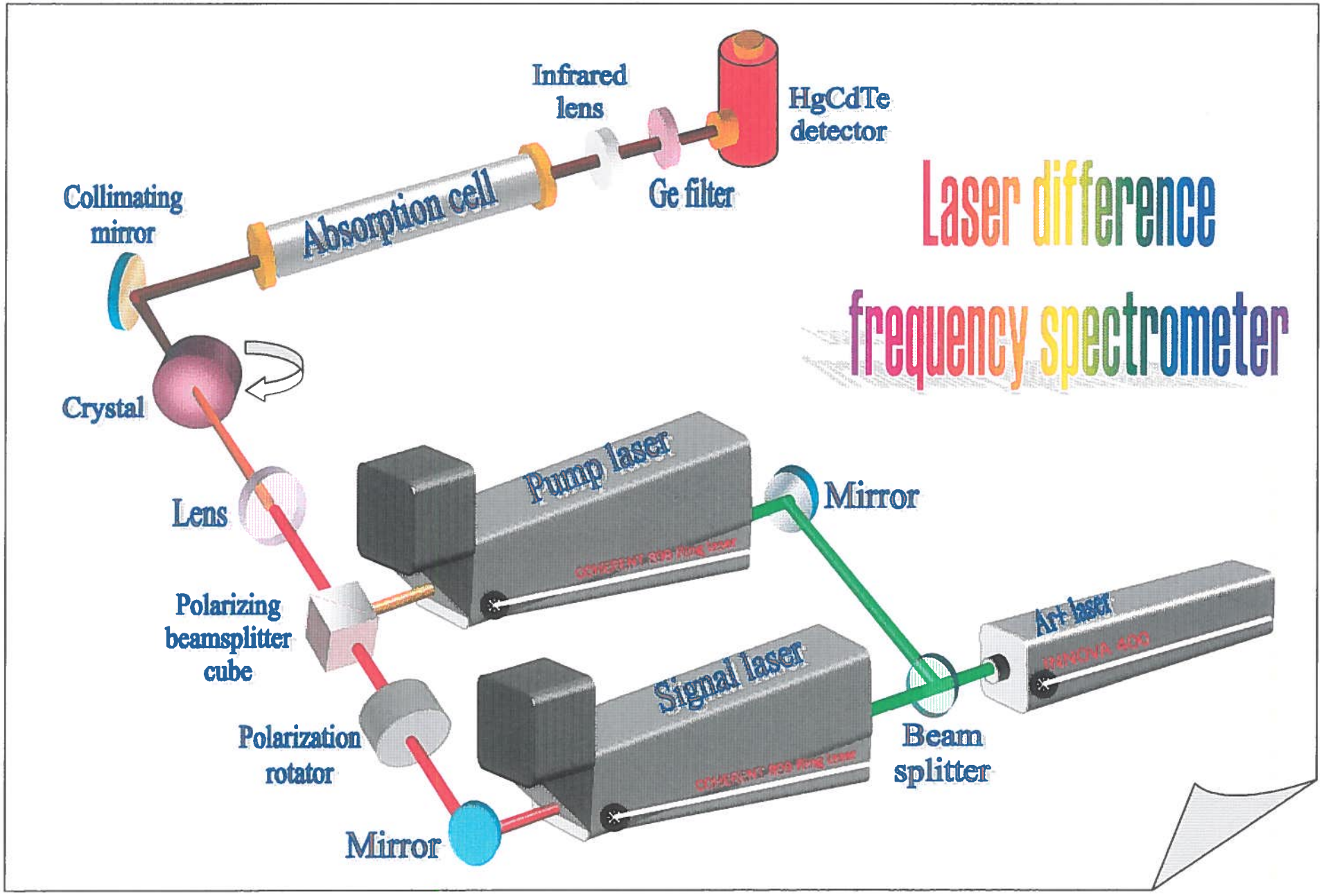
OUTLINE

- ⇨ *Motivation*
- ⇨ *Infrared spectrometer based on laser difference-frequency generation*
- ⇨ *Spectroscopic performances*
- ⇨ *Trace gas measurements by laser absorption spectroscopy*
- ⇨ *Conclusion & outlook*

Motivation

⇨ *Spectroscopic investigation of molecular line parameters ;*

⇨ *Environmental monitoring of trace gas, in particular volatile organic compounds, by laser absorption spectroscopy*


Infrared lens
HgCdTe detector
Ge filter
Absorption cell
Collimating mirror
Crystal
Lens
Pump laser
Mirror
Polarizing beamsplitter cube
Signal laser
Ar+ laser
Polarization rotator
Beam splitter
Mirror
Laser difference frequency spectrometer

Laser difference-frequency spectrometer

Spectral coverage

3.5-6.5 μm (DFG in QPM-PPRTA and $AgGaS_2$)

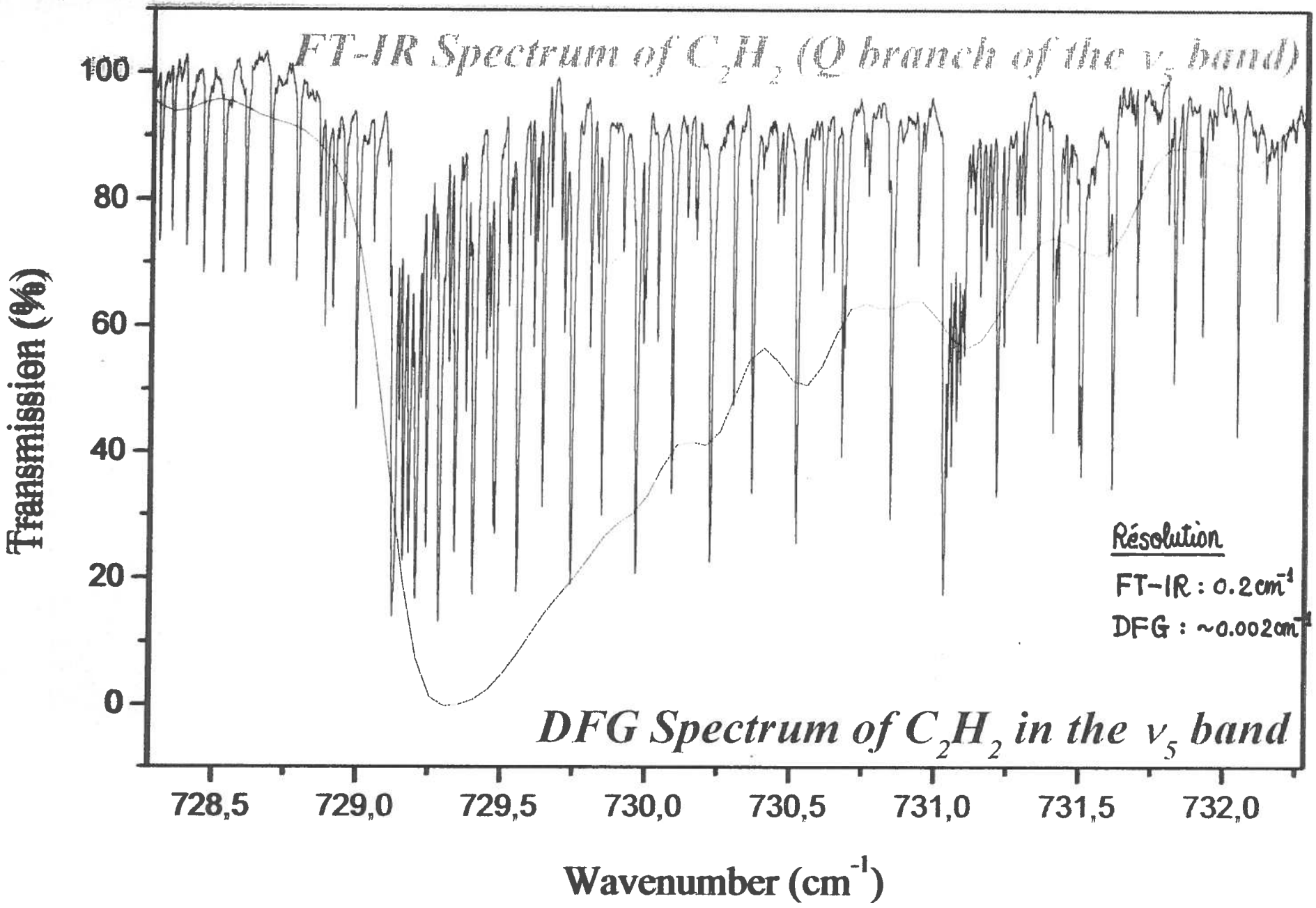
8-19 μm (DFG in GaSe)

cw power conversion

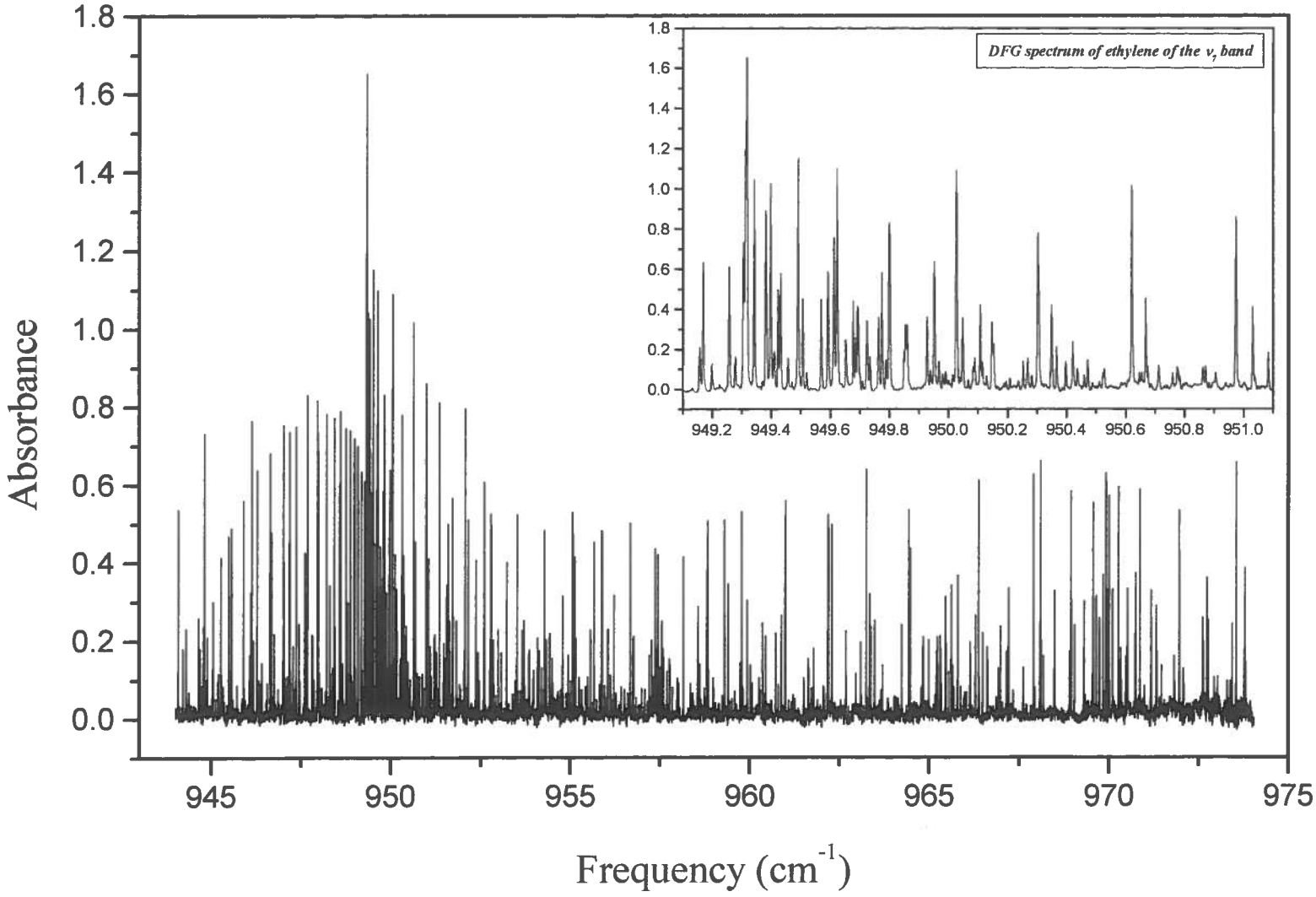
10-500 $\mu W/(W^2 . cm)$

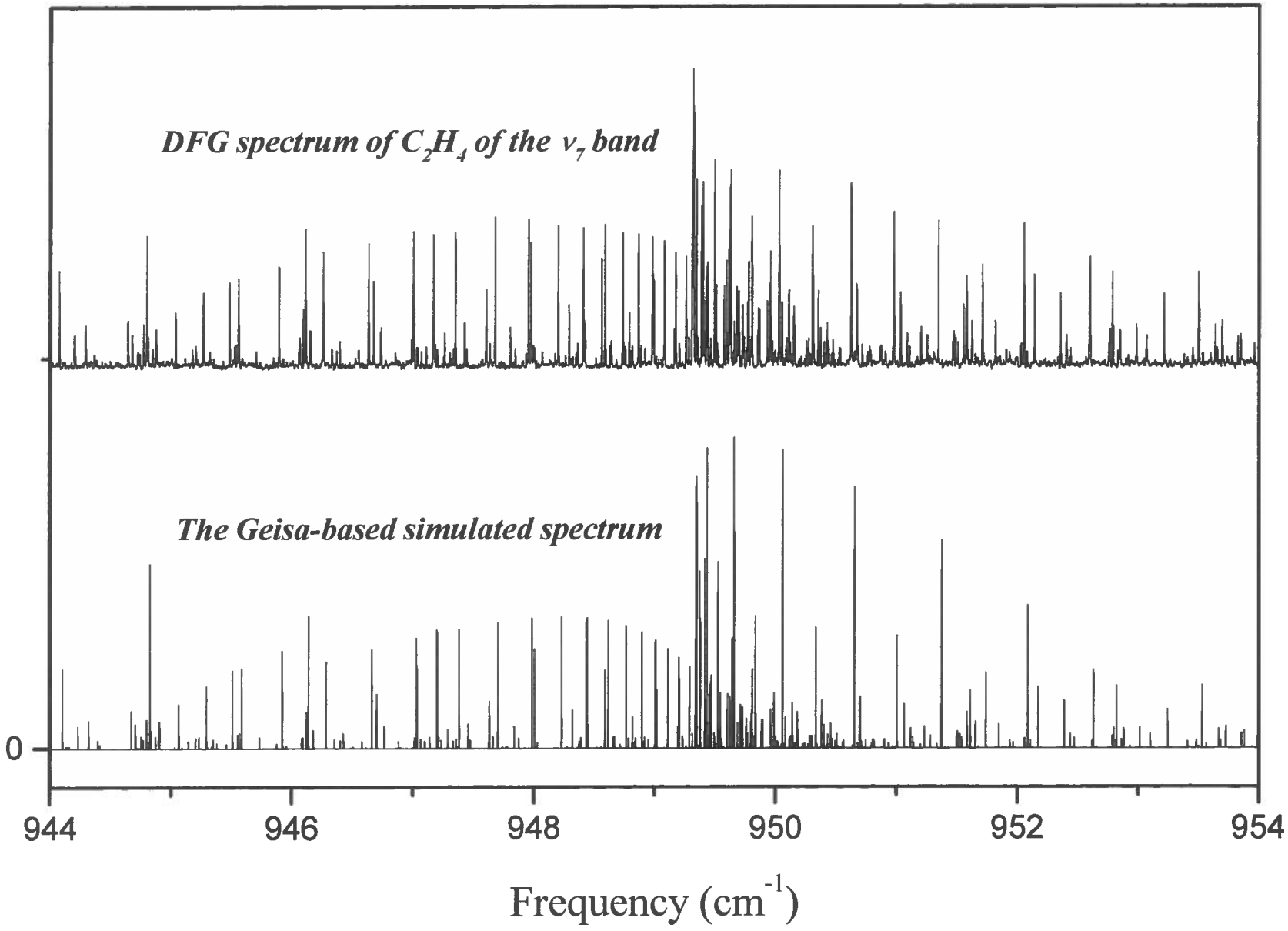
Spectral purity of the DFG source

< 1 MHz (~ 10^{-4} cm^{-1})

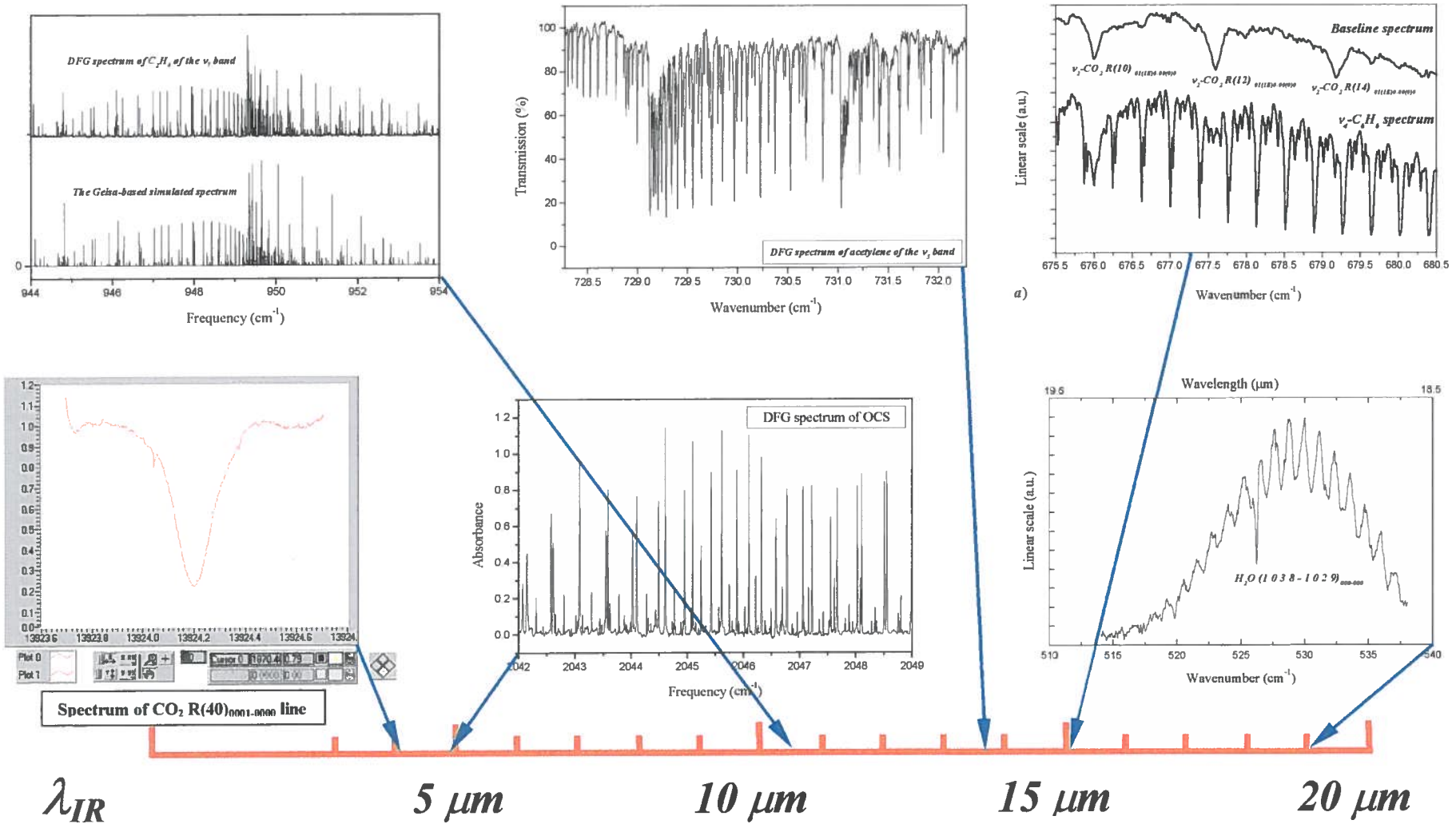

FT-IR Spectrum of C_2H_2 (Q branch of the ν_5 band)
Transmission (%)
100
80
60
40
20
0
728,5
729,0
729,5
730,0
730,5
731,0
731,5
732,0
Wavenumber (cm^{-1})
Résolution
FT-IR : 0.2cm^{-1}
DFG : ~0.002cm^{-1}
DFG Spectrum of C_2H_2 in the ν_5 band

High-resolution DFG spectrum of ν_7 C_2H_4 (@ 3.1 mbar & L=10 cm)

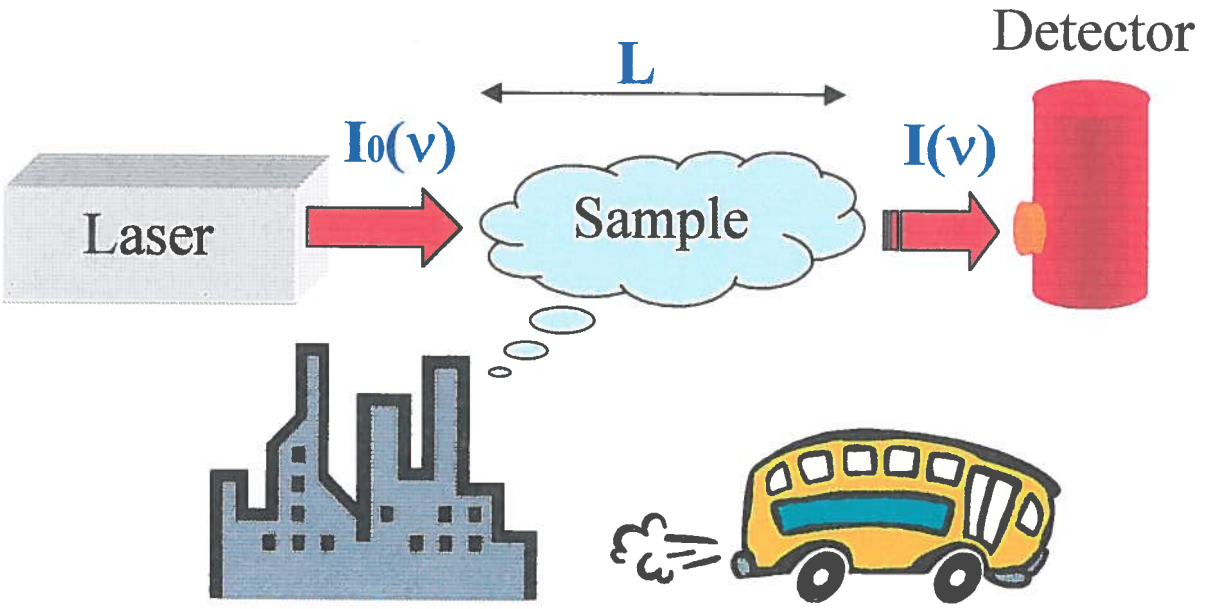



DFG spectrum of C_2H_4 of the ν_7 band
The Geisa-based simulated spectrum
0
944
946
948
950
952
954
Frequency (cm^{-1})

High-resolution Laser DFG Absorption Spectra



Trace Gas Detection Using Laser Absorption Spectroscopy



The Beer's law:

$$I(\nu) = I_0(\nu)\ exp\ (-\sigma(S, \gamma, \nu)\ C\ L)$$

Then the concentration:

$$C = ln\ (I_0 / I)/(\sigma(S, \gamma, \nu)\ L)$$

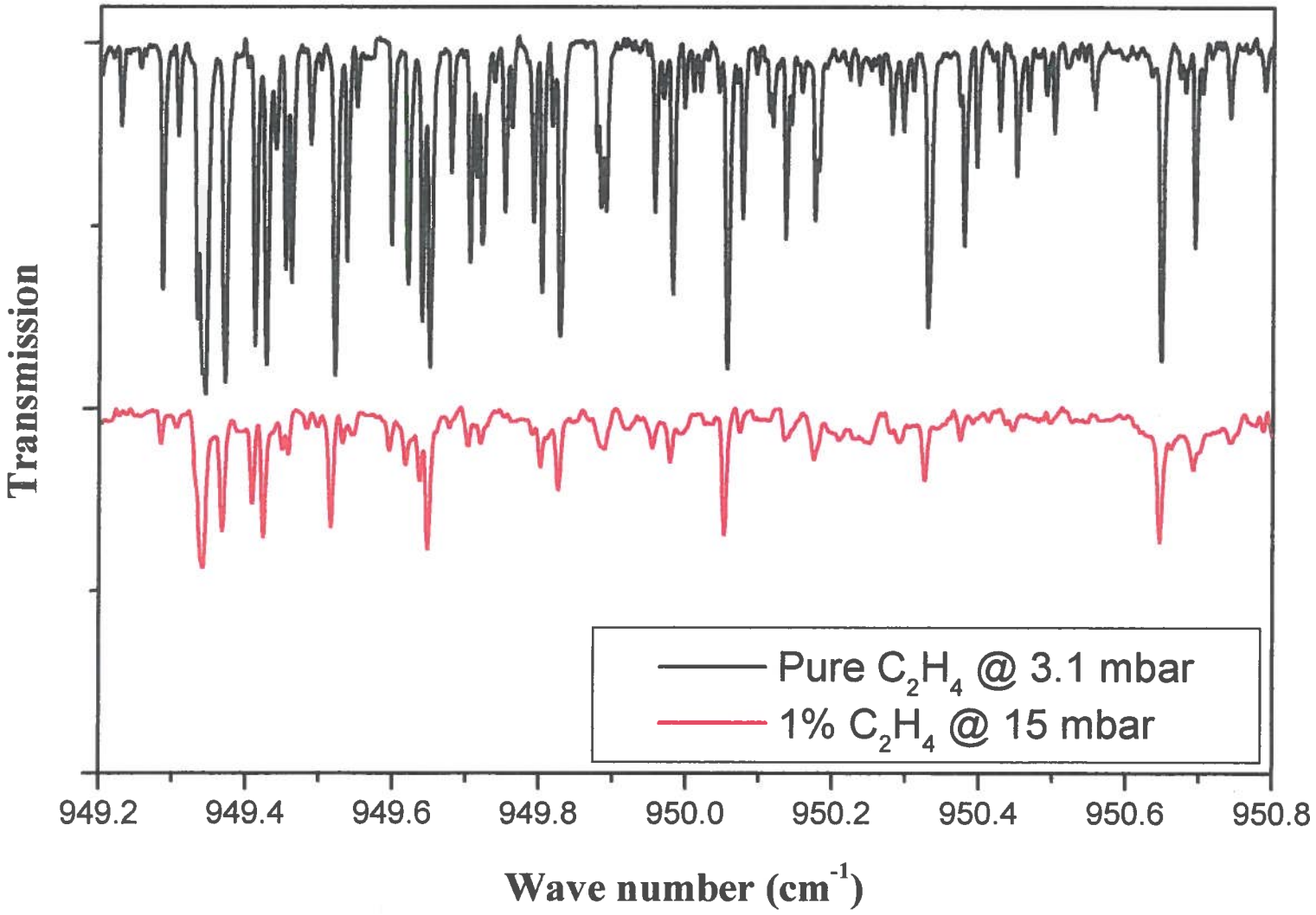
$I(\nu)$: the intensity after traversing a sample thickness L

$I_0(\nu)$: the incident intensity

$\sigma(S, \gamma, \nu)$: the absorption cross-section

C : the concentration of the absorbing species

High-resolution DFG spectra of ethylene of the ν_7 band

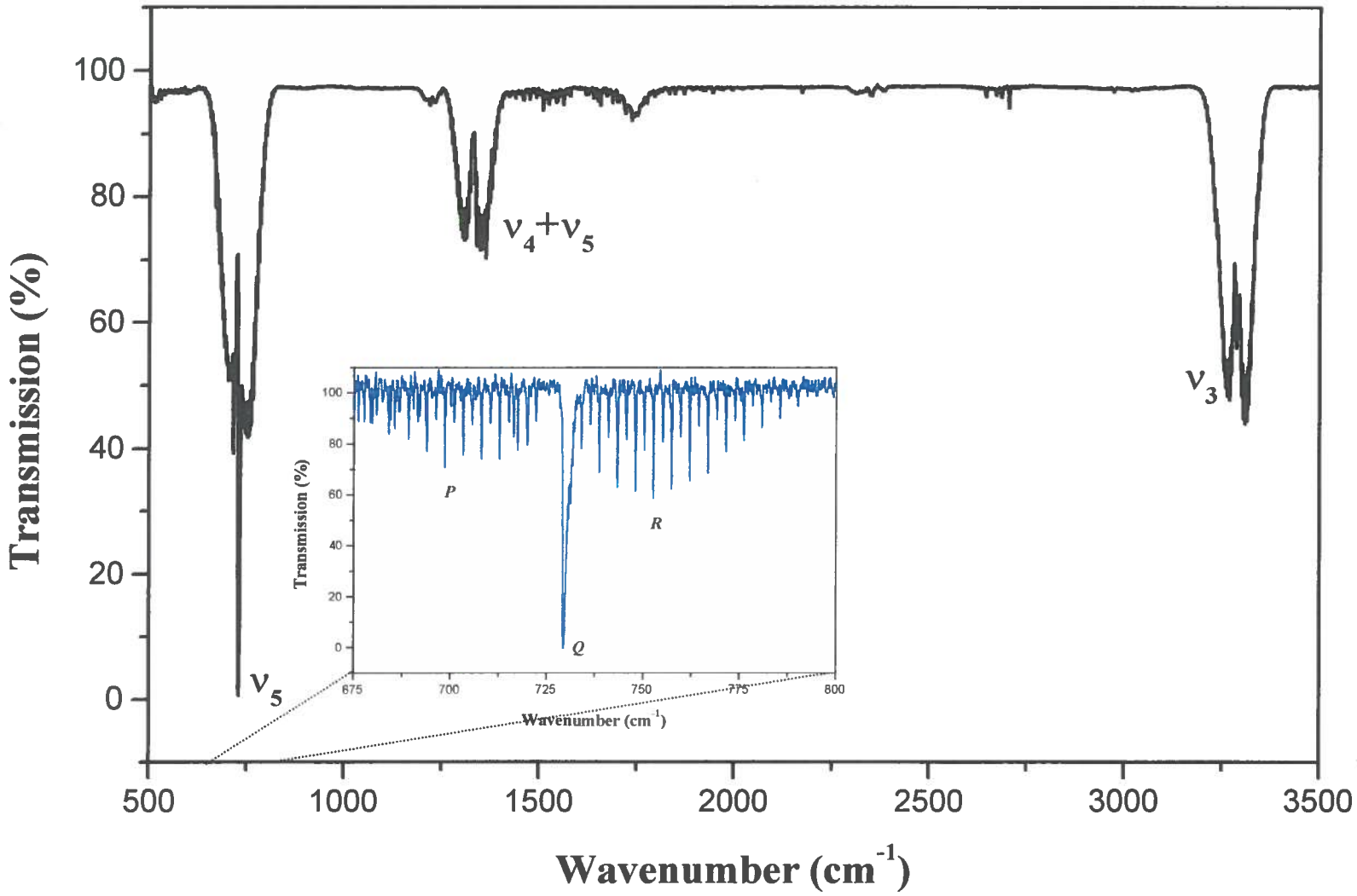


Absorption line selection

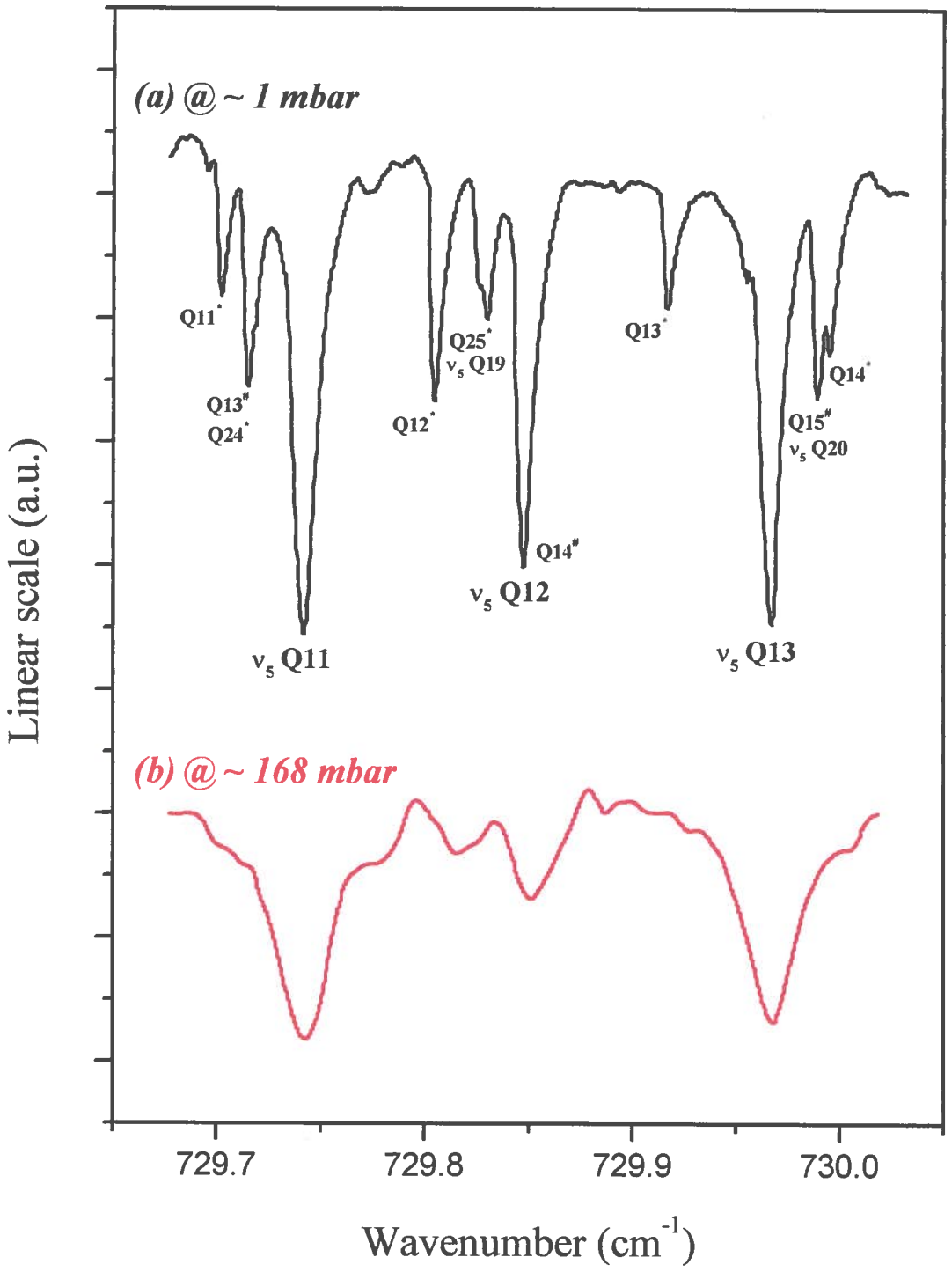
- ⇨ **Strong** for highly sensitive detection
- ⇨ **Isolated** for highly selective measurement

Selecting a strong absorption line for high sensitivity which at the same time should be isolated from interfering lines due to other gas species or from the same species.

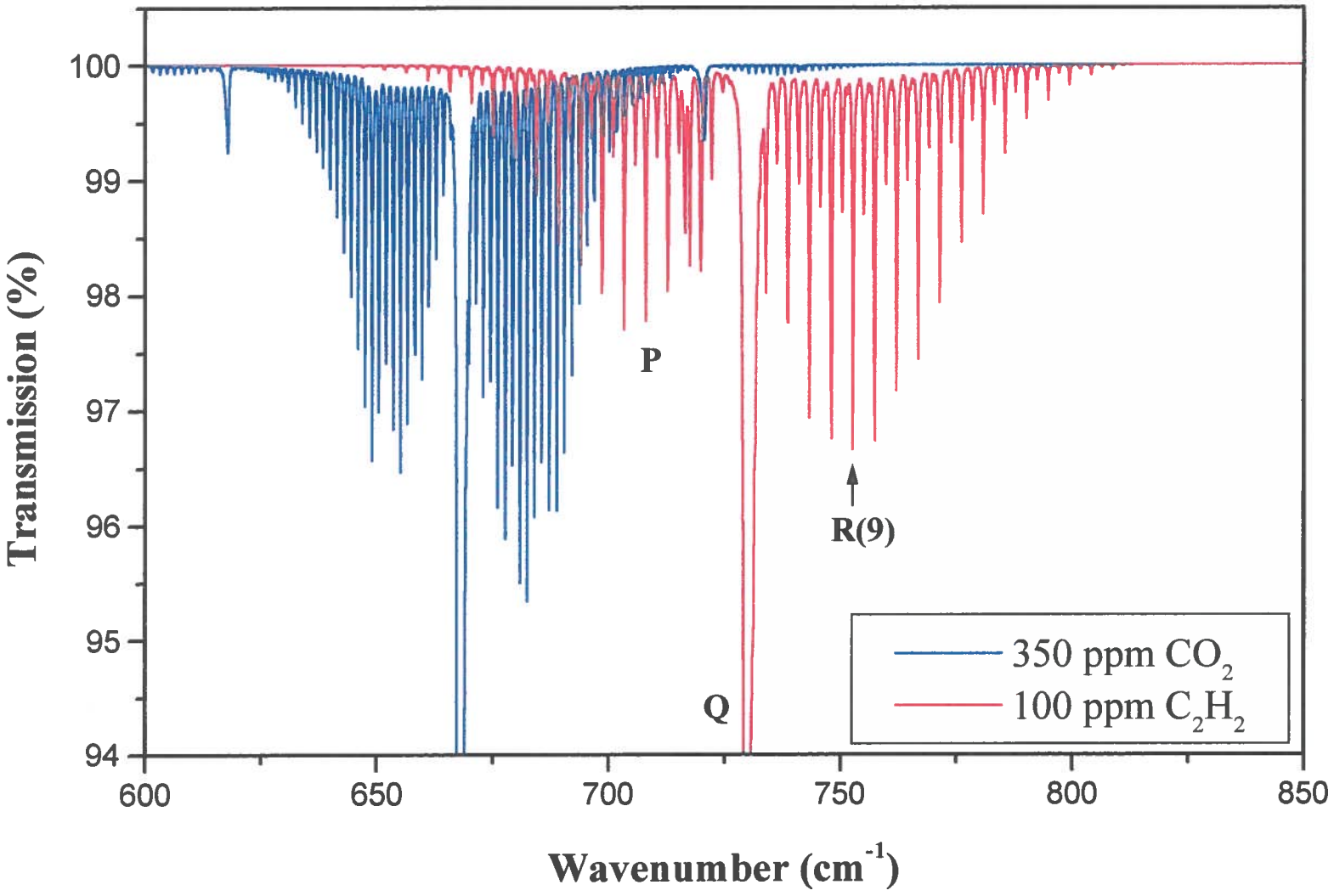
FT-IR absorption spectrum of C_2H_2 @ ~40 mbar (R=2 cm^{-1} with 64 scans)
The inset spectrum was obtained @ ~3 mbar (R=0.2 cm^{-1} with 16 scans)



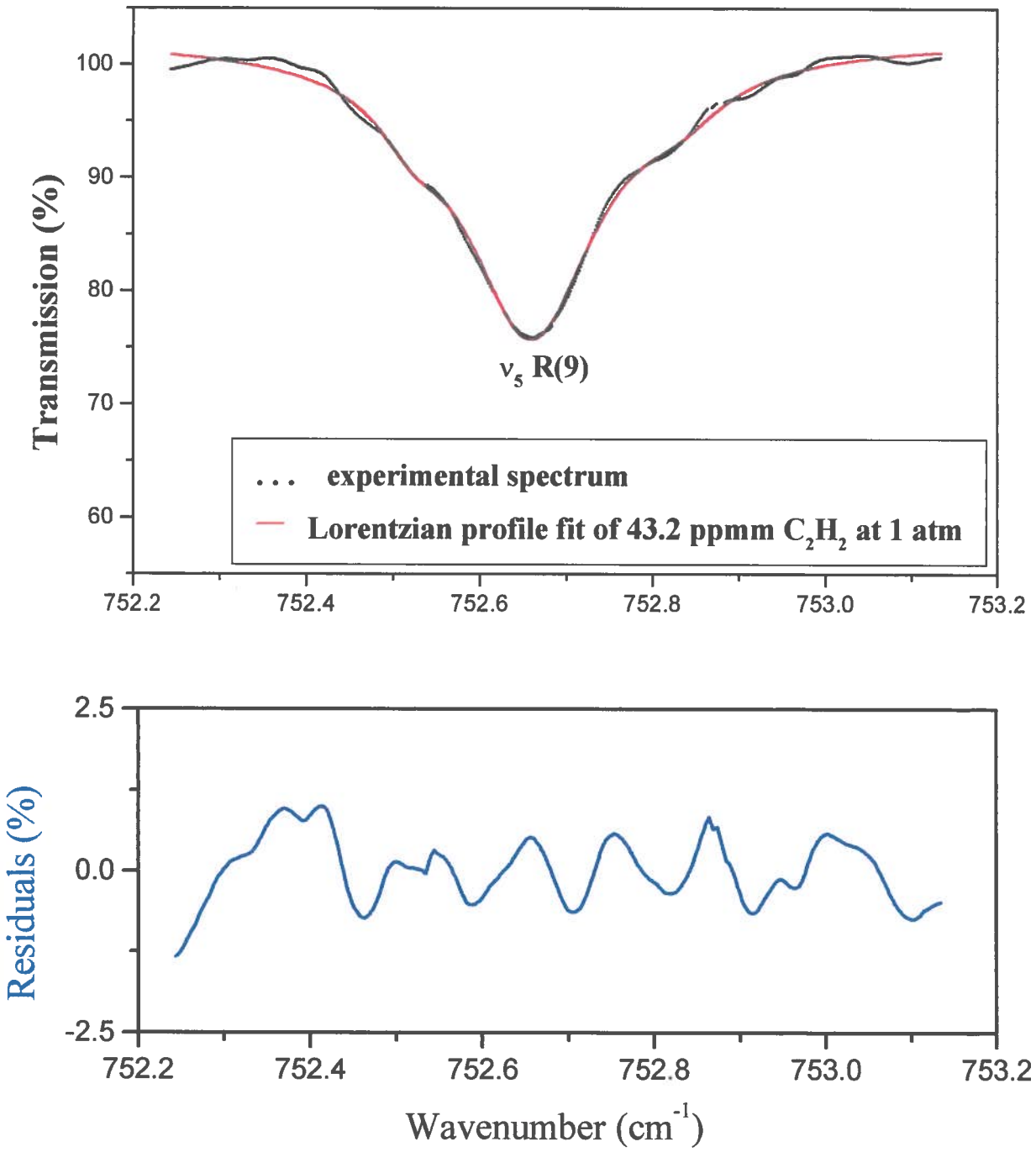
77 ppm C_2H_2 measurement using ν_5-Q11 and ν_5-Q13 lines (b)



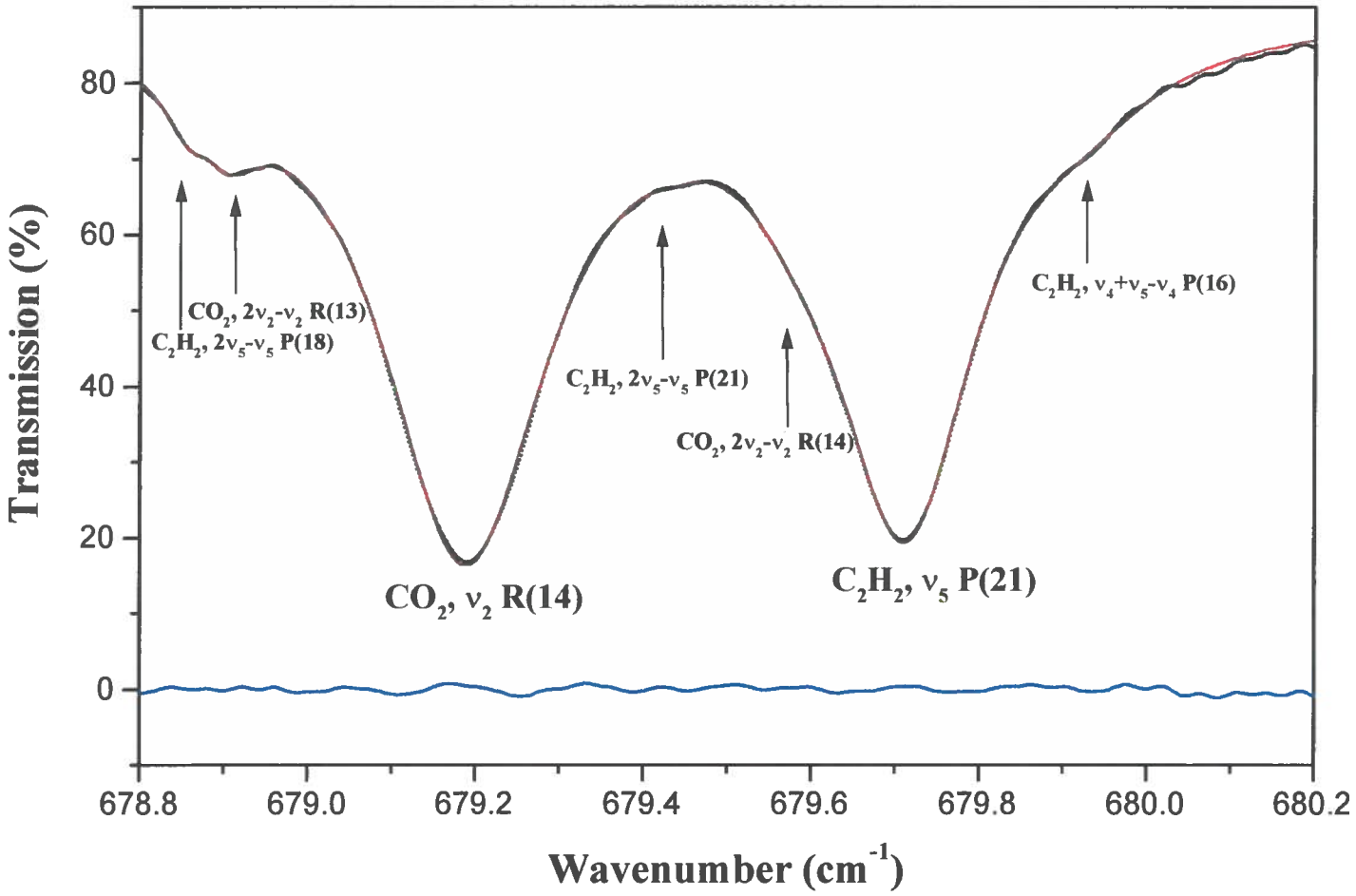
Simulated spectra of CO_2 and C_2H_2 @ atmospheric pressure



Spectrum of the ν_5 R(9) transition of C_2H_2 trace at atmospheric pressure



Spectrum of calibrated 1% CO_2 and C_2H_2 mixture around 679.5 cm^{-1} @ atmospheric pressure



Comparison of C_2H_2 trace detection using the P(21), Q(11) and R(9) lines of the ν_5 band

Rotational assignment (ν_5 band)	Transition frequency (cm^{-1})	Line strength (cm/mol.)	Absorption coefficient ($ppm^{-1}\ m^{-1}$)	Measured concentration-path (ppm m)	Pressure (Torr)	MDC* (ppb)
P (21)	679.7095	1.32^{E}-19	6.65^{E}-4	96.1	760	84.7
Q (11)	729.7380	1.08^{E}-18	2.68^{E}-2	7.7	126	2.4
R (9)	752.6589	6.82^{E}-19	2.88^{E}-3	43.2	760	20.7

** MDC is the 3σ-detection-limited minimum detectable concentration in ppb (part per billion, 10^{-9} atm.) using an optical path of 100-m.*

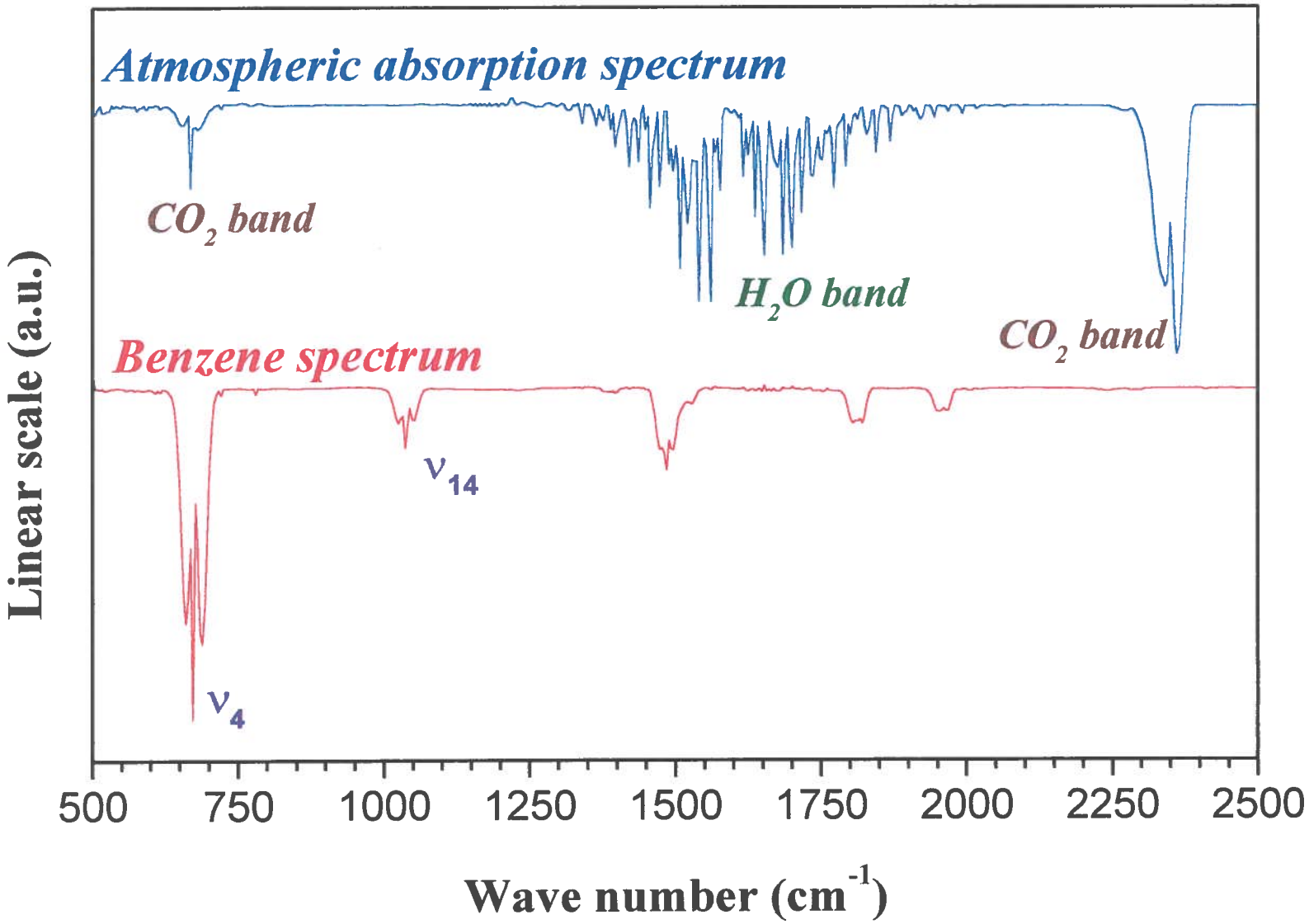
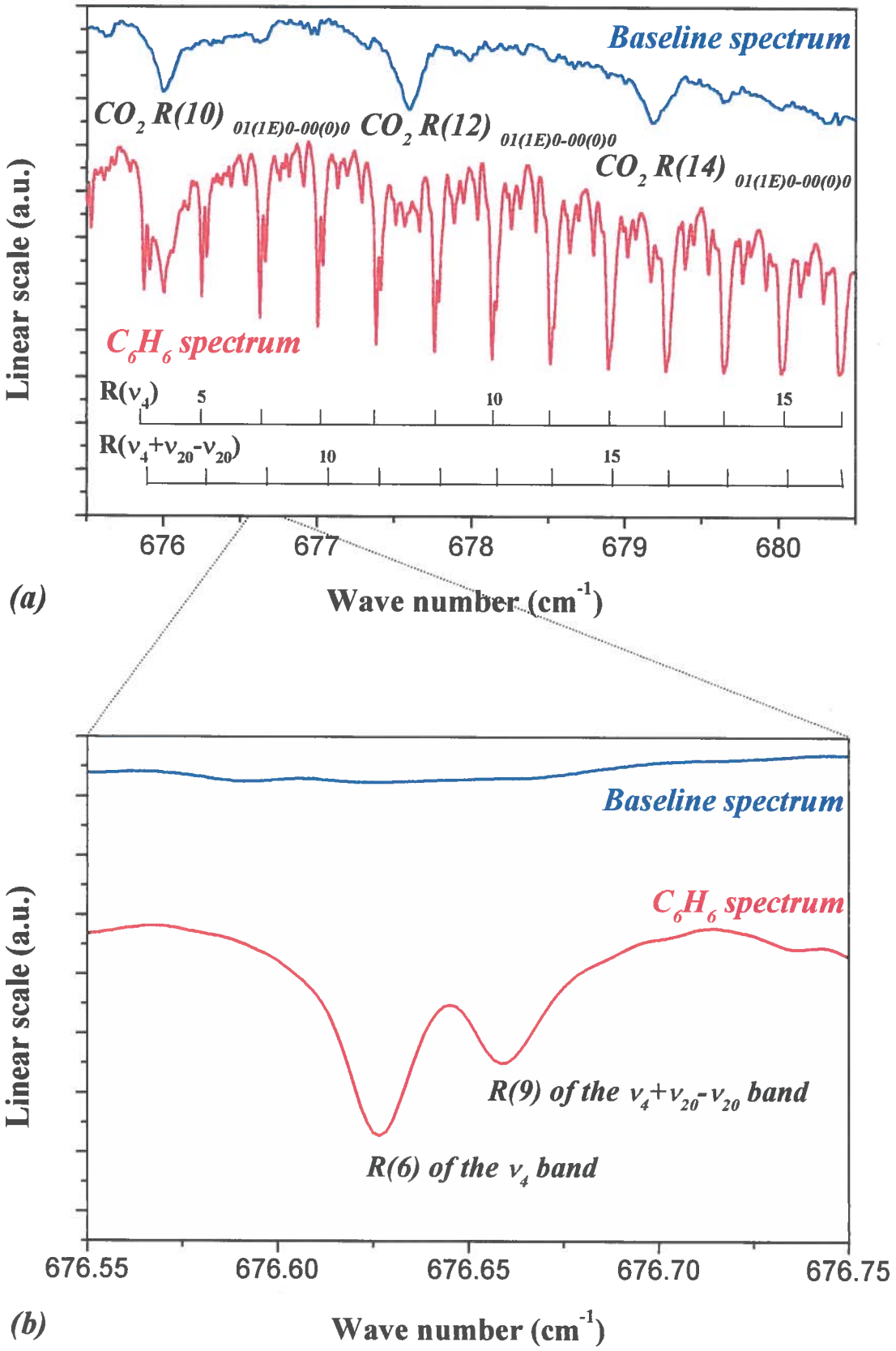

Atmospheric absorption spectrum
CO2 band
H2O band
CO2 band
Benzene spectrum
ν14
ν4
Linear scale (a.u.)
500
750
1000
1250
1500
1750
2000
2250
2500
Wave number (cm-1)

FIGURE 1

DFG spectrum of C_6H_6 in the ν_4 band



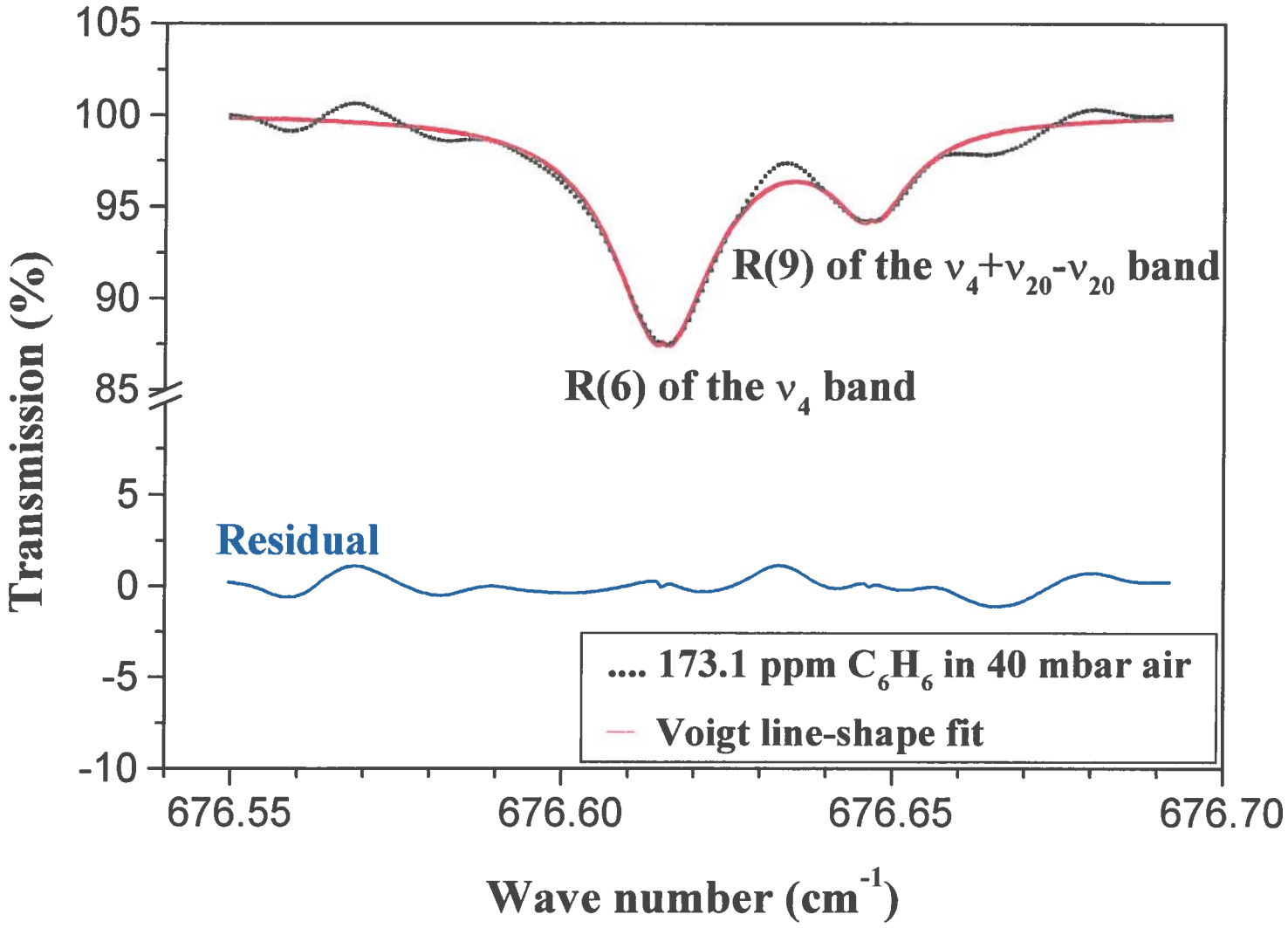
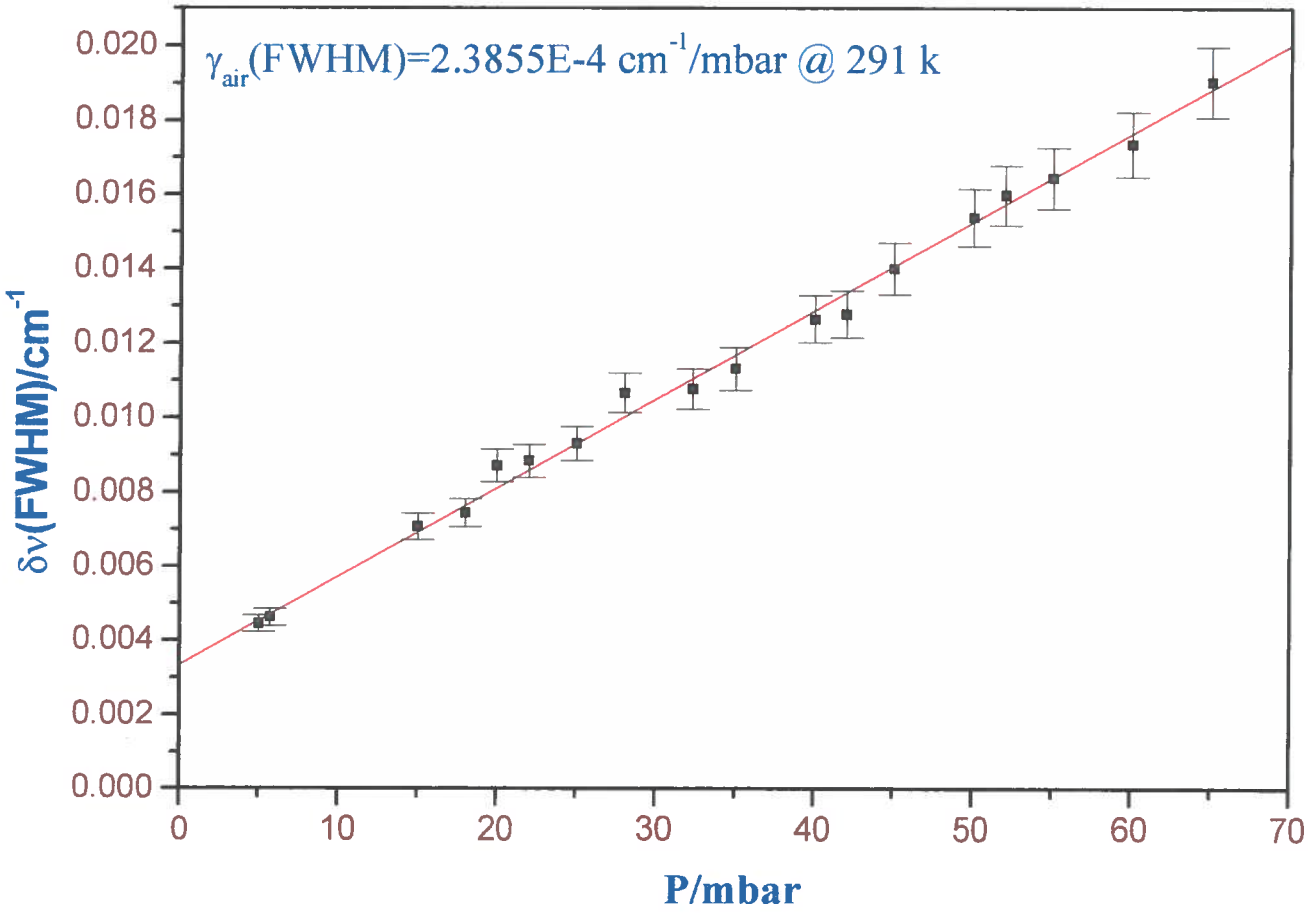

105
100
95
90
85
5
0
-5
-10
Transmission (%)
R(9) of the $\nu_4+\nu_{20}-\nu_{20}$ band
R(6) of the ν_4 band
Residual
.... 173.1 ppm C_6H_6 in 40 mbar air
Voigt line-shape fit
676.55
676.60
676.65
676.70
Wave number (cm^{-1})

FIGURE 5

Pressure dependence of the linewidth of the C_6H_6 line of the n4 R(6) branch @ 676.6258 cm^{-1}

Preliminary result: γ_{air} (FWHM)=0.23855 cm^{-1}/atm @ 291 k



SUMMARY

Laser absorption spectroscopy for environmental applications

- ⇨ High sensitivity and selectivity in the fundamental infrared region.
- ⇨ Measurements of trace amounts of various hydrocarbons: acetylene (ν_5 band), benzene (ν_4 band) and ethylene (ν_7 band) with a minimum detectable concentration of <ppm.

OUTLOOK

In situ and real time BTEX detection by means of diode laser based DFG employing QPM-GaAs crystal for the 8-16 μm region.