Quantum Cascade Laser Atmospheric Monitoring

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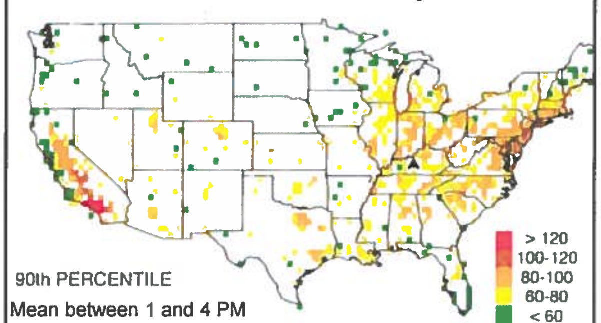
Talk outline

- A primer on urban smog
- Quantum cascade lasers
- Magnetic rotation spectroscopy
- Monitoring NO and NO_2

The components of smog

- H_2SO_3 and H_2SO_4 in killer London smogs. Different from U.S. urban smog.
- NO_x, organics, and sunlight produce classic summer urban smogs of Los Angeles and Houston
- Particulates

Distribution of high O_3 levels



Fiore, A.M., et al., *J. Geophys. Res.*, **103** 1471-1480 (1998).

The NO_x cycle

Compared with other relevant chemistry, the reactions below are fast.

(1) $NO_2 + h\nu \rightarrow NO + O$
(2) $O + O_2 \rightarrow O_3$
(3) $O_3 + NO \rightarrow NO_2 + O_2$

Setting up a steady state in O and O_3 gives.

$$[O_3] = \left(\frac{k_1[h\nu]}{k_3}\right)\frac{[NO_2]}{[NO]}$$

On a summer day, the factor in () is about 1/100 in ppm units. $[NO_2]/[NO]$ almost 10.

Sources of NO and NO_2

Although reduced by catalytic converters, NO comes primarily from vehicle exhaust.

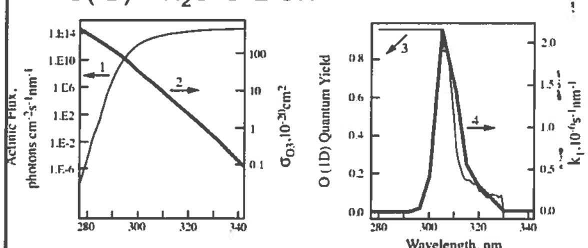
NO_2 is formed from NO by a series of reactions involving radicals.

$$OH + RH \rightarrow Rg + H_2O$$
$$Rg + O_2 \rightarrow RO_2$$
$$RO_2 + NO \rightarrow ROg + NO_2$$

When R=H, OH is regenerated among other processes making OH. HO_2 arises from the oxidation of CO.

Original OH source

$O_3 + h\nu(\lambda < 320\ nm) \rightarrow O(^1D) + O_2$
$O(^1D) + H_2O \rightarrow 2\ OH$



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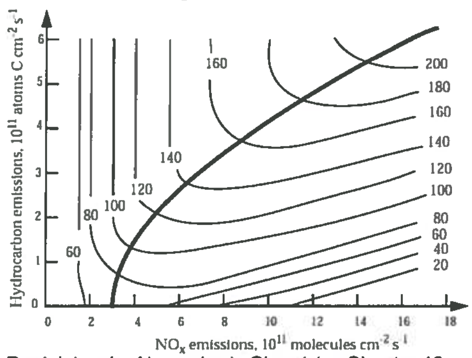
The oxidative chain

$OH + CO \rightarrow CO_2 + H$
$H + O_2 + M \rightarrow HO_2 + M$
$HO_2 + NO \rightarrow NO_2 + OH$
$NO_2 + h\nu \rightarrow NO + O(g.s.)$
$O + O_2 + M \rightarrow O_3 + M$
$O_3 + h\nu \rightarrow O_2 + O(^1D)$
$O(^1D) + H_2O \rightarrow 2\ OH$

Simulated O_3 concentrations (ppbv)



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Spectroscopic monitoring techniques

- OH (UV laser fluorescence)
- Radicals (NO,NO_2,HO_2?) IR Faraday Magnetic Rotation
- CO, CO_2, O_3 IR Photoacoustic Spectroscopy

OH monitoring

OH is extremely reactive. This almost requires an *in situ* monitoring scheme.

In situ detection by UV laser induced fluorescence can be done even though the fluorescence quantum yield at atmospheric pressure is tiny.

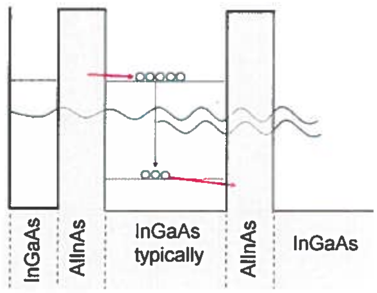
Converting its fluorescence signal into an OH concentration is difficult.

I believe no one is currently monitoring OH concentrations.

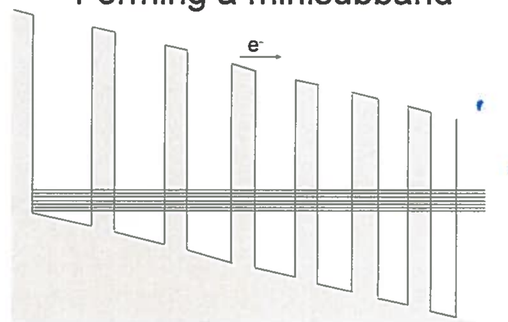
Quantum cascade laser (QCL)

"Quantum Cascade Laser",
Faist, J; Capasso, F; Sivco, DI; Sirtori, C; Hutchinson, Al; Cho, Ay. *Science* **264,** 553 (1994).

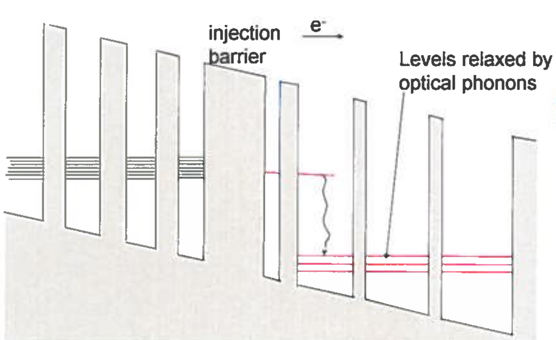
Quantum well lasing



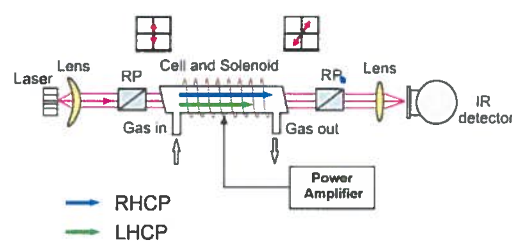
Forming a minisubband



Injection into upper state

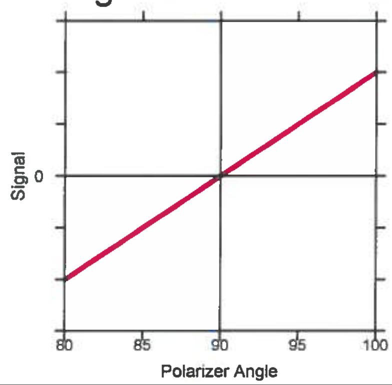


Faraday magnetic rotation

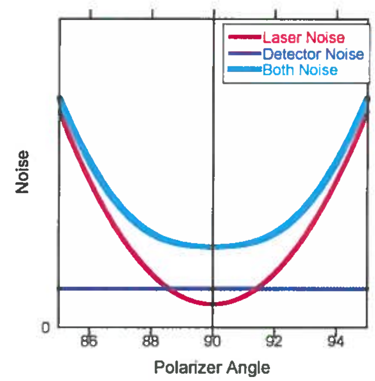


In gas phase, Faraday rotation arises from a difference in refractive indices for circular polarization when ΔM=+1 (or -1).

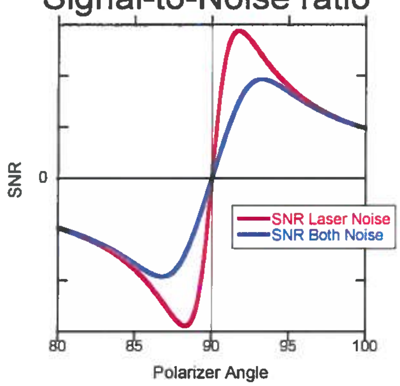
FRS Signal vs Polarizer Angle



Noise



Signal-to-Noise ratio



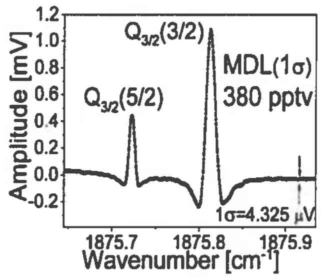
FRS and QCLs

Quantum cascade lasers are very quiet. Modulating at 1 kHz, for a QCL producing a few mW, sensitivity is determined by detector noise.

Recently QCL's producing 0.5 to 1 W cw are becoming available. For these sensitivity should be determined either by polarizer quality or power saturation.

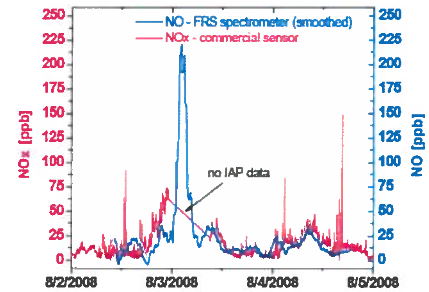
FRS observes refractive indices. These can power saturate, but far less easily than absorptions do.

Nitric oxide (NO) sensitivity

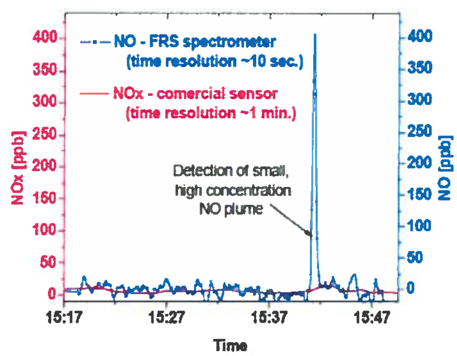


96 ppbv NO. Ambient NO ~5 ppbv

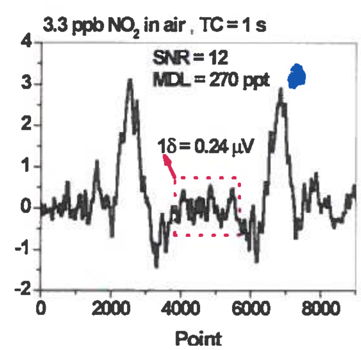
Beijing NO monitoring



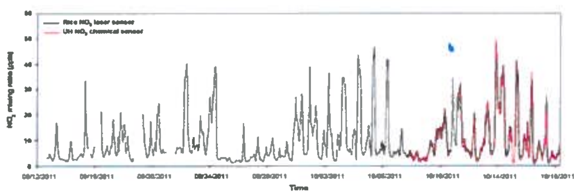
Fast detector response NO



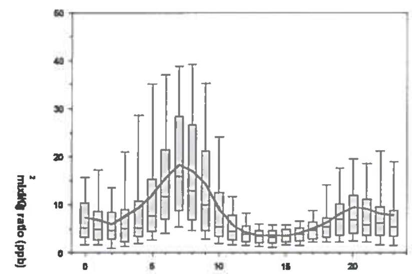
NO_2 sensitivity



NO_2 monitoring Houston



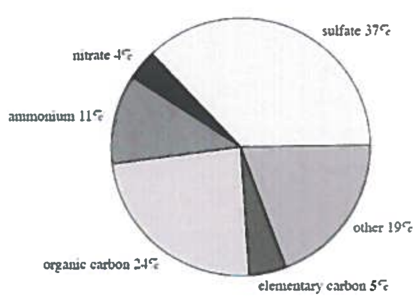
Diurnal NO_2 signal in Houston



9/12/2011
Sunrise 7:04; Sunset 7:32

11/21/2011
Sunrise: 6:51; Sunset:5:24

"Typical" particle



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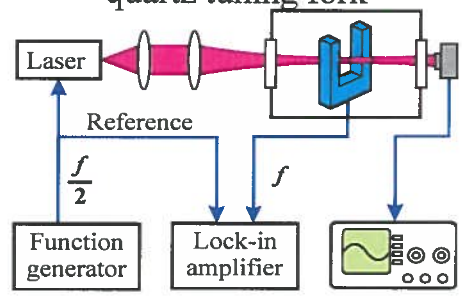
Houston area particle sources

- From elsewhere
  - Pollution from other urban areas
  - Remote fires: U.S. wildfires and Yucatan agricultural
  - Sea salt
  - Very fine sand from as distant as Sahara
- Our own particles
  - Vehicle exhaust (diesel especially)
  - Industrial emissions (SO_2, NH_3, organics)

Photoacoustic spectroscopy of nonmagnetic small molecules

- ➢Salt particle formation
  - ➢NH_3 (done)
  - ➢SO_2 (not yet done)
- ➢Small molecule components of smog
  - ➢CO (done)
  - ➢O_3 (not yet done)

Photoacoustic spectroscopy with a quartz tuning fork



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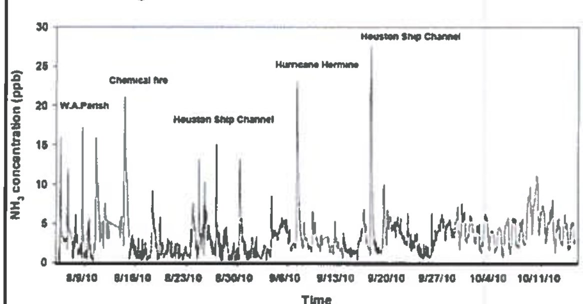
NH_3 monitoring in Houston



QCL IR Monitoring

- ➢Is sufficiently sensitive
- ➢Reliably selective for species
- ➢Can be applied to most small molecules
- ➢Responds rapidly
- ➢Can detect artifacts caused by pulses
- ➢Can be matched with wind direction
- ➢Is suitable for remote operations
- ➢Needs little downtime