

Optical remote sensing air monitoring techniques

Michael Yost, MS, PhD
Optical Remote Sensing Lab
University of Washington
Seattle, WA

Outline

- Introduction
- Techniques
 - Open Path Fourier Transform IR
OP-FTIR
 - Differential optical absorption spectroscopy
(DOAS)
- PM and open path sensing
- Discussion - summary

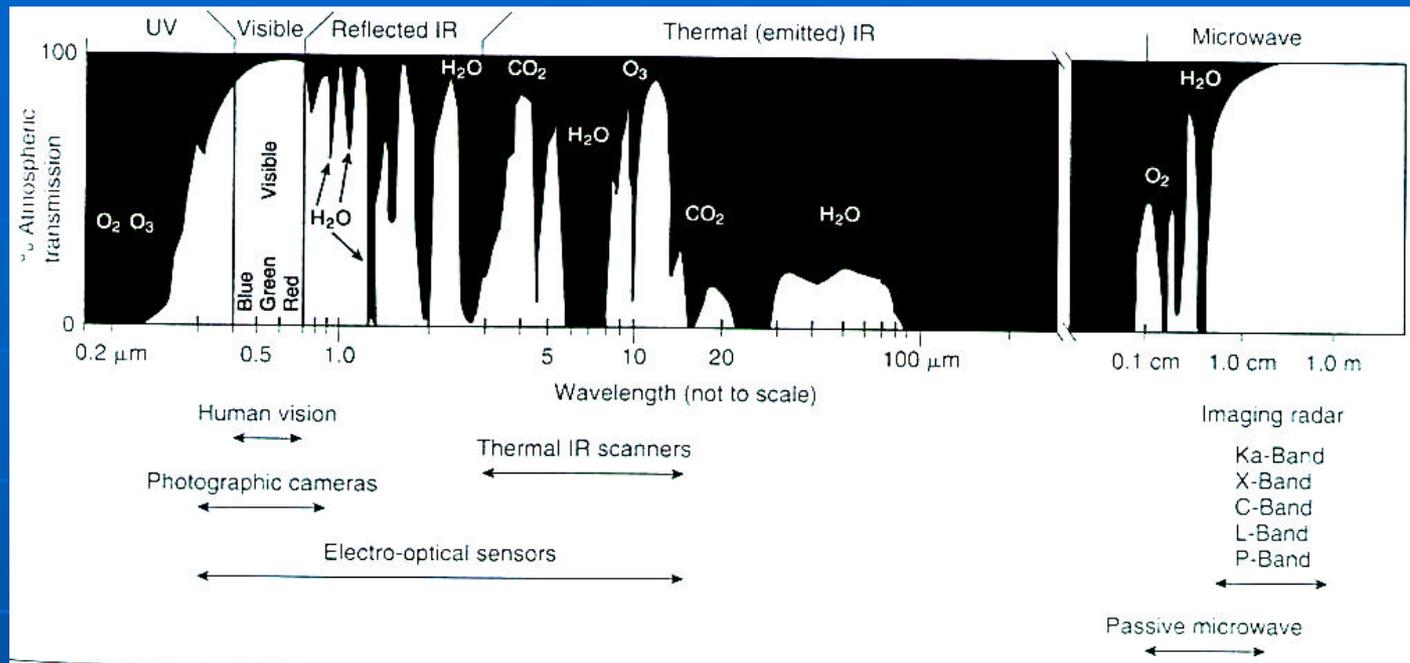
Introduction: Optical Remote Sensing

- Optical remote sensing
 - Includes visible and invisible light (UV & IR)
 - *In situ* measurements of a remote target or open path, usually in real time
 - Detects transmission, reflection, refraction or absorption of EM energy in the atmosphere
- Spectroscopic methods
 - Measures varying wavelengths (colors) of light to gather information on air components
 - Sensing can be passive or active
 - Can be broadband or narrow-band

Advantages with optical remote sensing

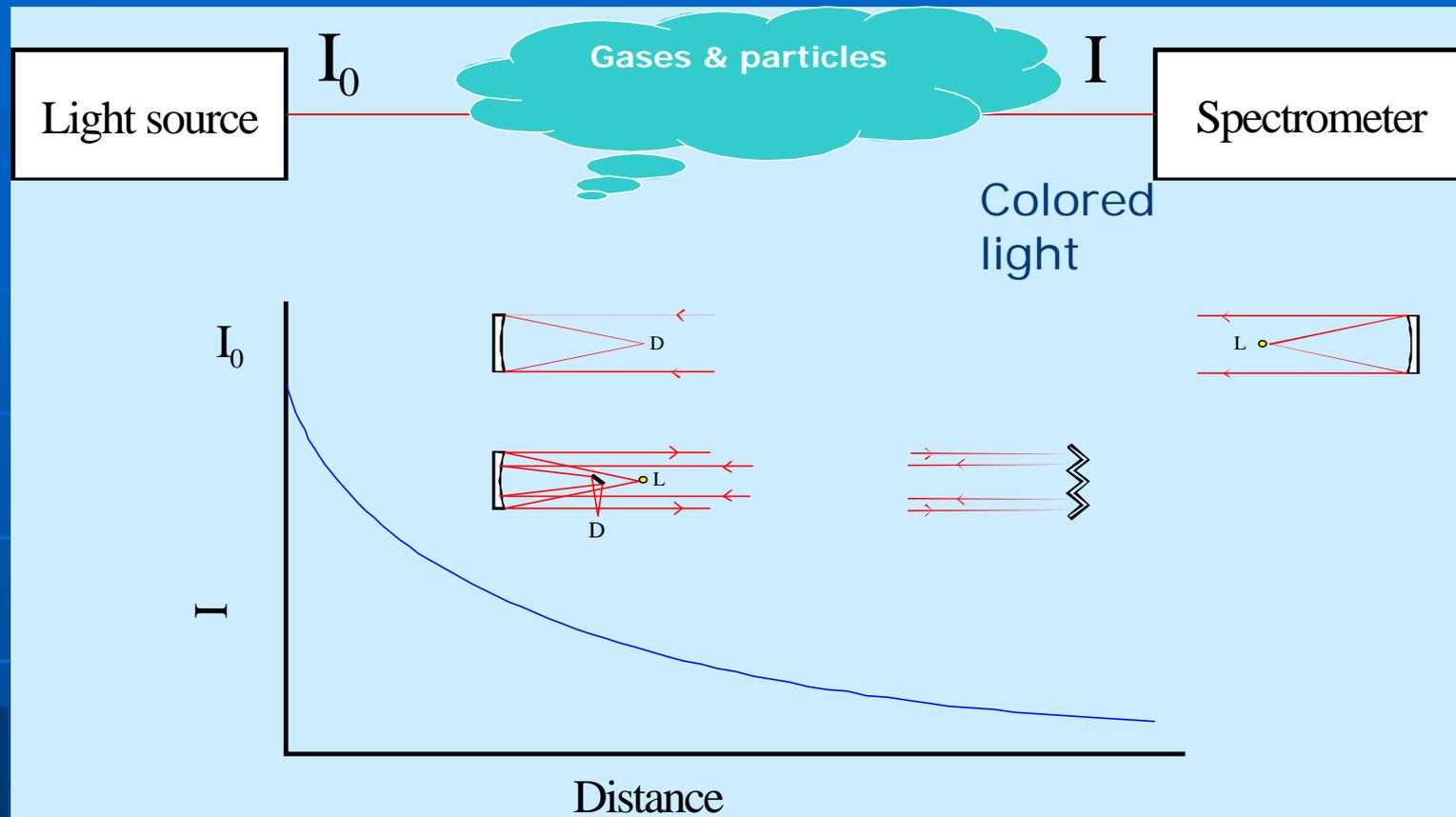
- Multi-component
- Line/area integrating
- Sensitive (ppb levels)
- Fast - time resolution
- Non-Invasive
- Easily automated

Atmospheric Transmission Windows



- 0.3 - 1.1μm UV, visible, near IR
- 1.5 - 1.8μm Mid IR
- 2.0 - 2.4μm Mid IR
- 3.0 - 5.0μm Mid IR
- 8.0 - 14.0μm Thermal IR (below O₃ layer)
- 10.5 - 12.5 Thermal IR

Absorption / Extinction spectroscopy



Atm. gases Rayleigh Mie

$$I(l) = I_0(l) \exp(-L(\sum (\mathbf{s}_i(l) c_i) + \mathbf{e}_R + \mathbf{e}_M))$$

Energy and Wavelength

- In the EM spectrum the Wavelength, Frequency and the Energy carried by the EM Field are directly connected

$$\lambda = c / \nu$$

$$\nu = \lambda^{-1}$$

$$E = h\nu$$

- The quantised energy carried by the beam of light is proportional to its Wavenumber (ν)
- Absorption of light occurs when the energy carried by one or more wavelengths of the light beam is correctly quantised to interact with the sample molecules

- Interaction can be from electron transitions, molecular vibrations and rotations, or band effects of free-carriers in solids
- For Mid-IR gas applications the vibrations, give a specific "fingerprint" for the molecules
- Elevated pressure causes collisional line broadening of IR features (@ 1Atm, FWHM > 0.25 cm⁻¹)

Vibrating Molecules – IR light

The diagram illustrates the interaction of IR light with two types of vibrating molecules. In the top section, a symmetrical diatomic molecule is shown with two red atoms. The vibrational wave function is labeled l_1 and the energy level is E_1 . The wave function is symmetric about the center, and the energy level is a single box. In the bottom section, a heteronuclear diatomic molecule is shown with a blue atom labeled (+) and a red atom labeled (-). The vibrational wave function is labeled l_2 and the energy level is E_2 . The wave function is asymmetric, and the energy level is a single box. A text box on the right explains that symmetrical molecules have no dipole and no absorption, while heteronuclear molecules have a changing dipole moment and absorb energy at $n = E_2 / h$.

Symmetrical Molecule:

No Dipole
No Absorption

Heteronuclear Molecule

$dm/dx \neq 0$
Absorbs Energy
at $n = E_2 / h$

ALL atomic gas or liquid species are IR transparent eg. He, Ne, Ar, Kr
ALL homonuclear diatomics are also IR transparent eg. H₂, N₂, O₂, F₂, Cl₂, Br₂ but not Heteronuclear HCl, CO₂, H₂O, CO, NO, CH₄

Quantification: How Much?

Transmission

$$\%T = (I/I_0)$$

Absorbance

$$A = -\log (I/I_0)$$

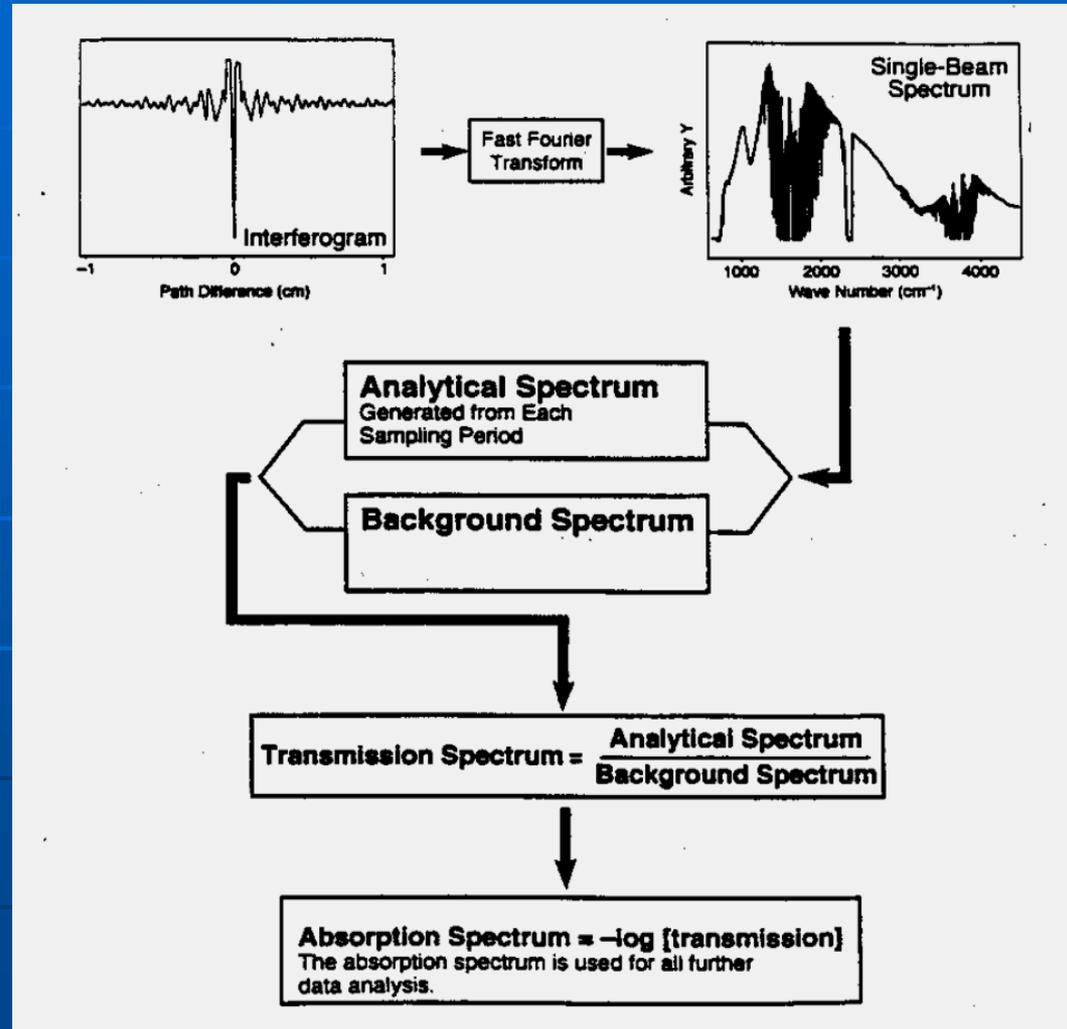
Absorbance = $f(\alpha, C, l)$ - in fact

$$A = \alpha Cl$$

Chosen to linearize the relationship between the spectrum response, pathlength and concentration of sample

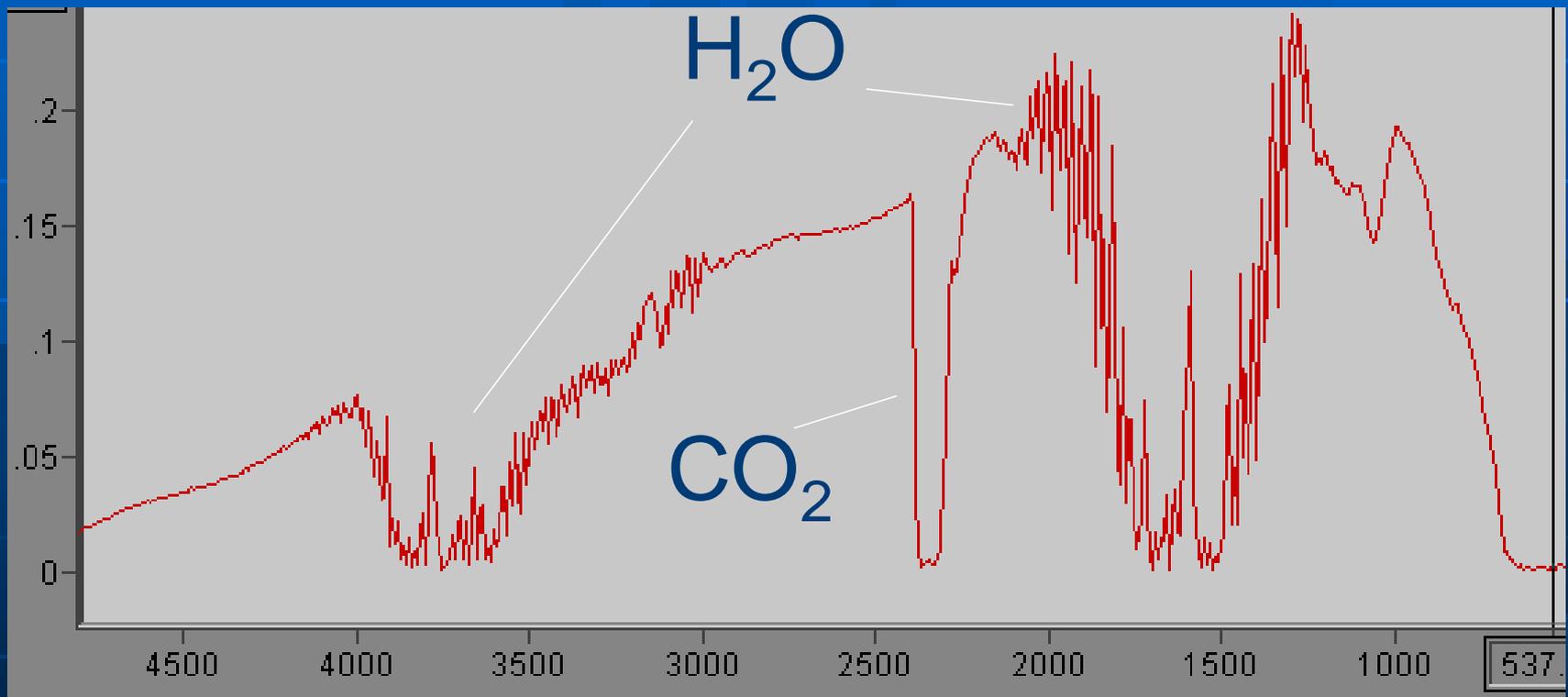
Flowchart of FTIR Data Analysis

- FFT (Interferogram) => Single beam spectrum
- Ratio Sample/Background & get Transmission spectrum
- Compute Absorbance
 $Abs = -\log(\%Trans.) = -aCL$
- CLS: linear regression (Beer-Lambert Law)
- Average conc. = integrated beam conc. / path length [i.e. (PPM) = (PPM-m) / (m)]

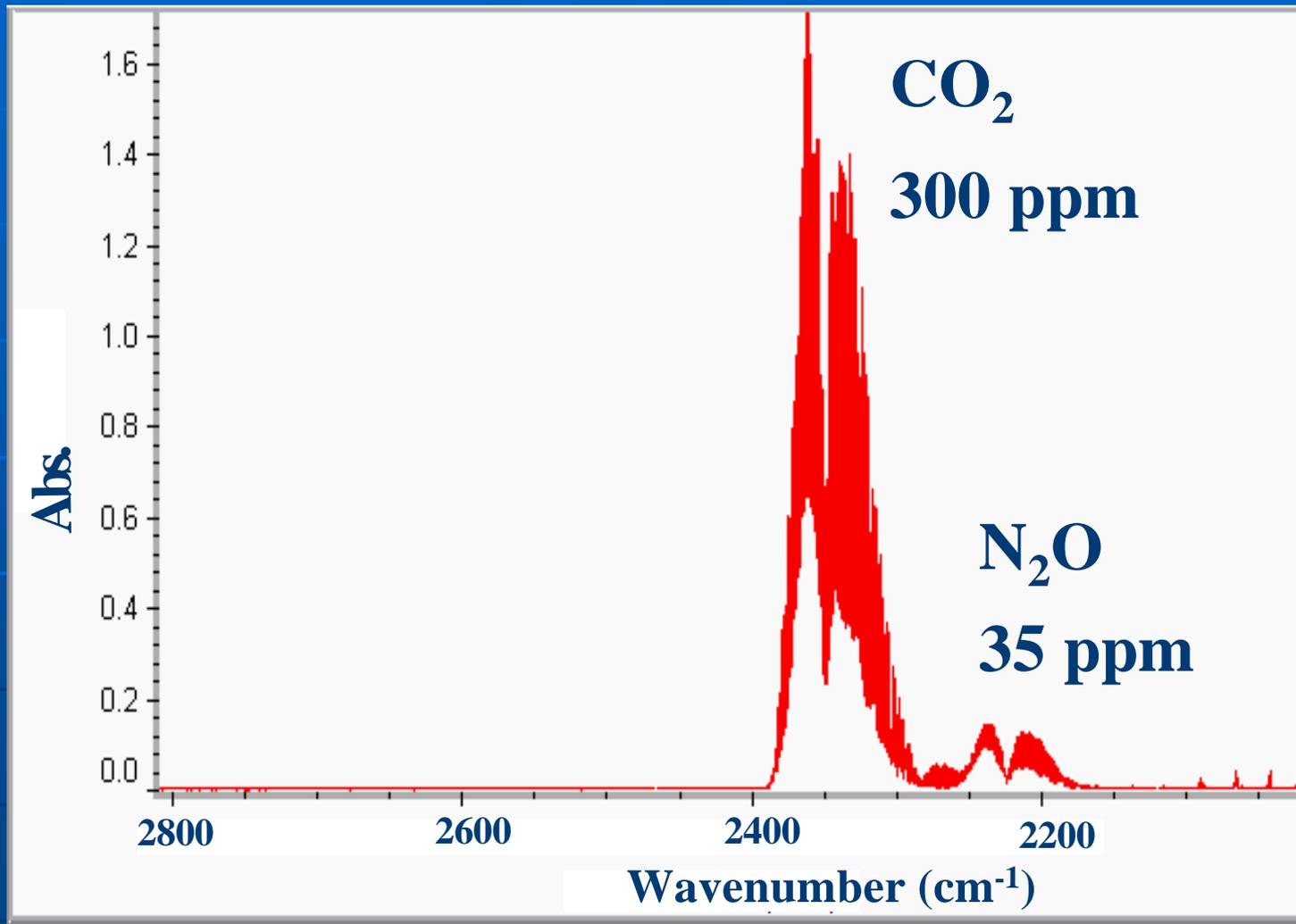


IR Single Beam Spectrum

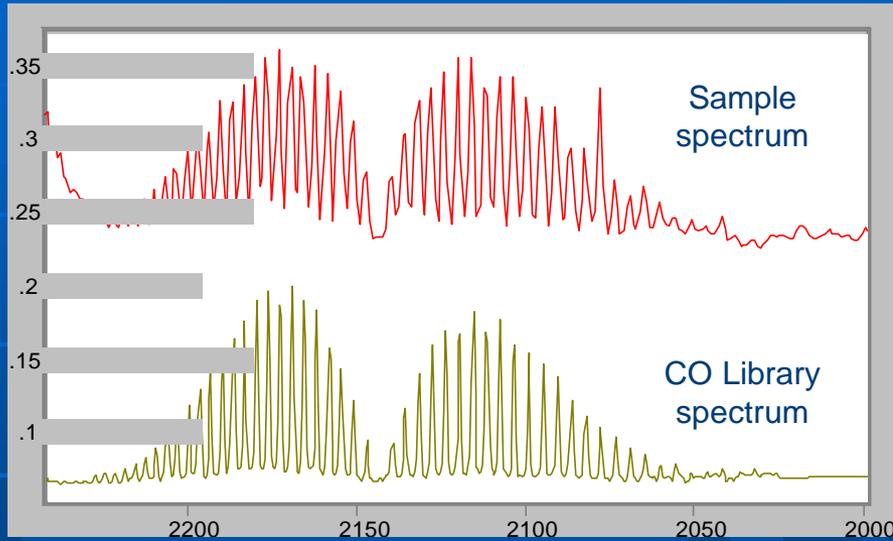
The shape of the spectrum depends on the black body emission of the source, transmission in the sample, and the detector response



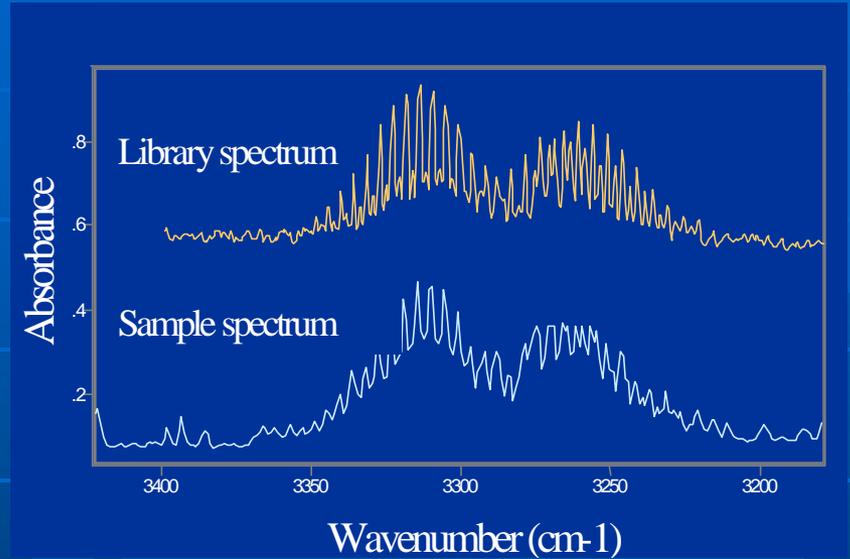
Double-Beam Absorbance Spectrum



FTIR Samples from Car Exhaust



Carbon Monoxide in Car Exhaust

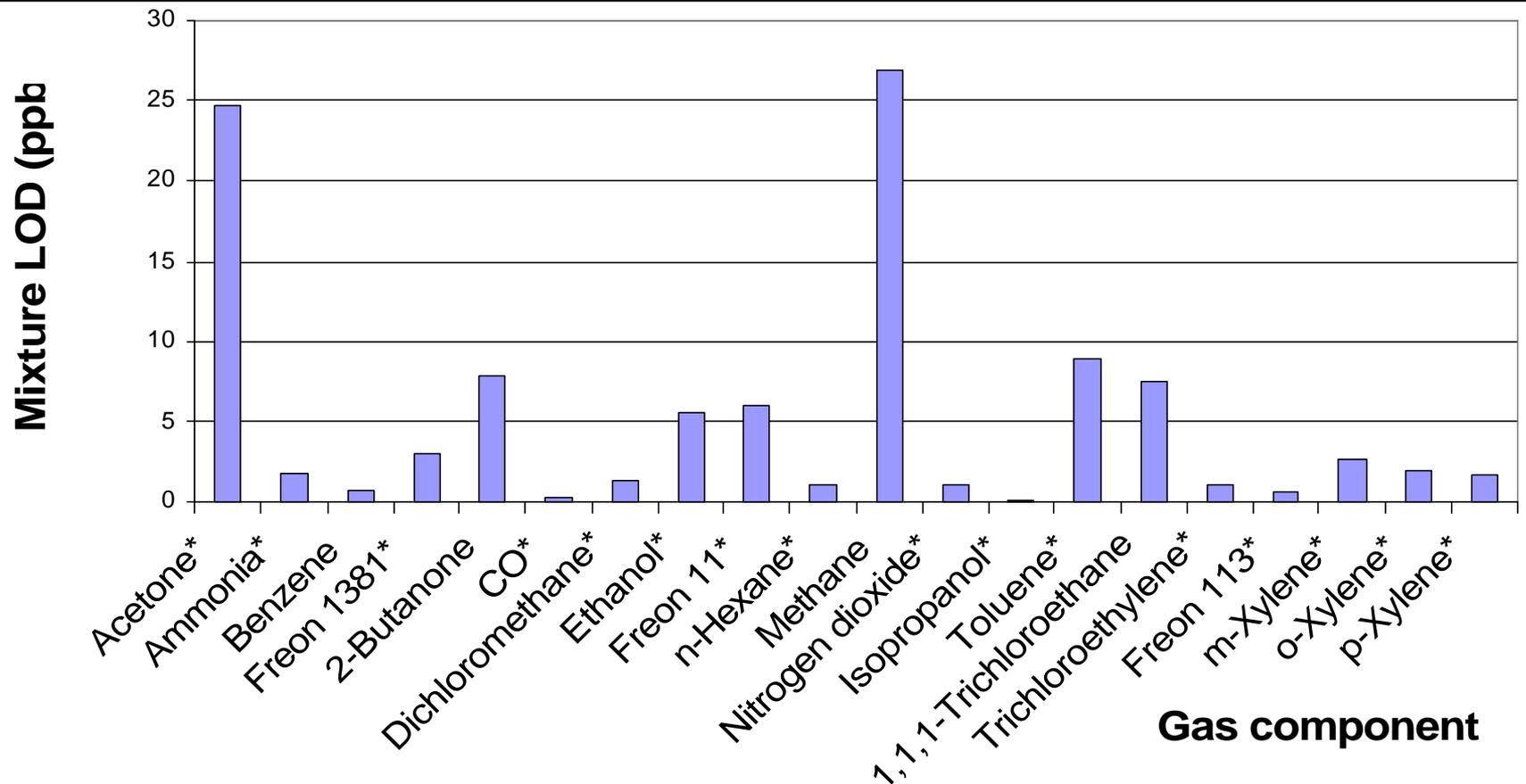


Acetylene in Car Exhaust

Advantages of FTIR spectrometers

- Good signal to noise ratios ($\gg 200$ typical)
- Both identification & quantification of samples
- Rapid scanning ($< 1\text{s}$ / scan)
- High resolution ($< 0.1\text{ cm}^{-1}$)
- High wavelength stability & accuracy
- High radiation throughput, no stray radiation
- Disadvantages
 - Moderate-low sensitivity (improves with $\sqrt{\#}$ scans)
 - Needs a fast detector : (Triglycine sulfate pyroelectric detector - TSPD; DTGS; MCT semiconductor type - LN_2 cooled)
 - Complex interpretation of data

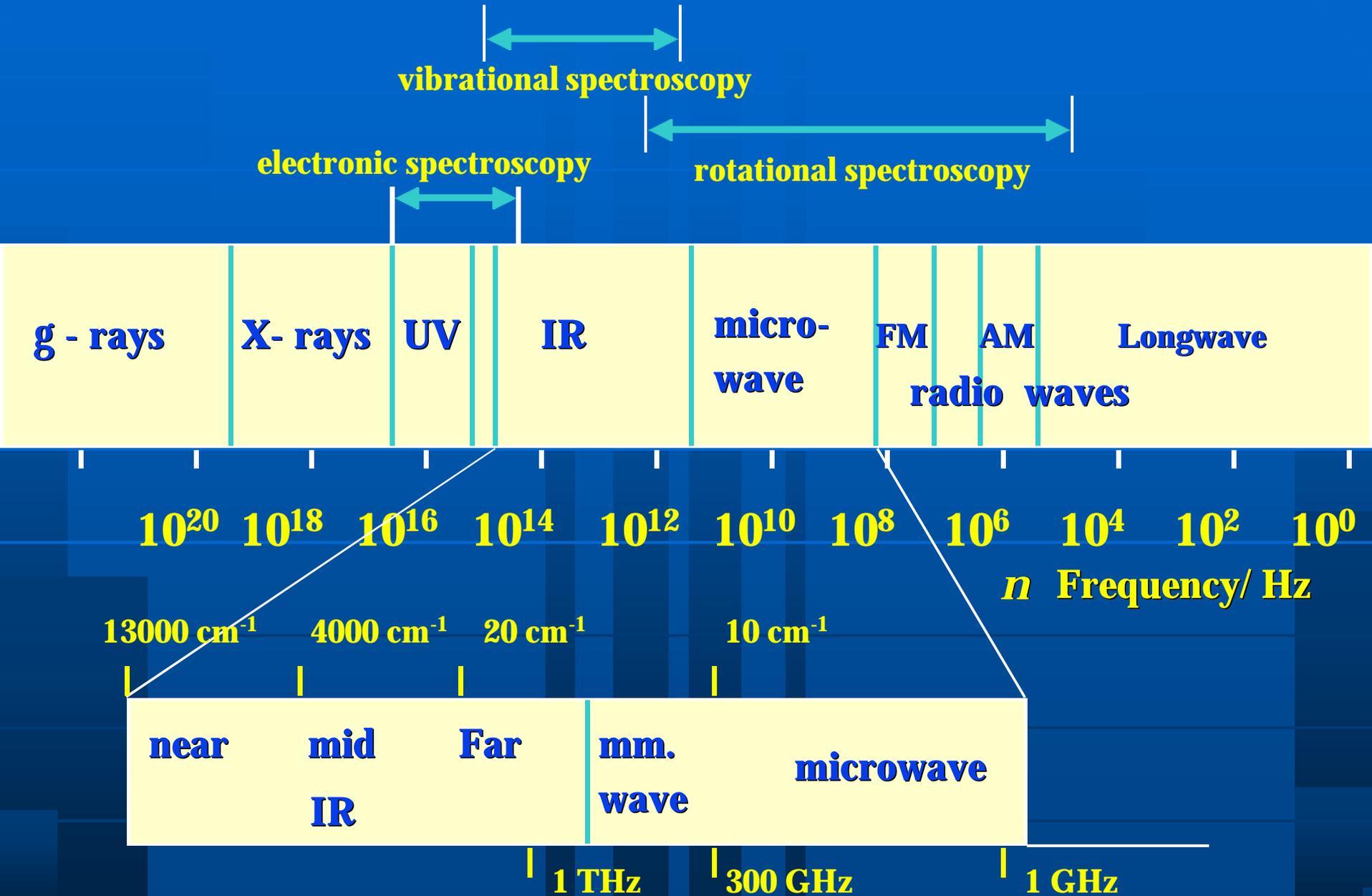
FTIR sensitivity for mixtures



Estimated LOD for mixtures based on 500m path with 1 min data collection at 0.5 cm⁻¹ resolution.

Based on ref: Monitoring of Gaseous Contaminants in Spacecraft Cabin Atmospheres,

DOAS & UV-Vis spectroscopy



Visible/Ultraviolet Spectroscopy

Visible Light 400

700 nm

UV

200

400nm

Vacuum UV 10

200nm

l (nm)	ν (Hz)	$\bar{\nu}$ (cm ⁻¹)	E (kJmol ⁻¹)
200	1.5×10^{15}	50000	598
400	7.5×10^{14}	25000	299
700	4.3×10^{14}	14285	171

NB. Typical Bond dissociation energies:

C - C 348 kJmol⁻¹

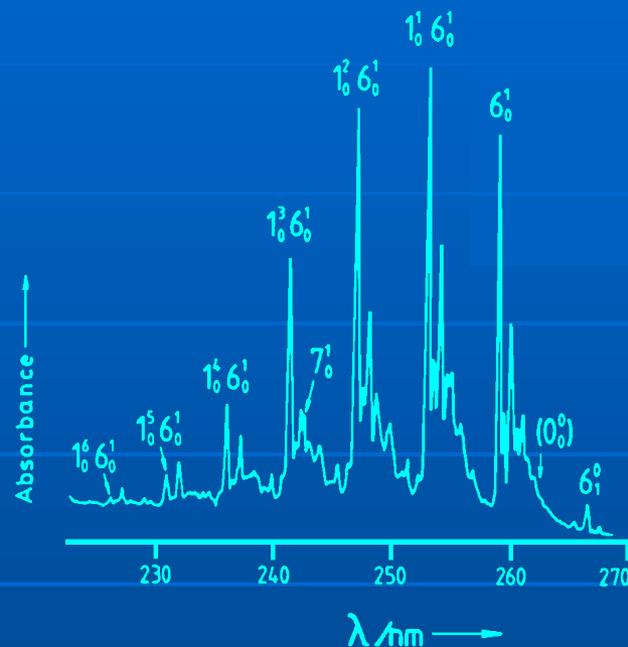
C - H 413 kJmol⁻¹

C - I 240 kJmol⁻¹

O = O 496 kJmol⁻¹

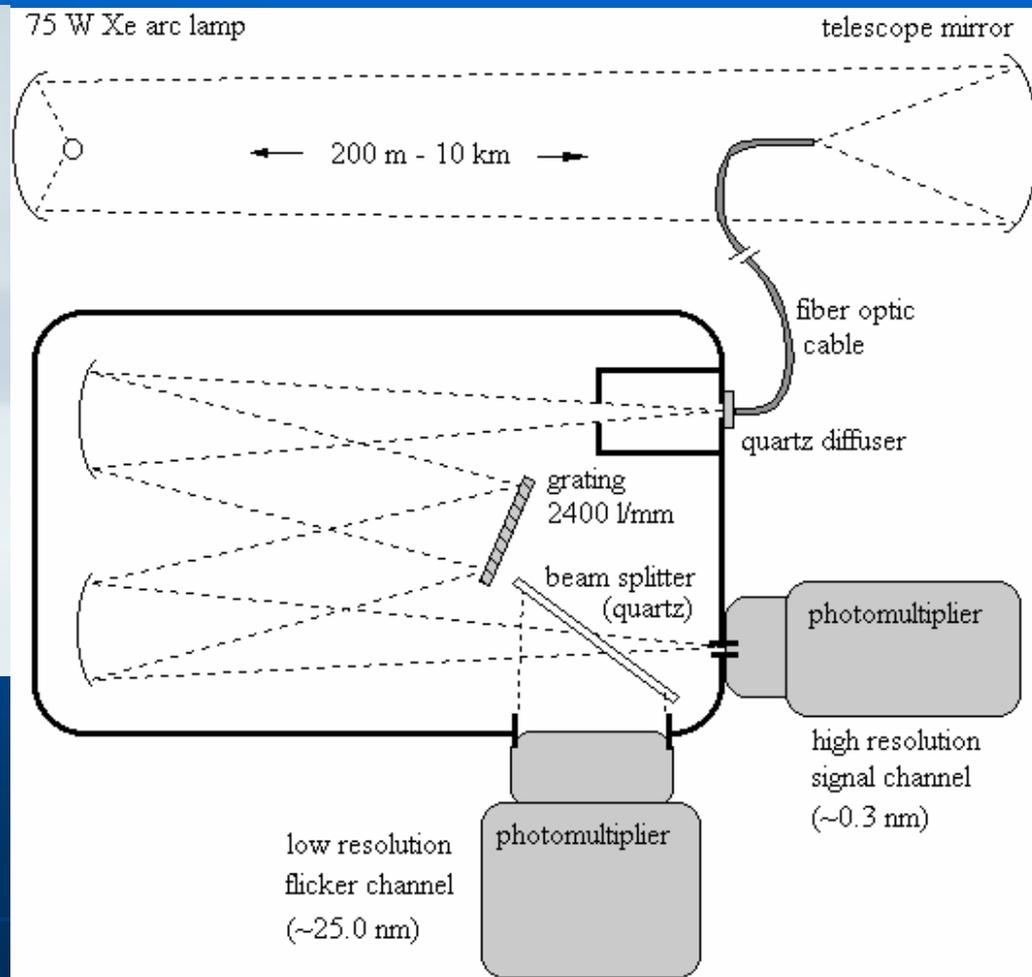
Application of Gas Phase Electronic Spectroscopy

- **Molecular identification**
- **Molecular dynamics**
- **Molecular constants**
- **Gas quantification**
 - good for homonuclear diatomics (N_2 , O_2 , Cl_2 etc) and for small molecules
 - Polyatomics: a little more complicated.
 - Usual broad band technique DOAS
 - uses Xe lamp source requires synthetic removal of background

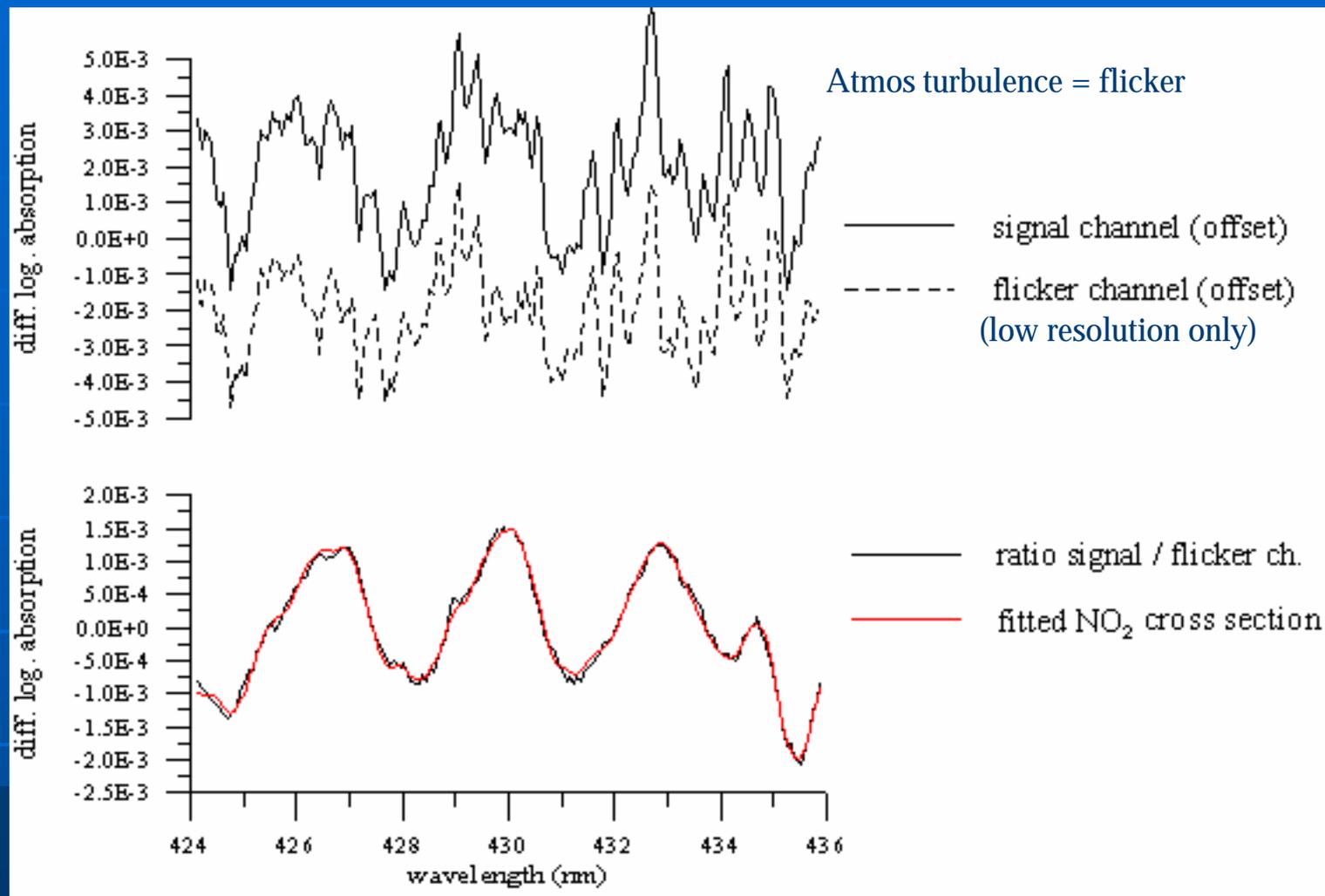


Benzene: Vibrational structure for an electronic transition

Typical DOAS system



DOAS for NO₂
Strong bands at
420-440nm

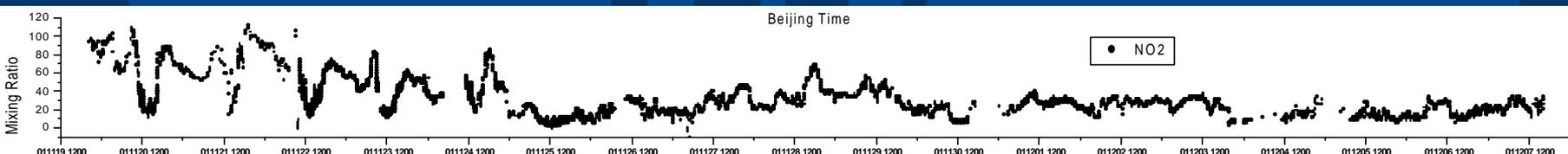
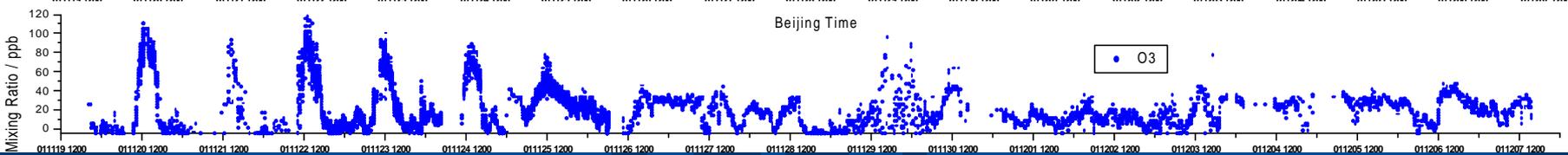
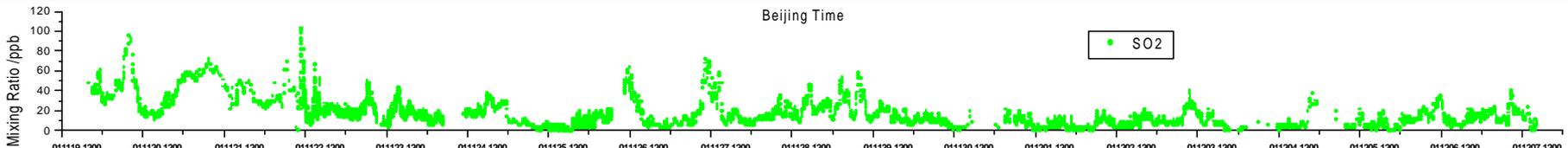
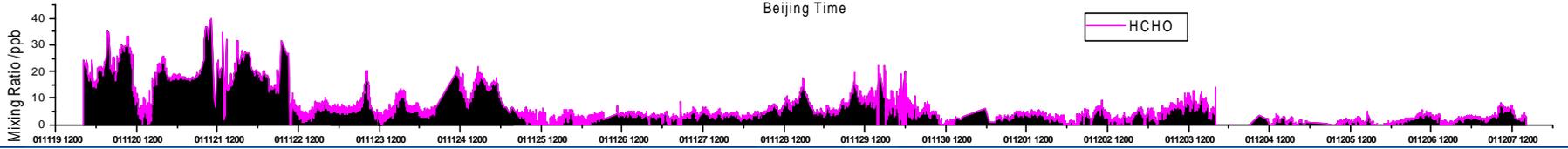
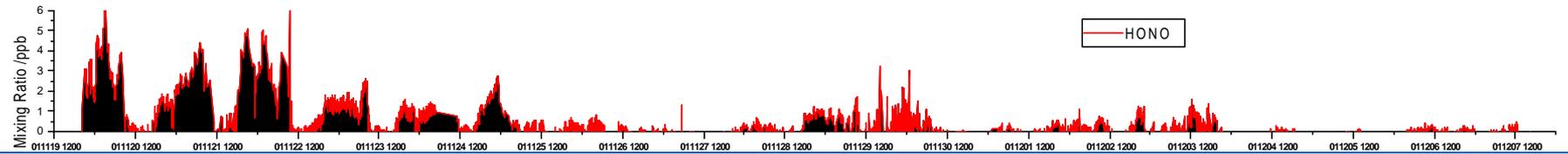


220m light path , 4 min measurement time.

red lower curve is a laboratory NO₂ cross section fitted to the ratio spectrum. The scaling factor gives an ambient mixing ratio of NO₂ of 8.5 ppb.

Also used for NO, SO₂, O₃ at ppb

DOAS measurements of HONO (nitrous acid), HCHO (Formaldehyde), SO₂, O₃ and NO₂ in Shanghai, Nov-Dec 2002



Beijing Time

DOAS applications

- Commercial systems

- atmospheric measurements of pollutants and trace gases
- environmental monitoring and atmospheric research
- industrial process control (e. g. on-line exhaust analyses)
- detection of inorganic trace gases: NO_2 , SO_2 , O_3 , HONO, HCHO, NO_3 , BrO, IO, ClO, CS_2 , and others
- detection of organic trace gases: benzene, toluene, phenol, benzaldehyde, cresols, dimethylphenols, and others

Example: <http://www.hmm.de/DOAS/doas.html>

Typical Gases Measured w DOAS

Species	Max Optical Path Length	**LDL (ppb)
Nitrogen Dioxide	2,000 m	0.2
Nitrogen Trioxide	2,000 m	0.02
Formaldehyde	1,000 m	0.5
Ozone	1,000 m	0.5
Sulphur Dioxide	1,000 m	0.2
Benzene	800 m	0.5
Toluene	800 m	0.5
p-Xylene	800 m	0.5
m-Xylene	800 m	1.0
o-Xylene	800 m	5.0

**Typical Lower Detection Limits (LDL's) based on 5 minute averaging time.

DOAS advantages

- in-situ measurements of some highly diluted volatile gases, simultaneous measurement of several species
- high specificity and high sensitivity
- "contactless" detection by optical absorption technique
- good time resolution down to 30 seconds
- automatic / unattended operation
- "calibration free" operation
- less maintenance than FTIR
- adaptation to customer specifications
- Less complex spectral data interpretation

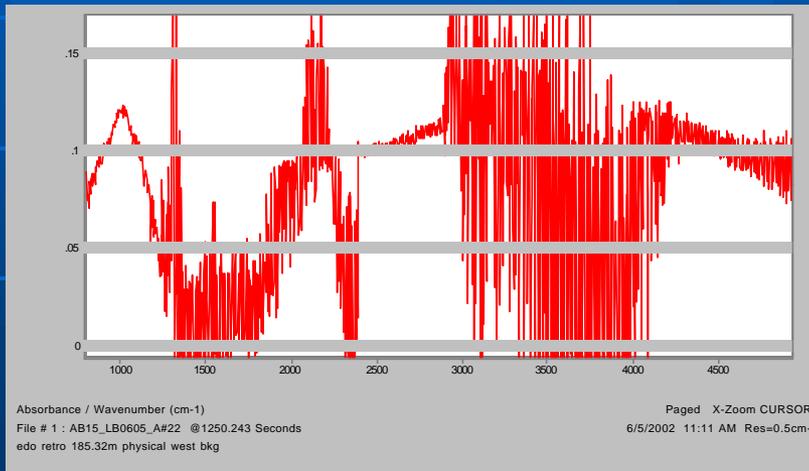
Particles & OP-methods

- Can we measure PM?
- What range of particle sizes?
- Can we tell soot from dust?
- What assumptions are needed?

W/ Special Thanks to Dr. Ram Hashmonay at Arcadis in RTP for the materials!

Method Overview

OP-FTIR is an accepted method for gas measurements (TO-16) Particulate matter (PM) presence also reveals a unique baseline structure (see below)

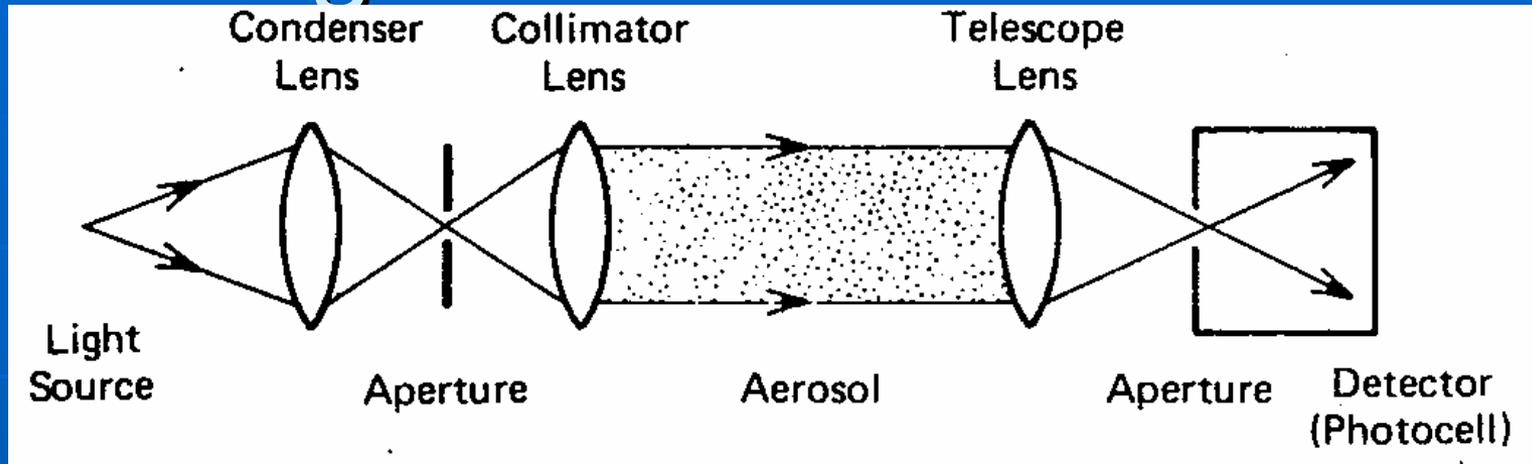


- Baseline structure can be predicted for a given size distribution and optical constants using Mie theory
- We developed an inversion algorithm to retrieve the aerosol size distribution from extinction (scattering + absorption) measurements
- Optical properties (constants) of specific PM may be determined using a bench-top FTIR spectrometer

Atmospheric Scattering

- Scattering process disperses radiation in all directions
- Important scattering agents include: gases, aerosols & clouds
- 3 types of atmospheric scattering are important in remote sensing:
 - Rayleigh (molecular) scattering
 - - primarily due to oxygen and nitrogen molecules ($d < 0.1 \times \text{wavelength}$)
 - - most influential in UV-Vis region at altitudes above 4.5km
 - - scattering inversely proportional to fourth power of wavelength
 - Mie (non-molecular) scattering
 - - occurs for particles w/ mean diameter ~ 0.1 to 10 times $>$ wavelength
 - - E.g. water vapor, smoke, dust, volcanic ejecta, sea salt crystals
 - - most pronounced in lower 4.5km of atmosphere
 - - wavelength dependence varies $\sim 1/\text{wavelength}$
 - dependent on size distribution, concentration & refractive index
 - Nonselective scattering
 - - occurs when sufficient # of particles w/ mean diameters > 10 wavelengths
 - - E.g. larger particles, water droplets and ice crystals in clouds and fogs
 - - scattering is independent of wavelength (near UV, visible, near infrared)
 - clouds appear brilliant white - colorless water drops and ice scatter all wavelengths equally well

Light Extinction ← Filtration of photons!



■ Bouguer's Law

$$\frac{I}{I_0} = \exp(-s_e L)$$

Extinction Efficiency

$$Q_e = \frac{\text{radiant power scattered and absorbed by a particle}}{\text{radiant power geometrically incident on the particle}}$$

Extinction Coefficient

$$s_{e_i} = \frac{\rho}{4} \sum_j Q_{e_{ij}} N_j d_j^2$$

- s_{e_i} - extinction for the i^{th} wavelength
- $Q_{e_{ij}}$ - dimensionless extinction efficiencies
- N_j - number density for the j^{th} aerosol size
- d_j - is the aerosol j^{th} size class (diameter)

Mie theory for scattering spheres

Size Parameter a

$$a = \frac{pd}{l}$$

d - particle diameter

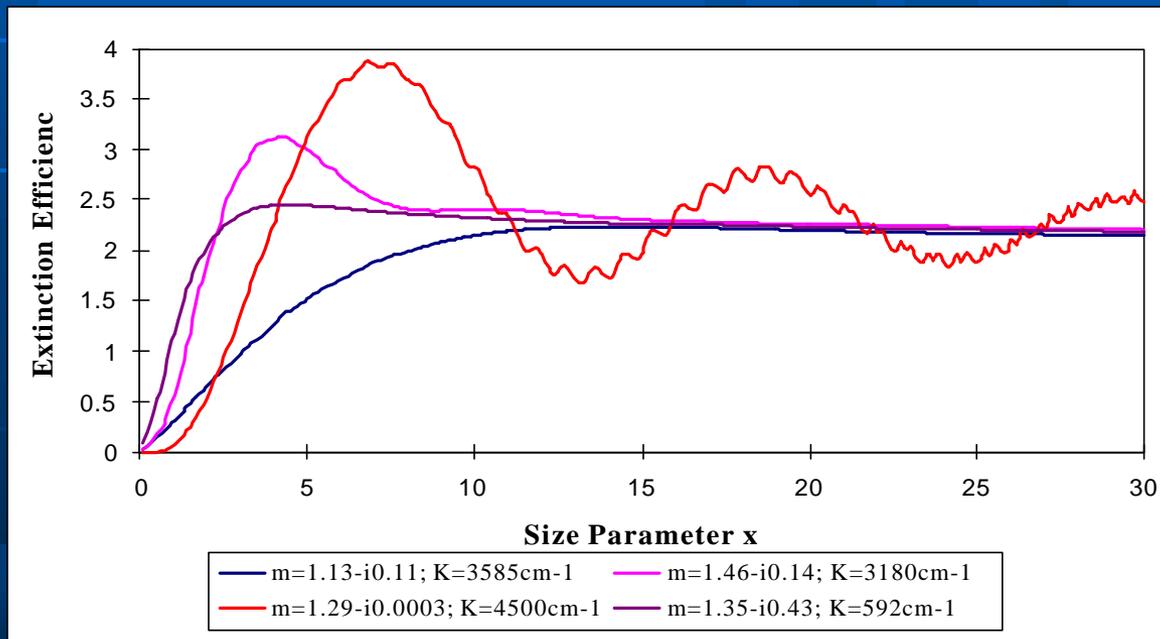
l - wavelength

Complex Refractive Index

$$m(\mathbf{l}) = n(\mathbf{l}) - ik(\mathbf{l})$$

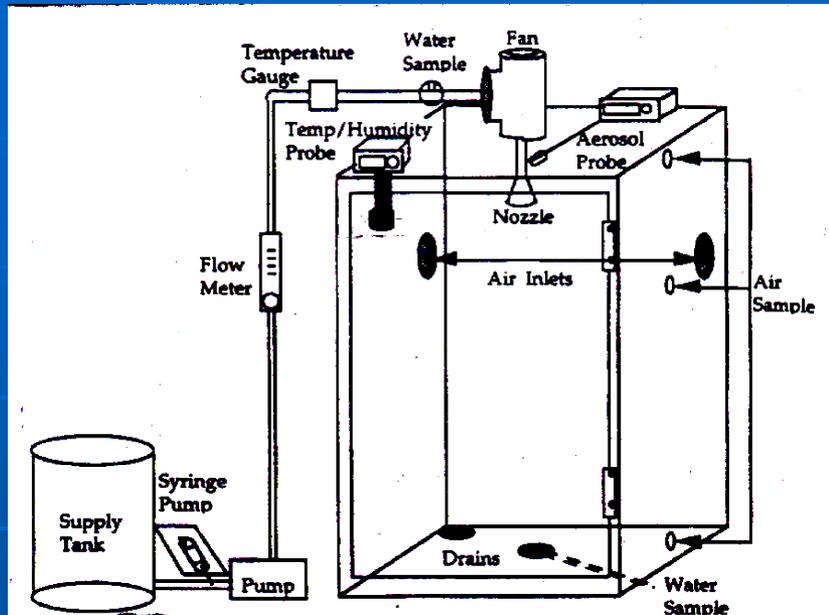
n – scattering term
(refraction and reflection)

k – absorption term

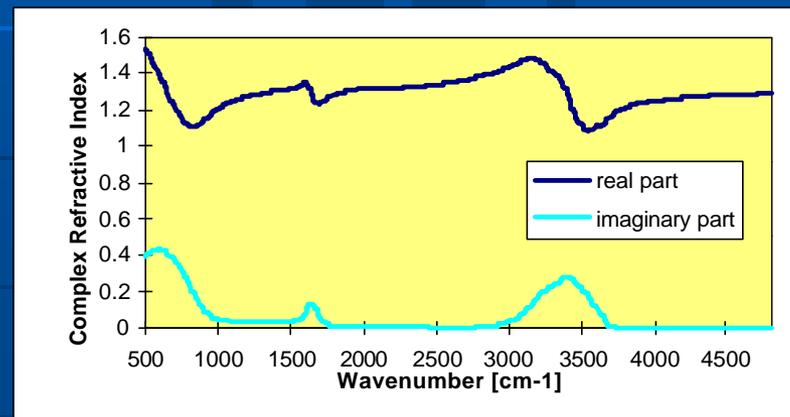


- Extinction efficiency of water in different parts of the spectrum

Shower Experiment

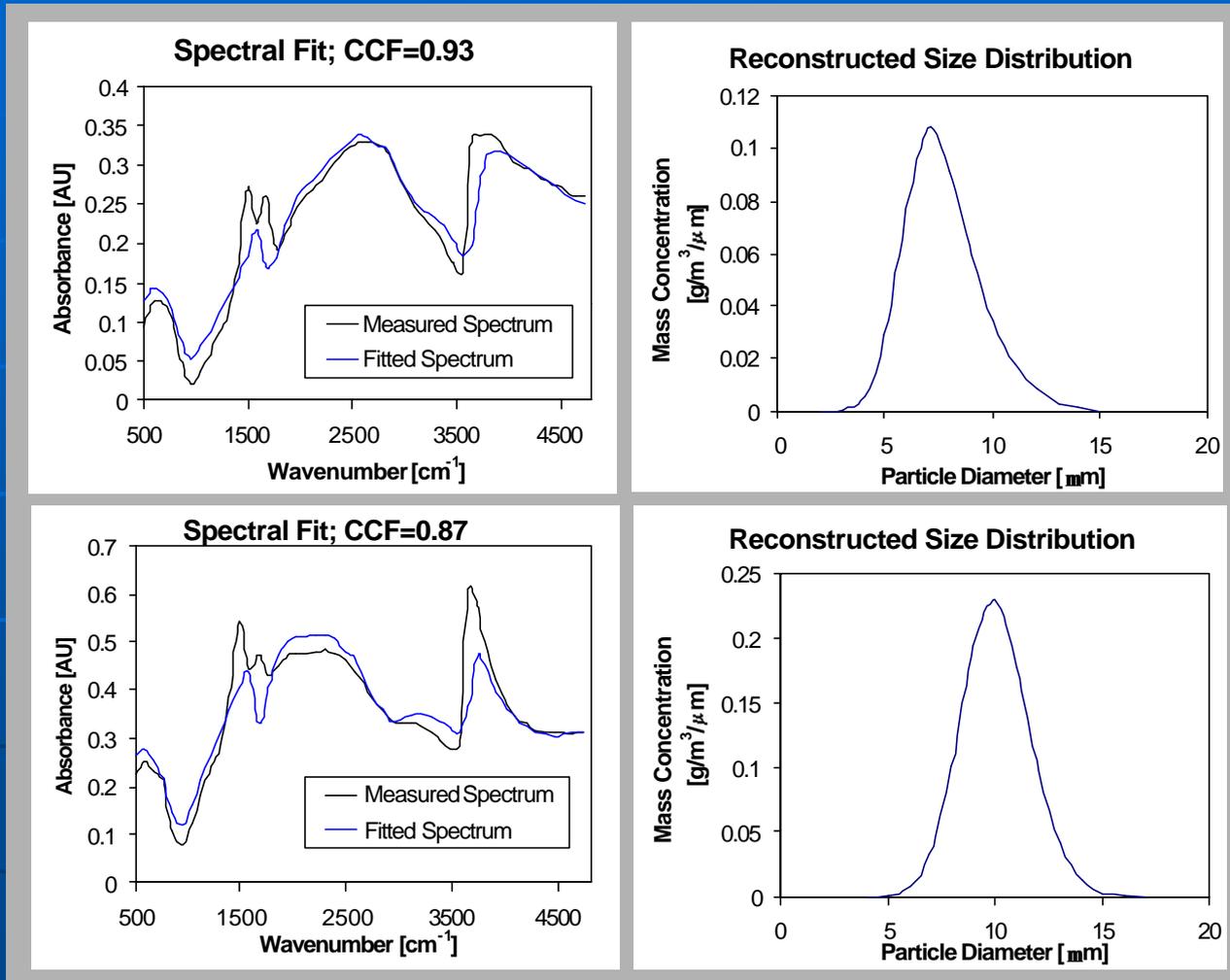


- OP-FTIR beam through water condensation aerosol
- Size distribution confirmed by aerosol probe
- Known optical constants (see below)

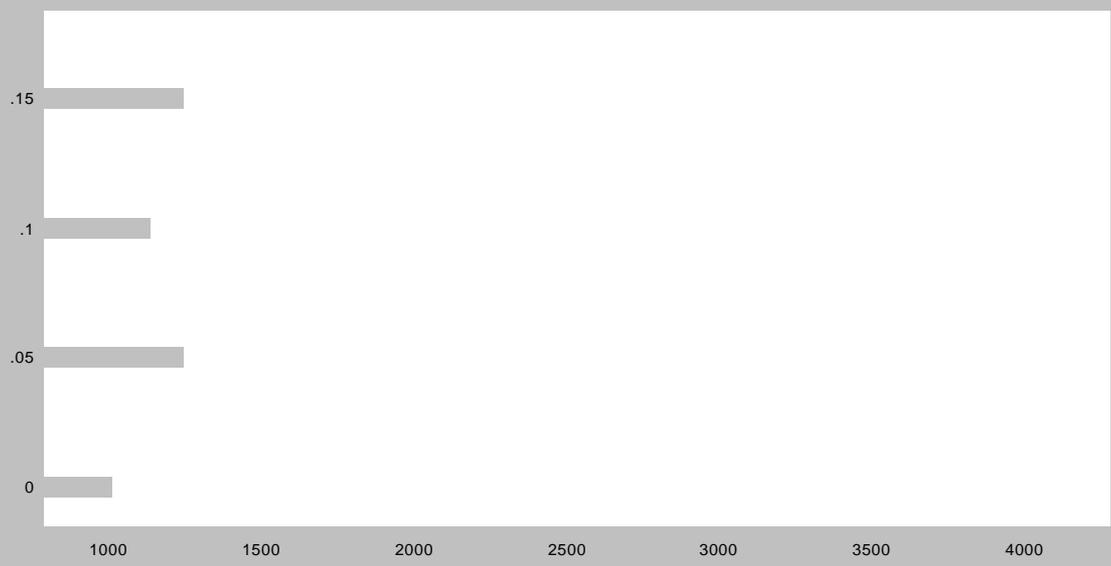


Complex refractive index of water

Shower Experiment Results



Smoke PM Extinction



Observed spectrum

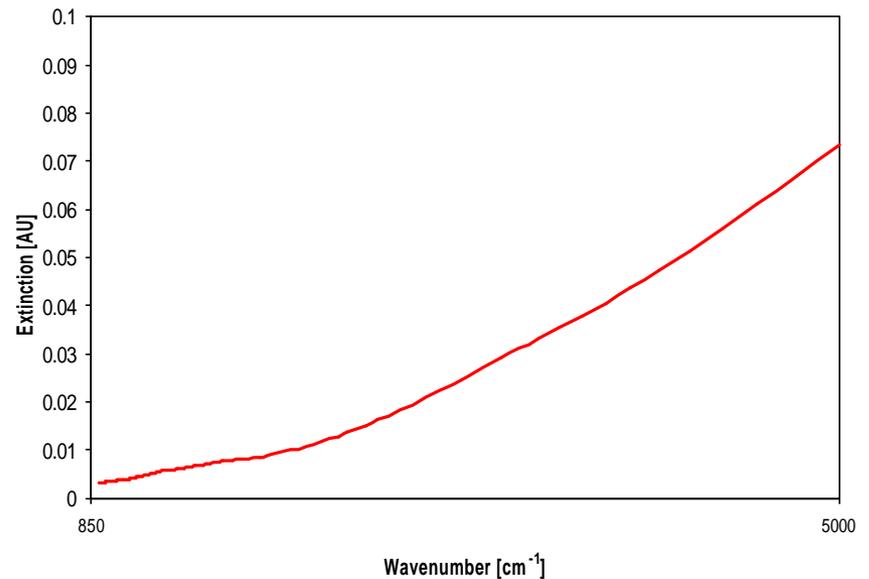
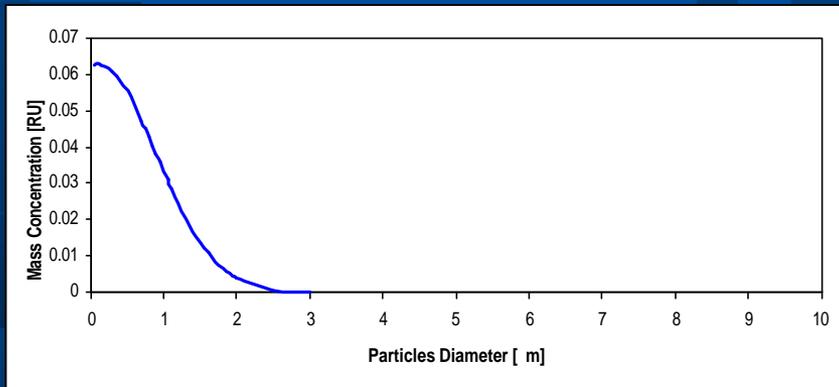
Calculated extinction

Absorbance / Wavenumber (cm-1)

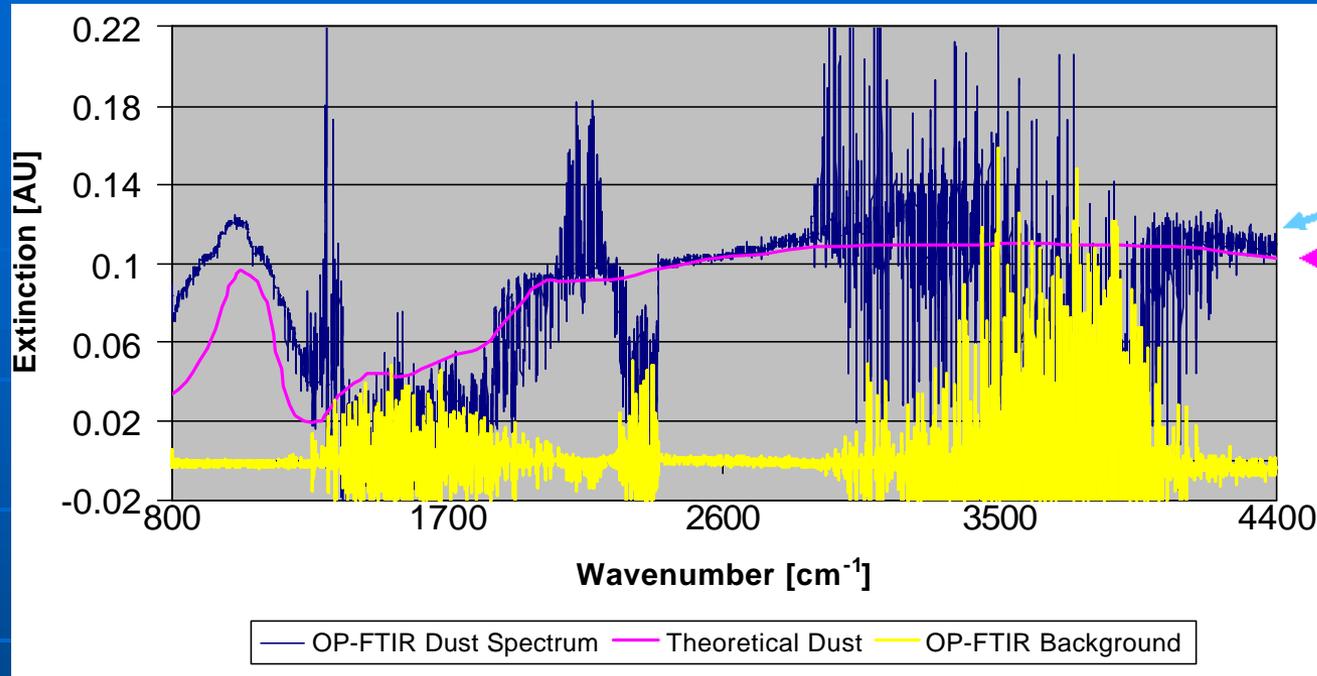
File # 1 : ABS-SMOKE-KAGAN#17 @-5.25 Wavenumber (cm-1)

Burn Test

Calculated Size distribution



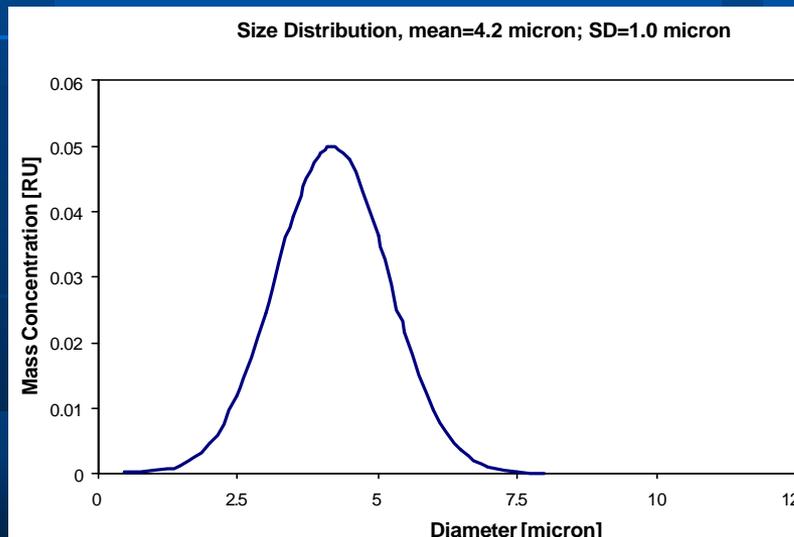
Louisville Landfill Dust



Spectrum with Dust

Calculated Extinction

Background Spectrum



OP-FTIR Beam

D

Landfill

U

Discussion:

Where do we go from here?

- The first time we have shown an open-path optical techniques to obtain real-time sizing & concentration of fugitive dust and other aerosols like water or pesticides
- OP-FTIR can be used in field to measure multiple gases and PM concentration data simultaneously
- Extending the spectral range to the UV/VIS range will allow sizing of submicron PM (~.25 μm and up)
- Research needed on practical issues: interferences, optical properties of urban aerosols, shape effects
- Should be able to use concurrent data from point monitoring networks to refine results
- Mapping and source localization also possible

Questions?