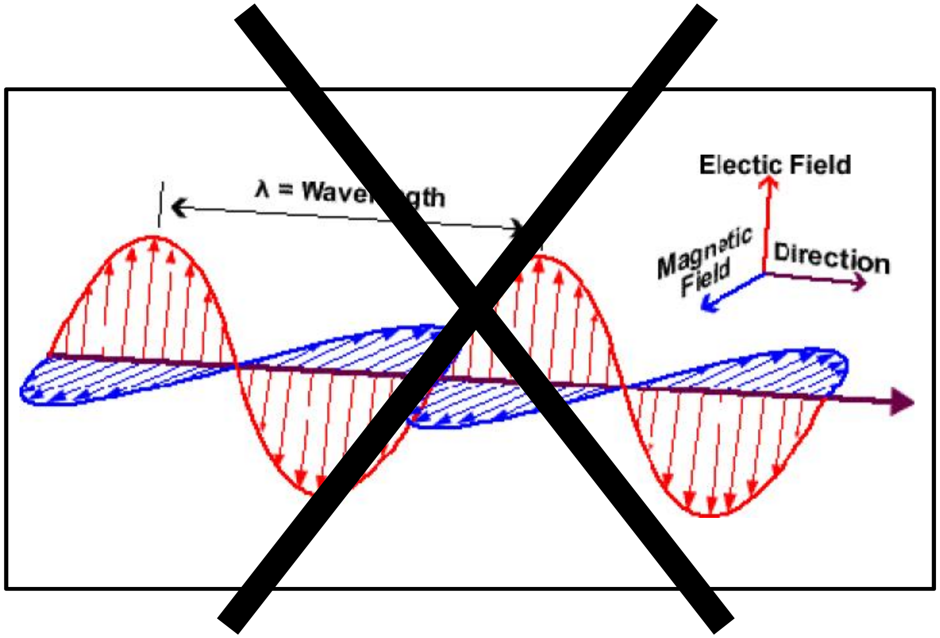
Atmospheric Field Measurements using Cavity Enhanced Spectroscopy

Rebecca Washenfelder
NOAA / University of Colorado



Electromagnetic Fields

Field Measurements

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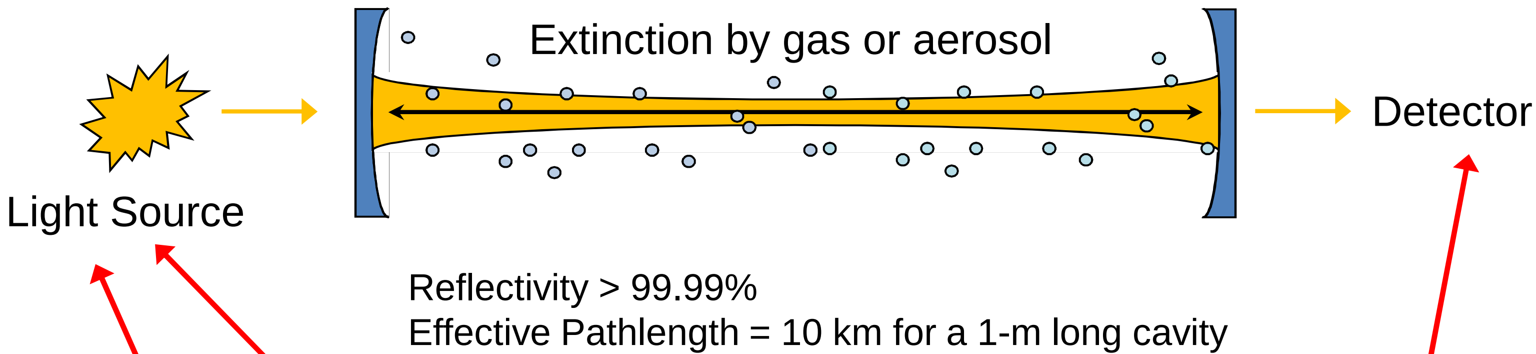
Four Ways to Describe CES Field Instruments

① Atmospheric Species (scientific question)



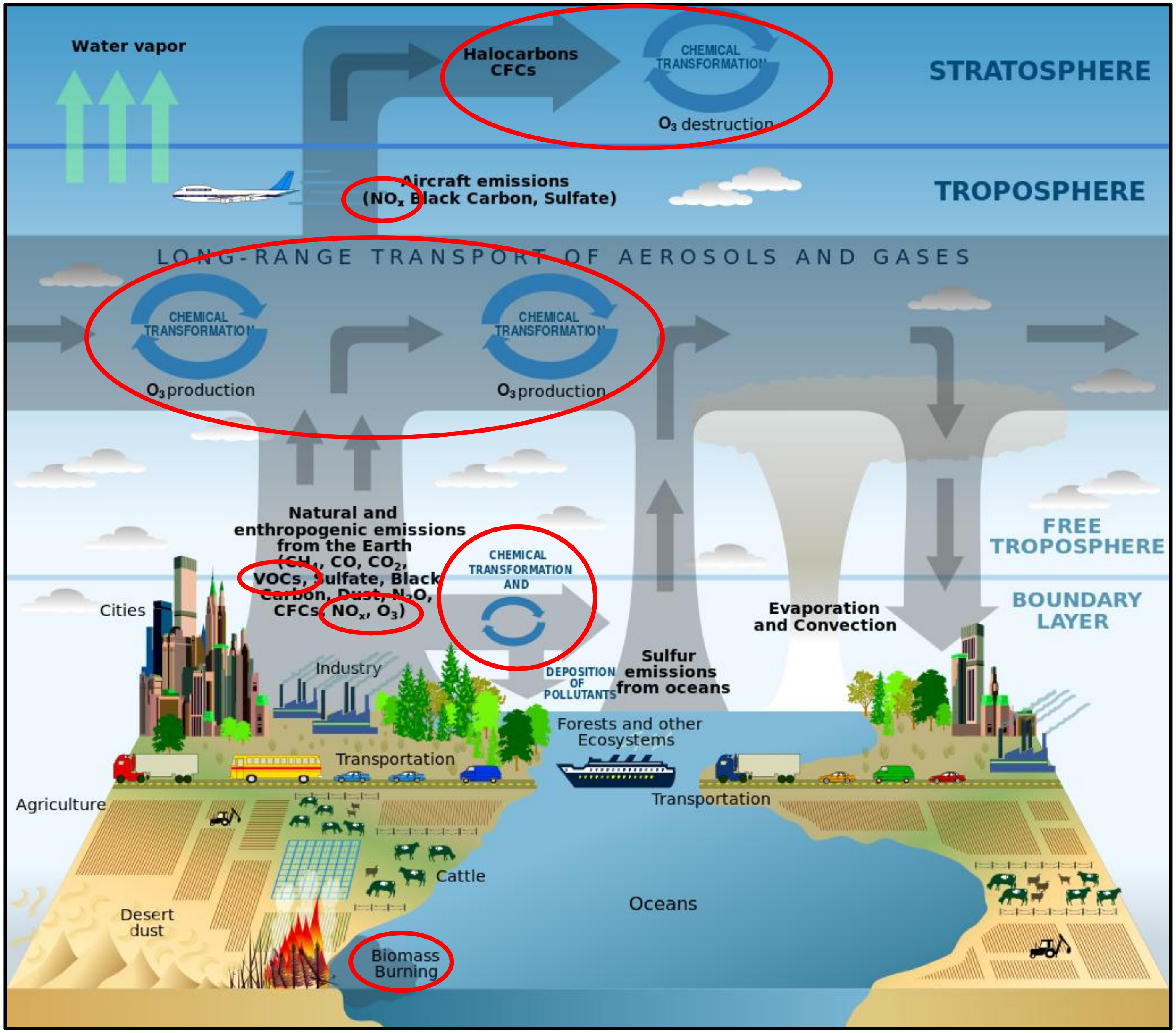
② Technique (CRDS, BBCEAS, ICOS…)

③ Spectral Region

④ Measurement Platform (tower, van, ship, aircraft…)

① Scientific Questions in Atmospheric Chemistry

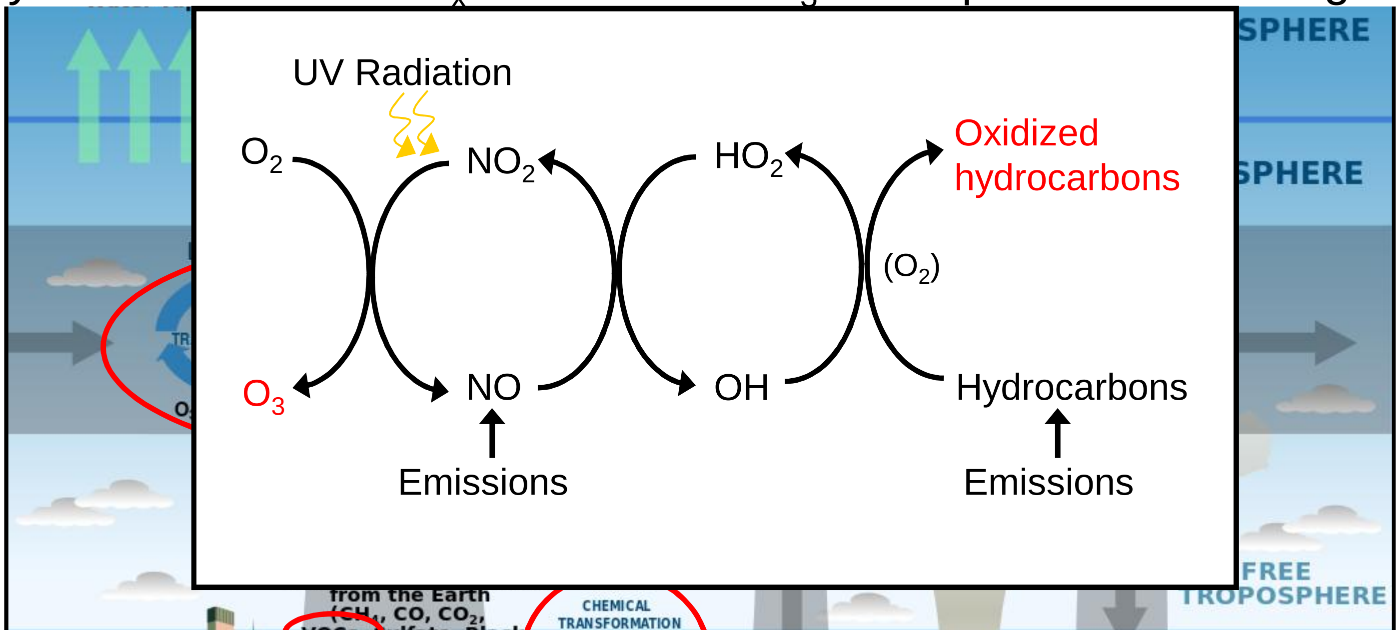
Photochemical Reactions:



① Scientific Questions in Atmospheric Chemistry

Photochemical Reactions:

Hydrocarbons and NO_x react to form O_3 in the presence of sunlight.



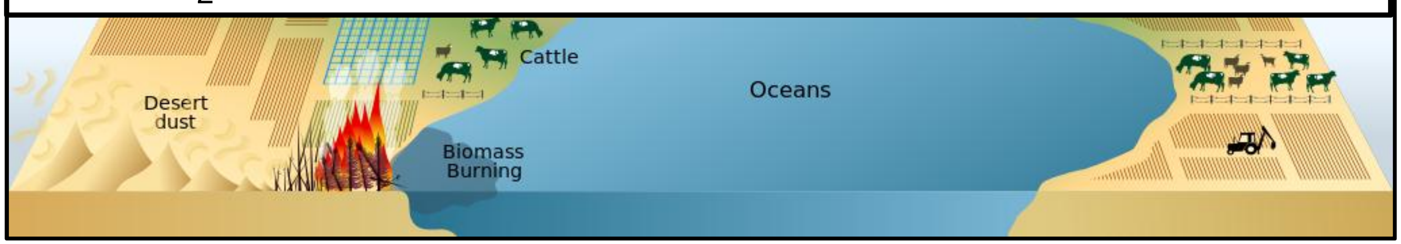
Important Measurements (Blue = CES)**:**

NO, NO_2, HONO, NO_3, N_2O_5, HNO_3

O_3

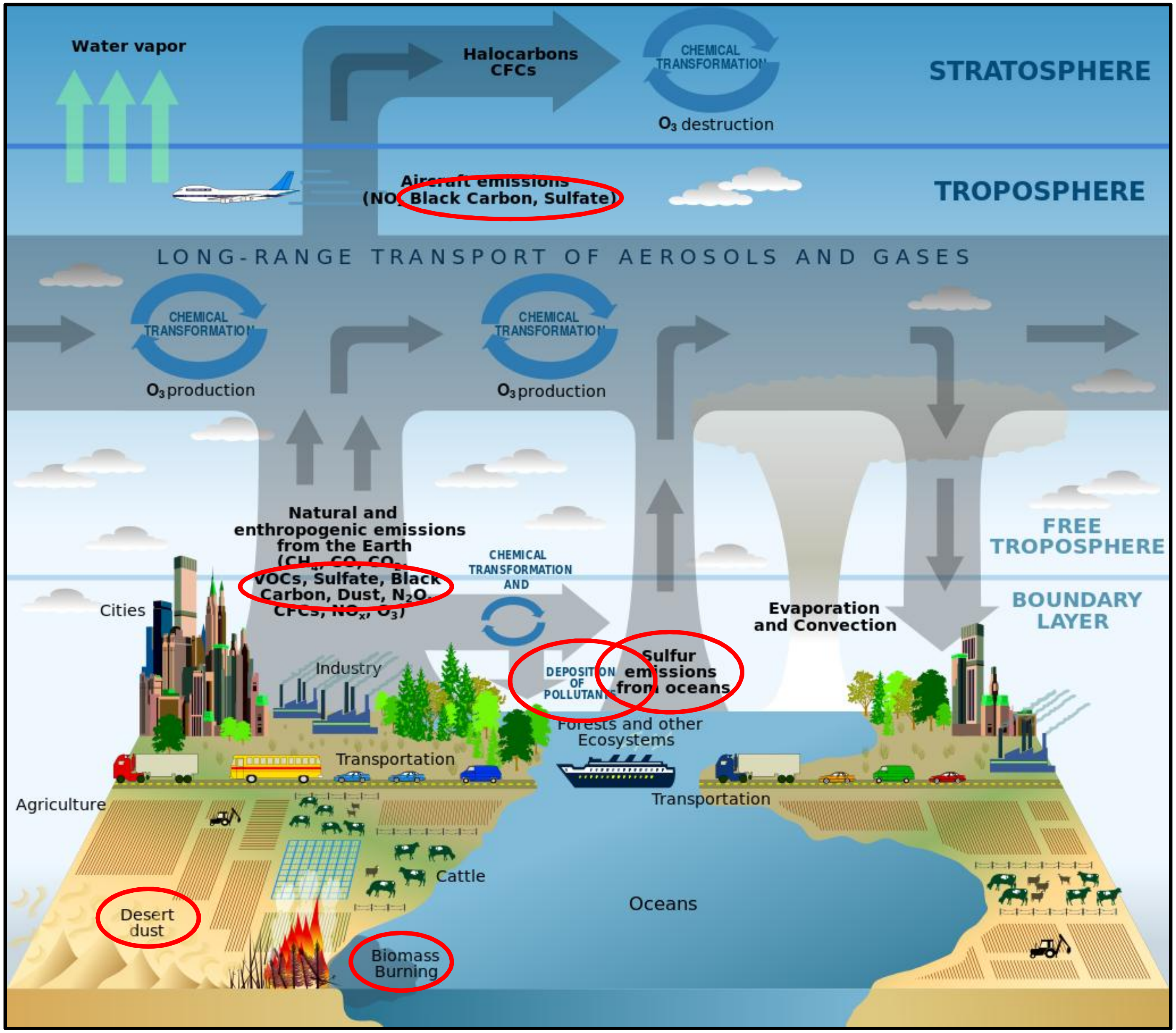
Hydrocarbons (or Volatile Organic Carbon, VOCs)

OH, HO_2



① Scientific Questions in Atmospheric Chemistry

Aerosol Concentration, Sources, and Properties:



① Scientific Questions in Atmospheric Chemistry

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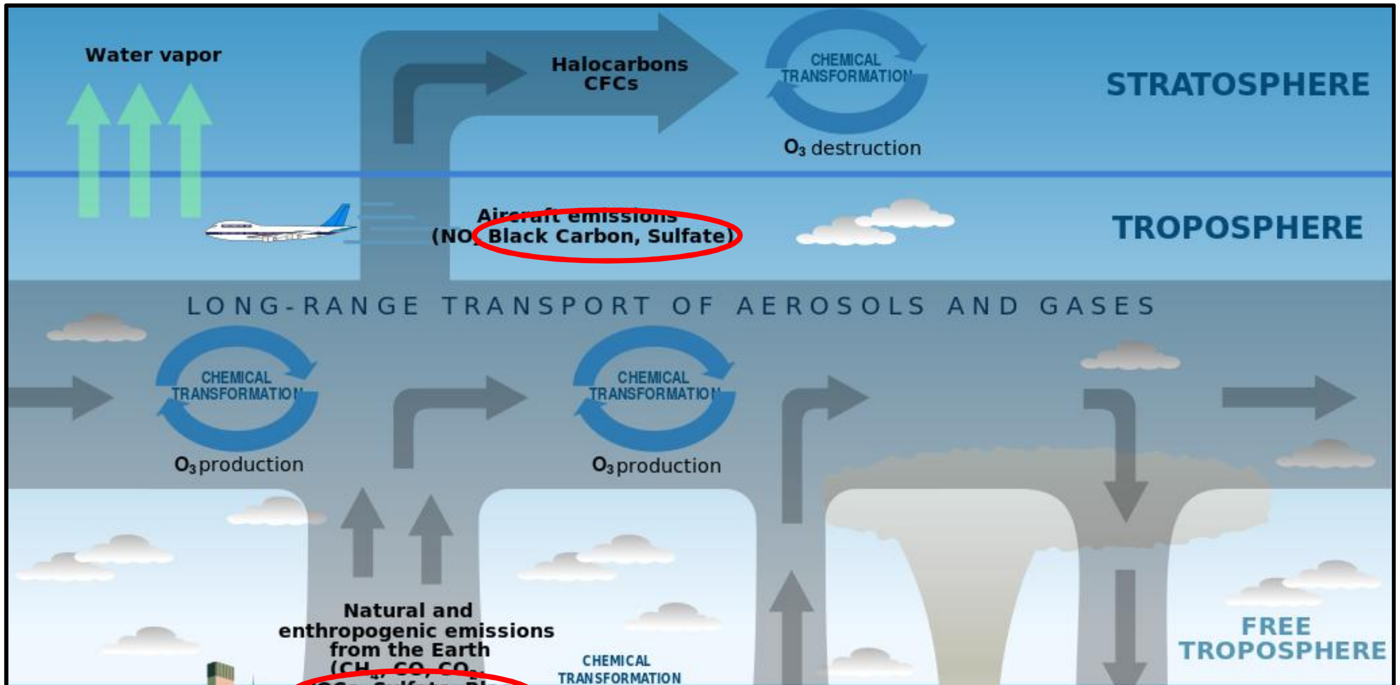


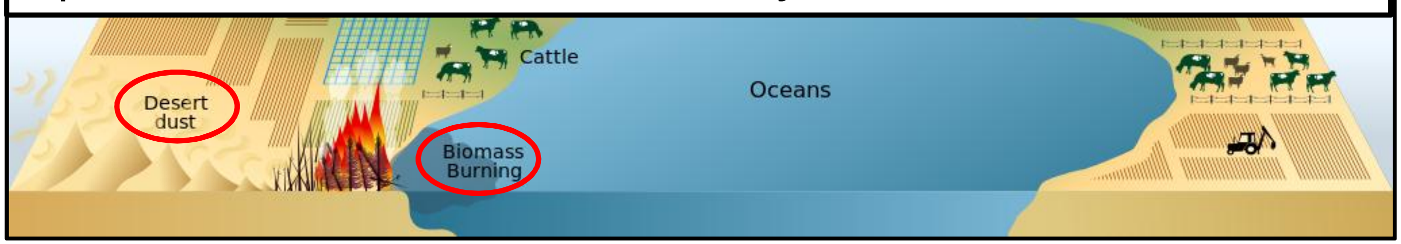
Important Measurements (Blue = CES)**:**

Number and size distribution of particles

Aerosol absorption, scattering, and extinction

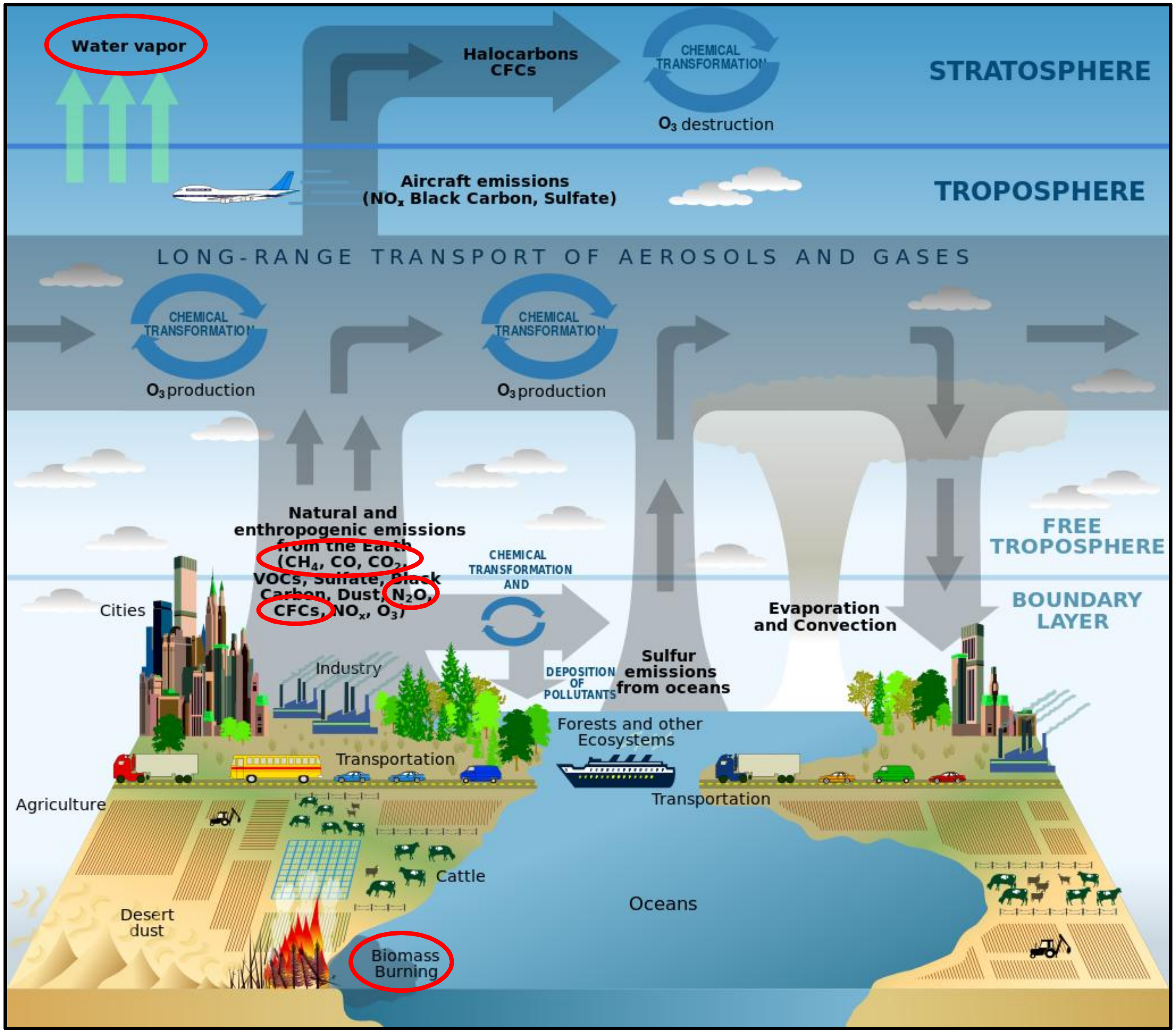
Emissions of primary aerosol

Species that contribute to secondary aerosol mass



① Scientific Questions in Atmospheric Chemistry

Greenhouse Gases



① Scientific Questions in Atmospheric Chemistry

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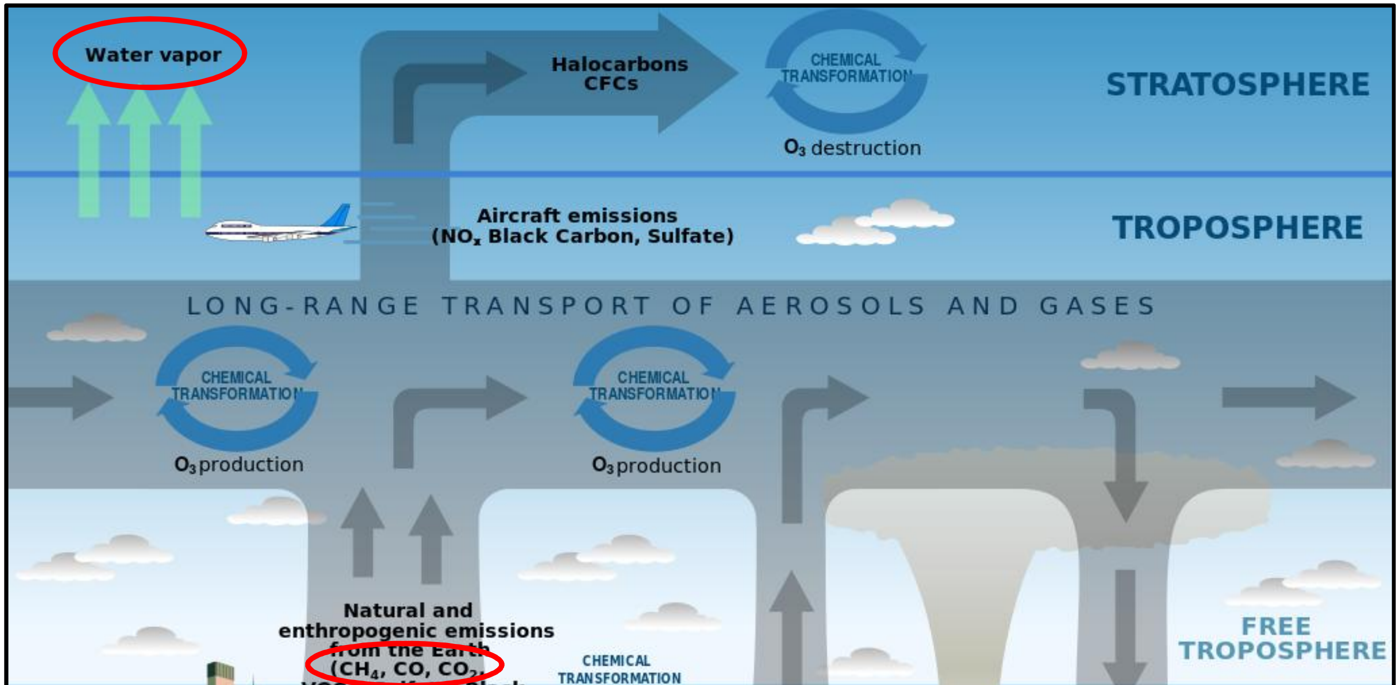


Important Measurements (Blue = CES)**:**

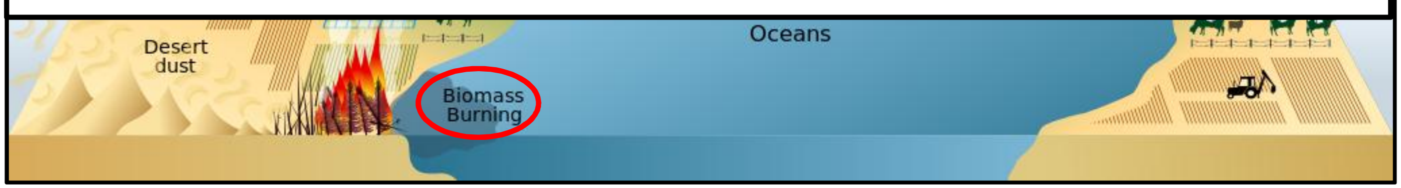
H_2O

CO_2, CH_4, CO

N_2O

O_3

CFCs



① Scientific Questions in Atmospheric Chemistry

Every atmospheric sample contains a mixture of species:

Non-Reactive Gases

Gas	Average Mixing Ratio (ppmv*)
Nitrogen (N_2)	780,840
Oxygen (O_2)	209,460
Argon (Ar)	9,340
Carbon dioxide (CO_2)	397
Neon (Ne)	18
Helium (He)	5.2

Particles

Aerosol Mass	5 – 30 μg m^{-3}

Reactive Gases

Gas	Average Mixing Ratio (ppmv*)
Methane (CH_4)	1.8
Hydrogen (H_2)	0.6
Nitrous oxide (N_2O)	0.31
Carbon monoxide (CO)	0.12
Ozone (O_3)	0.01 – 0.1
NO_x (NO and NO_2)	0.001 – 0.05
Ammonia (NH_3)	0.0001 – 0.005
Sulfur dioxide (SO_2)	0.0001 – 0.001
Others: hydrocarbons, nitrogen compounds (HONO, NO_3, N_2O_5), CFCs	

At standard temperature and pressure, density is 2.4 x 10^{19} molecules cm^{-3}.

***1 part per million by volume (ppmv) = 2.4 x 10^{13} molecules cm^{-3}.**

② Cavity Enhanced Spectroscopy Technique

	Narrowband	**Broadband**
Pulsed Light	Cavity Ringdown Spectroscopy (CRDS)	Broadband Cavity Ringdown Spectroscopy (BBCRDS)
Continuous Light	Integrated Cavity Output Spectroscopy (ICOS)	Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS)

All of these techniques are described by the same basic equation:

$$\frac{dI_{in}(\lambda)}{dt} = c\left(-\frac{1-R(\lambda)}{d} - \sum_i \alpha_i(\lambda)\right) I_{in}(\lambda) + c k_s I_{source}(\lambda)$$

where
I_{source}(ª) = intensity of external source
k_s = coupling efficiency of light into the cavity
I_{in}(ª) = light intensity inside cavity
c = speed of light
R = mirror reflectivity
d = distance between mirrors
~$_i$(ª) = extinction by species *i*

Scherer et al., Chemical Reviews, 1997

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Continuous Light Techniques

$$\frac{dI_{in}(\lambda)}{dt} \rightarrow 0$$

$$\frac{dI_{in}(\lambda)}{dt} = c\left(-\frac{1-R(\lambda)}{d} - \sum_i \alpha_i(\lambda)\right) I_{in}(\lambda) + c k_s I_{source}(\lambda)$$

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Pulsed Light Techniques

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Aerosol measurements use extinction.

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Gas-phase measurements use extinction to determine number density:

$$N_i = \frac{\alpha_i(\lambda)}{\sigma_i(\lambda)}$$

where ~$_i$(ª) = extinction by species *i* (units of cm^{-1})

±$_i$(ª) = absorption cross section of species *i* (units of cm^2 $molecule^{-1}$)

N_i = number density of *i* (units of molecules cm^{-3})

② Cavity Enhanced Spectroscopy Technique

Light Sources

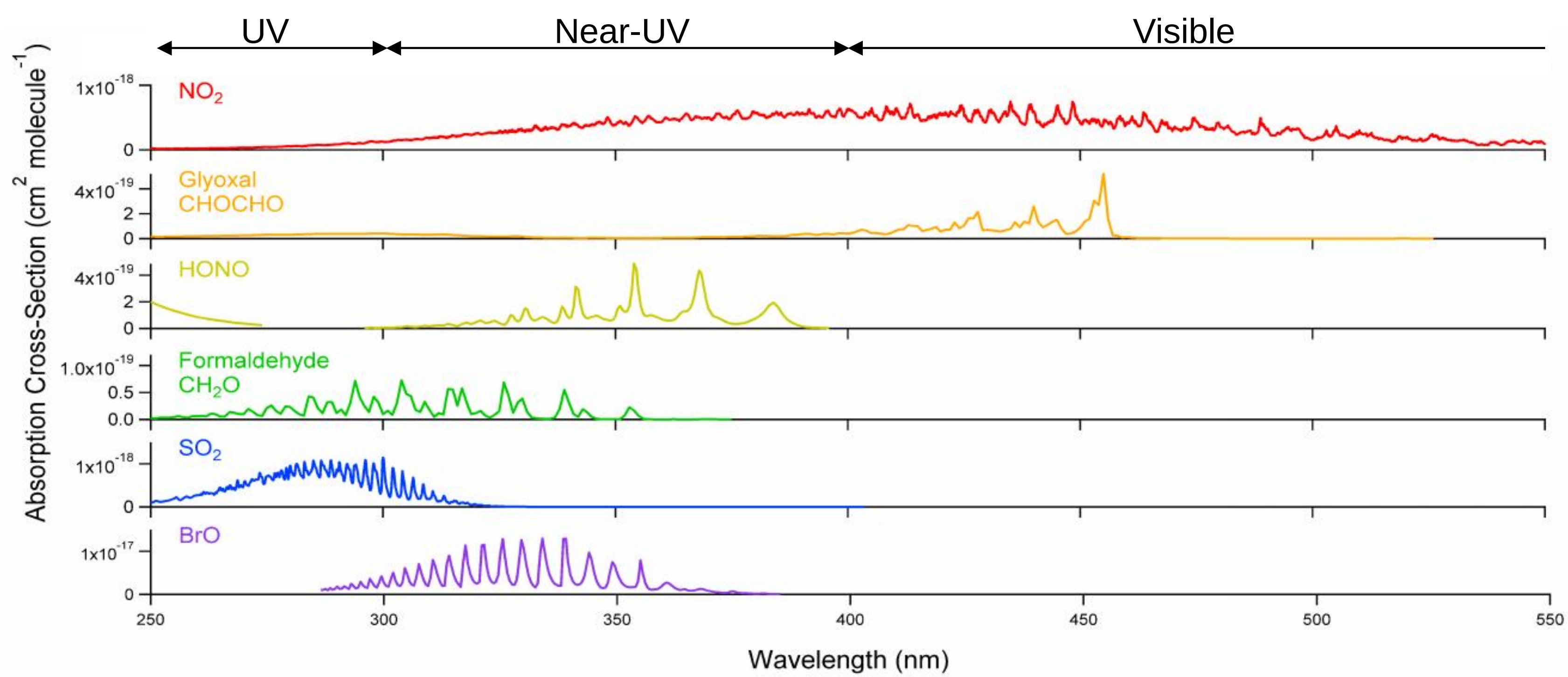
	Narrowband	Broadband
Pulsed Light	Nd:YAG laser, excimer laser, pulsed dye laser, optical parametric oscillator (OPO)	Nd:YAG-pumped dye laser, arc lamp, light emitting diode (LED)
Continuous Light	Diode laser, HeNe laser, Ar-ion laser, Nd:YAG laser	Arc lamp, LED

Detectors

	Narrowband	Broadband
Pulsed Light	Photomultiplier tube, avalanche photodiode	Grating spectrometer with array detector
Continuous Light	Photomultiplier tube, photodiode	Fourier transform spectrometer, Grating spectrometer with array detector

③ Spectral Regions and Target Species

Spectral Region	Wavelength (nm)	Transitions	Selected Species
Ultraviolet	100 – 290	Electronic	NO_2, CH_2O, SO_2, O_3
Near-Ultraviolet	300 – 400	Electronic	NO_2, HONO, CH_2O, SO_2, BrO, O_3…
Visible	400 – 750		O_3, H_2O, NO_3, CHOCHO
Near-Infrared	750 – 2,500	Ro-vibrational	CO_2, CH_4, N_2O, H_2O, CO
Mid-Infrared	2,500 – 10,000	Ro-vibrational	CO_2, CH_4, N_2O, H_2O, CO, hydrocarbons, CFCs, NH_3, many others



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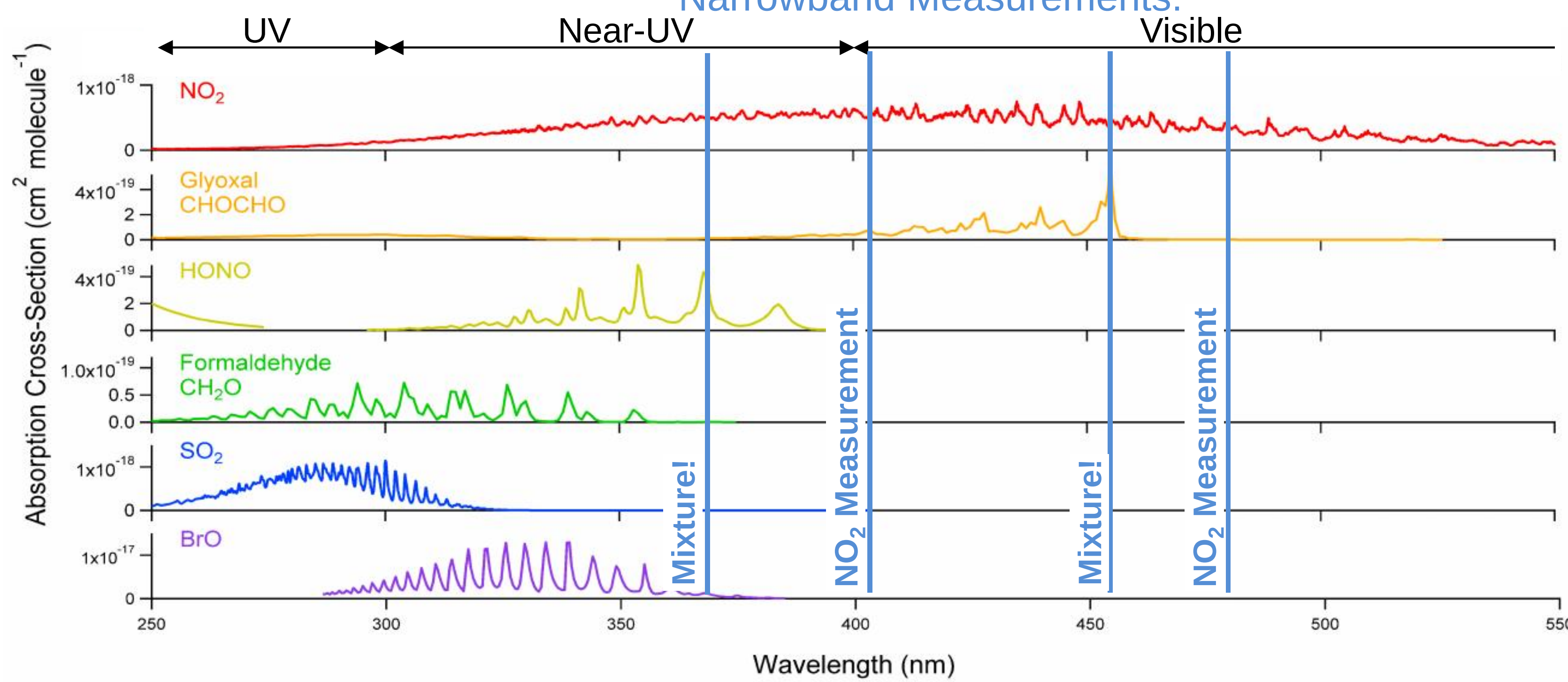
Narrowband Measurements:



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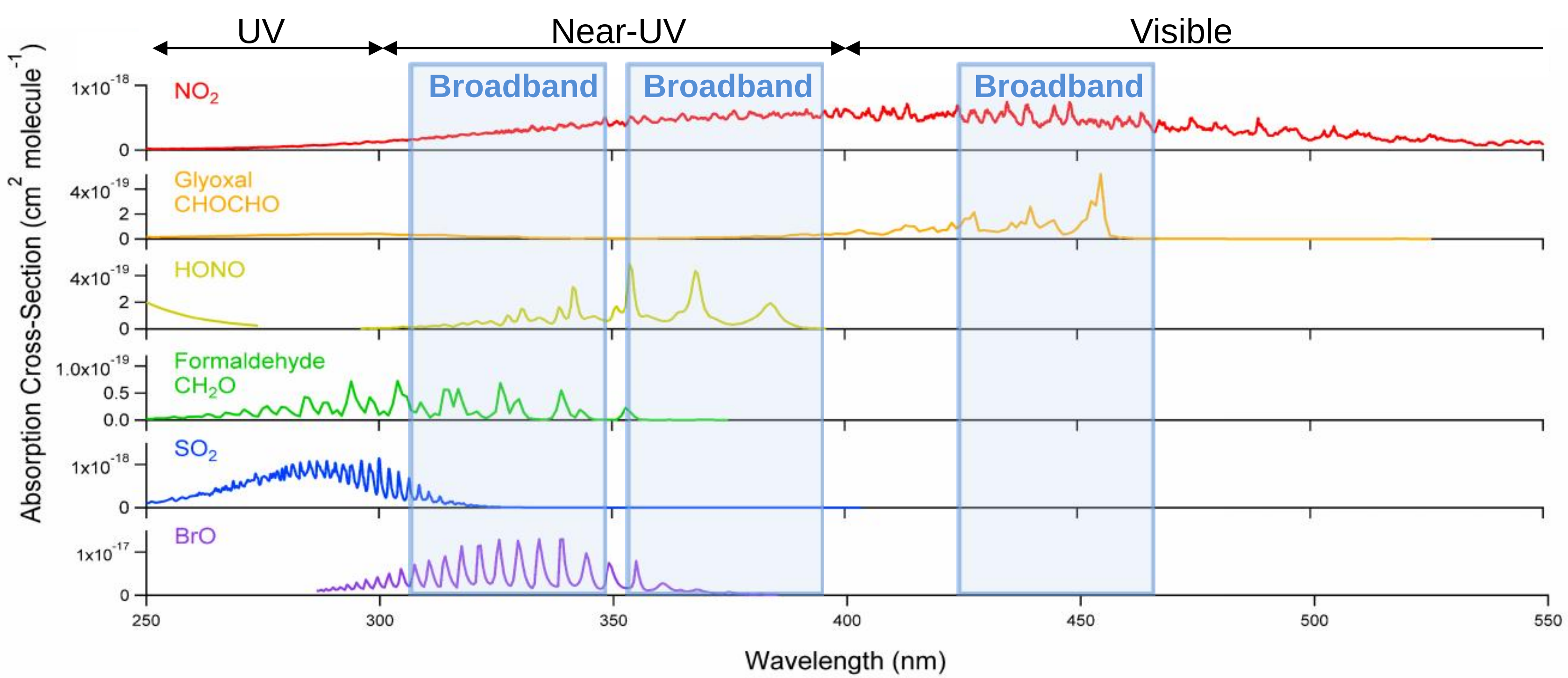

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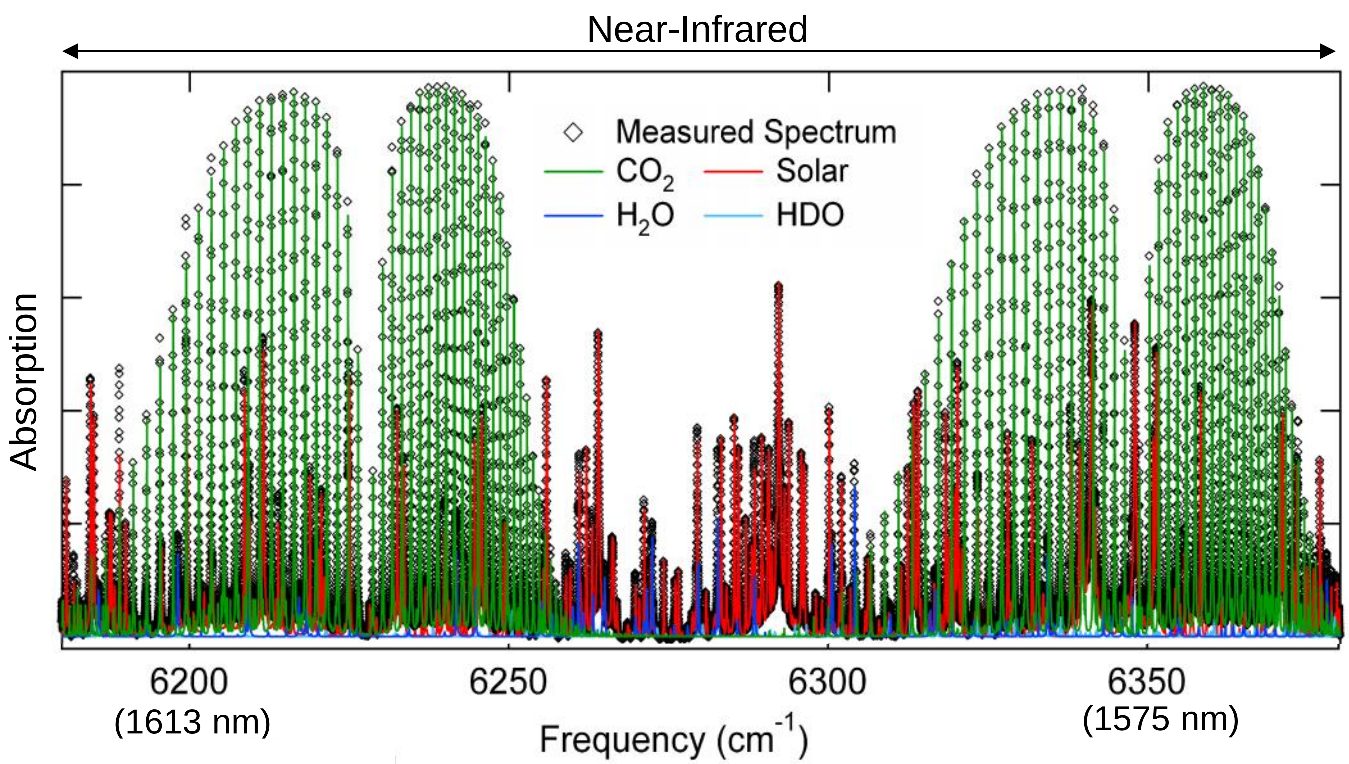


④ Measurement Platform

Increasing Complexity

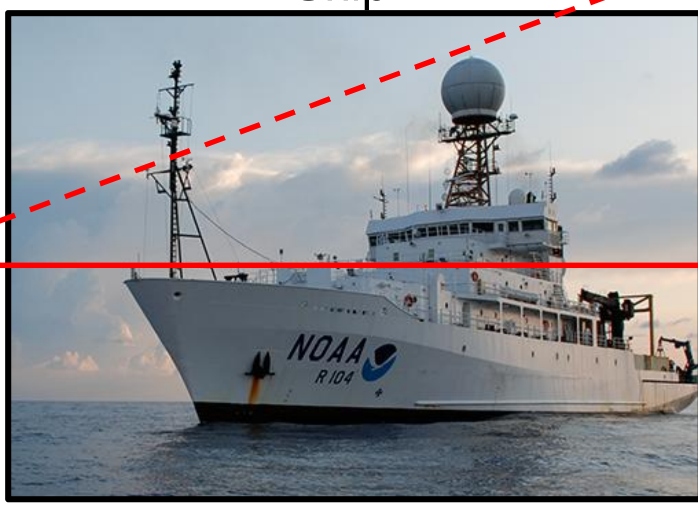
Ground and Tower Sites

Southern Oxidant and Aerosol Study – Alabama 2013
BBCEAS measurements of aerosol extinction

Mobile Ground Sites

Agricultural and Oil/Gas Study – Colorado 2014
CRDS measurements of NH_3

Ship



Air Quality and Climate Study – California 2010
CRDS measurements of NO, NO_2, and N_2O_5

Aircraft

Air Quality and Climate Study – California 2010
CRDS measurements of aerosol extinction

Other Considerations for a Field Instrument

Sampling time

Precision and detection limit

} Closely related

Method for acquiring zeros (I_0)

Method for calibration or validation

Materials for sample handling

Optical stability and mirror cleanliness

Engineering requirements: Size, weight, and portability

Automation and ease of use

Sampling Time Must Be Appropriate For Platform

Ground and Tower Sites

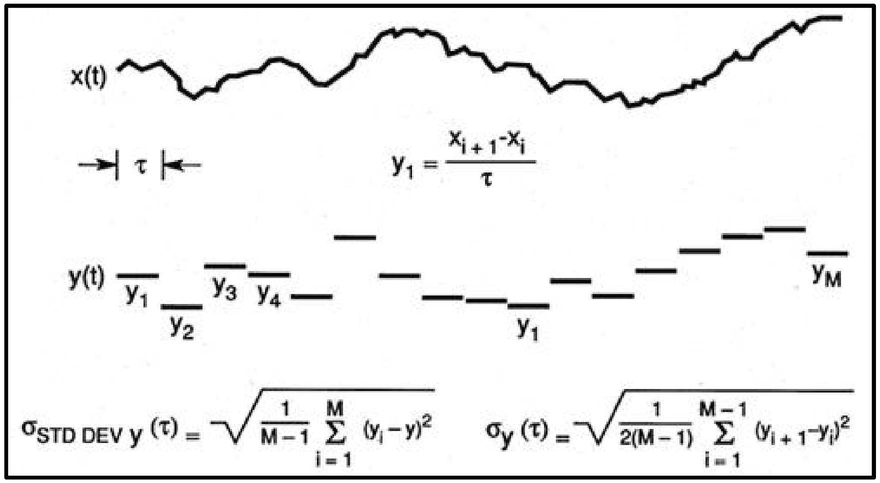
Mobile Ground Sites

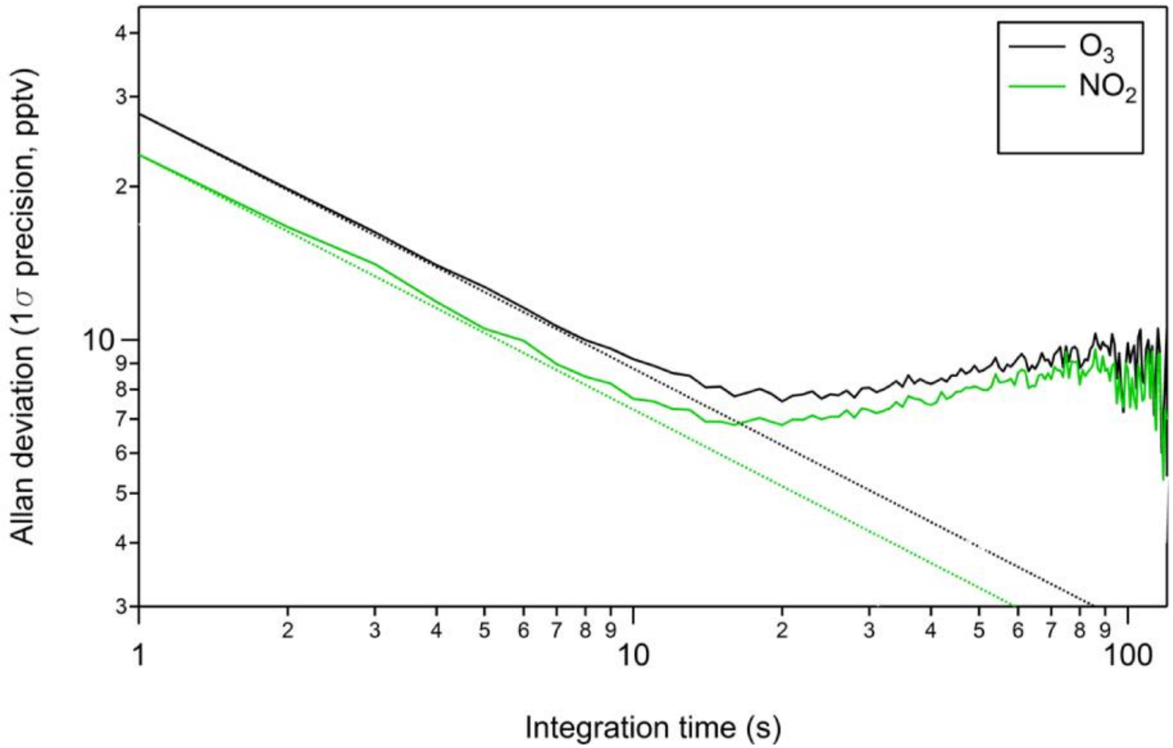
Ship

Aircraft

Detection Limit and Precision

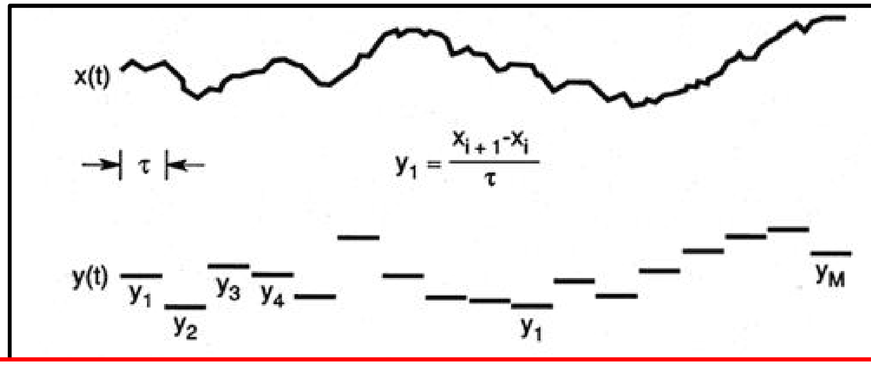
Allan Deviation



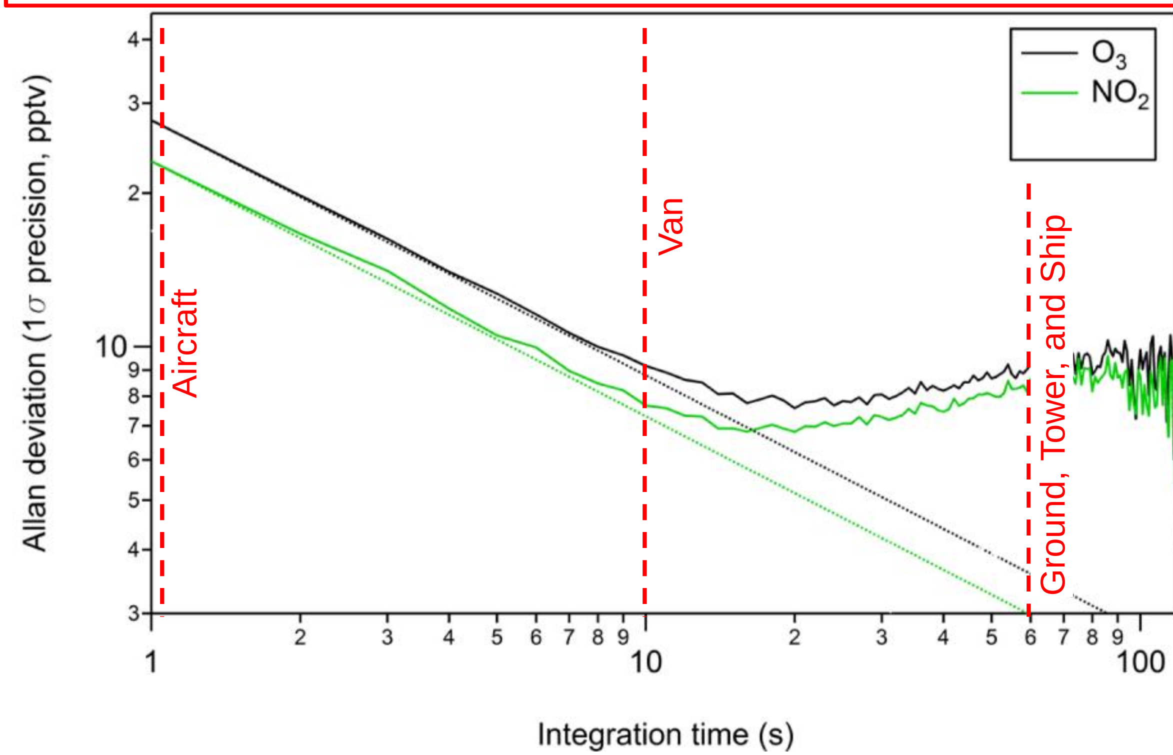


Detection Limit and Precision

Allan Deviation



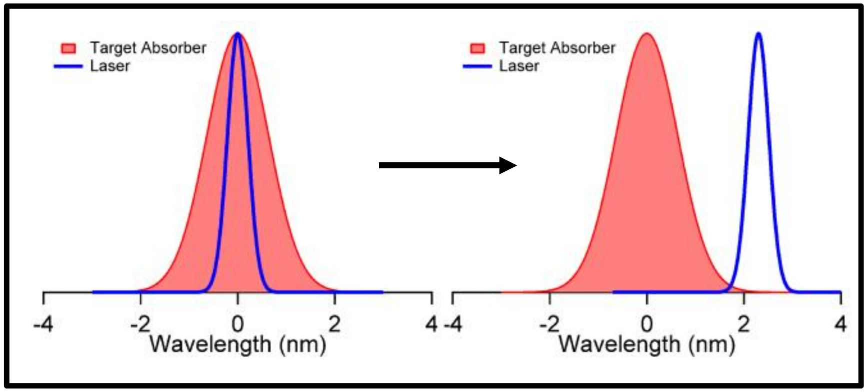
The precision must be sufficient to measure ambient concentrations on the time scale of the measurement platform.



Methods for Determining I_0

All cavity enhanced spectroscopy techniques are described by light extinction that follows Beer's Law. It is necessary to measure a known reference extinction, I_0.

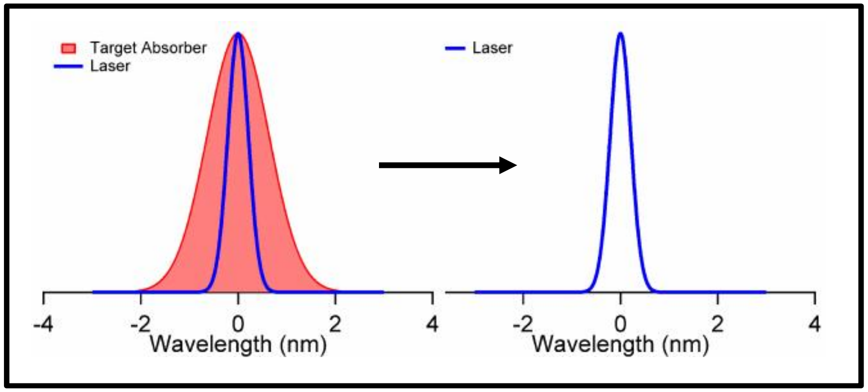
Scan the wavelength.
Example: CO_2 measurement in the mid-IR



Fill the cavity with synthetic "zero air".
Example: Most NOAA field instruments

Remove the target species.
Example: NO_3 scrubbed with NO

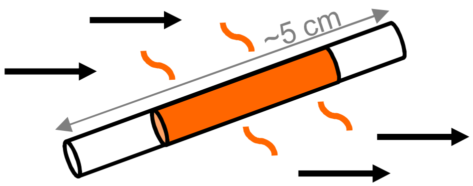
Filter the sample.
Example: Aerosol measurements



Methods for Calibration and Validation

CES instruments directly measure absolute extinction. However, they may be affected by sample losses, chemical interferences, or errors in I_0.

Generate a known gas concentration from a permeation tube:



Sealed teflon tube contains volatile species.
Output depends on temperature and tube length.
Manufacturers: Kin-Tek; Vici

Generate a known gas concentration from a cylinder:

Must be a stable species.
Manufacturers: Scott-Marin, Scott Specialty Gas, NOAA

Generate a known gas concentration from a real-time reaction:

Example:
HCl (permeation tube) + H_2O + $NaNO_2$ → HONO

Generate known aerosol samples:

Generate and dry particles from solution.

Measure the size distribution and number with a scanning mobility particle sizer.

Methods for Sample Handling

Two concerns:
- Contaminating the sample.
- Losing sample to surfaces.

GAS SPECIES

<u>Reactive trace gases:</u>
- Teflon is used for all parts in contact with sample air.

- For "sticky" trace gases (NH_3, acids), minimize the inlet length, number density, and residence time.

<u>Unreactive trace gases:</u>
- Teflon or metal is used.

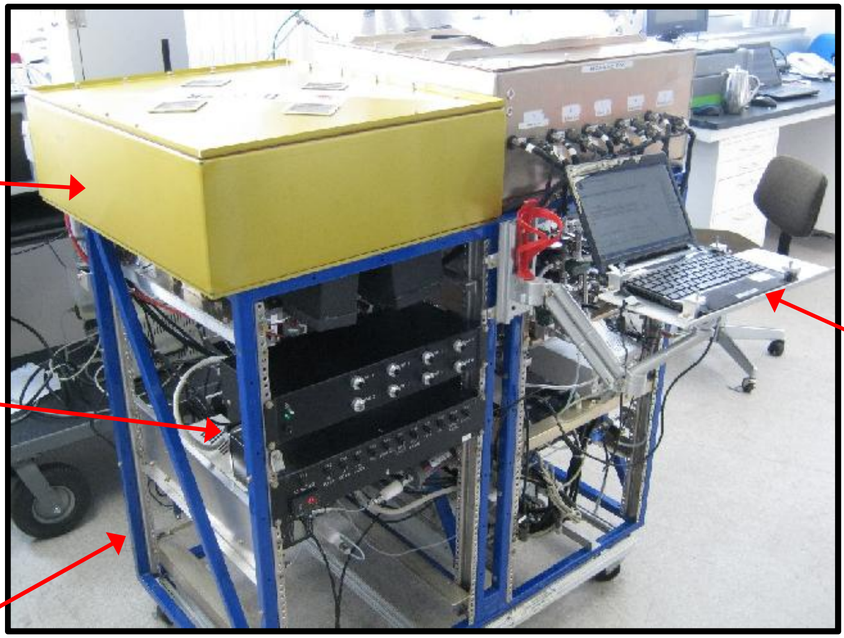
AEROSOL PARTICLES

- Plastics can easily accumulate a static charge that attracts particles. Only metal and electrically-conductive tubing can be used.

- Aerosol particles can be lost inertially. It is necessary to calculate and minimize the inertial losses from sharp bends in the flow path.

Case Study #1: Aerosol Extinction

Scientific problem: Aerosol extinction
Technique: Cavity ringdown spectroscopy (narrowband, pulsed)
Spectral region: 405, 532, and 660 nm
Platform: Aircraft



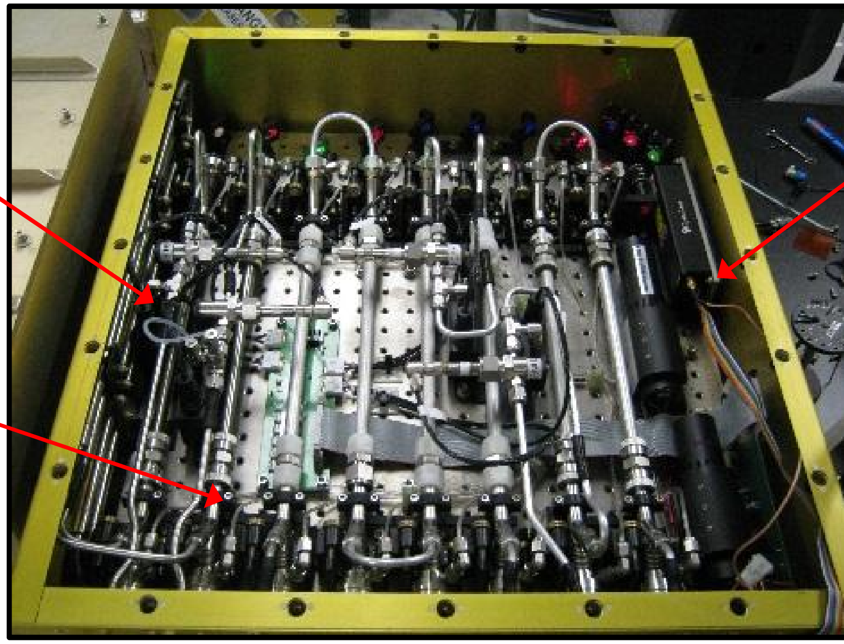
Nick Wagner, Justin Langridge, and Bernie Mason

Case Study #1: Aerosol Extinction

Eight optical cavities

Instrument is built on an optical "breadboard."

Each mirror has a small flow of filtered air to prevent particles from collecting on the mirrors.



Three channels are humidified and one is denuded to remove volatile species.

NO_2 and O_3 (which absorb at 405 and 532 nm) are removed using activated charcoal.

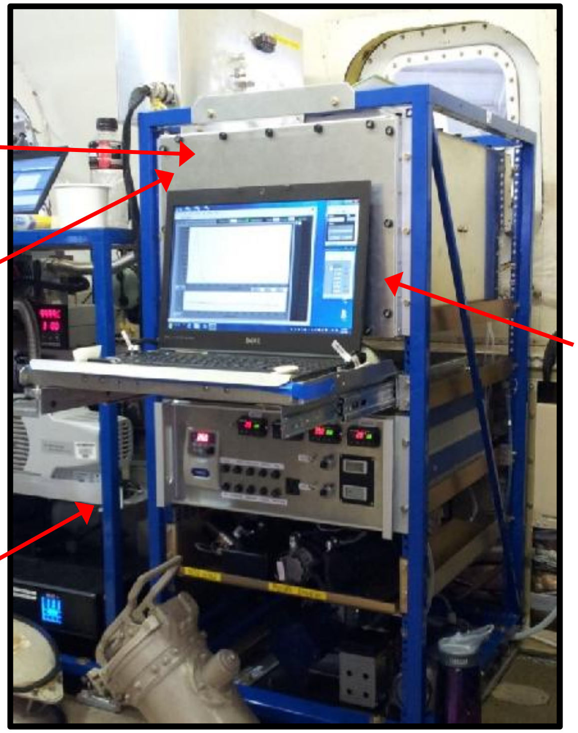
Sampling time:	1 second (1000 ringdowns)
Sensitivity:	0.1 $Mm^{-1} = 10^{-9}$ cm^{-1} in 1 second
Method for acquiring zeros:	Ambient air is filtered
Method for validation:	Comparison with scattering instrument
Materials:	Metal cells with conductive tubing
Engineering:	~1.2 m x 0.05 x 0.05 m; 90 kg
	Fully automated

Participated in four aircraft field campaigns since 2010.

Nick Wagner, Justin Langridge, and Bernie Mason

Case Study #2: Glyoxal and Nitrous Acid

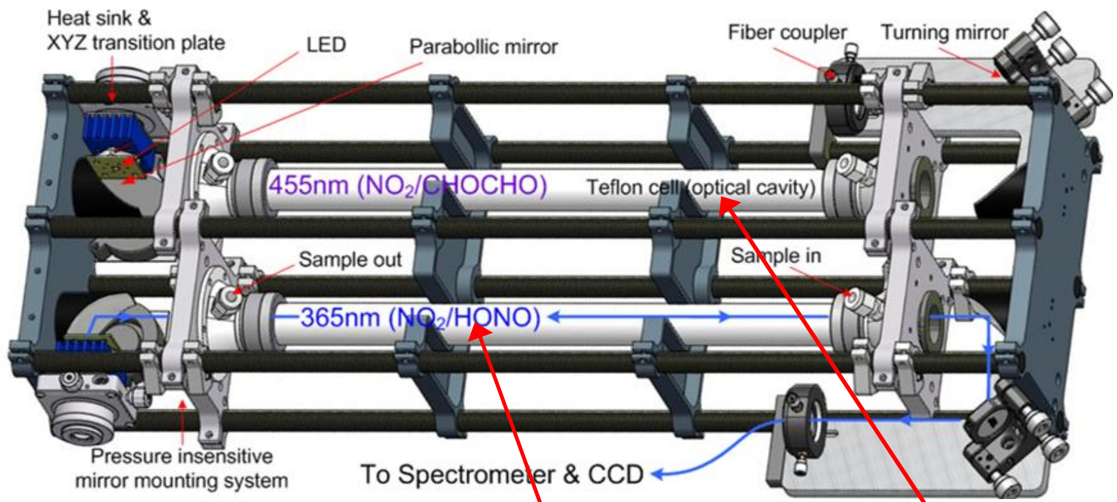
Scientific problem: Photochemical reactions; aerosol chemistry
Technique: Broadband cavity enhanced spectroscopy
Spectral region: 360 – 390 nm; 440 – 470 nm
Platform: Aircraft



Kyung-Eun Min, Kyle Zarzana, Rebecca Washenfelder

Case Study #2: Glyoxal and Nitrous Acid

Instrument is built in a cage system.



Aerosol particles are removed with an inlet filter. No mirror purge flows are used.

HONO and NO2 are measured at 360-390 nm

CHOCHO and NO_2 are measured at 440-470 nm

Sampling time:	5 sec
Sensitivity:	3 x 10^{-9} cm^{-1} at 368 nm; 7 x 10^{-10} cm^{-1} at 455 nm in 5 sec
Method for acquiring zeros:	Inlet is overflowed with zero air
Method for validation:	Standard additions of NO_2
Materials:	Teflon
Engineering:	~1.0 m x 0.06 x 0.05 m; 102 kg
	Fully automated

Participated in two aircraft field campaigns since 2013.

Kyung-Eun Min, Kyle Zarzana, Rebecca Washenfelder

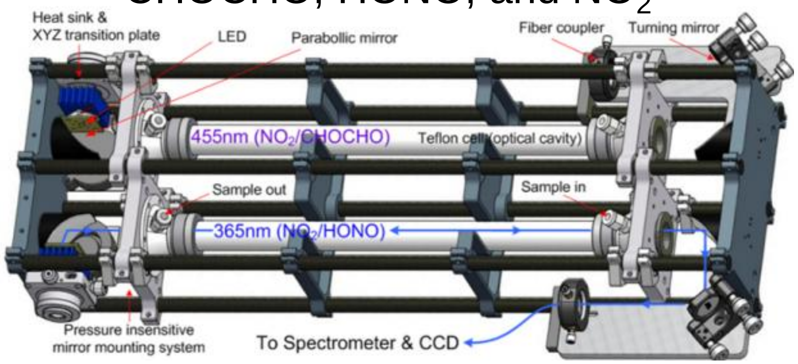
NOAA Tour – Wednesday 5 pm

CRDS and ICOS instruments to measure NH_3, CO_2, CH_4, CO, H_2O, and N_2O installed in van

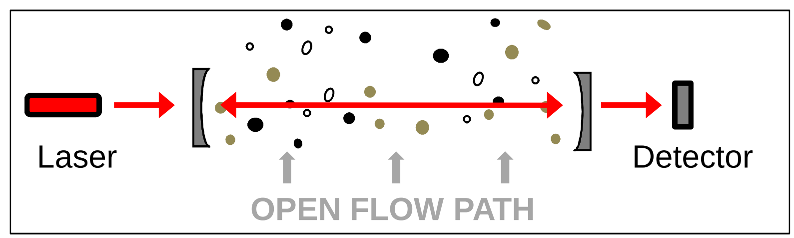
Broadband instrument to measure aerosol extinction at 360 – 420 nm

CRDS instrument to measure NO, NO_2, NO_y, and O_3

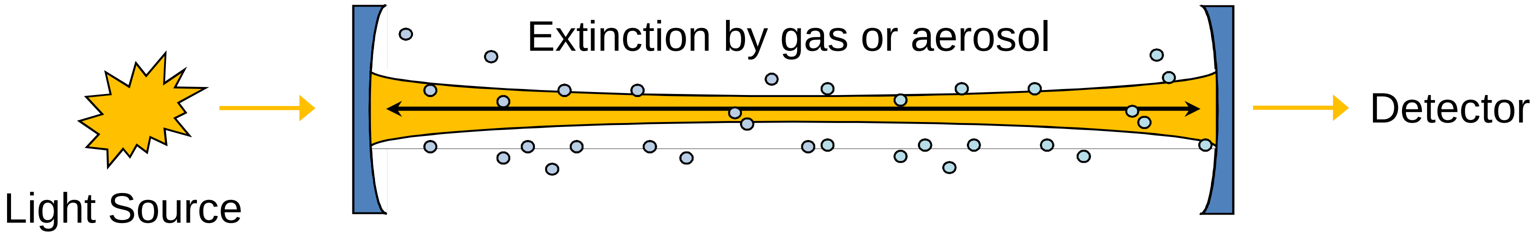
Broadband instrument to measure CHOCHO, HONO, and NO_2



Open-path CRDS instrument to measure aerosol extinction



Conclusions



The defining categories for an atmospheric field instrument are:

① Atmospheric species (scientific question)
② Analytical technique (CRDS, ICOS, BBCRDS, BBCEAS)
③ Spectral region
④ Measurement platform

Other important considerations are:

Sampling time
Precision and detection limit
Method for acquiring zeros (I_0)
Method for calibration or validation
Materials for sample handling
Optical stability and mirror cleanliness
Engineering requirements: Size, weight, and portability
Automation and ease of use