Applications of cavity enhanced spectroscopy techniques in atmospheric chemistry

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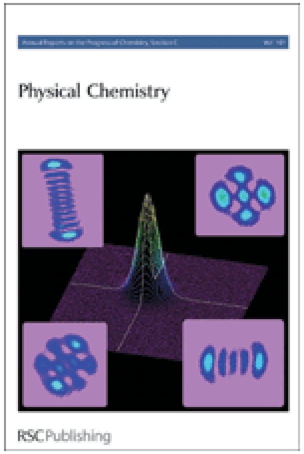
Outline

- Quantitative measurement of trace atmospheric species
- Optical extinction by atmospheric aerosols



Cavity ring-down and cavity enhanced spectroscopy using diode lasers.

M.I. Mazurenka, A.J. Orr-Ewing, R. Peverall and G.A.D. Ritchie, Annual Reports C **101**, 100 – 142 (2005).

Quantitative measurement of trace atmospheric species

Why use absorption spectroscopy to measure trace atmospheric constituents?

- Quantitative determination of mixing ratios
- Rapid and specific measurements
- Measurement of reactive species such as radicals

but absorption spectroscopy is generally insensitive.

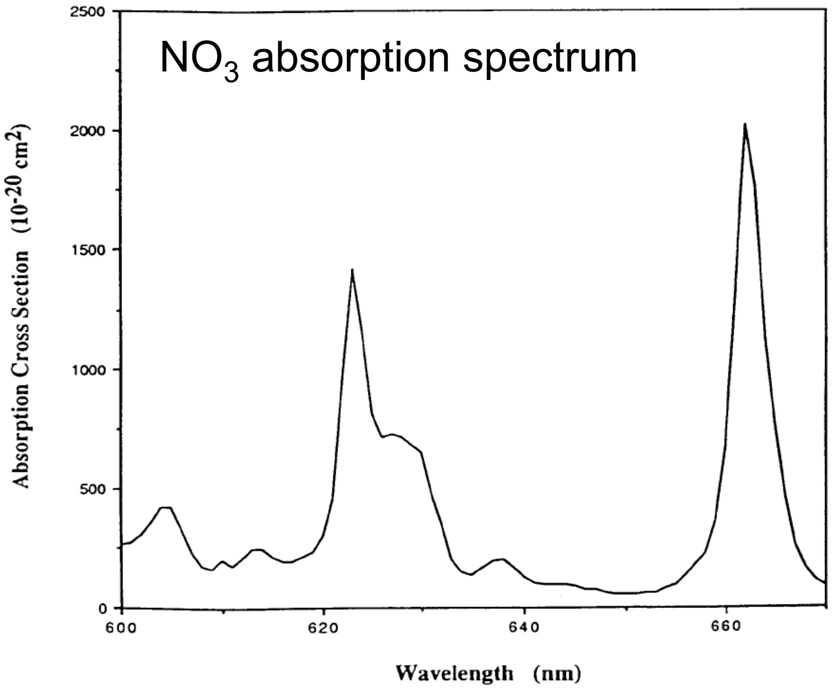
Strategies for atmospheric measurements:

- Long path differential optical absorption spectroscopy (DOAS)
- Laser induced fluorescence (LIF) and FAGE
- Multi-pass absorption spectroscopy with tuneable diode lasers
- Cavity enhanced absorption techniques – CRDS and CEAS

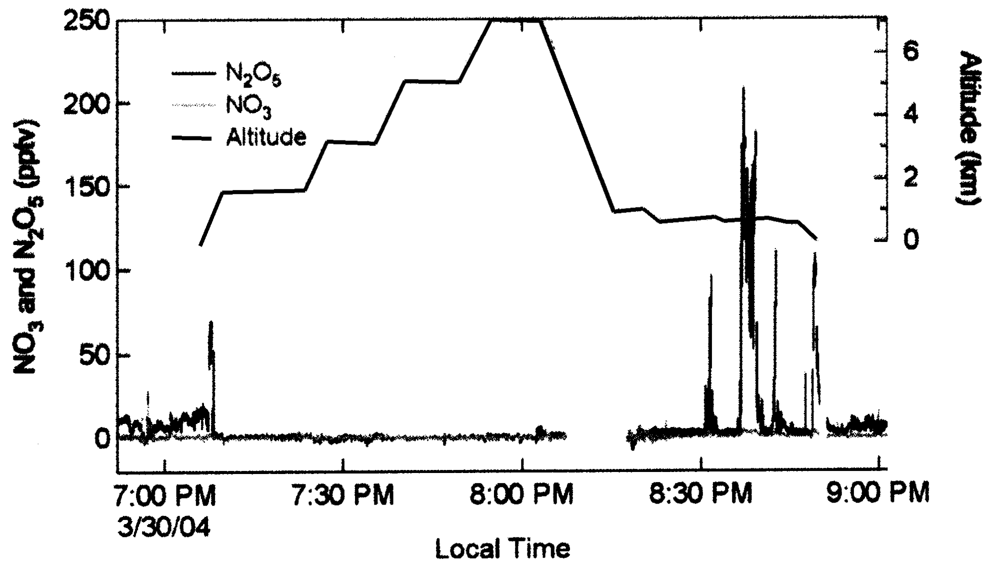
An example – measurement of N_2O_5 and NO_3 in air

Measurement of **N_2O_5** and **NO_3** in air with (sub)-pptv sensitivity by:

- Brown and Ravishankara (dye laser CRDS)
- Simpson (diode laser CRDS)
- Ball and Jones (broadband dye laser CRDS)

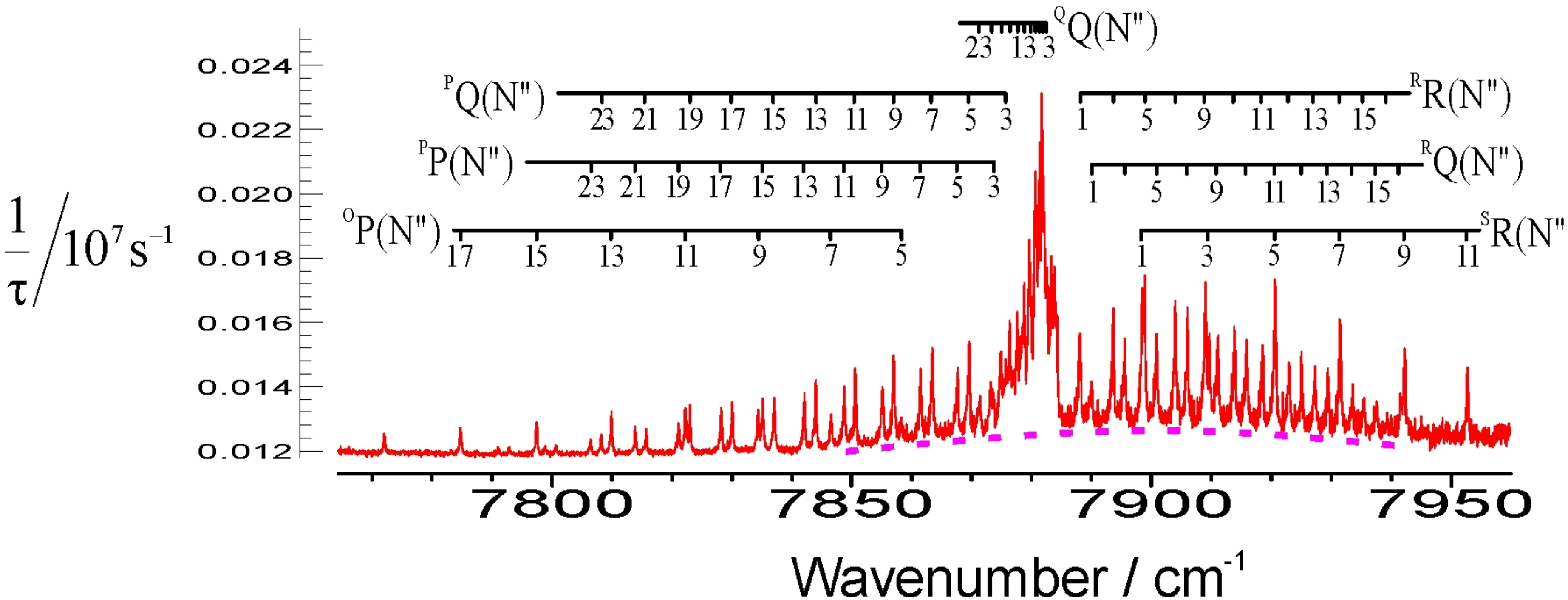


NO_3 and N_2O_5 by aircraft CRDS instrument
(Dubé et al. Rev. Sci. Inst. **77**, 034101 (2006))



"Forbidden" transition in O_2

$$O_2\ a^1\Delta_g \leftarrow X^3\Sigma_g^- \quad (v'=0 \leftarrow v''=0)$$

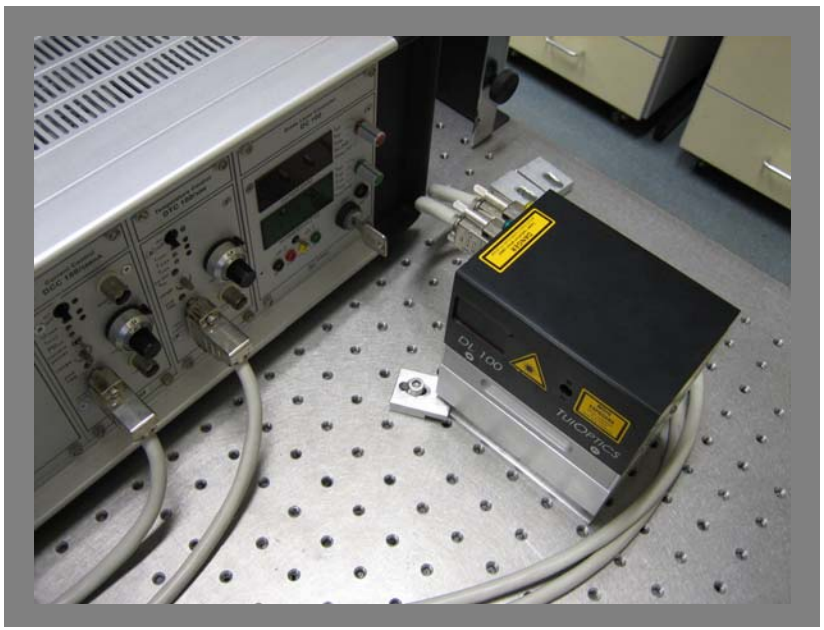


$A = 2.256 \times 10^{-4}\ s^{-1} \quad \tau_{rad} = 73.9$ min

S.M. Newman *et al.*, J. Chem. Phys. **110**, 10749 (1999)

Diode laser based sensors

- Compact, relatively cheap lasers
- Low power requirements
- Potential for very high sensitivity
- Limited wavelength range
- Quantum cascade lasers for mid-IR

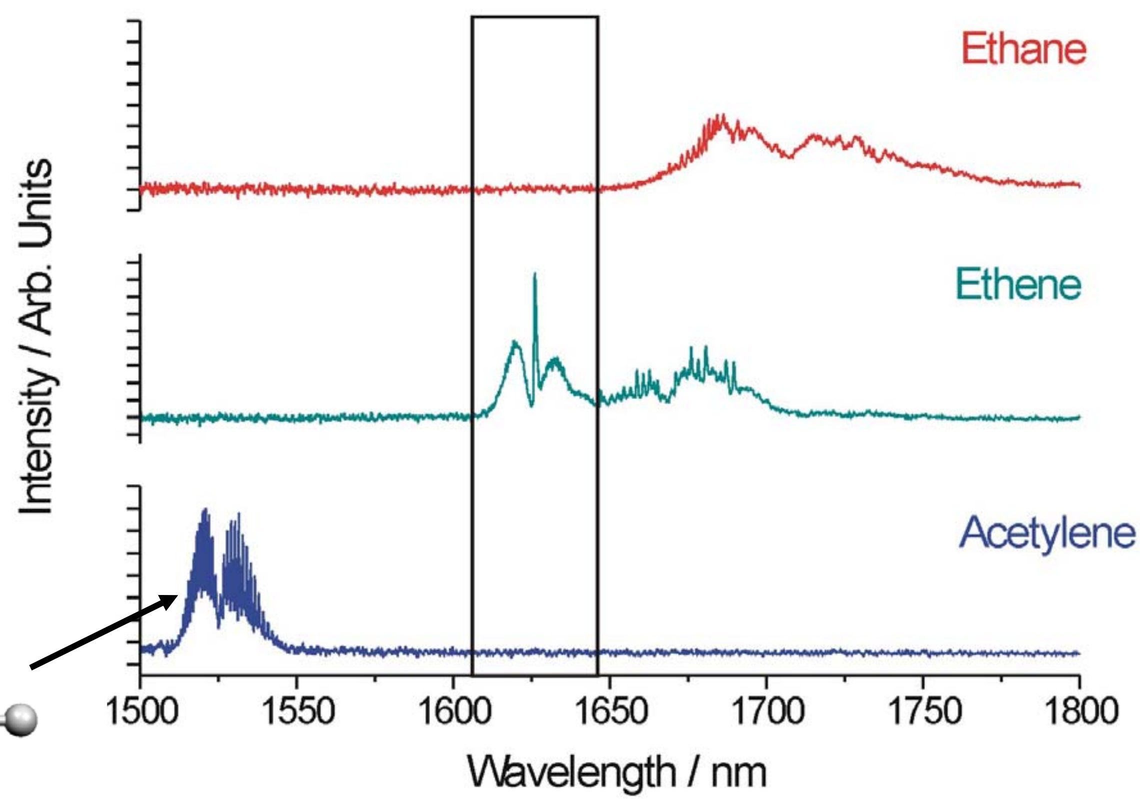


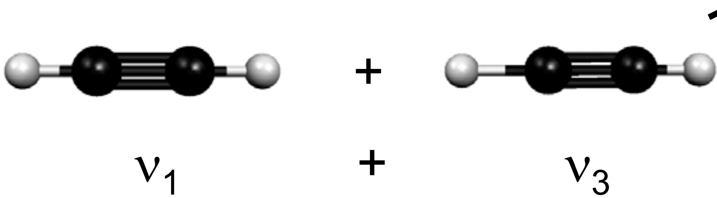
External cavity diode laser
(ECDL)

Distributed feedback diode laser
(DFB)

Trace volatile organic compounds (VOCs)

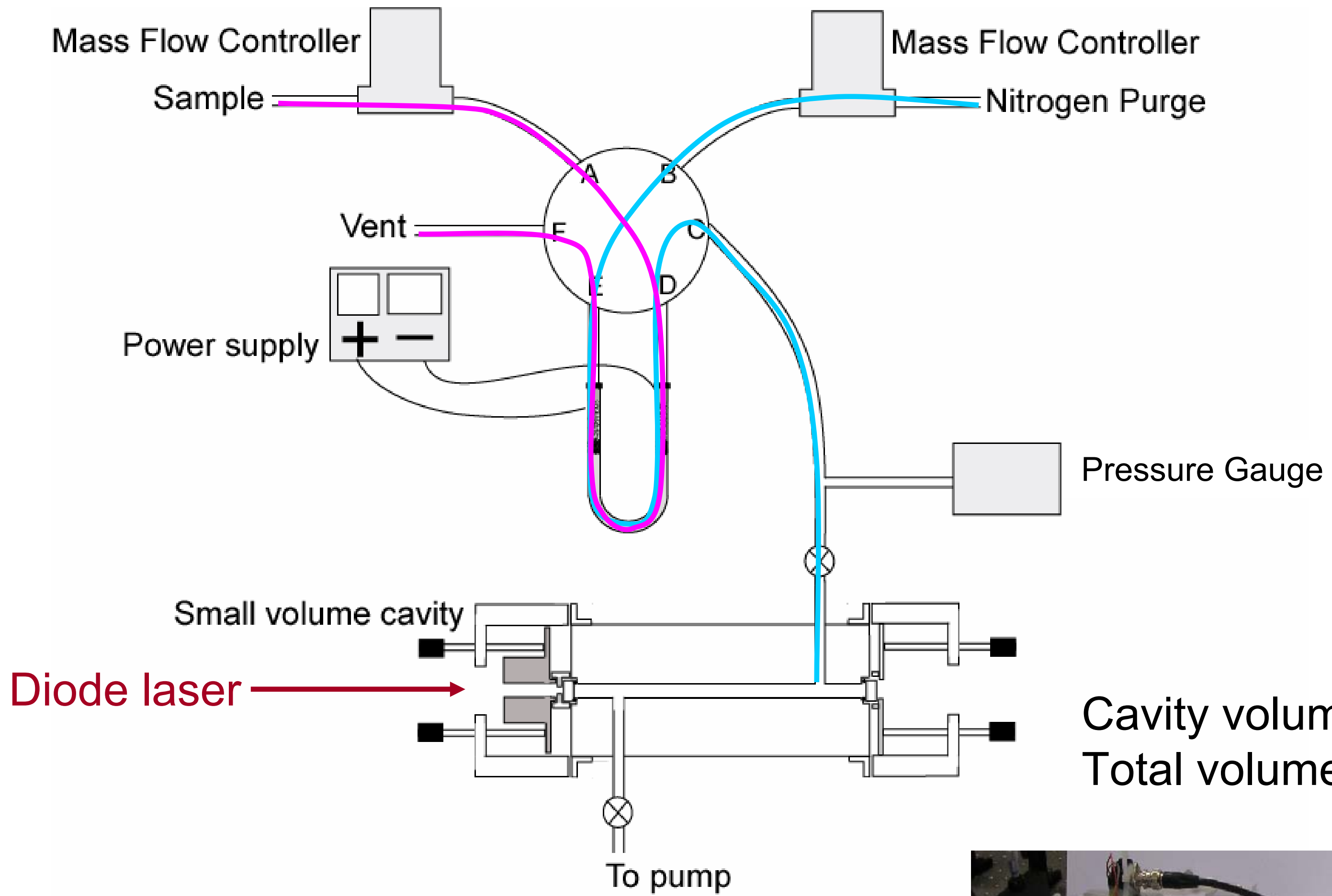
- VOCs emitted from anthropogenic and natural sources
- Can contribute to pollution events in troposphere and aerosol formation
- Implicated in many acute health issues (e.g. 1,3-butadiene is carcinogenic)
- Detect VOCs via near-IR vibrational overtones or combination bands.
- Detection limits can be a few ppbv for small VOCs.
- Pressure broadening can degrade sensitivity.





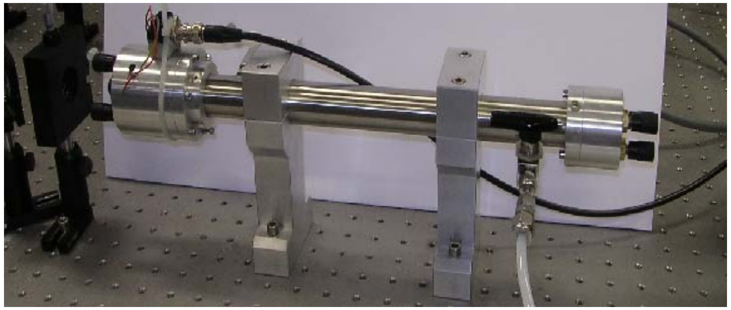
B.L. Fawcett *et al.*, Analyst **128**, 960 (2003)

Pre-concentration to access the ppb and ppt range



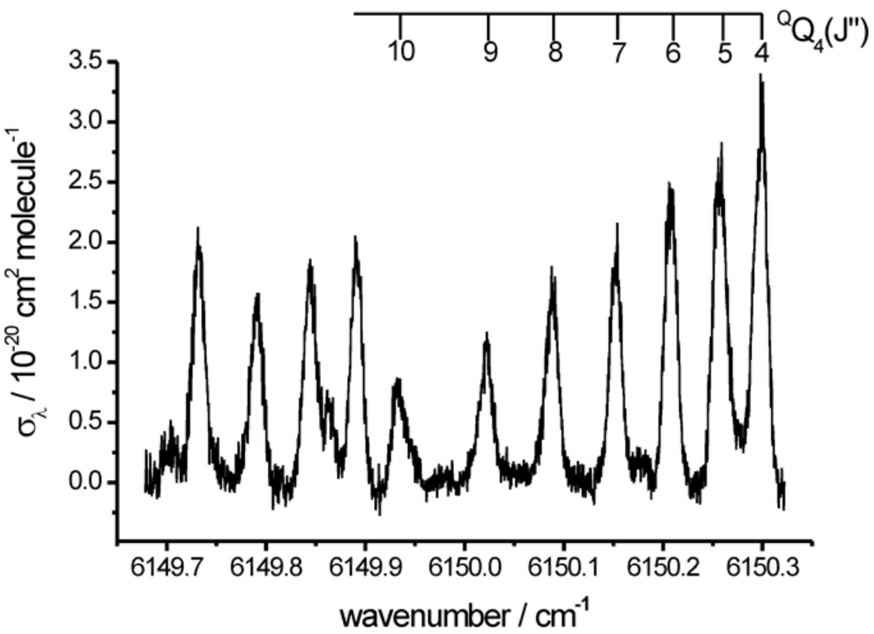
Cavity volume = 6 cm^3
Total volume = 29.5 cm^3

- Quantitative trace detection of VOCs
- No GC separation required



Ethene in a multi-component standard

Measuring ethene in a standard (NPL) sample containing 27 different hydrocarbons with mixing ratios ranging from 5 – 64 ppbv.

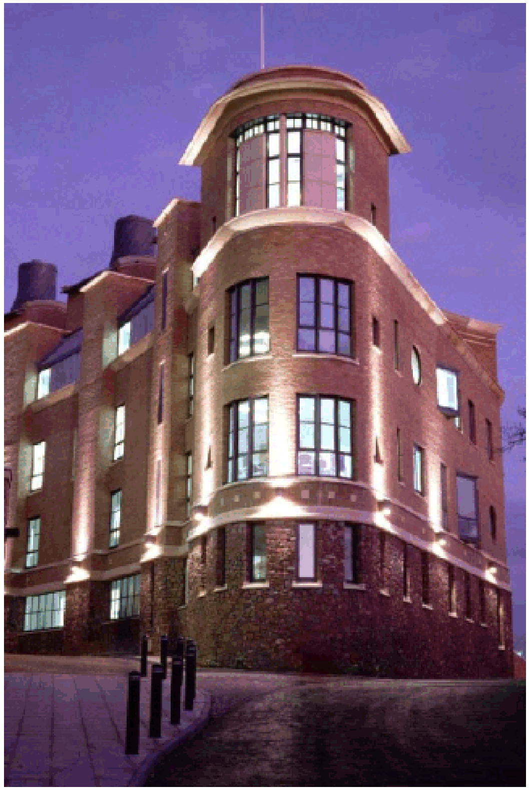


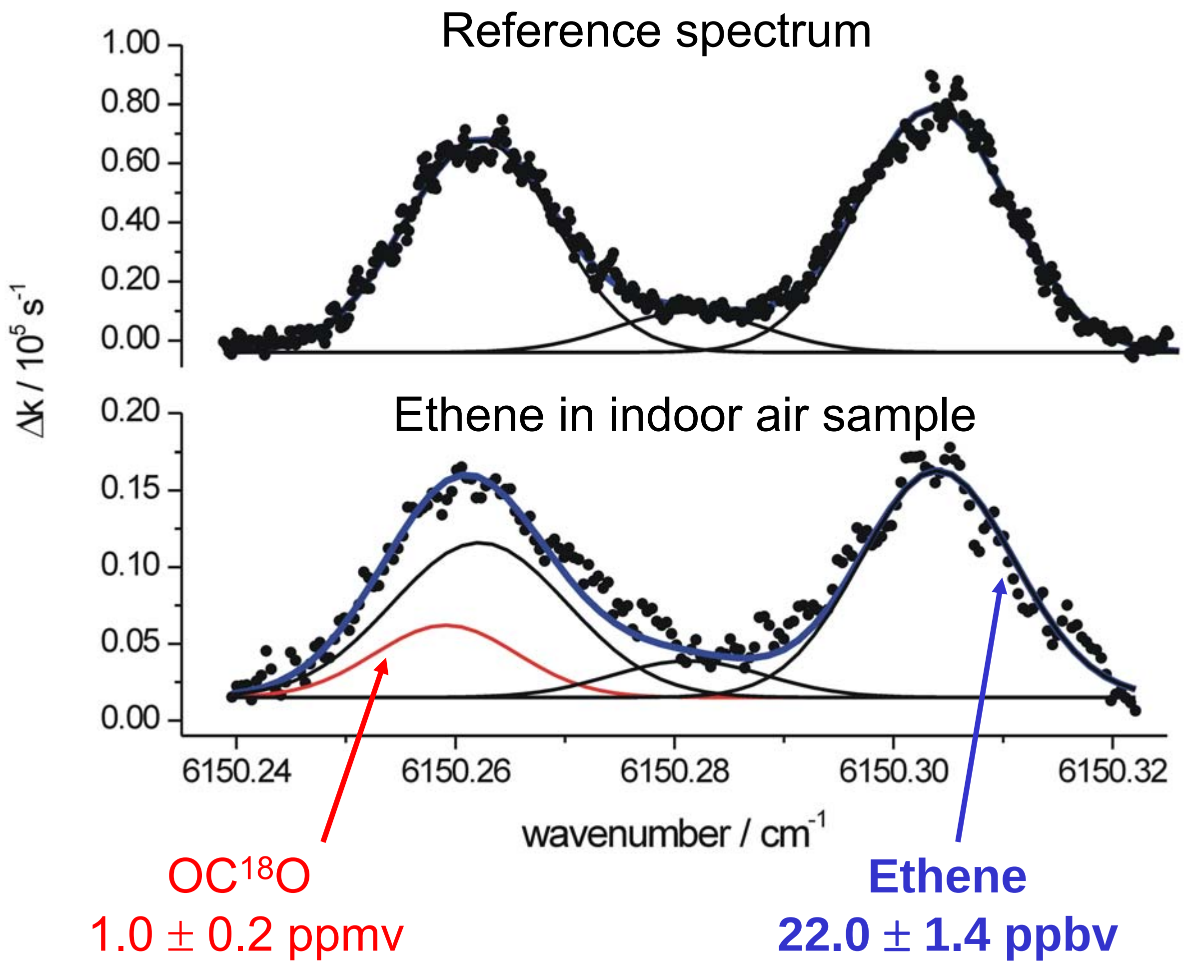
Ethene $\nu_5 + \nu_9$ band

Sample	Peak Area / s^{-1} cm^{-1}	Mixing ratio / ppbv
1	240.8 ± 5.4	20.39 ± 0.41
2	236.8 ± 7.2	20.05 ± 0.61
3	240.3 ± 5.9	20.34 ± 0.51
Mean		**20.26 ± 0.89**

19.1 ppbv ethene in NPL standard

Ethene in Bristol air





Ethene in outdoor air

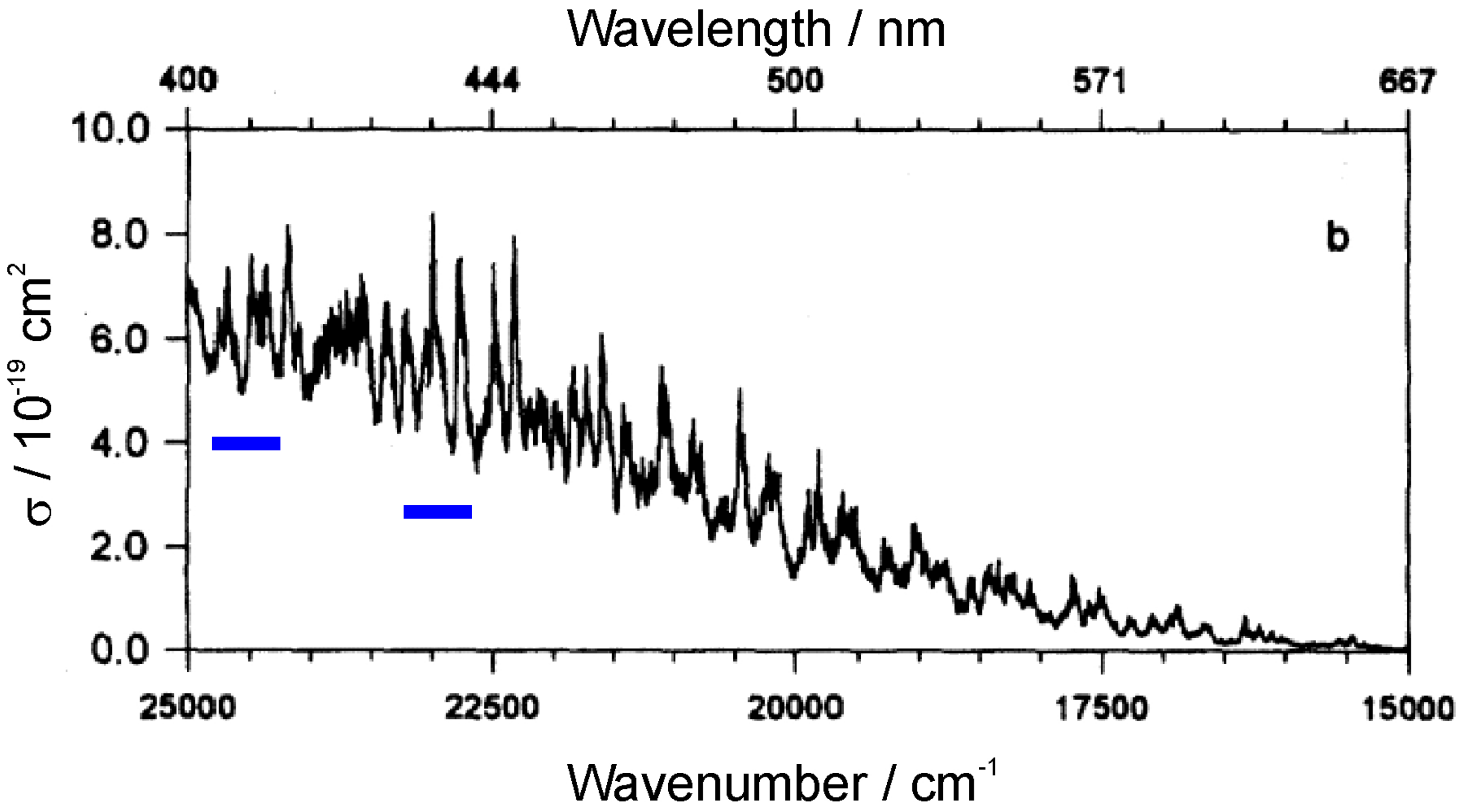
5.8 ± 0.3 ppbv

Trap contains MS 5A

A.M. Parkes *et al.*, Anal. Chem. **76**, 7329 (2004)

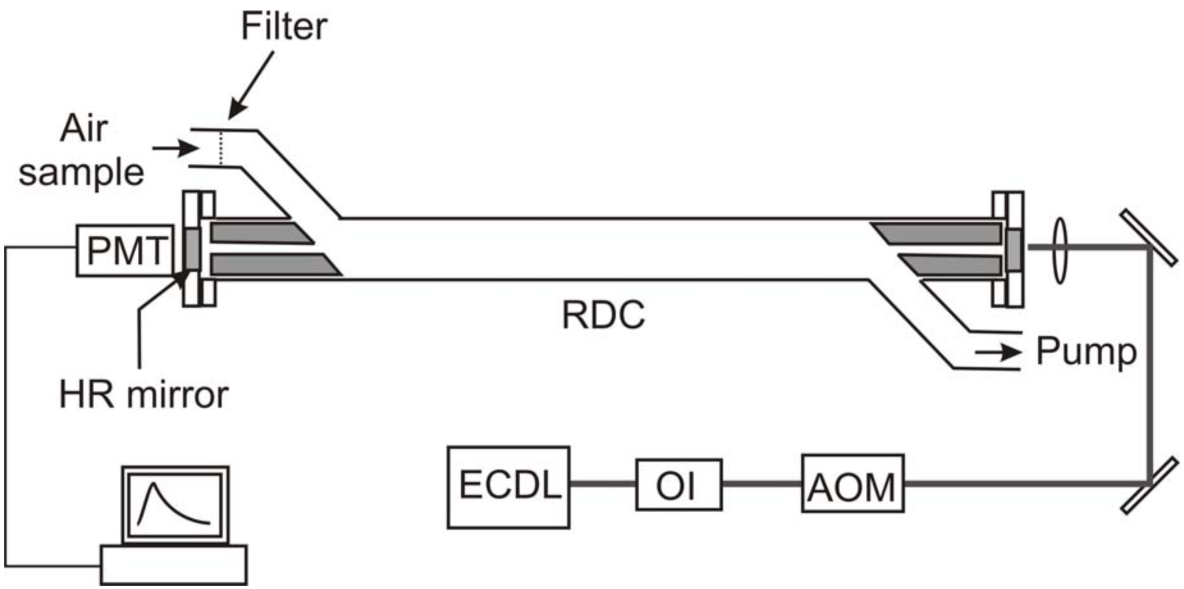
Blue diode laser CRDS detection of atmospheric NO_2

- NO_2 forms in polluted troposphere and produces ozone.
- $[NO_2] < 100$ ppt in remote sites and ≥ 5 ppb in urban air.



M. Mazurenka *et al.*, Chem. Phys. Lett. **367**, 1 (2003) and Appl. Phys. B **81**, 135 (2005)

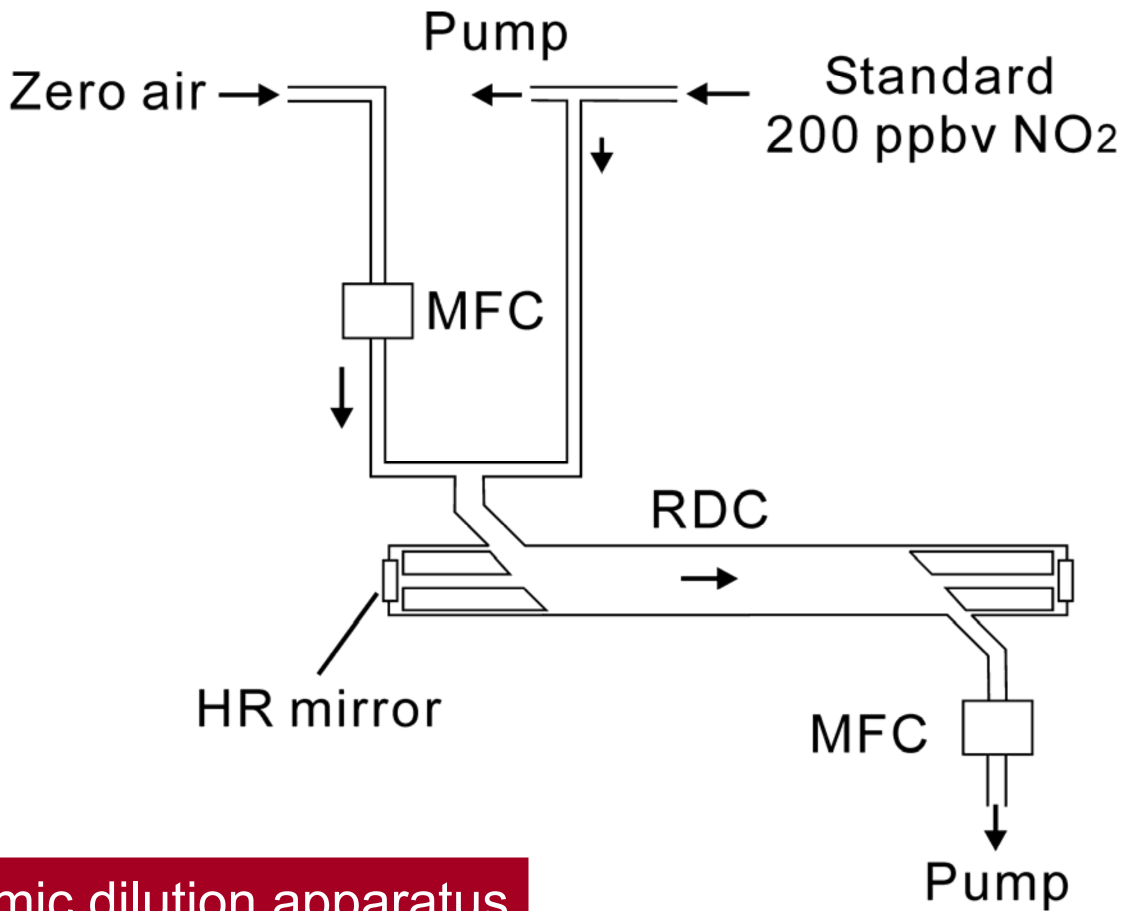
Trace detection of NO_2 in air



- Ring-down system has τ = 32.5 μs
- Detection limit for NO_2 is ~ 100 pptv (in ~ 50 s)
- 1 μm teflon membrane filter in inlet to remove aerosols
- Pass air through coil of stainless steel tube to obtain NO_2 free reference

R. Wada *et al*., Analyst **130**, 1595 (2005)

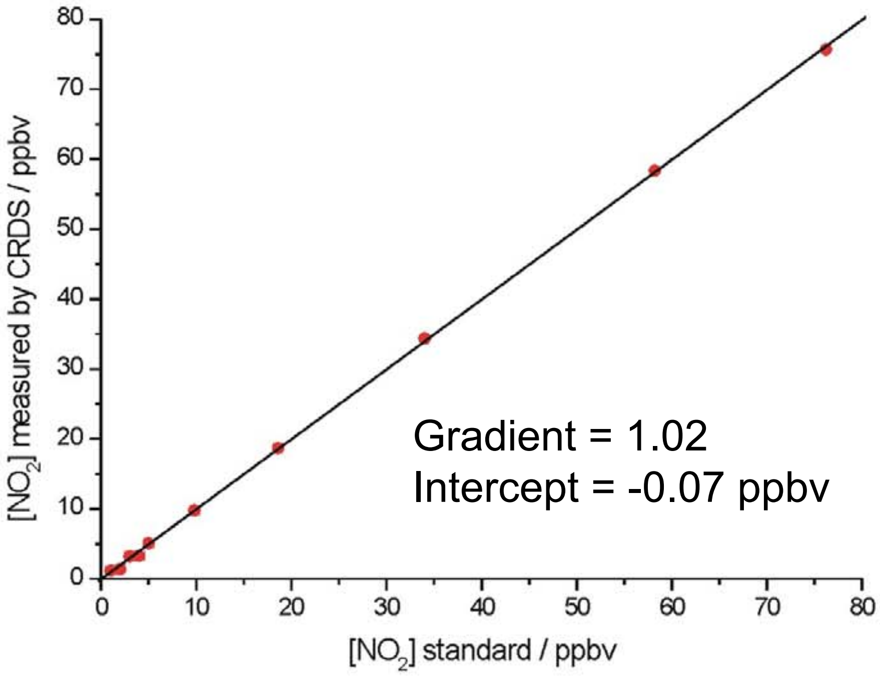
Tests of instrument performance down to 0.2 ppbv

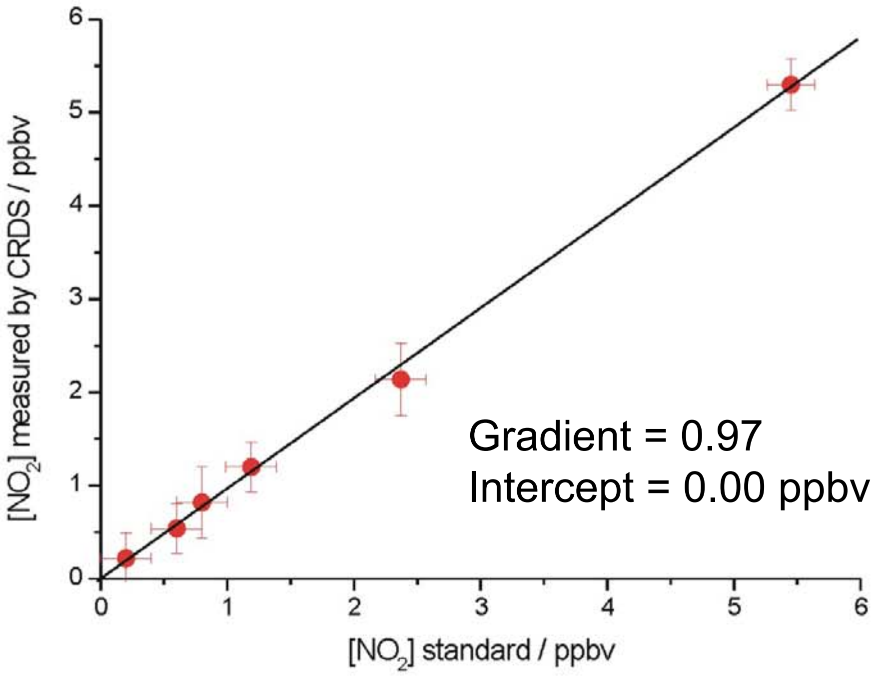


Dynamic dilution apparatus

R. Wada *et al*., Analyst **130**, 1595 (2005)

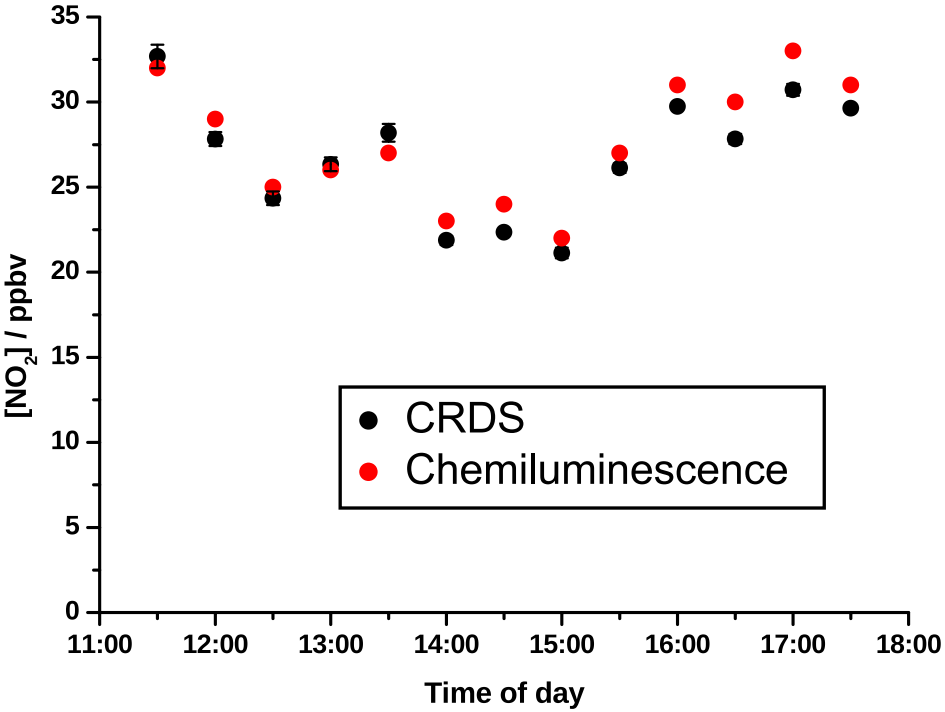
Trace detection of NO_2 at 410 nm – tests of dynamic range

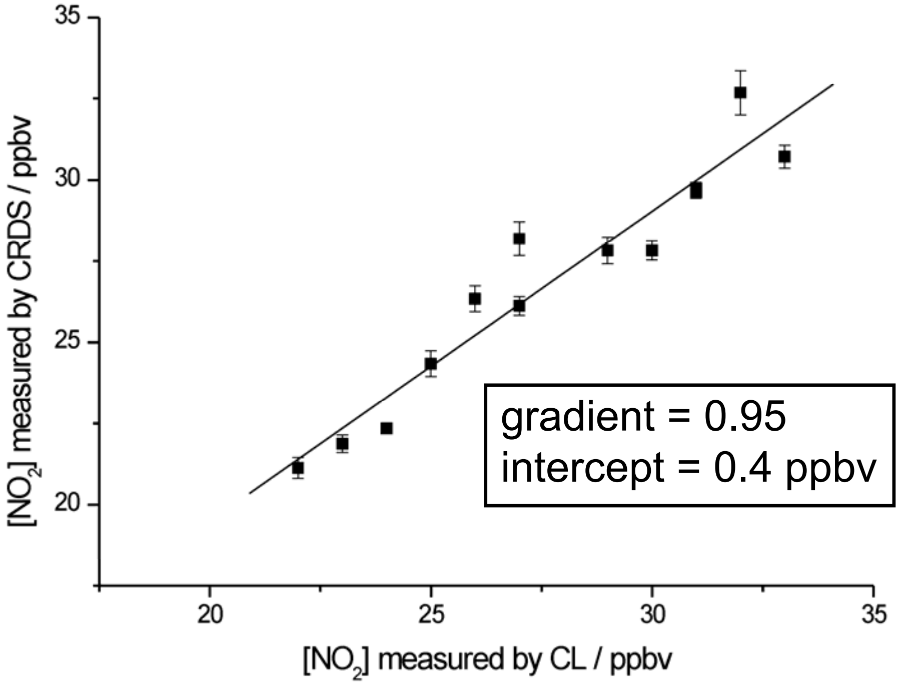




NO_2 in Bristol air – comparison of CRDS and chemiluminescence

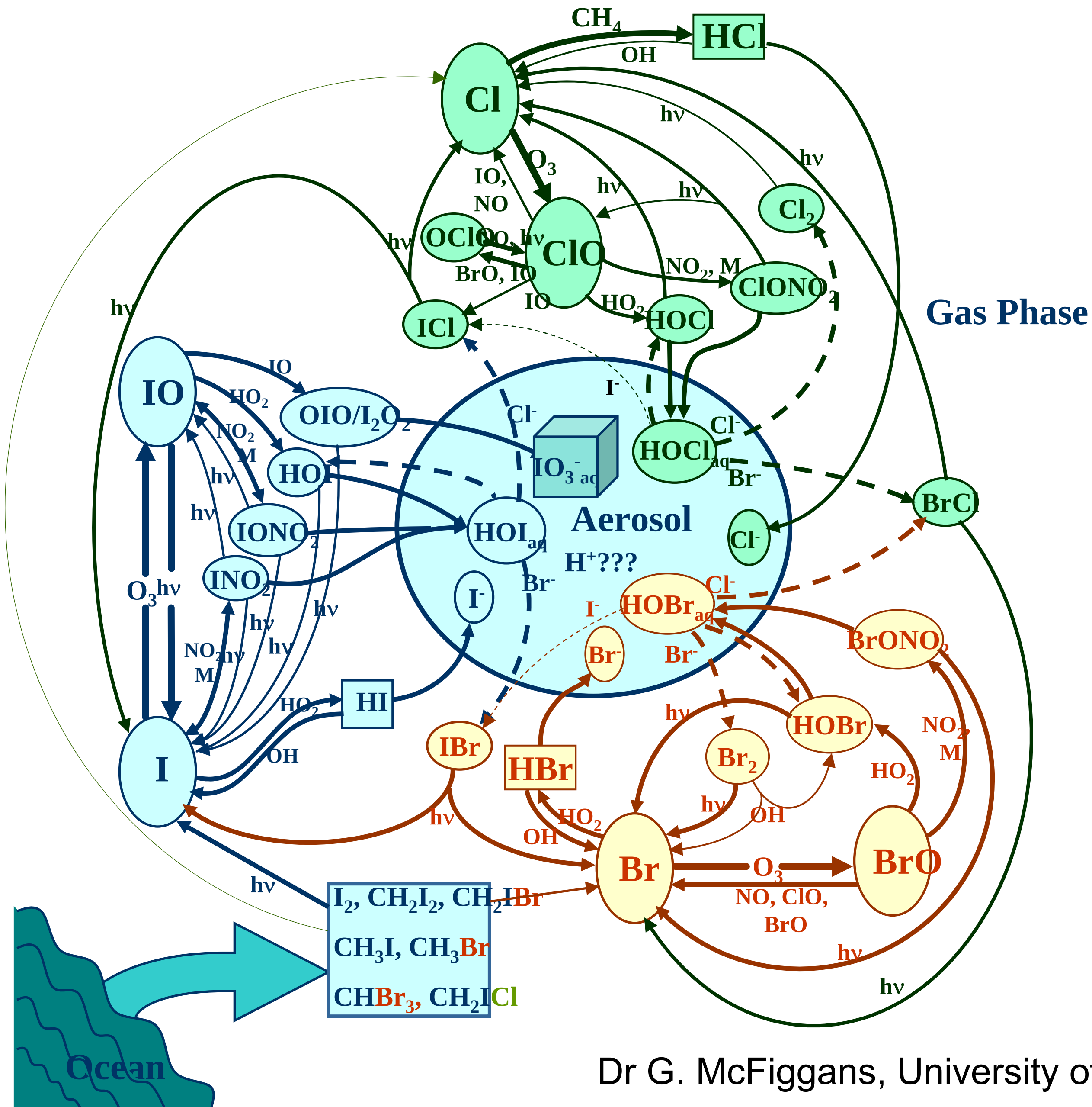
NO_2 in Bristol air on 25 March 2005





R. Wada *et al*., Analyst **130**, 1595 (2005)

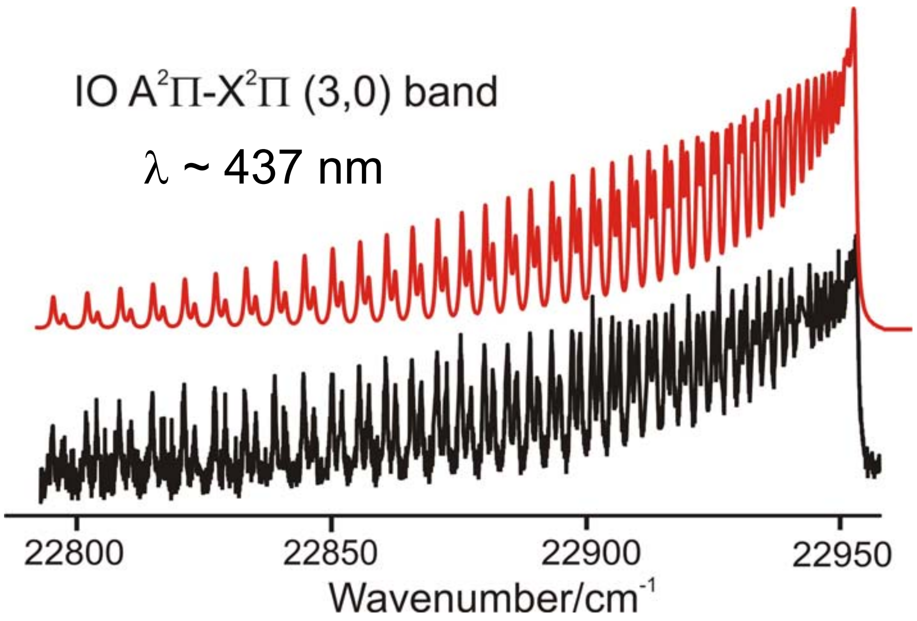
Halogen chemistry in the marine boundary layer

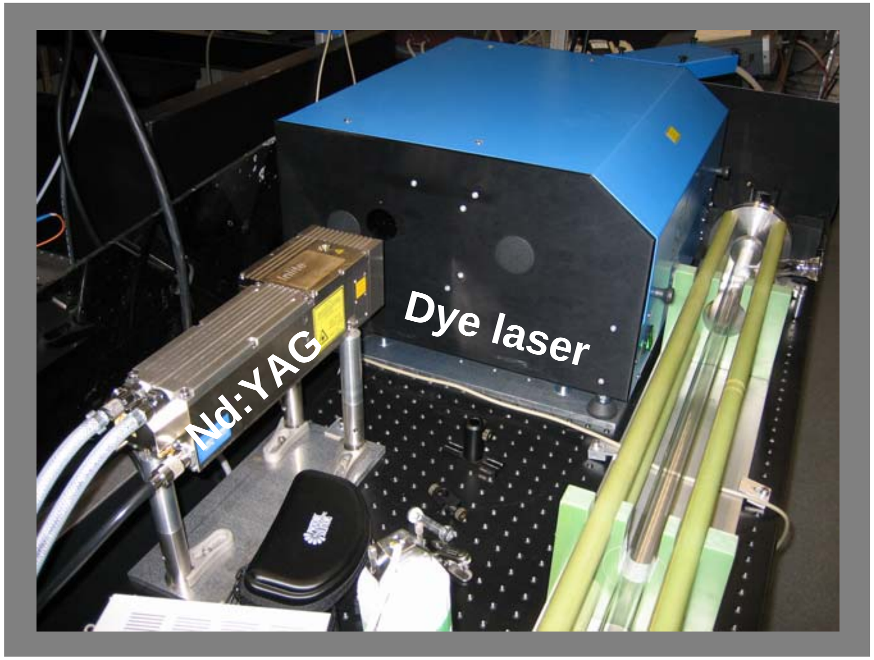


Dr G. McFiggans, University of Manchester

IO detection – work in progress

- IO (1–6 ppt) identified in MBL at coastal sites by long-path (4 km) DOAS
  B. Alicke *et al*., Nature **397**, 572, 1999.
- Localized mixing ratios may be **~ 60 - 100 pptv**.





- For a 32 μs ring-down time, **$[IO]_{min}$ = 7 x 10^7 cm^{-3} (3 pptv)**.
- Wall losses in ring-down cell must be quantified – or use open path cell.

Reactive Halogens in the Marine Boundary Layer – September 2006

Pulsed laser CRDS apparatus deployed in Roscoff to measure atmospheric I_2 and IO.

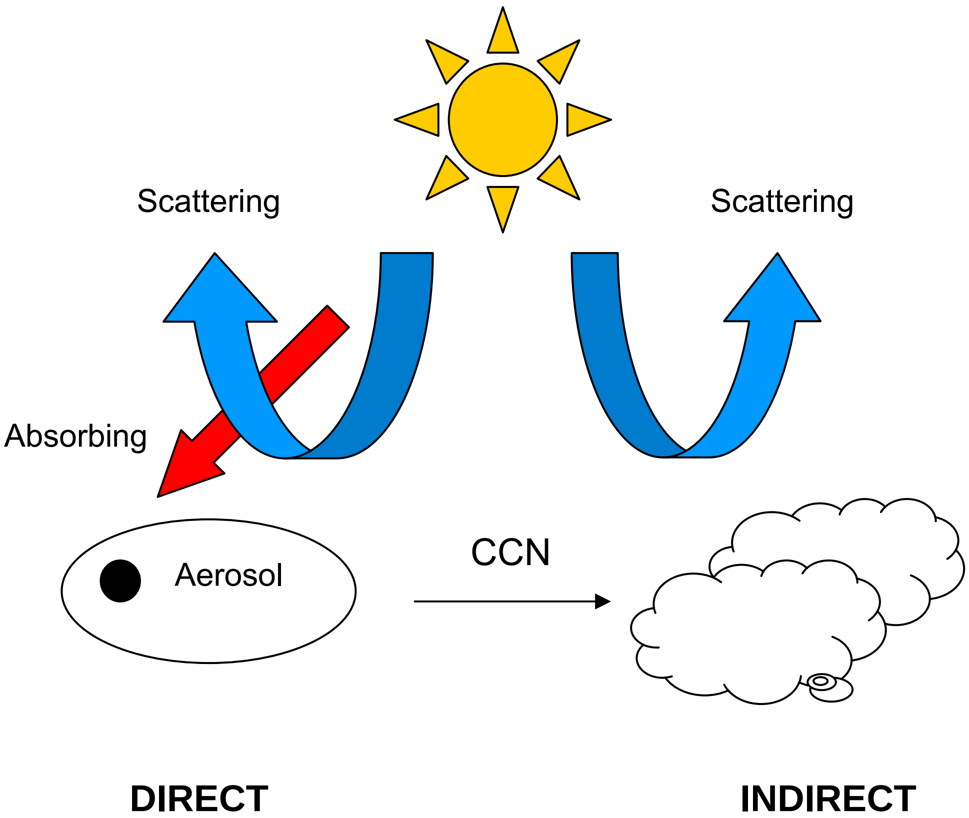
Intercomparison with DOAS and LIF/FAGE instruments.

IO successfully measured by open path CRDS.

Peak IO concentrations occur before low tide.

Optical properties of atmospheric aerosol particles

- Aerosol particles have both **direct** and **indirect** effects on the radiative balance of the atmosphere.
- Uncertainties in their influence on radiative forcing remain large.



Atmospheric aerosols

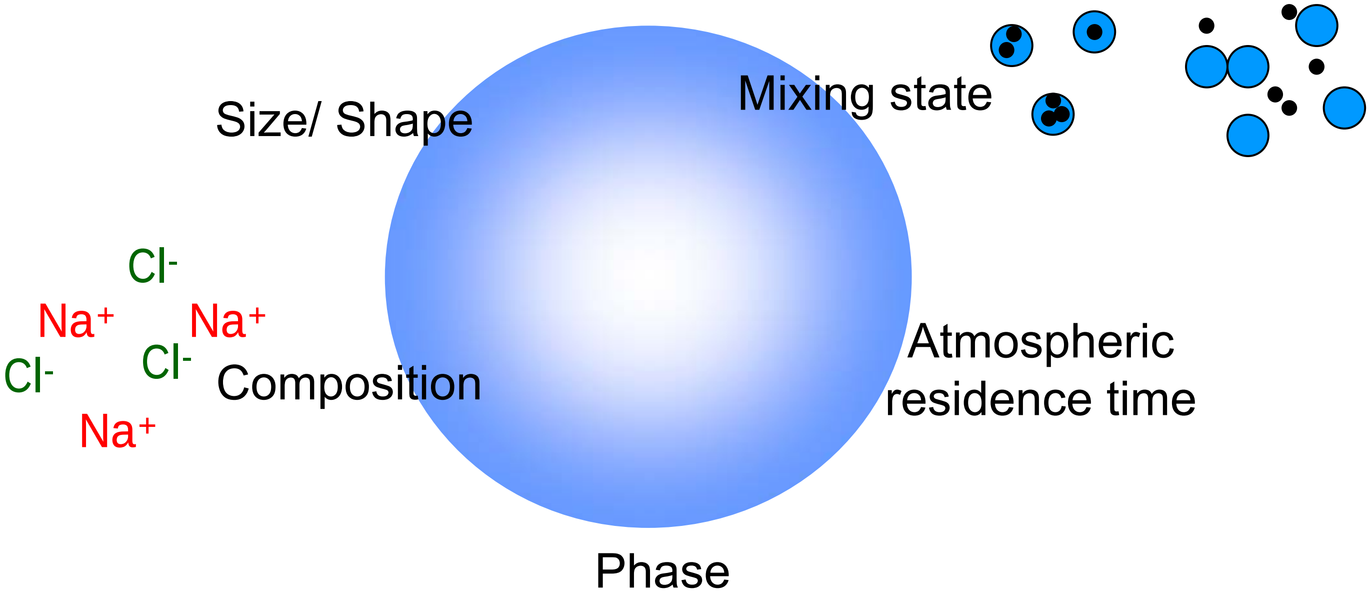
Aerosol particles in the atmosphere:

- Mineral dust
- Combustion (fossil fuels, biomass)
- Sulphuric acid
- Sea salt
- Oxidation of organic molecules

etc.

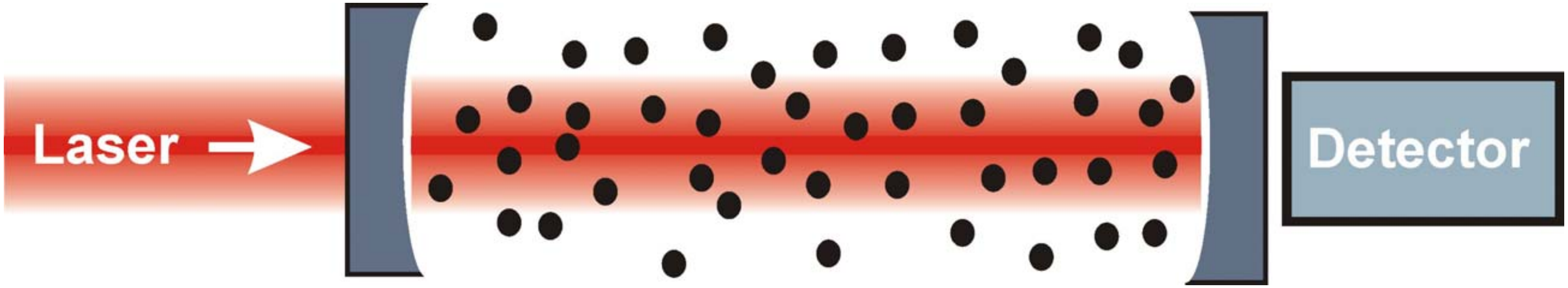
Scattering and absorption contribute to aerosol extinction:

$$\alpha = \alpha_{scat} + \alpha_{abs}$$



CRDS measurement of atmospheric aerosol extinction

Prior work by **Atkinson** (Portland), **Ravishankara** (NOAA), **Strawa** (NASA-Ames), **Arnott** (Nevada), **Winefordner** (Florida) and others to measure atmospheric aerosol extinction by CRDS.

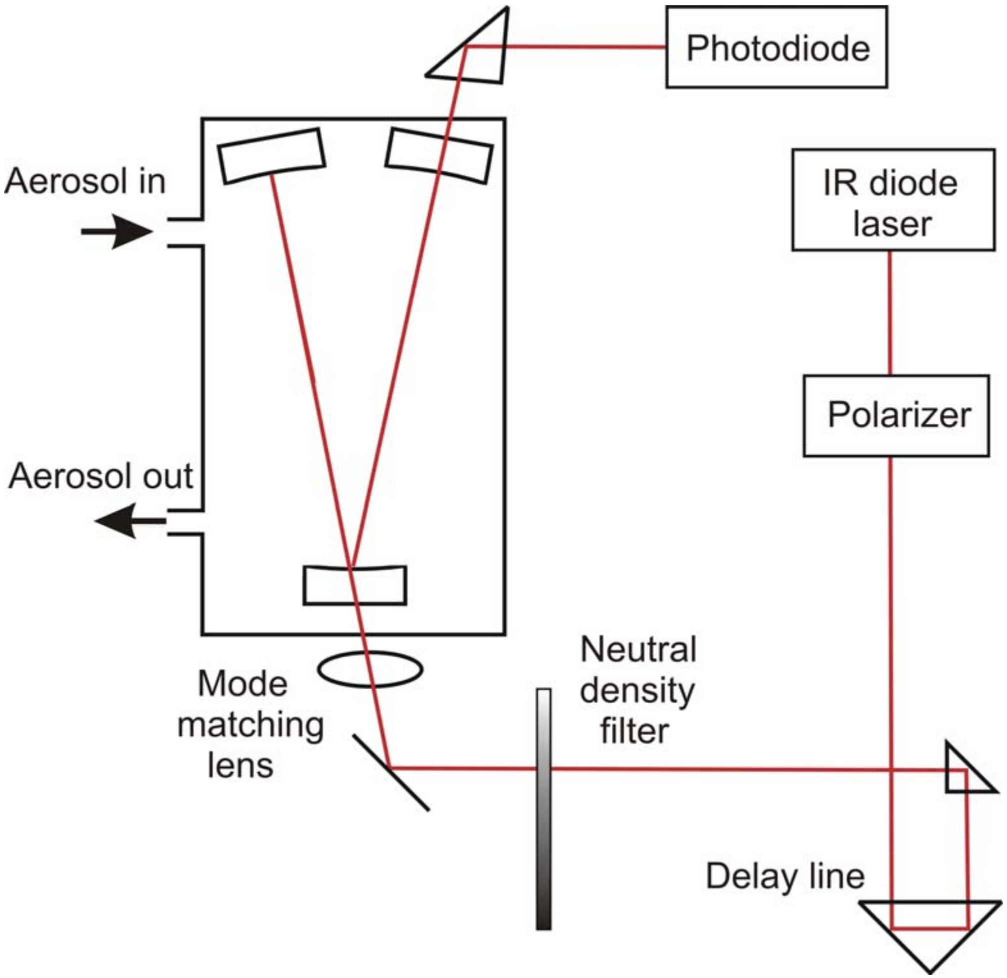


- Statistical fluctuations associated with low particle number densities can dominate the uncertainty in the measurement of extinction.

- Analysis of the Poisson statistics of cavity losses to extract information on the aerosol particles, e.g.,

  Pettersson *et al*., *J. Aerosol Sci*. **35**, 995 (2004)
  Bulatov *et al*., *Anal. Bioanal. Chem.* **384**, 155 (2006)

Optical feedback CRDS for rapid aerosol measurements



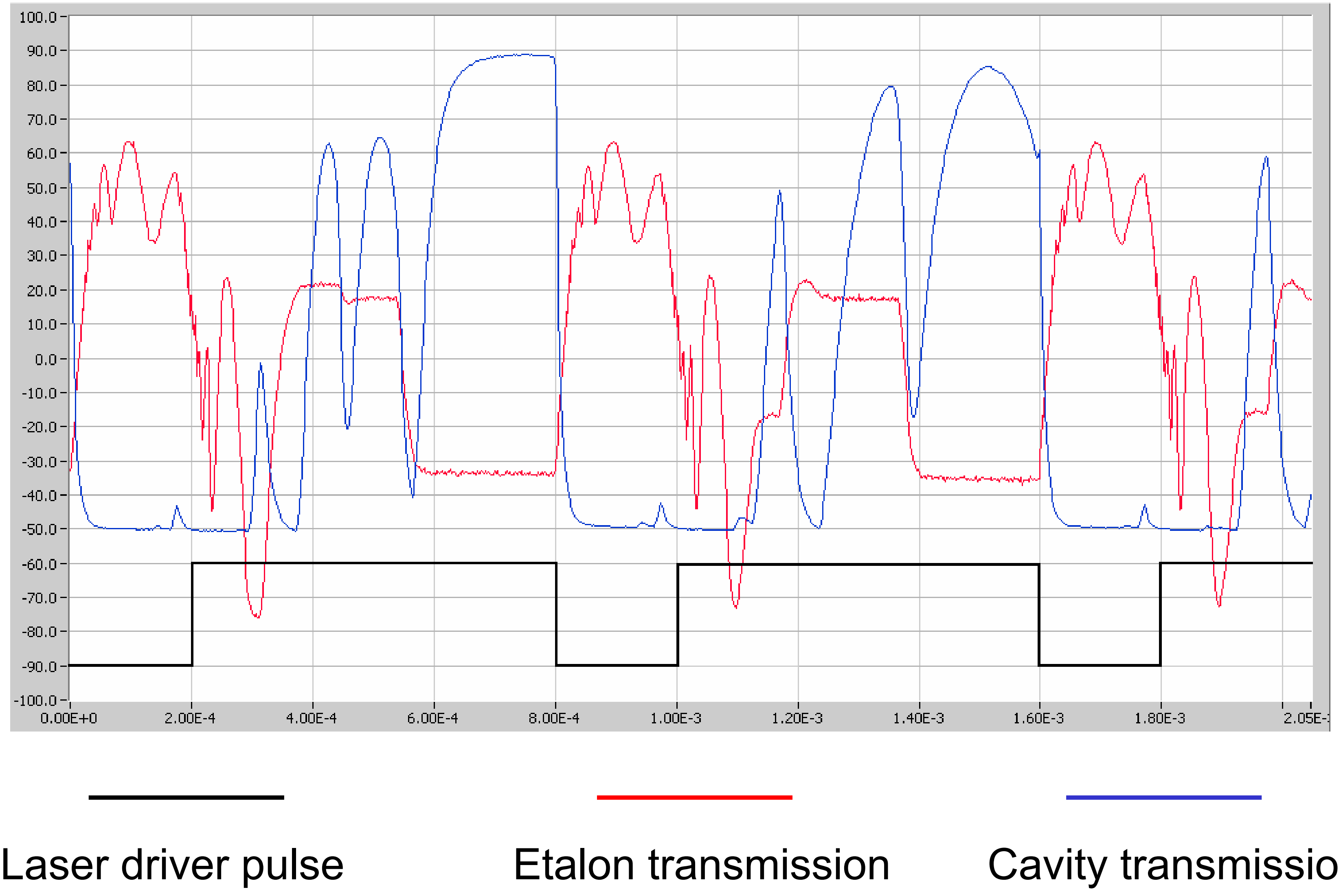
OF-CRDS first demonstrated by Morville *et al*., Appl. Phys. B **78**, 465 (2004)

Feedback of light from cavity forces laser into resonance with cavity mode and narrows laser bandwidth.

Rapid and efficient build-up of light intensity in cavity.

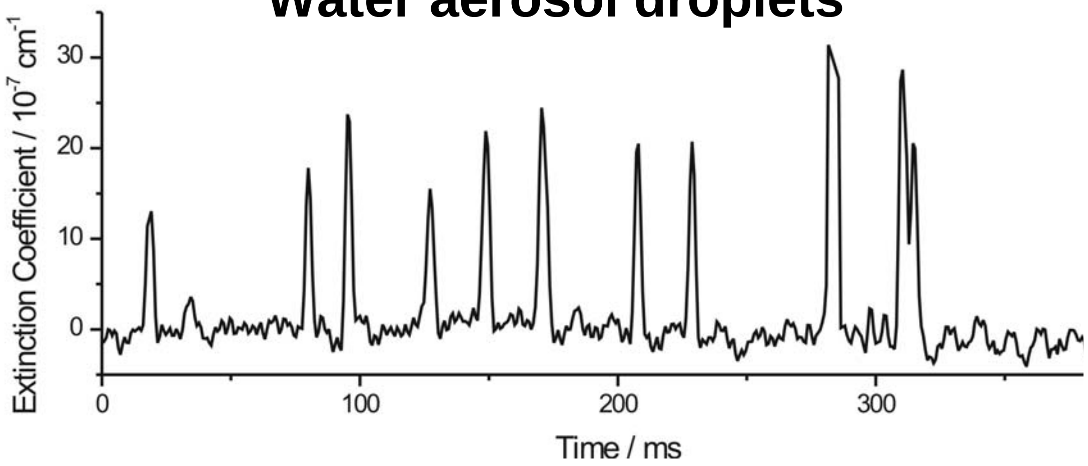
Make measurements at >1 kHz.

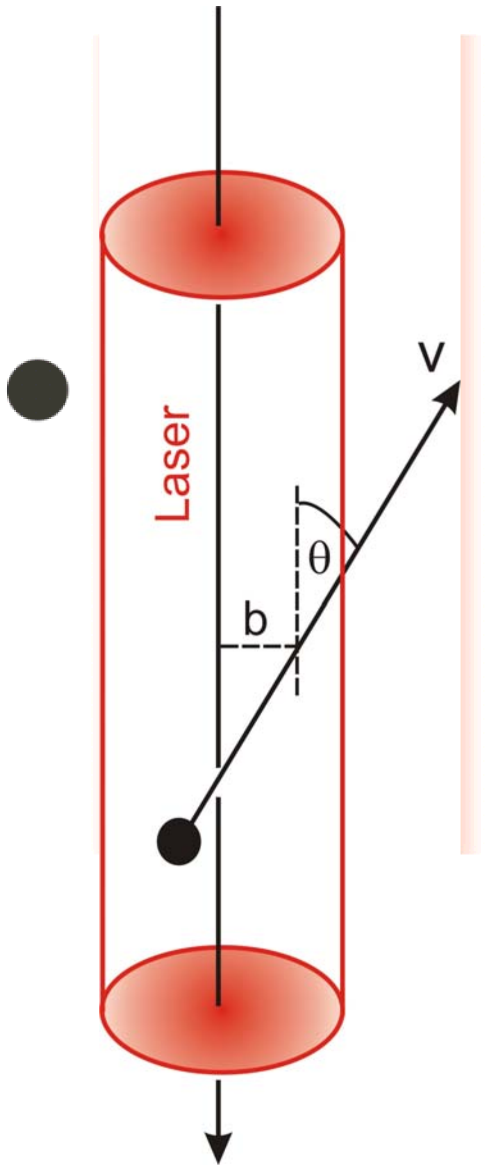
OF-CRDS measurement of atmospheric aerosol extinction



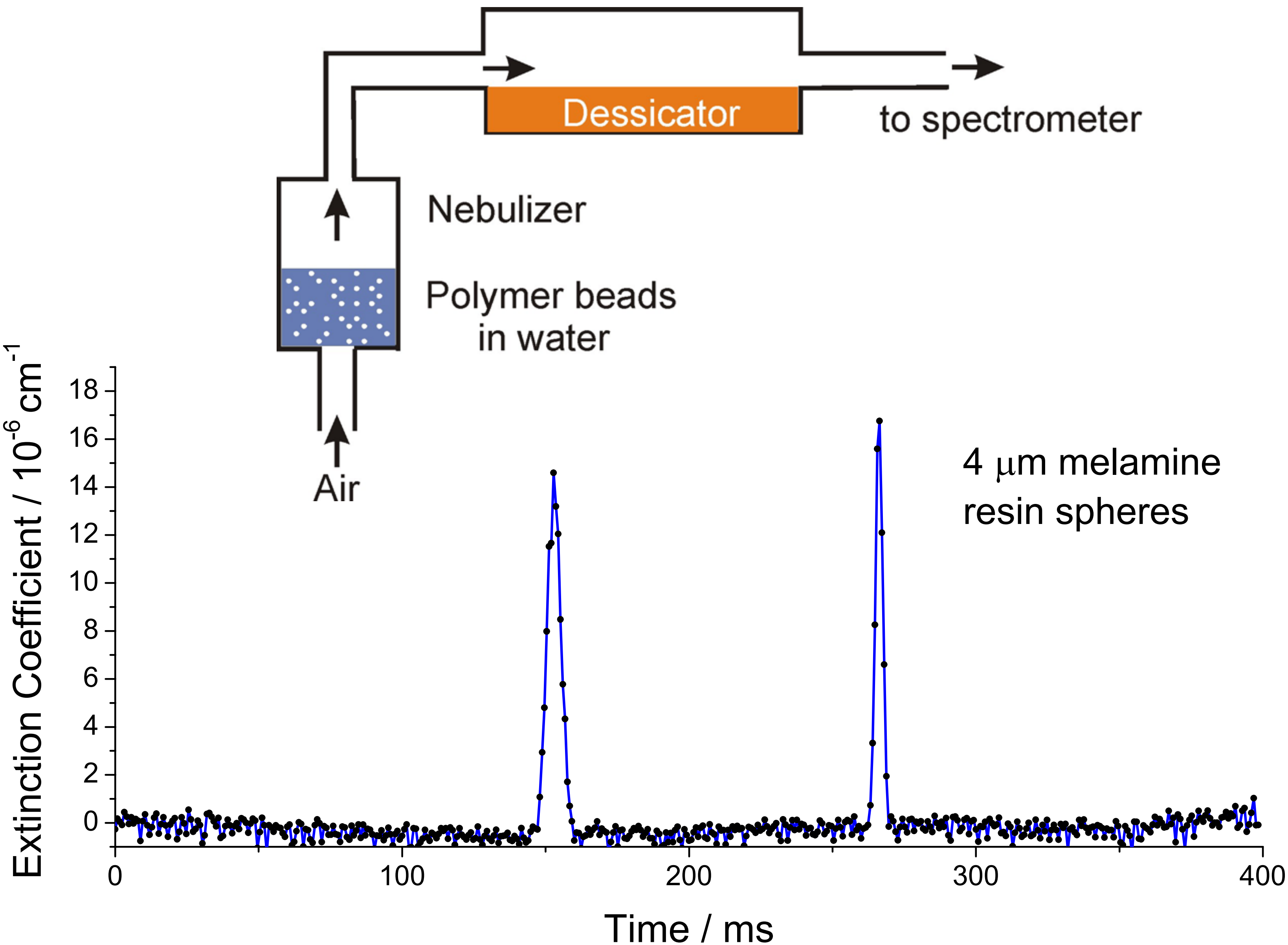
OF-CRDS of single aerosol particles

Water aerosol droplets

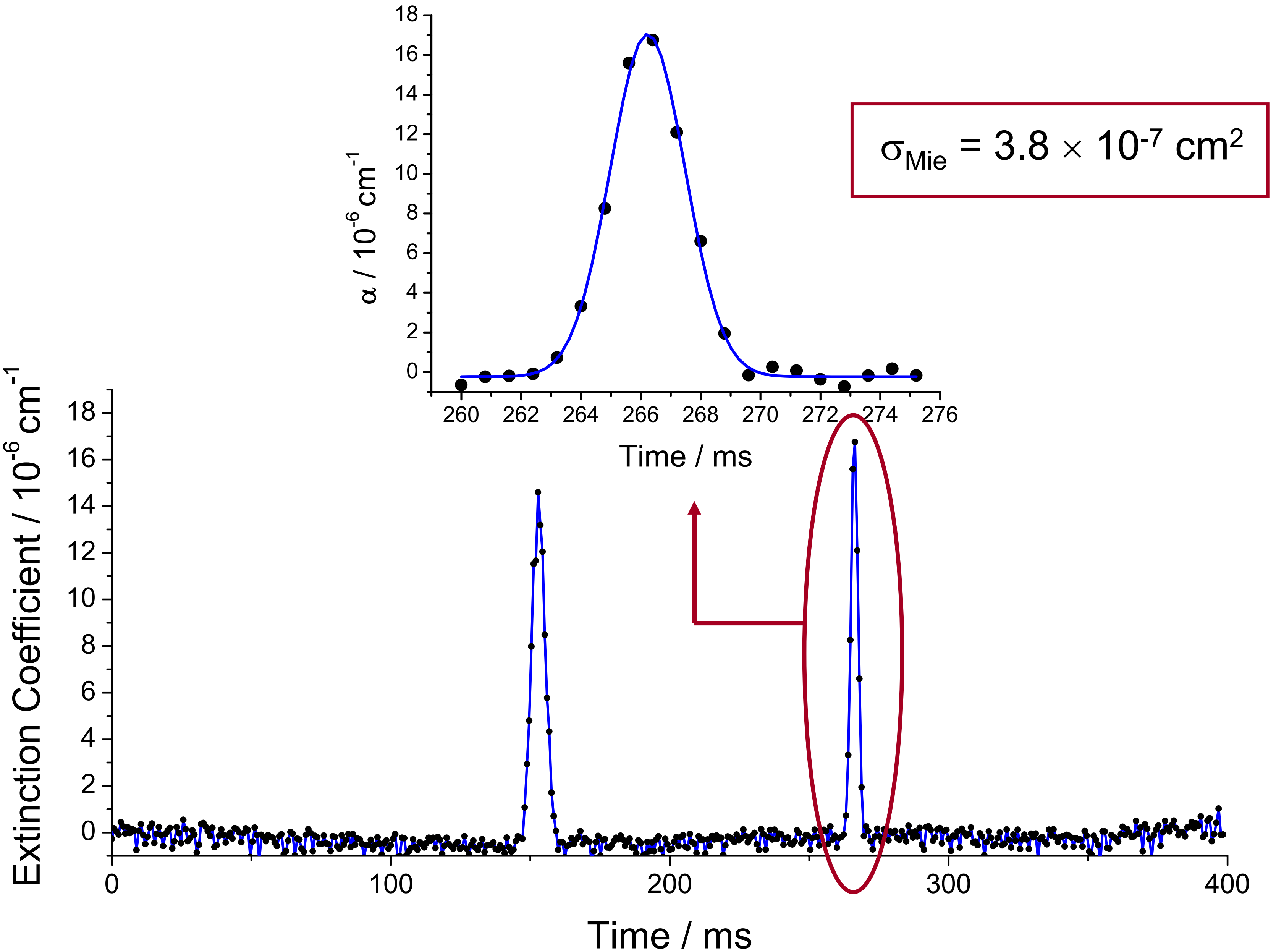




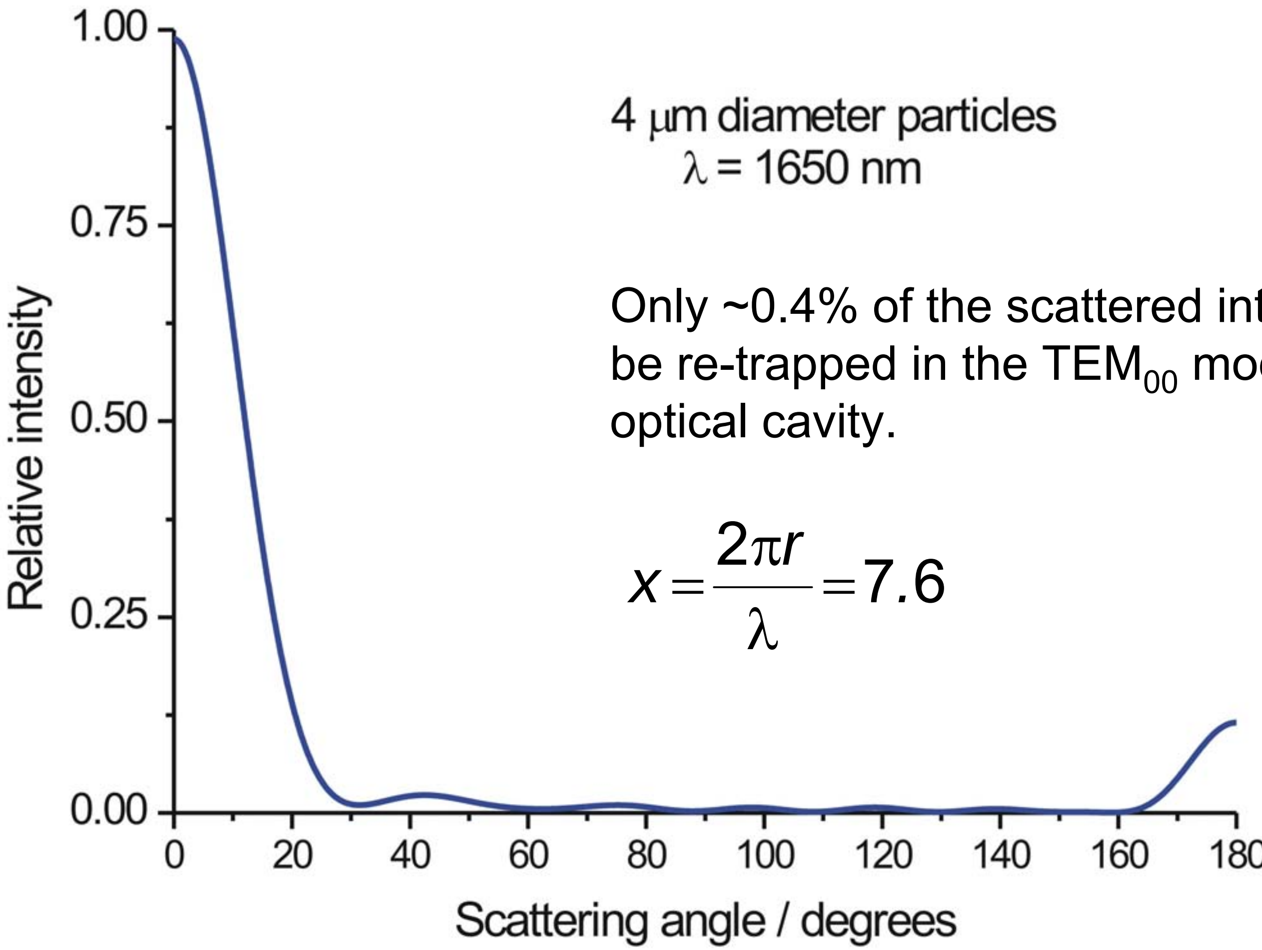
OF-CRDS of single aerosol particles



OF-CRDS of single aerosol particles



Differential scattering by aerosol particles



Only ~0.4% of the scattered intensity will be re-trapped in the TEM_{00} mode of the optical cavity.

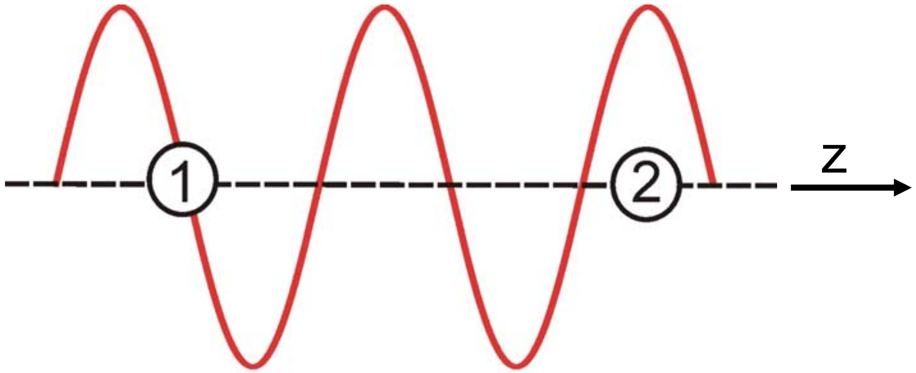
$$x = \frac{2\pi r}{\lambda} = 7.6$$

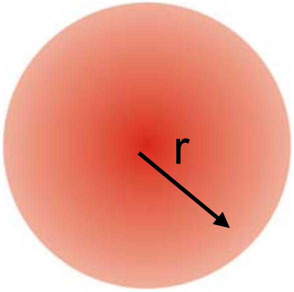
- Much sharper forward scatter for $r \approx 28$ μm particles at $\lambda = 560$ nm ($x \approx 300$).
- Severe underestimation of extinction cross sections.

CRDS measurement of aerosol extinction

Cavity losses depend on location of particle(s) in the laser beam:

- *z*-dependence of **standing** wave for cw cavity excitation (effects of phase).
- *r*-dependence of intensity of Gaussian beam TEM_{00} mode.





Treatment requires:

- Modified Mie theory.
- Effects of averaging from motion of particle during RD measurement.
- Poisson statistics for particles in **Gaussian** beam.
- Effects of averaging of many particles in cavity.

Outcomes:

- Scattering for single particles does depend on phase and particle location.
- Averaging effects wash out the phase dependence.

Conclusions

- Cavity enhanced spectroscopy techniques provide the sensitivity necessary for quantitative measurements of a variety of trace atmospheric constituents (NO_3, NO_2, small VOCs, IO *etc*.).

- Relatively low cost diode lasers can be used as the light source.

- Wavelength coverage of present diode lasers is restrictive.

- Cavity enhanced methods can be used to study the extinction of single aerosol particles or ensembles of aerosols.

- Separation of absorption and scattering losses remains a challenge.

Acknowledgements

VOC measurements

Ruth Lindley
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Aerosol measurements

Dr Johanna Miller
Tim Butler

HCHO photochemistry

Carina Smith
Dr Francis Pope
Dr Anne-Louise Holloway

EPSRC
Engineering and Physical Sciences Research Council

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