Spectroscopic techniques for atmospheric analysis

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Introduction-Educational Background

- 1991 Ph.D. University of Iowa, *Atomic Molecular and Laser Physics.*
- 1987 International Center for Theoretical Physics; Trieste, Italy.
- 1985 M.S. Addis Ababa University Physics: *Surface Science.*
- 1977 B.S. Addis Ababa University *Physics Sec. Education/Math minor*

- ***1-B. Area of field of specialization***

- Experimental and Theoretical (Computational) Atomic, Molecular and Optical Physics /and Chemical Physics

Current Research

Research in my group involves the use of spectroscopic techniques and theoretical methods for atmospheric applications: The focus is measuring in the laboratory and the field the optical and physio-chemical properties of Biomass Burning (BB) aerosol to understand the role of BB Aerosol on climate, regional weather, air quality, urban heat and health. We investigate:

- **Laboratory:**

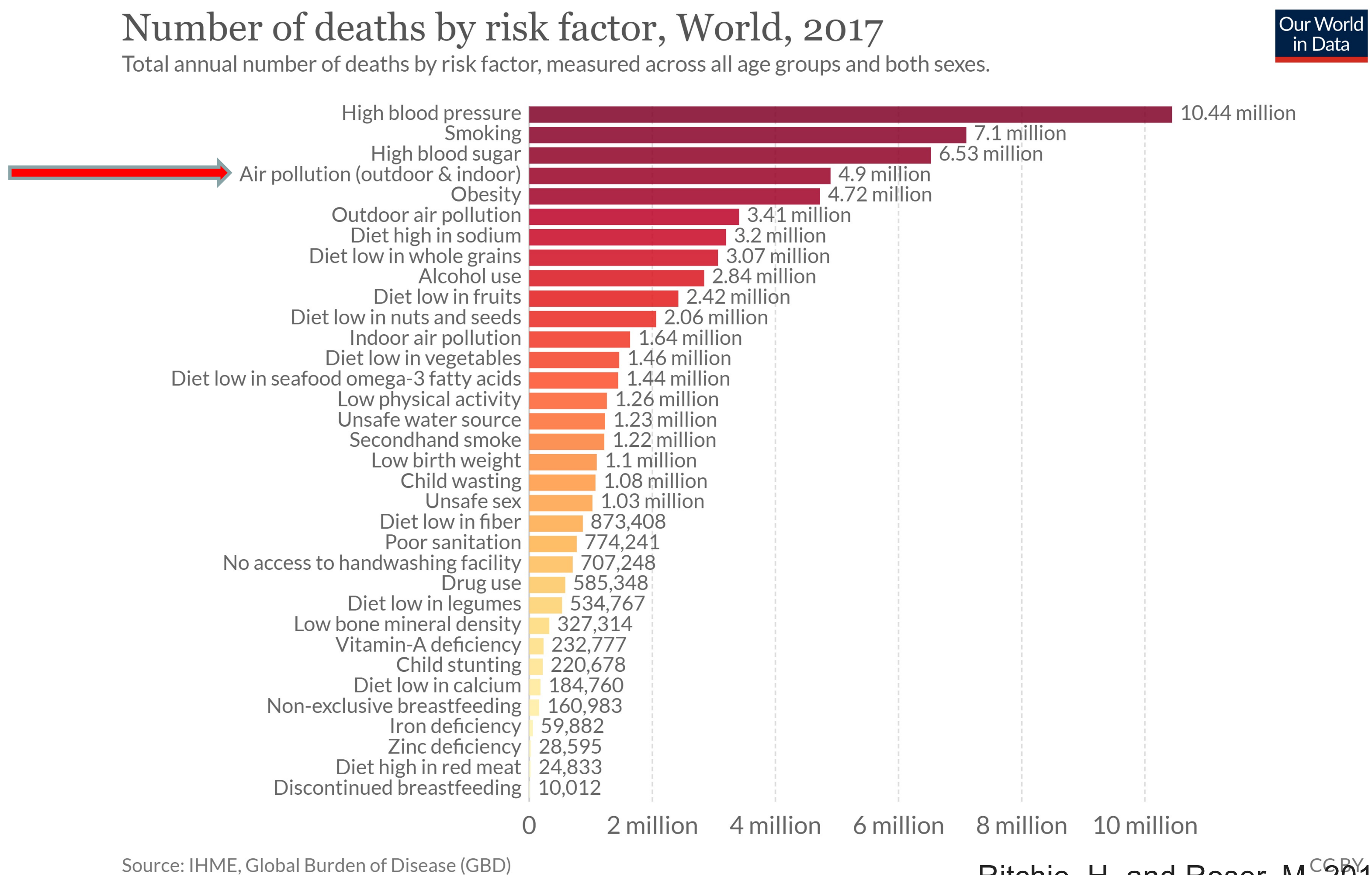
1) How do relative humidity (RH) photochemical aging morphology and burn conditions, fuel type influence the size distribution, optical properties, chemical properties and emission factors of BB aerosols produced from sub-Saharan Africa Biomass Fuels.
2) Drivers of Toxicity of Complex Aerosols from Biomass Burning

- Modeling: Extract Refractive Indices using T-Matrix and RDG Theory using High resolution TEM images from Filter samples

- Field Studies: Field measurements of power plant emissions and wildfire emissions and their impact on Air Quality.
- **Interdisciplinary research that depends on contributions from physicists, chemists, chemical engineers, atmospheric scientists, epidemiologists, computational scientists.**

What motivated me to do this?

- Air pollution kills an estimated seven million people worldwide every year. WHO data shows that 9 out of 10 people breathe air that exceeds WHO guideline limits containing high levels of pollutants (Murray et al., 2020; WHO, 2019).
- Death rates from air pollution are highest in low-to-middle income countries, with more than 100-fold differences in rates across the world.
- pollutants can lead to health complications including ischemic heart disease, lung cancer, stoke, and chronic obstructive pulmonary disease (COPD)
- Recent studies link air pollution to brain health and **Alzheimer's** disease (PNAS, 2021)
- Accelerated decline in episodic memory was associated with long-term $PM_{2.5}$ exposure
- **Air pollution linked to neurodegeneration markers (Nature, 2021)**
- Air pollution linked to dementia and cardiovascular disease (JAMA-NEUROLOGY, 2020)



Ritchie, H. and Roser, M. 2018

Outline

- Available analytical techniques and environmental constraints for field work
- Gas detection- IR, Chemiluminescence and fluorescence techniques
- Optical techniques-Cavity ring down spectroscopy
- Scattering of light-Nephelometry
- Photoacoustic Spectroscopy- absorption measurements

Available analytical techniques

- Mass Spectrometry
- Gas Chromatography
- Chemical Methods
- Solid State Sensors
- Optical Techniques

Optical Techniques

- Photoacoustic
- Laser Induced Fluorescence
- Direct Absorption

Analytical Techniques in Atmospheric applications

Concentration Scale: ppm (10^{-6}) - ppt(10^{-12}) and below !

Method	Examples	Signal	Background	Sensitivity	Calibration
Mass Spectrometry	CIMS	Ion Counts	Dark	Excellent, Rapid	Relative
Fluorescence Spectroscopy	LIF CL	Photon Counts	Dark	Excellent, Rapid	Relative
Chromatography	GC-MS Liquid Chrom.	Elution Time	Dark	Excellent, Slow	Relative
Chemical Separation	Mist Chamber Denuder			Good, Slow	Relative
Direct Absorption Spectroscopy	DOAS IR Absorption	I/I_0	Bright	Poor* *Depends on path length	Absolute

Environmental Constraints

The outside world is harsh unlike laboratories

- **Electromagnetic Interference**
- Power Supplies:
- Possible different line voltages on board aircraft and Vehicles.
- Ambient Temperature: remote standalone instruments Can undergo very wide temperature ranges. Temperature range can go from –60 ^{o}C to 80^{o}C
- No optical tables with tuned vibrations absorbers,

Environmental Constraints

- **No Clean rooms leading to dirt in optical components, corrosion explosion**

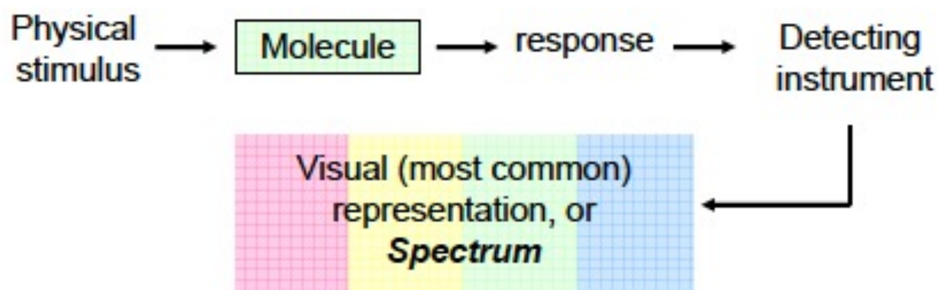
- **No Pressure Stability- leading to poor mechanical stability, optical stability and thermal stability**

- **Unattended operation**:

No fulltime dedicated people. This creates problems with maintenance, calibration and long-term overall stability.

- No freedom on dimensions and weight- severe constraints

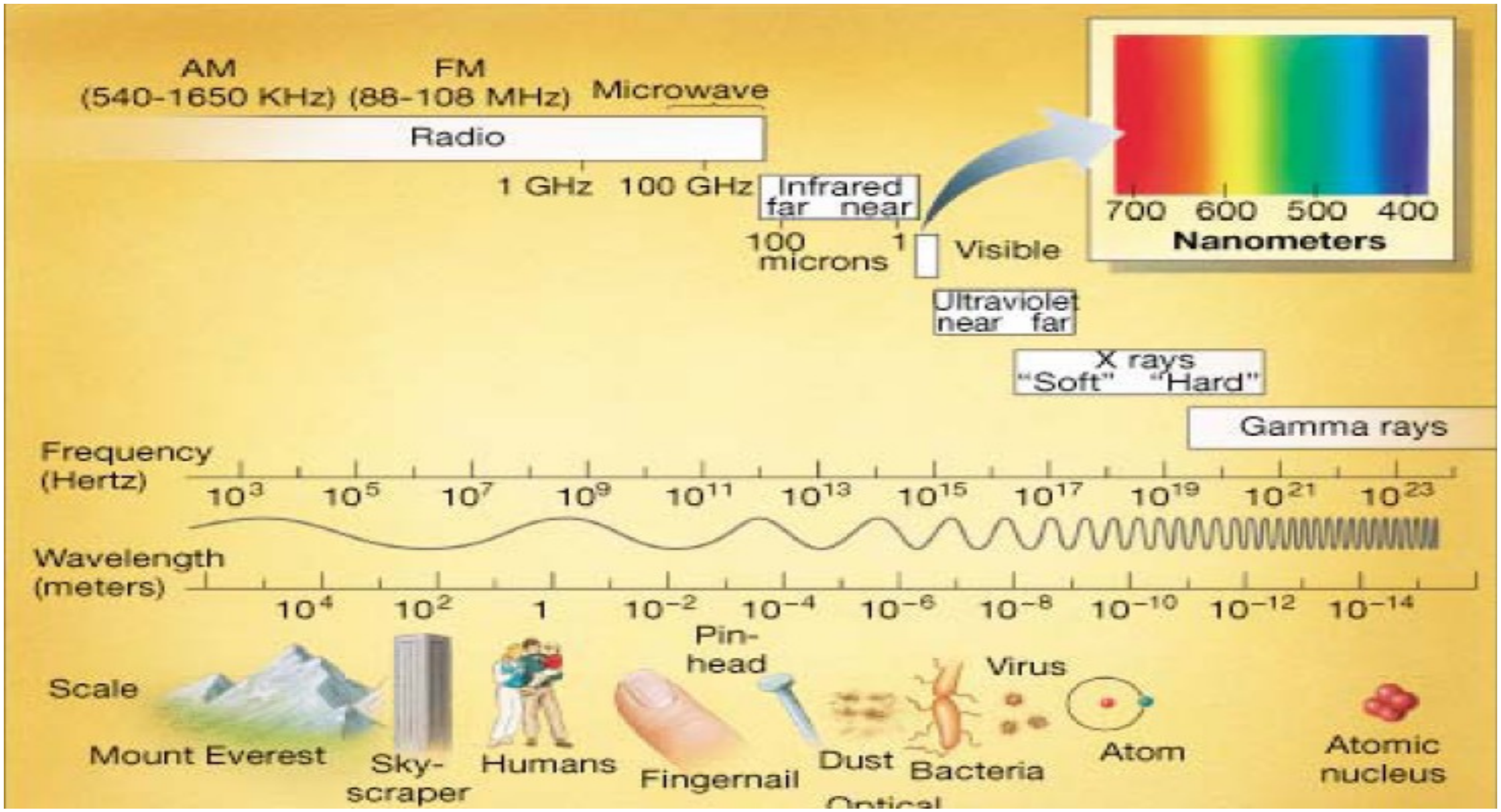
SPECTROSCOPY - Study of spectral information



Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum.

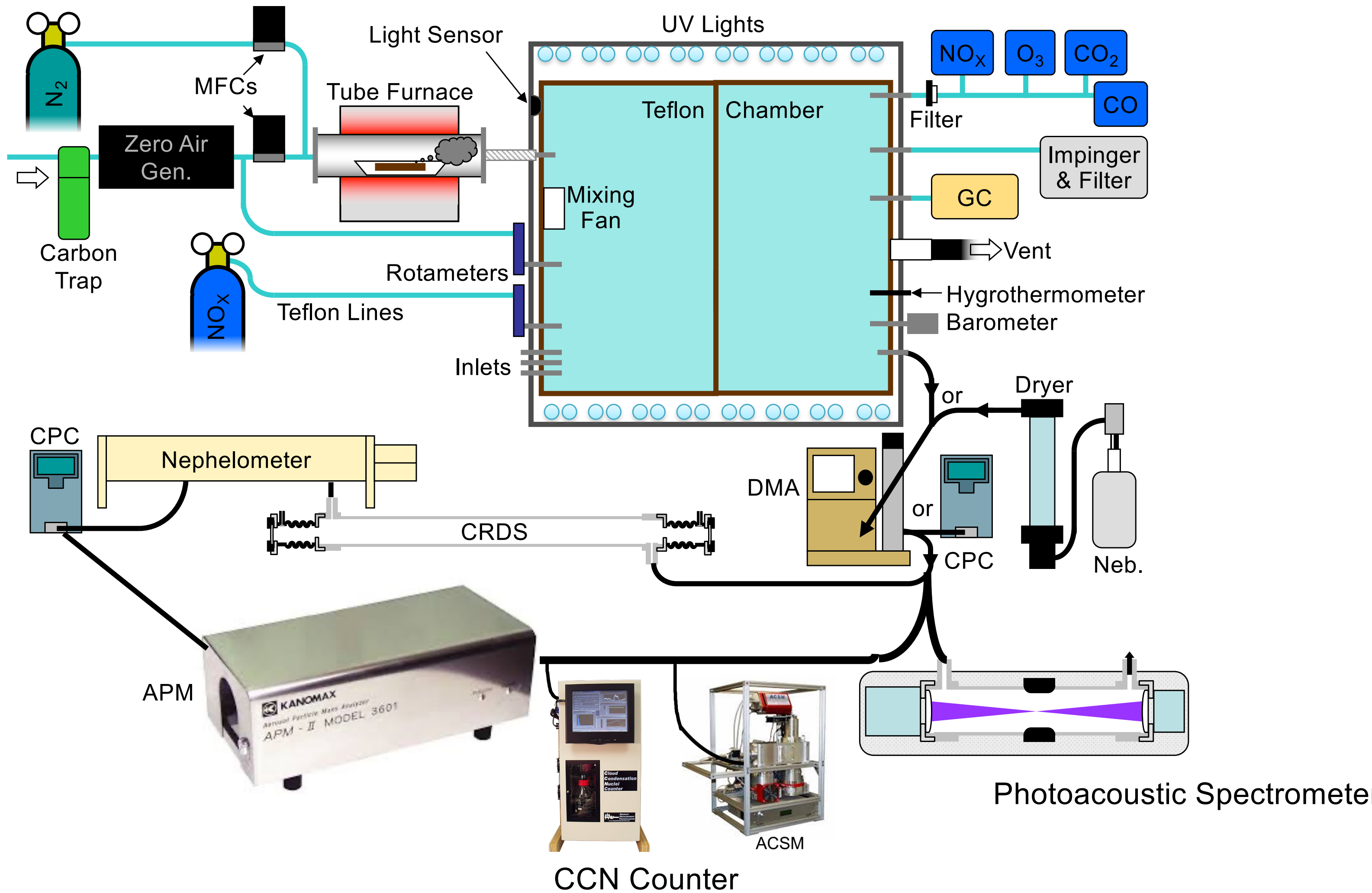
Wide Range of Types of Electromagnetic Radiation in nature.

1. Only a small fraction (350-780 nms. is visible light).
2. The complete variety of electromagnetic radiation is used throughout spectroscopy.
3. Different energies allow monitoring of different types of interactions with matter.



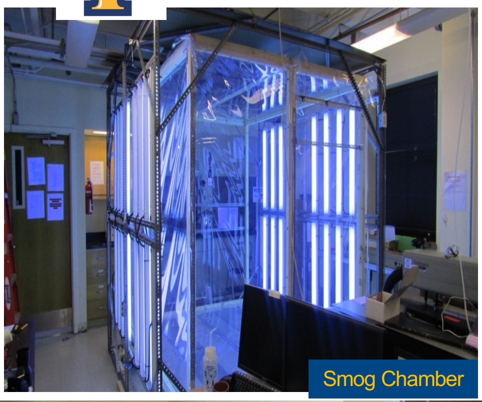
Common Spectroscopic Methods Based on Electromagnetic Radiation

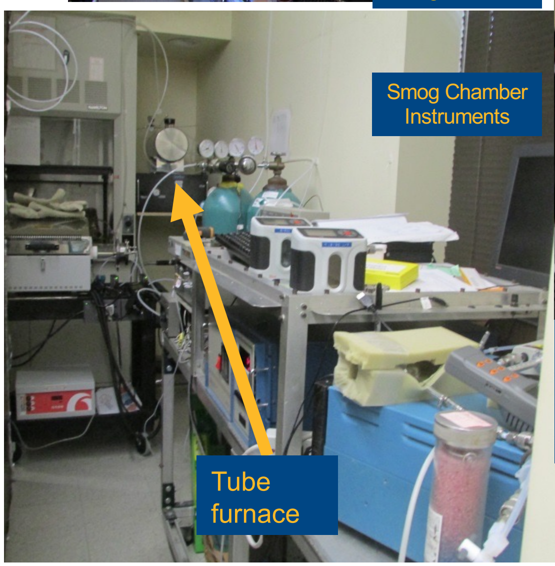
Type of Spectroscopy	Usual Wavelength Range	Usual Wave number Range, cm^{-1}	Type of Quantum Transition
Gamma-ray emission	0.005-1.4 Å	_	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1-100 Å	_	Inner electron
Vacuum ultraviolet absorption	10-180 nm	$1x10^6$ to $5x10^4$	Bonding electrons
Ultraviolet visible absorption, emission, fluorescence	180 -780 nm	$5x10^4$ to $1.3x10^4$	Bonding electrons
Infrared absorption and Raman scattering	0.78-300 μm	$1.3x10^4$ to $3.3x10^1$	Rotation/vibration of molecules
Microwave absorption	0.75-3.75 mm	13-27	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6-10 m	$1.7x10^{-2}$ to $1x10^3$	Spin of nuclei in a magnetic field

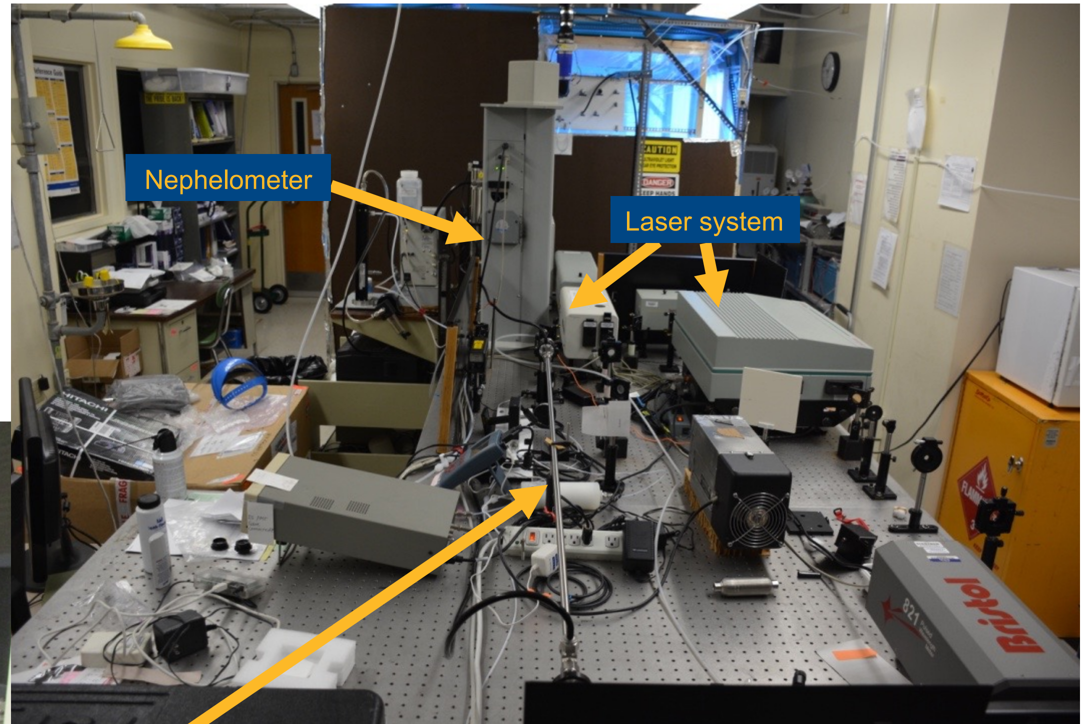


N2
MFCs
Light Sensor
UV Lights
NOX
O3
CO2
CO
Filter
Tube Furnace
Teflon
Chamber
Zero Air Gen.
Impinger & Filter
Carbon Trap
Mixing Fan
GC
Vent
Rotameters
NOX
Teflon Lines
Hygrothermometer
Barometer
Inlets
or
Dryer
CPC
Nephelometer
DMA
or
CRDS
CPC
Neb.
APM
KANOMAX
Aerosol Particle Mass Analyzer
APM - II MODEL 3601
ACSM
Photoacoustic Spectrometer
CCN Counter

Optical Properties Measurement Facility



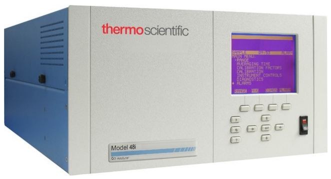


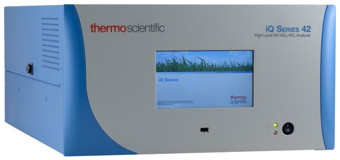


Optical Properties Instruments

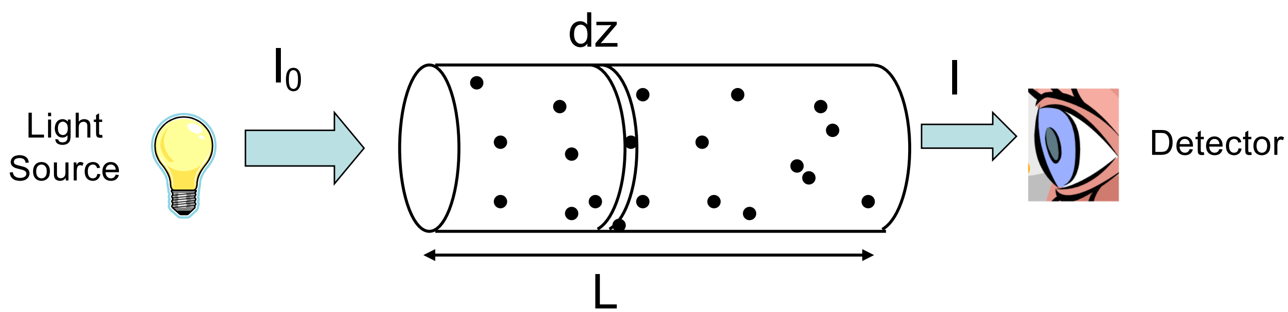
Most gas detection uses spectroscopy

- Interaction of matter with electromagnetic radiation
  - UV, visible light, or IR
  - X-rays, gamma rays
- Absorption spectroscopy
  - Target molecule absorbs the light
- Emission spectroscopy
  - Incident radiation causes molecule to emit light at a new wavelength





Beer's Law (a.k.a. Lambert-Beer Law)



$$dI = -\alpha \times I \times dz$$

$$\int_{I_0}^{I} \frac{dI}{I} = -\alpha \int_{0}^{L} dz$$

$$\boxed{I(z) = I_0 \exp[-\alpha L]}$$

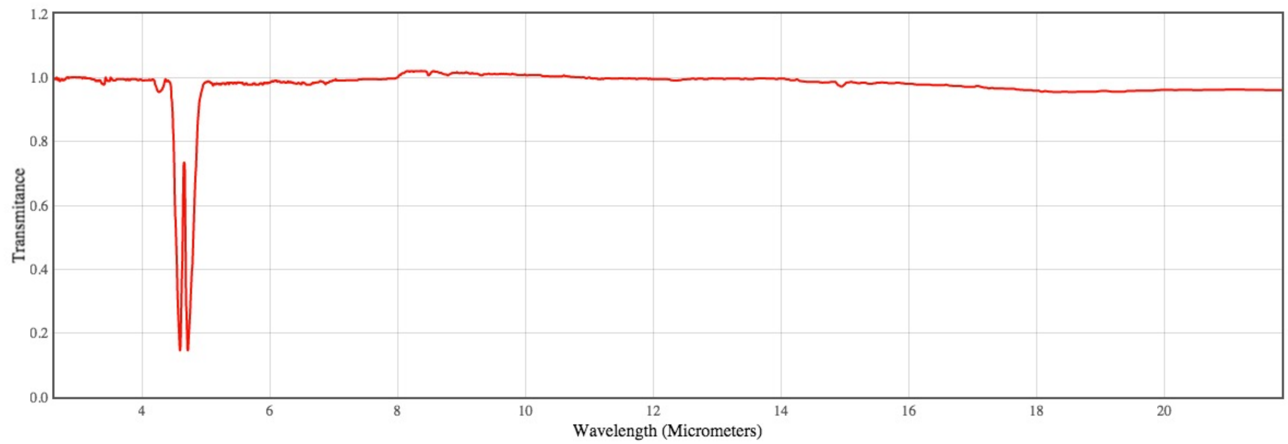
$\alpha \equiv$ Absorption (Extinction) Coefficient

α (cm^{-1}) = N_{Abs} (cm^{-3}) σ (cm^2)

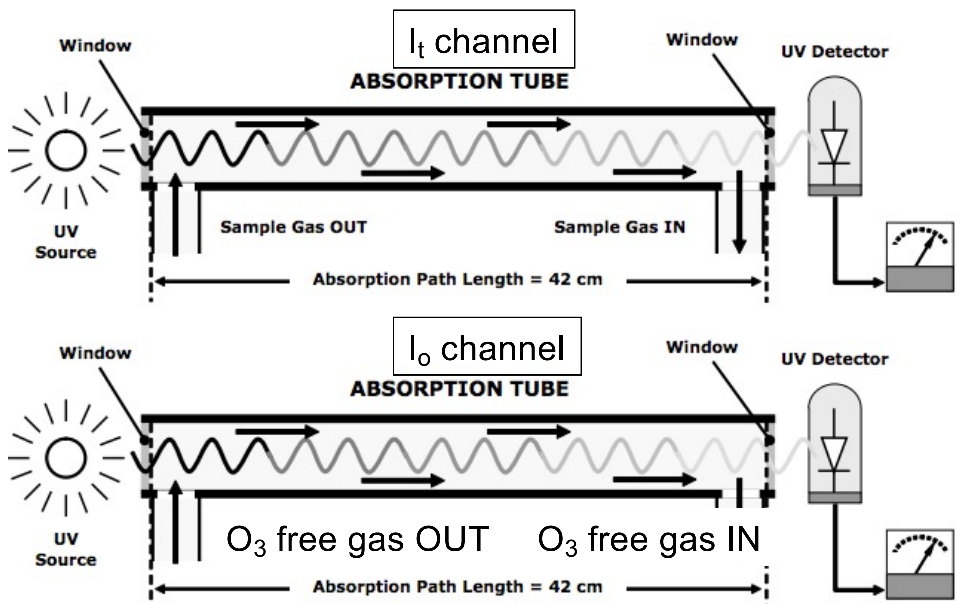
If σ is known, N can be determined *absolutely*

CO absorbance spectrum (IR)

Fraction of light passing through

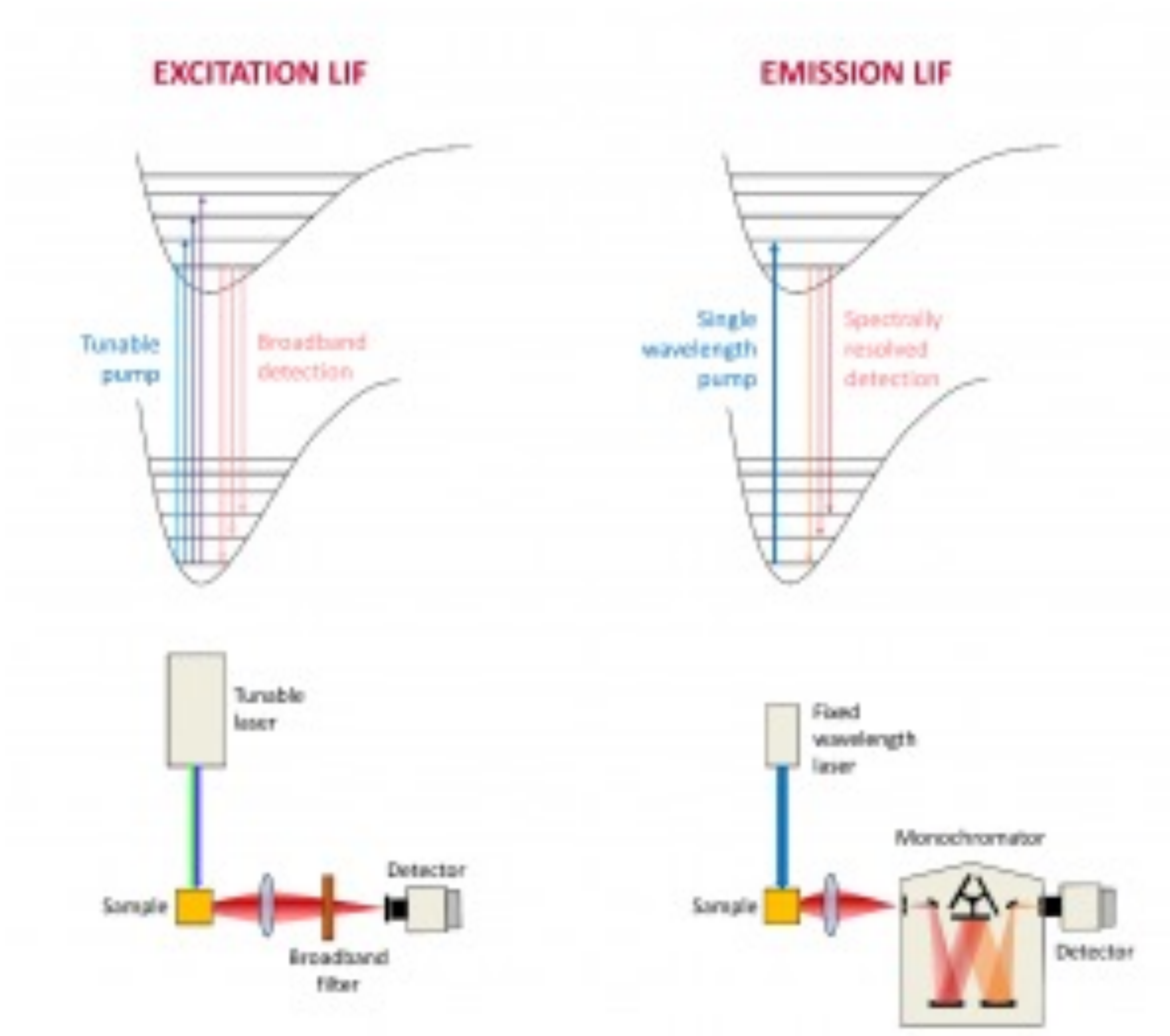


CO and O_3: Absorption



Many SO_2 monitors use fluorescence

- $SO_2 + h\nu_{214nm} \rightarrow SO_2^*$
- $SO_2^* \rightarrow SO_2 + h\nu_{330nm}$
- Signal at 330 nm is a function of:
  - Intensity of 214 nm light
  - Absorption coefficient of SO_2
  - Decay rate of SO_2^* to SO_2


EXCITATION LIF
EMISSION LIF
Tunable pump
Broadband detection
Single wavelength pump
Spectrally resolved detection
Tunable laser
Sample
Detector
Broadband filter
Fixed wavelength laser
Monochromator
Sample
Detector

Field Research

- **Field studies: WINTER- [Wintertime INvestigation of Transport, Emissions, and Reactivity]**

Instruments are rack mounted
Inlets are located along the fuselage.
An SO_2 analyzer utilizing on UV fluorescence detection.
Airborne Ring-down Nitrogen Oxide Laser Detector (A.R.N.O.L.D.),
a Particle Into Liquid Sampler (PILS2) with fraction collector,
a time-of- flight Aerosol Mass Spectrometer (AMS) and a CO/CO_2 analyzer

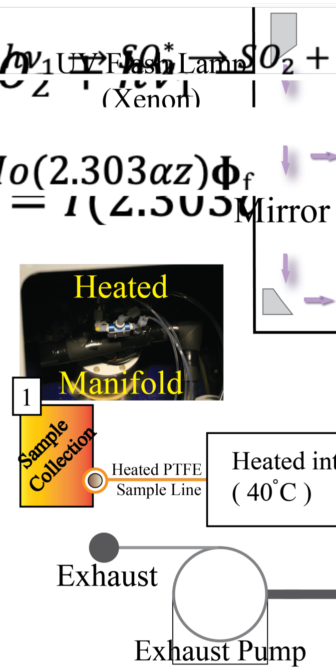
SPECTROSCOPIC INSTRUMENTATION ON BOARD NSF-C-130 PLANE

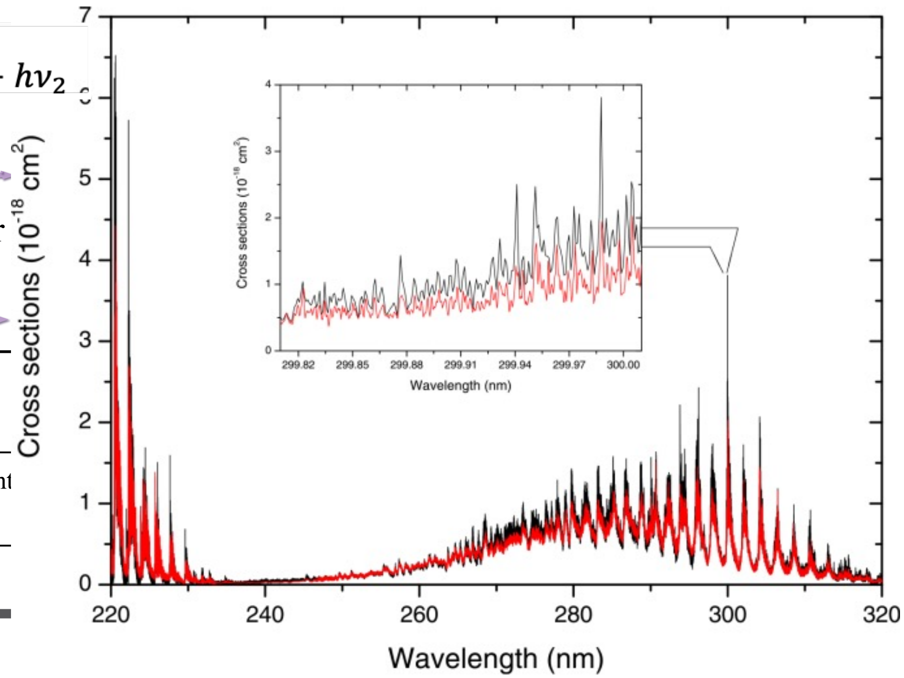
Dr. Greene
NCAT Graduate

Pulsed Fluorescence Spectrometry

(1) $SO_2 + h\nu_1 \rightarrow SO_2^* \rightarrow SO_2 + h\nu_2$

(2) $I = Io(2.303\alpha z)\Phi_f$





Natural Sources of Atmospheric SO_2

- Volcanic activity
  - Episodic violent activity
  - Fuming and venting
- Oceanic Sulfur Cycle
- Forest Fires

Anthropogenic Sources of Atmospheric SO_2

- Power Plant Emissions
  - >Coal – Boiler power generation
- Transportation
- Urban
  - >Diesel / Gasoline
  - >Wood burning

Part I : Literature Review

Why Investigate Atmospheric SO_2

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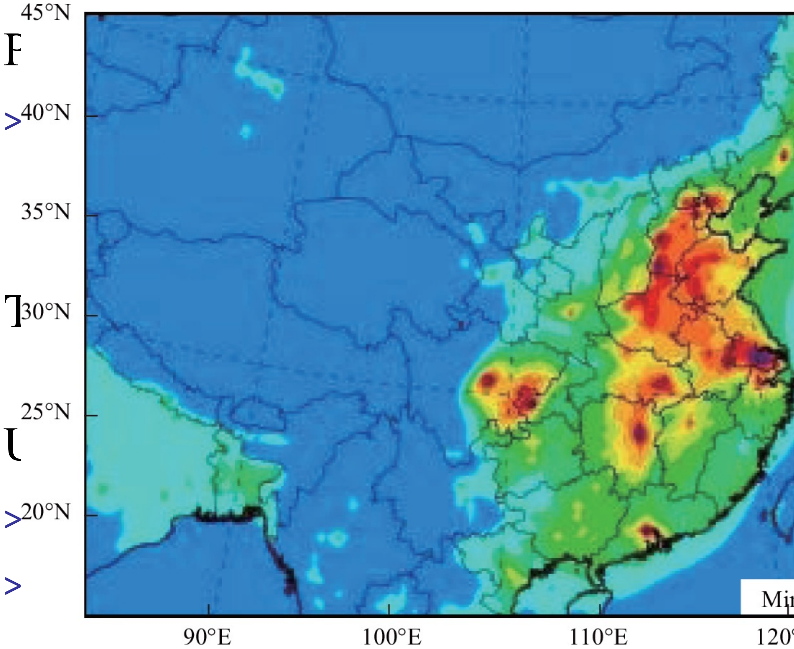
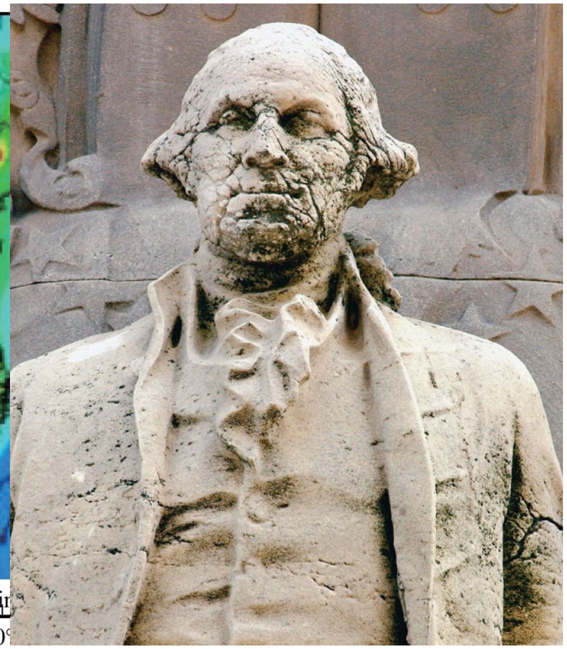




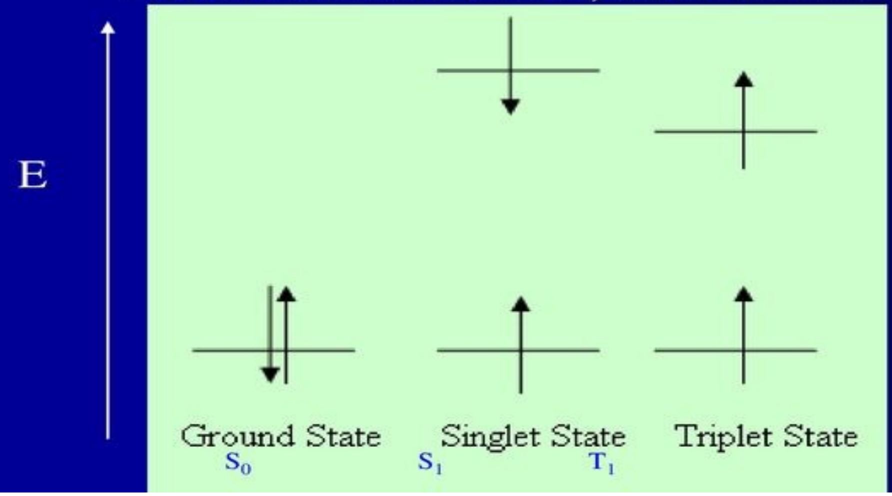
Luminescence

Emission of radiation, which occurs during returning of excitated molecules to ground state

Fluorescence, phosphorescence – excitation is caused by absorption of radiation

Chemiluminiscence – excitation is caused by chemical reaction

Other type of luminiscence – e.g. triboluminiscence, catodoluminiscence, radioluminiscence

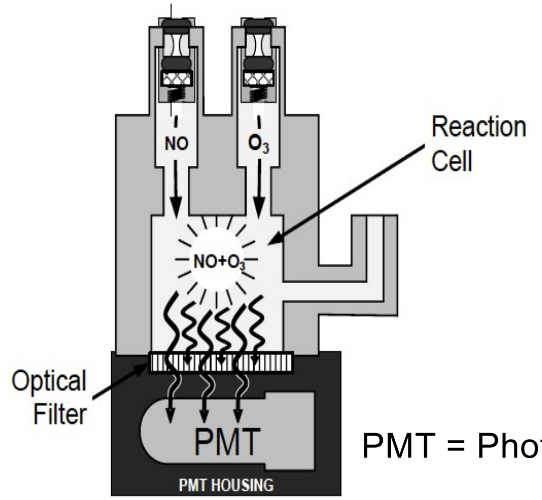


Singlet state - spins of two electrons are paired

Triplet state - spins of two electrons are unpaired

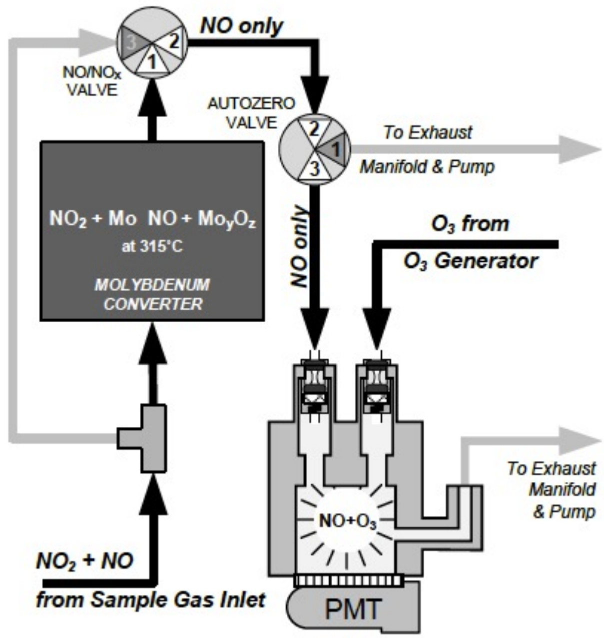
NO_2 chemiluminescence

- Older technology
- $NO + O_3 \rightarrow NO_2^* + O_2$
- Dominant pathway: $NO_2^* + M \rightarrow NO_2$
- Minor pathway: $NO_2^* \rightarrow NO_2 + h\nu_{1200nm}$



PMT = Photo multiplier tube

Detect NO and NO_2 by converting NO_2 to NO

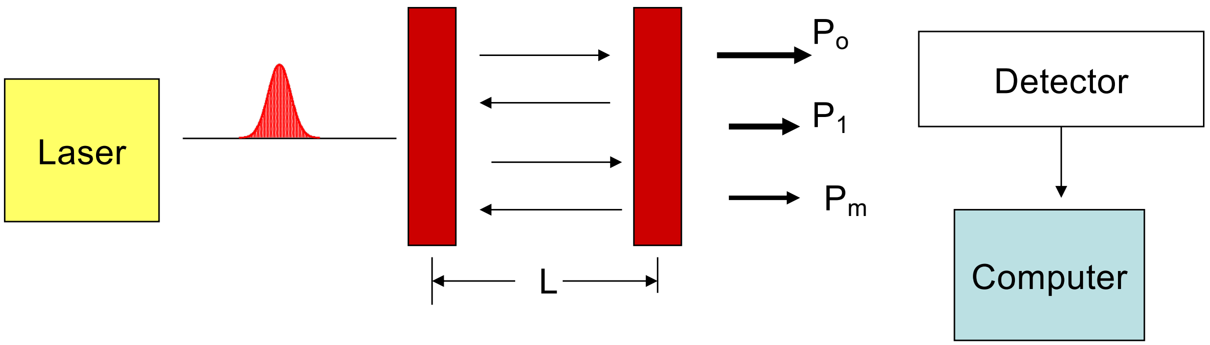


Chemiluminescent NO_2 challenges

- NO_2 is not detected directly
- Many species can interfere and appear as “NO_2”
- Mo catalyst can become saturated or degrade over time
- Problematic when NO_2 is low

Cavity Ring Down Spectroscopy

- A very sensitive technique
- Sample placed between two highly reflective mirrors
- Only decay time dependence of light measured
- Effective absorption path length (dependent on mirror reflectivity) can be very long (several kms)
- Easy to build



- Power of first transmitted pulse is

$$P_1 = T^2 e^{-\alpha L} P_0$$

α is the absorption coefficient

- After each round trip the pulse power decreases by an additional factor

$$R^2 Exp(-2\alpha L)$$

THEORY

$$P_m = (\mathrm{R}e^{-\alpha L})^{2m} P_1 = [(1 - T - A)e^{-\alpha L}]^{2m} P_1$$

$$P_m = P_1 e^{2m[\ln R - \alpha L]} \approx P_1 e^{-2m[T + A + \alpha L]}$$

$$\tau_1 = \frac{L/c}{T + A + \alpha L}$$

- Decay time τ_1
- With out a gas $\alpha = 0$
- The decay time will be lengthened to $\tau_2 = \frac{L/c}{T + A}$

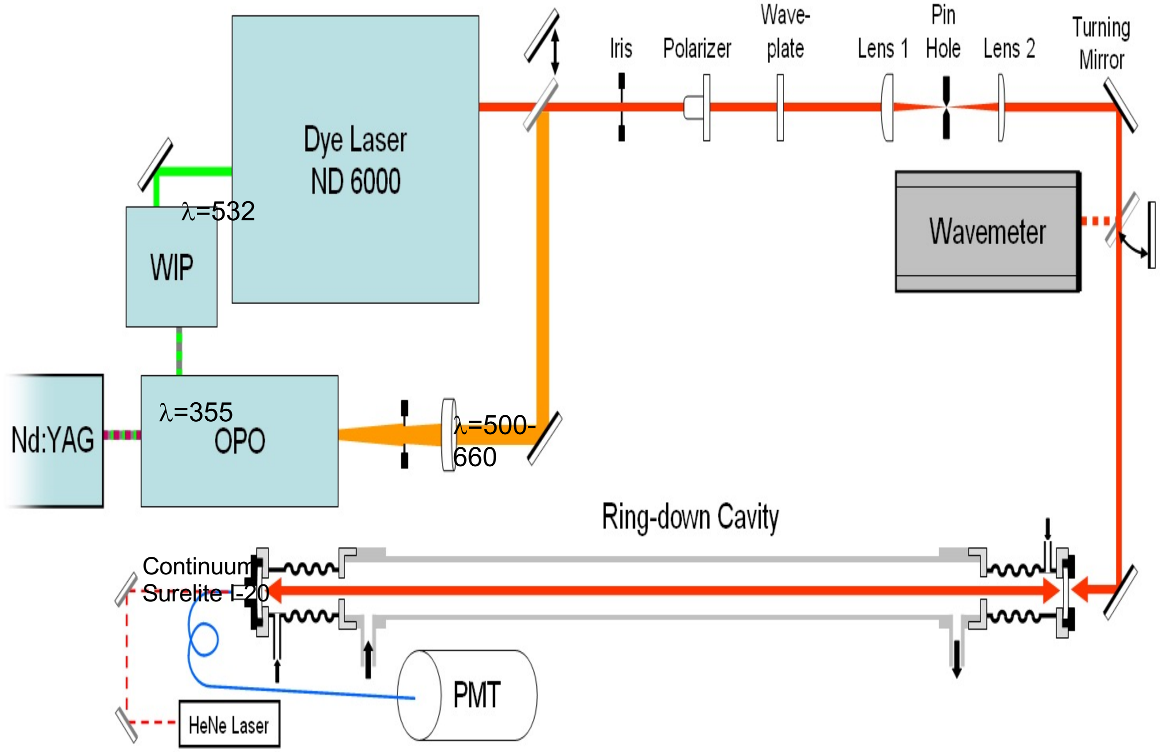
THEORY

- From the difference $$\Delta\tau = \tau_2 - \tau_{1;};$$
- The product

$$\alpha L = (1-R)\,\Delta\tau/\tau_1$$

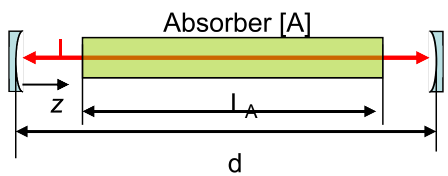
of the absorption coefficient α and cavity length L can be determined as a function of the laser wavelength λ.

- Minimum detectable absorption is limited by the reflectivity R, the unavoidable losses A of the resonator and accuracy of measuring τ_2 and τ_1



Spectra recorded at 2 nm intervals, with 200 shots averaged at each wavelength

Cavity Ring-Down Absorption (Extinction) Spectroscopy



Mirror reflectivity = R

Define $$R_L \equiv \frac{d}{L_A}$$

Beer's Law: $$\frac{dI}{I} = -\alpha dz$$

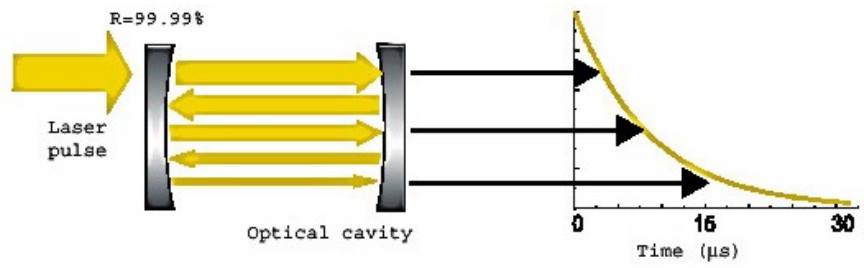
Differential Cavity Loss: $$\frac{dI}{I} = -\left(\frac{c\alpha}{R_L} + \frac{c}{d}(1-R)\right)dt = -\left(\frac{c\alpha}{R_L} + \frac{1}{\tau_0}\right)dt$$

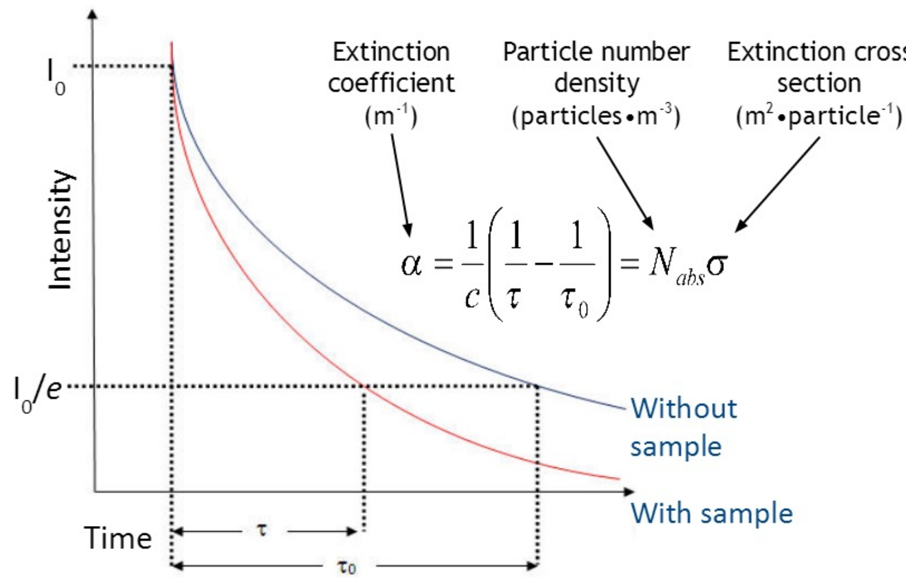
Integrated Cavity Loss: $$I(t) = I_0 \exp\left[-\left(c\alpha/R_L + 1/\tau_0\right)t\right] = I_0 \exp\left(-t/\tau\right)$$

Cavity Time Constant: $$1/\tau = c\alpha/R_L + 1/\tau_0$$

Absorption (Extinction) Coefficient: $$\boxed{\alpha = [A]\sigma = \frac{R_L}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)}$$

Absolute determination of α in terms of τ, τ_0


R=99.99%
Laser pulse
Optical cavity
0
15
30
Time (µs)


I0
I0/e
Intensity
Time
τ
τ0
Extinction coefficient (m-1)
Particle number density (particles•m-3)
Extinction cross section (m2•particle-1)
$\alpha = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) = N_{abs}\sigma$
Without sample
With sample

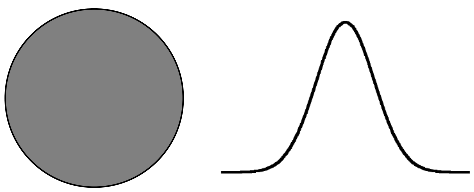
CONDITIONS

- Incoming laser beam has to be mode matched to the fundamental TEM_{00q} resonator mode otherwise transverse modes is excited with higher diffraction losses.

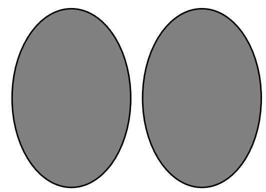
- Due to the spectral bandwidth of the laser pulse many fundamental resonator modes within the bandwidth $\delta\omega_R$ can be excited. Therefore, in order to resolve absorption lines the laser bandwidth $\delta\omega_L$ should be smaller than the absorption width.

- The relaxation time of the resonator must be longer than that of excited molecules, i.e. $R > 0.9999$ and careful alignment.

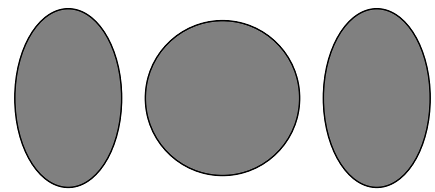
Transverse Electric Modes (TEM)



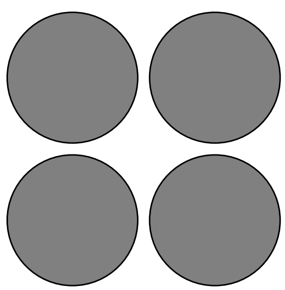
TEM_{00}



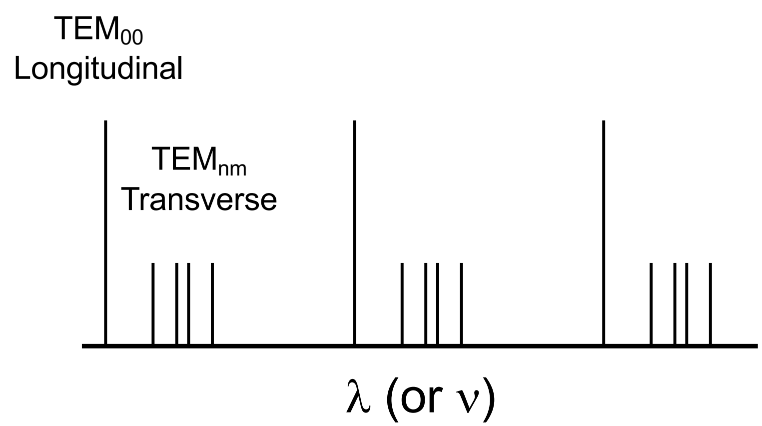
TEM_{10}



TEM_{20}

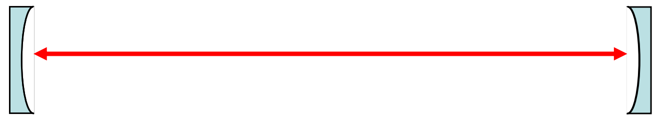


TEM_{11}

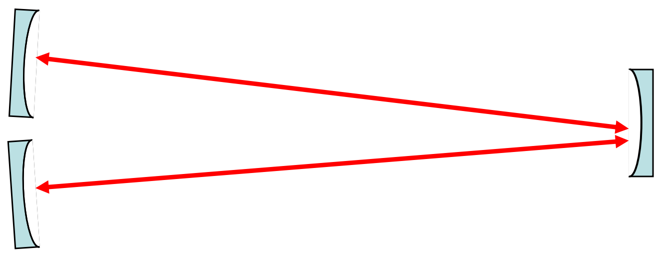


What is an Optical Cavity ?

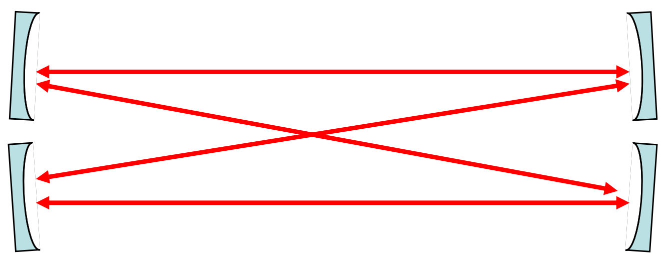
"A region bounded by two or more mirrors that are aligned to provide multiple reflections of light waves"



2 mirror



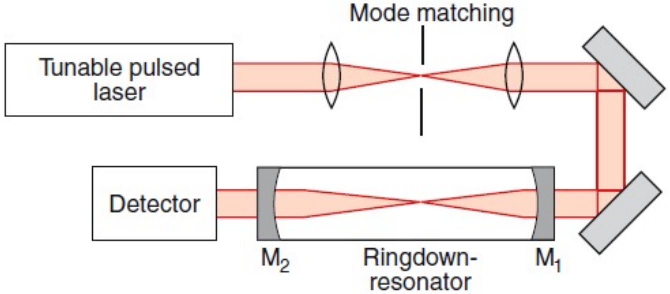
Triangular

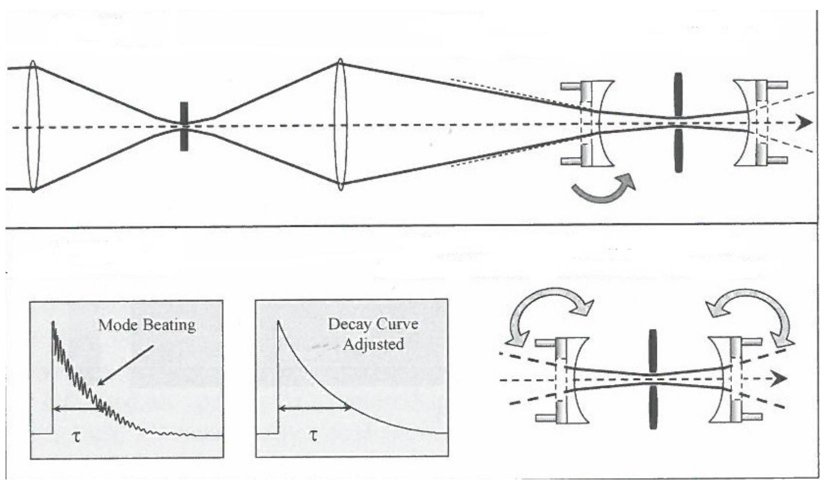


Bow-Tie

Mode Matching- Coupling of the Laser Pulse to the Cavity Mode

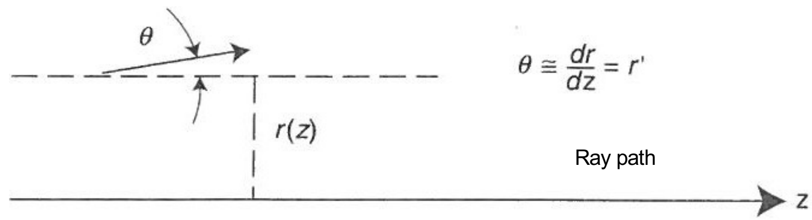
•Mode matched Laser mode to the fundamental TEM_{00} resonator mode.
•Mode of laser in resonance
With a mode of the cavity





Stability of the Cavity-Review of Optics

ABCD ray matrices Represent propagation through optical elements



$$\theta \cong \frac{dr}{dz} = r'$$

z_1

Propagation through a distance *d* in a medium with index of refraction of 1

$$r(z_2) = r(z_1) + r'(z_1)(z_2 - z_1),$$
$$r'(z_2) = r'(z_1).$$

$$\begin{bmatrix} r(z_2) \\ r'(z_2) \end{bmatrix} = \begin{bmatrix} 1 & z_2 - z_1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} r(z_1) \\ r'(z_1) \end{bmatrix}.$$

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix} = \begin{vmatrix} 1 & L \\ 0 & 1 \end{vmatrix}$$

$$L = z_2 - z_1$$

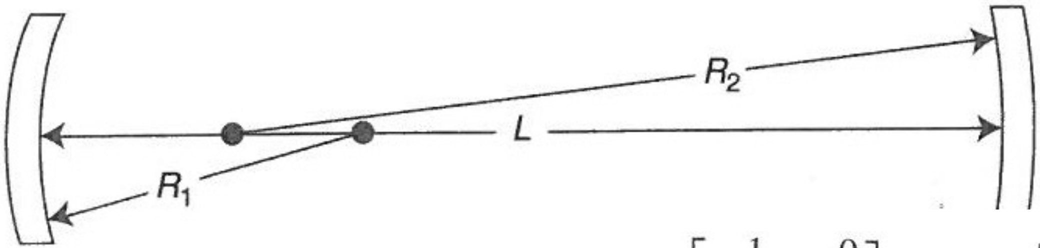
A thin lens with focal length *f*

$$\begin{bmatrix} 1 & 0 \\ -1/f & 1 \end{bmatrix}$$

Reflection from a Spherical mirror of Radius R

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ -\frac{2}{R} & 1 \end{vmatrix}$$

CAVITY STABILITY



$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ -\dfrac{2}{R_1} & 1 \end{bmatrix} \begin{bmatrix} 1 & L \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -\dfrac{2}{R_2} & 1 \end{bmatrix} \begin{bmatrix} 1 & L \\ 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 - \dfrac{2L}{R_2} & 2L - \dfrac{2L^2}{R_2} \\ \dfrac{4L}{R_1R_2} - \dfrac{2}{R_1} - \dfrac{2}{R_2} & 1 - \dfrac{2L}{R_2} - \dfrac{4L}{R_1} + \dfrac{4L^2}{R_1R_2} \end{bmatrix}.$$

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix}^N$$

For N round trips of the Beam

Stable Optical Resonators

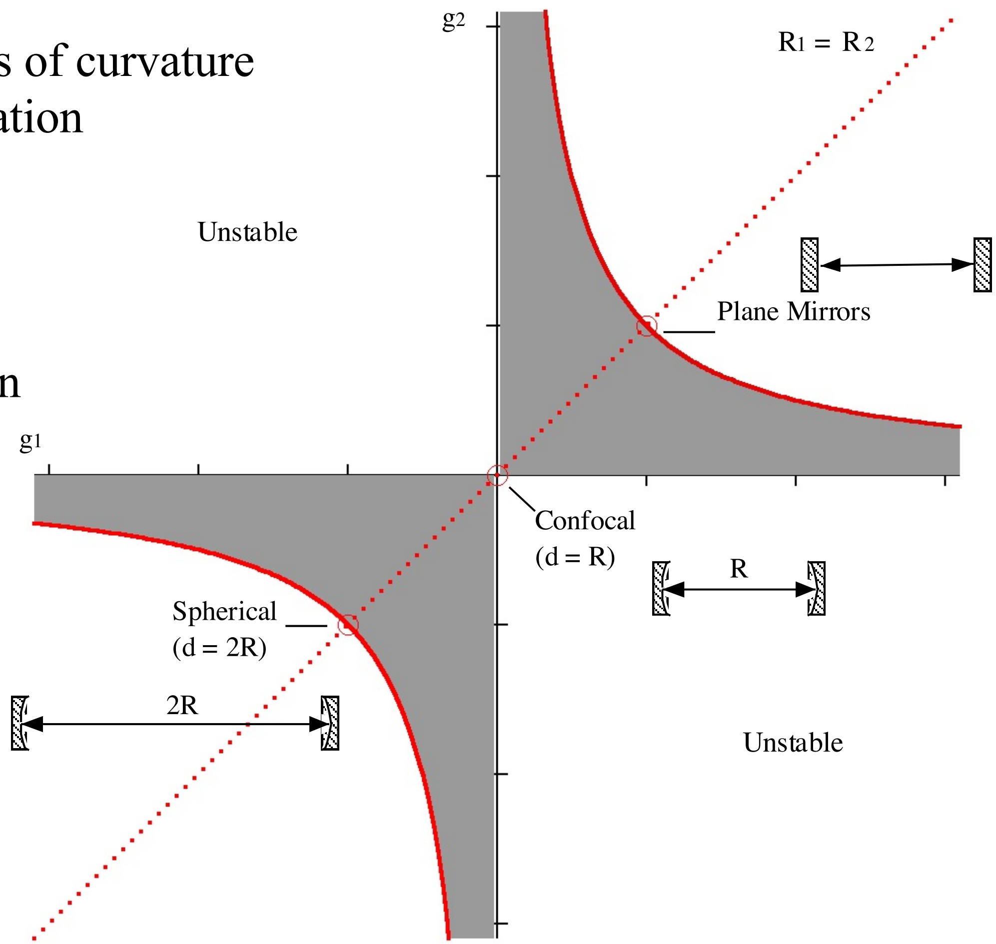
R = mirror radius of curvature
d = mirror separation

"g parameter"

$$g_{1,2} = 1 - \frac{d}{R_{1,2}}$$

Stability condition

0 Ł $g_1 g_2$ Ł 1



ABCD Matrix for the CRD

$$q_{out} = \frac{Aq_{in} + B}{Cq_{in} + D}$$

$$\frac{1}{q_{in}} = \frac{1}{r_{in}} - i\frac{\lambda}{\pi w_{in}^2}$$

$$\frac{1}{q_{out}} = \frac{1}{r_{out}} - i\frac{\lambda}{\pi w_0^2}$$

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \begin{bmatrix} 1 & d/2 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & \frac{n_1}{n_2} \cdot e \\ \frac{n_2 - n_1}{n_1 \cdot r_m} & 1 \end{bmatrix} \begin{bmatrix} 1 & d_2 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -1/f & 1 \end{bmatrix} \begin{bmatrix} 1 & d_1 \\ 0 & 1 \end{bmatrix}$$

Resonances in Optical Cavities

"Longitudinal Modes"

$$\nu\frac{2d}{c}=\frac{2d}{\lambda}=q$$

q = integer

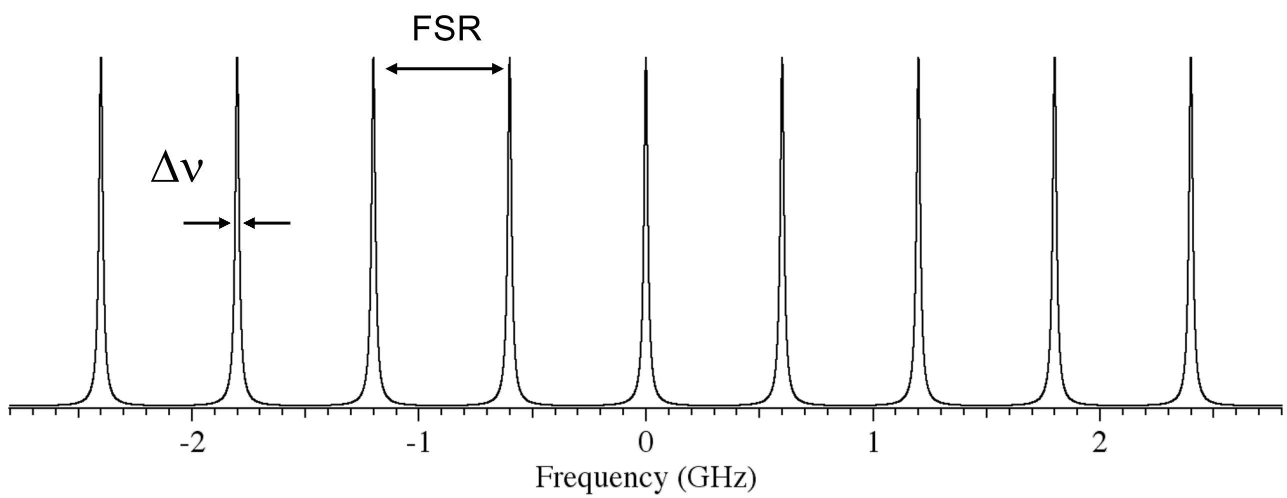
Resonant

Non-resonant

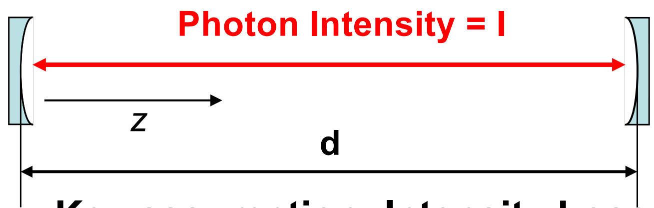
Cavity Transmission $$T(\nu)=\frac{(1-R)^2}{(1-R)^2+4R\sin^2\left(\frac{2\pi\nu d}{c}\right)}$$

Free Spectral Range $$FSR=\frac{c}{2d}$$

Full Width Half Max $$\Delta\nu=\frac{c}{2d}\frac{1-R}{\pi\sqrt{R}}$$



Photon Lifetime in an Optical Cavity



Mirror reflectivity = R

Key assumption: Intensity Loss at Mirror = (1-R)

1-R ≈ T, Transmission, if other losses (e.g. absorption, scattering) are not severe

$$\frac{dI}{dz} = -\frac{1-R}{d} I$$

$$x = ct$$

$$dx = cdt$$

c = speed of light
≈ $3\text{x}10^4$ cm μs^{-1}

$$\boxed{\frac{dI}{I} = -\frac{c}{d}(1-R)dt}$$

$$\int_{I_0}^{I_t} \frac{dI}{I} = -\frac{c}{d}(1-R)\int_0^t dt$$

$$\ln\left(\frac{I(t)}{I_0}\right) = -\frac{c}{d}(1-R)t$$

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_0}\right)$$

$$\boxed{\tau_0 = \frac{d}{c(1-R)} \approx \frac{d}{cT}}$$

Photon Lifetime

CRDS Sensitivity

$$\alpha = \frac{R_L}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

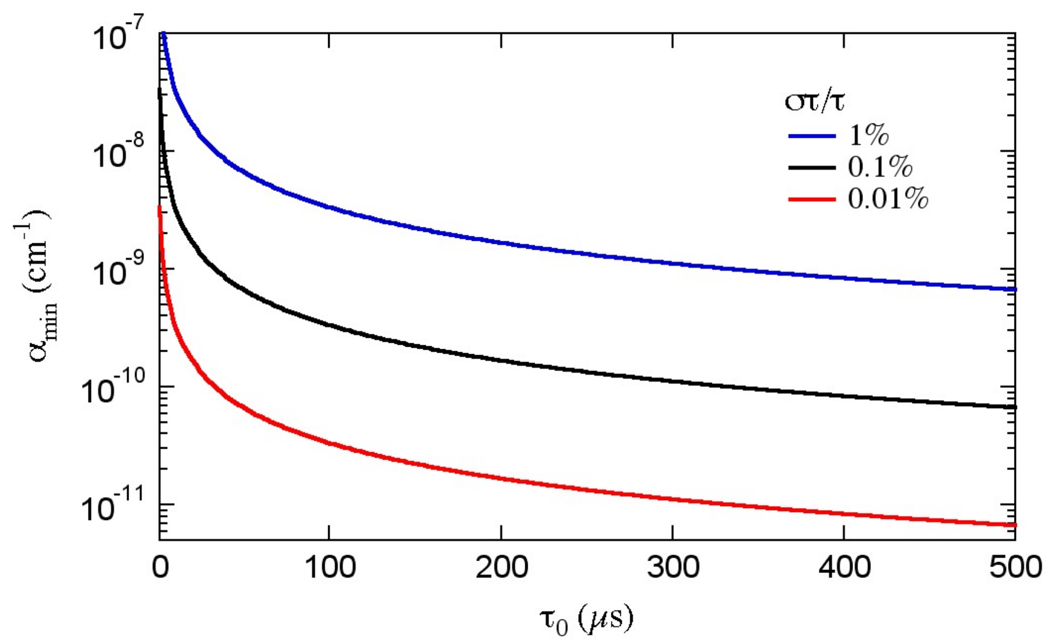
$$\alpha_{\min} = \frac{R_L}{c}\frac{\sqrt{2}\sigma(\tau)}{\tau_0^2}$$

$$\boxed{\alpha_{\min} = \sqrt{2}\,\frac{R_L}{c}\frac{\delta(\tau)}{\tau_0}}$$

$$\alpha_{\min} = \frac{R_L}{c}\frac{(\tau_0 - \tau)_{\min}}{\tau \times \tau_0}$$

$$\delta(\tau) = \frac{\sigma(\tau)}{\tau_0}$$

Note: Light intensity does not matter !



Limitations on τ_0 (effective path length)

1. Mirror Reflectivity

   Best achievable is T ≈ 5 ppm

   Strong function of λ

2. Cavity Length
3. Rayleigh scattering

   $\sigma_{Rayliegh} \propto \lambda^{-4}$!

4. Mie Scattering - Aerosol

   Also scales steeply with λ

   Aerosol extinction can be large!

5. Interfering absorbers

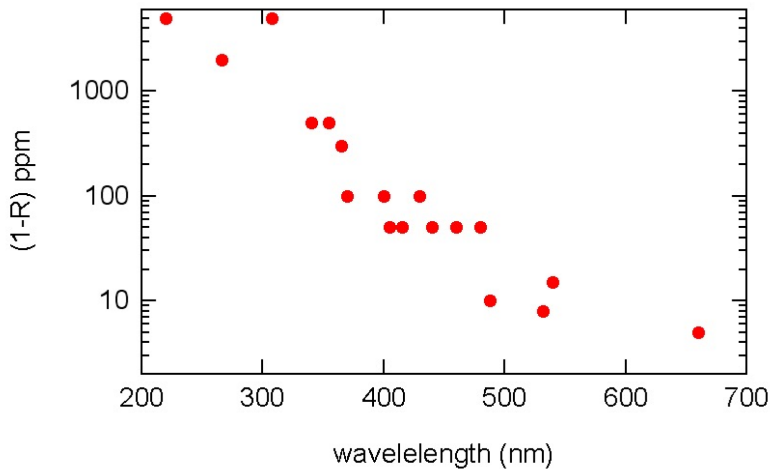
$$\tau_0 = \frac{1}{c}\left(\frac{(1-R)}{L} + \alpha_{Rayleigh} + \frac{\alpha_{Mie}}{R_L} + \frac{1}{R_L}\sum_i \alpha_i\right)^{-1}$$

"Empty" Cavity Loss = Mirror Transmission + Rayleigh Scattering + Mie Scattering + Interfering Absorptions

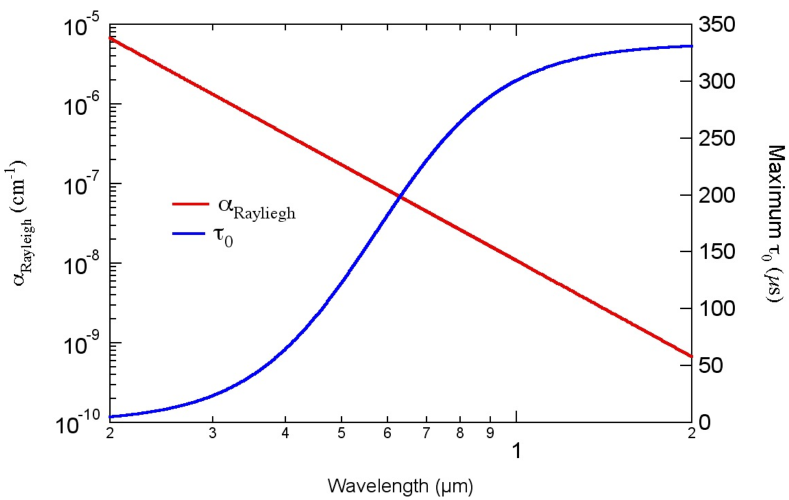
1-2 specific to CRDS

3-5 common to *any* direct absorption measurement

but … particularly acute when $\alpha_{min} < 10^{-8}$ cm^{-1}



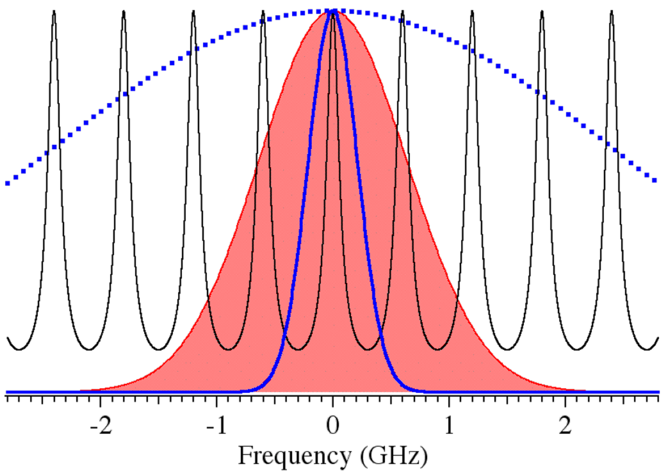
Mirror reflectivity vs wavelength

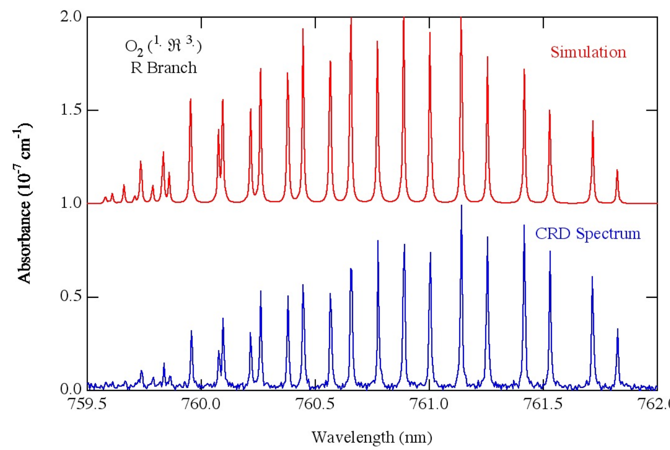


Rayleigh Scattering: τ_0 is commonly pressure dependent

Practical consequence: sensitivity may be *invariant* with pressure in some regimes

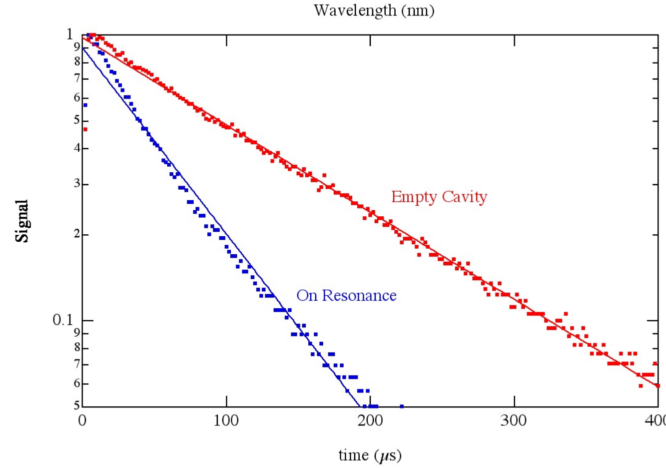
Quantitative Spectroscopy I - Linewidth Effects





$$I(t) = I_0 \sum_i \exp\left[-(1/\tau_0 + c\alpha_i)t\right]$$

$$\neq I_0 \exp\left[-t/\tau\right]$$



- Decays are *not* single exponential
- Limits applicability of pulsed CRDS to discrete spectroscopy - e.g. rovibrational lines in small molecules
- Effect can be corrected for small absorptions - e.g., $\alpha < 10^{-8}$ cm^{-1}

Quantitative Spectroscopy II - Mode Beating

• Pulsed laser envelope excites multiple TEM modes

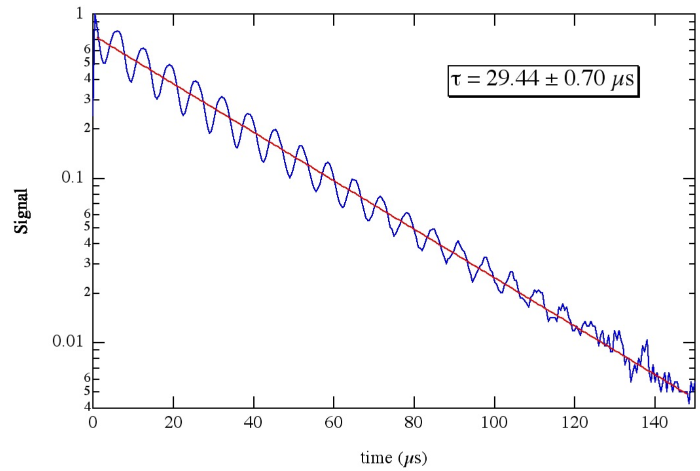
• Frequency difference between modes leads to a beat frequency superimposed on the ring-down transient

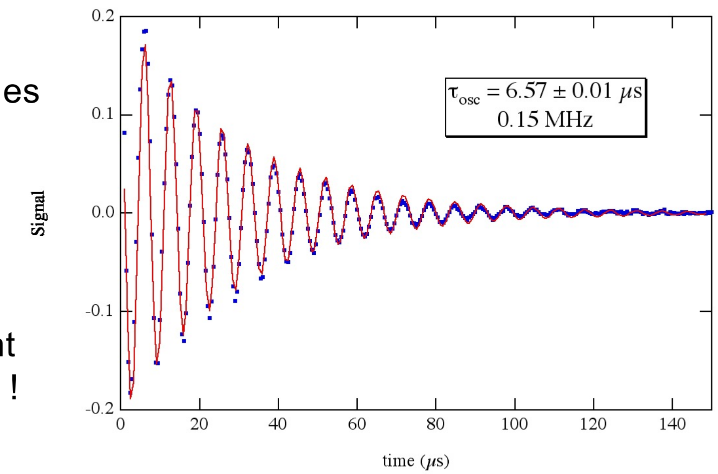
$$I(t) = I_0 \exp[-t/\tau]\sin(\omega t + \phi)$$

• If small number of modes, can in principle determine which TEM modes contribute to the spectrum

• Typically *very* sensitive to cavity alignment

• Interference effects are still present in cavities pumped by pulsed lasers !





Light Sources II - Continuous Wave (cw) Lasers

- Examples: Diode lasers, He:Ne, Ar-ion laser, Nd:YAG, etc

  Many, many ways to generate cw light !

  Spectral coverage from visible to mid infrared

  Recent advances in telecommunications have made near infrared diodes available, cheap and high performance

- Advantages: Lightweight, may be very inexpensive, lower power consumption, etc.
- Disadvantages: Typically limited tunability (e.g. temperature tuning of diode lasers)
- Coupling between laser source and cavity must be *active*
- Fast switch required to shutter light source to record ring-down transient

	UV 0.2 - 0.4 µ	VIS 0.4 - 0.7 µ	Near IR 0.7 - 2.5 µ	Mid IR 2.5 - 20 µ
Molecular Absorptions	Electronic Absorption Bands	Low Electronic High Vibrational	Vibrational Overtones	Vibrational Fundamentals
Absorption Cross Sections	Moderate - Strong 10^{-19} - 10^{-17} cm^2	Weak - Strong 10^{-23} - 10^{-17}	Weak - Moderate 10^{-21} - 10^{-19} cm^2	Moderate - Strong 10^{-19} - 10^{-18} cm^2
Examples	O_3 Aromatics Halogens	Nitrogen oxides Glyoxal Water vapor	Small VOCs X-OH molecules HO_2, RO_2	Anything ! (except N_2, O_2)
Mirrors	Poor 100 - 5000 ppm	Good-Excellent 5-50 ppm	Excellent 5-10 ppm	Moderate 100-300 ppm
Light Sources	Pulsed Lasers Broadband	Pulsed (dye lasers) cw (diode lasers)	Pulsed (OPO's, Raman shifted dye) cw (Telecom diode)	cw Pb Salt cw Quant. Cascade cw DFG
Detectors	Excellent	Good-Excellent	Moderate	Fair
Rayleigh + Mie Scattering	Strong	Moderate	Weak	N/A

Applications to Atmospheric Science

- Measurements of small absorption cross sections
- Laboratory chemical kinetics
- Laboratory measurements of radicals - e.g., photochemistry
- Field measurements I - Atmospheric trace gas detection
- Field measurements II - Aerosol extinction

Gaussian Beams-Theory

A. Gaussian beam

The electromagnetic wave propagation is under the way of Helmholtz equation

$$\nabla^2 U + k^2 U = 0$$

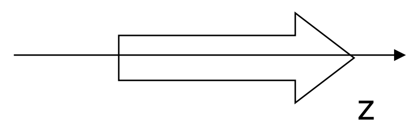
Normally, a plan wave (in z direction) will be

$$U = U_0 \exp\{-i(\omega t + \mathrm{k}\cdot\mathrm{r})\} = U_0 \exp(-ikz)\exp(-i\omega t)$$

When amplitude is not constant, the wave is

$$U = A(x, y, z)\exp(-ikz)\exp(-i\omega t)$$

An axis symmetric wave in the amplitude



$$U = A(\rho, z)\exp(-ikz)\exp(-i\omega t)$$

frequency $\omega = 2\pi\nu$

Wave vector $k = \dfrac{2n\pi}{\lambda}$

Paraxial Helmholtz equation

Substitute the *U* into the Helmholtz equation we have:

$$\nabla_T^2 A - i2k\frac{\partial A}{\partial z} = 0$$

where

$$\nabla^2{}_T = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

One simple solution is spherical wave:

$$A(\vec{r}) = \frac{A_1}{z}\exp(-jk\frac{\rho^2}{2z})$$

$$\rho^2 = x^2 + y^2$$

The equation $$\nabla_T^2 A - i2k\frac{\partial A}{\partial z} = 0$$

has the other solution, which is Gaussian wave：

$$U(\vec{r}) = A_0 \frac{W_0}{W(z)} \exp[-\frac{\rho^2}{W^2(z)}] \exp[-ikz - ik\frac{\rho^2}{2R(z)} + i\xi(z)]$$

where

$$W(z) = W_0[1+(\frac{z}{z_0})^2]^{1/2}$$

z_0 is ***Rayleigh range***

$$R(z) = z[1+(\frac{z_0}{z})^2]$$

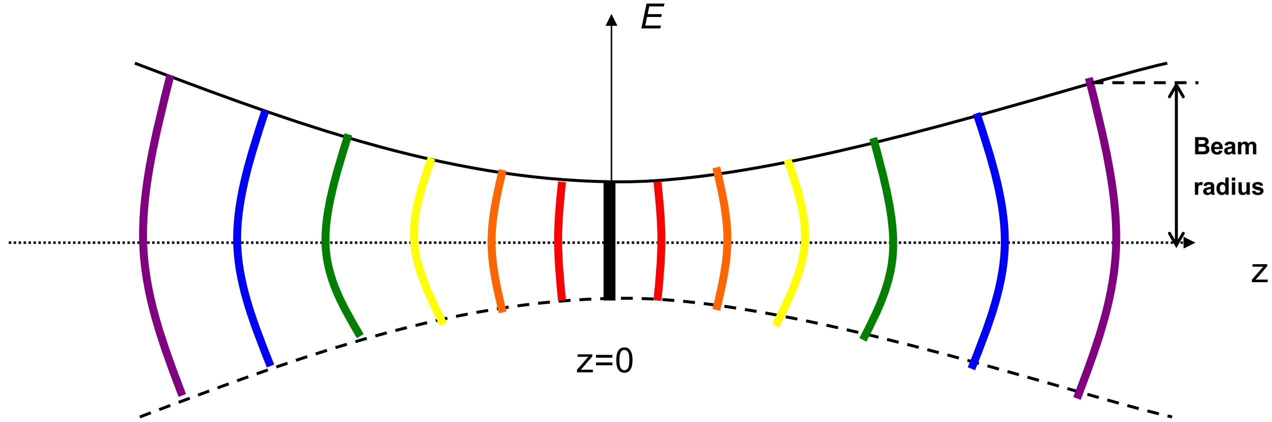
q ***parameter***

$$\frac{1}{q(z)} = \frac{1}{R(z)} - i\frac{\lambda}{\pi W^2(z)}$$

$$\xi(z) = \tan^{-1}\frac{z}{z_0}$$

$$W_0 = (\frac{\lambda z_0}{\pi})^{1/2} = W(z)\big|_{z=0} = W(0)$$

Gaussian Beam



Electric field of Gaussian wave propagates in z direction

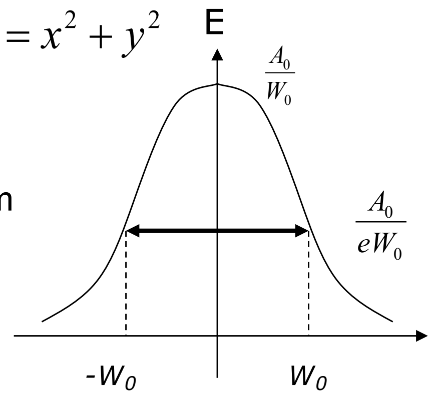
$$E(x,y,z)=\frac{A_0}{W(z)}\exp[\frac{-(x^2+y^2)}{W^2(z)}]\cdot\exp[-ik(\frac{x^2+y^2}{2R(z)}+z)+i\xi(z)]$$

Physical meaning of parameters

- Beam width at z $\boxed{W(z)=W_0[1+(\frac{z}{z_0})^2]^{1/2}}$
- Waist width $W_0=W(0)$ $z_0=\frac{\pi W_0^2}{\lambda}$
- Radii of wave front at z $R(z)=z[1+(\frac{\pi W_0^2}{\lambda z})^2]=\boxed{z[1+(\frac{z_0}{z})^2]}$
- Phase factor $\xi(z)=\arctan\frac{\lambda z}{\pi W_0^2}=\boxed{tg^{-1}\frac{z}{z_0}}$

Gaussian beam at z=0

$$E(x,y,0)=\frac{A_0}{W_0}\exp[-\frac{r^2}{W_0^2}]$$ where, $r^2=x^2+y^2$



Beam width:

$$W(z)=W_0[1+(\frac{z}{z_0})^2]^{1/2}$$ will be minimum

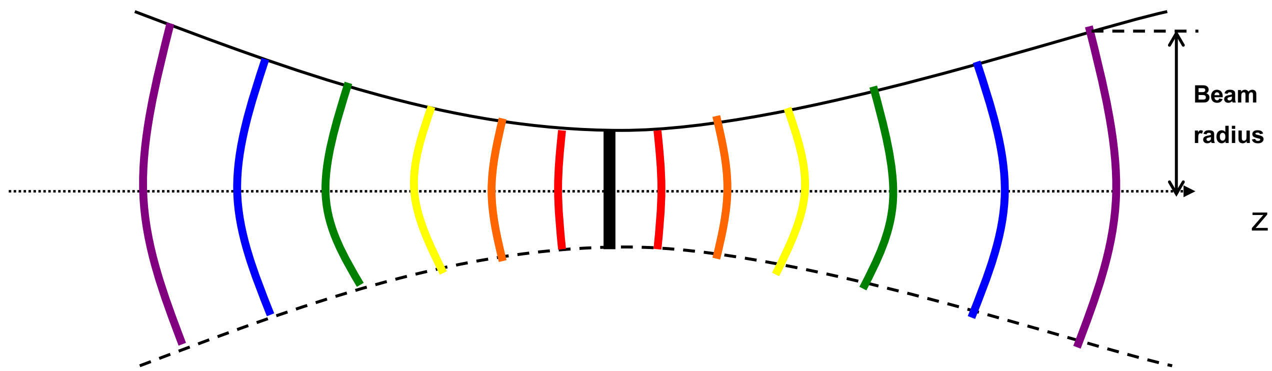
wave front

$$\lim_{z\to 0}R(z)=\lim_{z\to 0}\left\{z\left[1+\left(\frac{\pi W_0^2}{\lambda z}\right)^2\right]\right\}=\infty$$

at z=0, the wave front of Gaussian beam is a plan surface, but the electric field is Gaussian form

***W_0* is the waist half width**

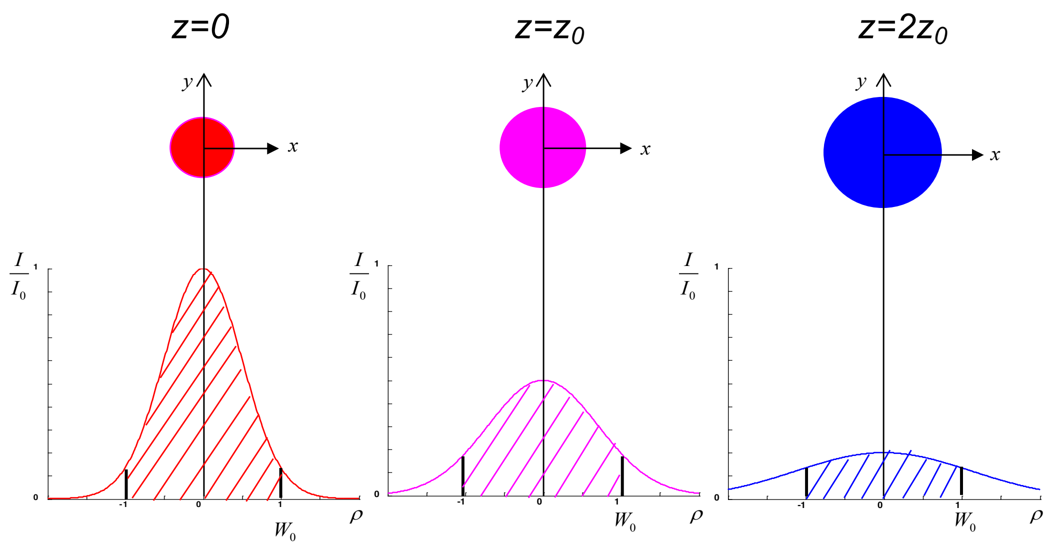
B. The characteristics of Gaussian beam



Gaussian beam is a axis symmetrical wave, at z=0 phase is plan and the intensity is Gaussian form, at the other z, it is Gaussian spherical wave.

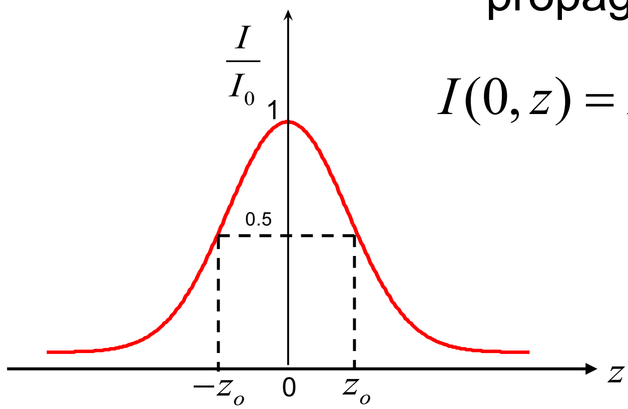
Intensity of Gaussian beam

- Intensity of Gaussian beam $$I(\rho,z)=I_0[\frac{W_0}{W(z)}]^2\exp[-\frac{\rho^2}{W^2(z)}]$$



The normalized beam intensity as a function of the radial distance at different axial distances

On the beam axis (ρ = 0) the intensity



Variation of axial intensity as the propagation length z

$$I(0,z) = I_0[\frac{W_0}{W(z)}]^2 = \frac{I_0}{1+(\frac{z}{z_0})^2}$$

z_0 is ***Rayleigh range***

$$z_0 = \frac{\pi W_0^2}{\lambda}$$

The normalized beam intensity I/I_0 at points on the beam axis (ρ=0) as a function of z

Power of the Gaussian beam

The power of Gaussian beam is calculated by the integration of the optical intensity over a transverse plane

$$P = \frac{1}{2} I_0 \pi W_0^2$$

So that we can express the intensity of the beam by the power

$$I(\rho, z) = \frac{2P}{\pi W^2(z)} \exp[-\frac{2\rho^2}{W^2(z)}]$$

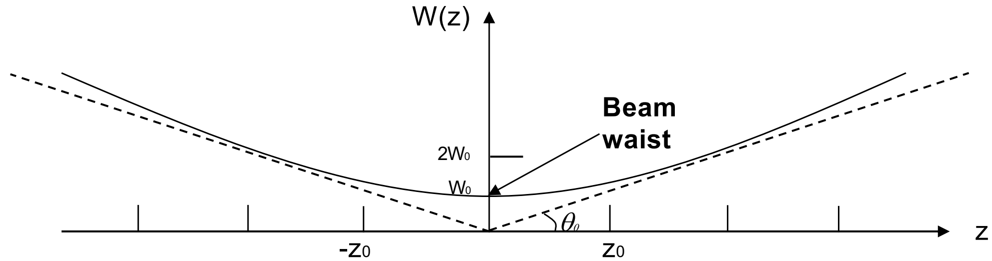
The ratio of the power carried within a circle of radius ρ. in the transverse plane at position z to the total power is

$$\frac{1}{P}\int_0^{\rho_0} I(\rho, z) 2\pi\rho d\rho = 1 - \exp[-\frac{2\rho_0^2}{W^2(z)}]$$

Beam Radius $W(z)=W_0[1+(\frac{z}{z_0})^2]^{1/2}$ $W(z)\approx\frac{W_0}{z_0}z=\theta_0 z$

$\because$ $\boxed{z_0=\frac{\pi W_0^2}{\lambda}}$

$$\boxed{\theta_0=\frac{\lambda}{\pi W_0}}$$

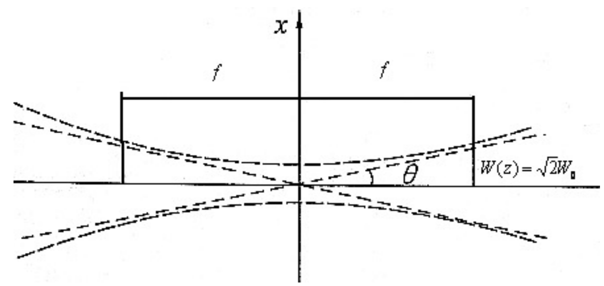


The beam radius *W(z)* has its minimum value W_0 at the waist (*z=0*) reaches $\sqrt{2}W_0$ at $z=\pm z_0$ and increases linearly with z for large z.

Beam Divergence $$2\theta=2\frac{dW(z)}{dz}=\frac{2\lambda z}{\pi W_0}[(\frac{\pi^2W_0^2}{\lambda})^2+z^2]^{-\frac{1}{2}}$$

$$\boxed{\theta_0=\frac{\lambda}{\pi W_0}}$$

The characteristics of divergence angle



- z=0, $2\theta=0$
- z=$\pi W_0^2 / \lambda = z_0$ $\quad 2\theta=\sqrt{2}\lambda / \pi W_0$
- z→∞ $\quad 2\theta=\dfrac{2\lambda}{\pi W_0}$ or $2\theta=\lim\limits_{x\to\infty}\dfrac{2W(z)}{z}$

z_0 is ***Rayleigh range***

Define $f=z_0$ as the ***<u>confocal parameter of Gaussian beam</u>*** $\quad f=z_0=\dfrac{\pi W_0^2}{\lambda}$

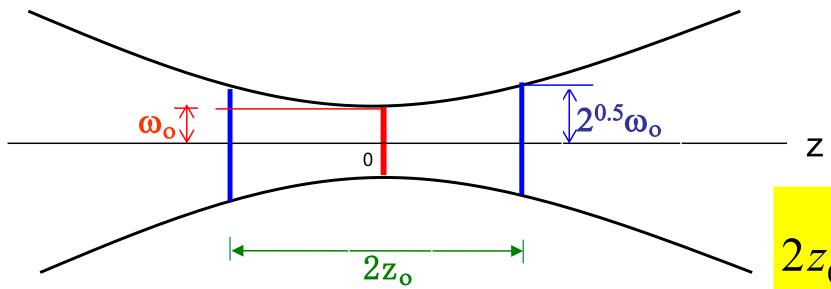
The physical means of f : the half distance between two section of width

$W(z)=\sqrt{2}W_0$

$$2\theta=\lim_{z\to\infty}\frac{2W(z)}{z}=\lim_{z\to\infty}\frac{2\sqrt{\frac{f\lambda}{\pi}(1+\frac{z^2}{f^2})}}{z}=2\sqrt{\frac{\lambda}{f\pi}}$$

Depth of Focus

Since the beam has its minimum width at z = 0, it achieves its best focus at the plane z = 0. In either direction, the beam gradually grows “out of focus.” The axial distance within which the beam radius lies within a factor $2^{0.5}$ of its minimum value (i.e., its area lies within a factor of 2 of its minimum) is known as the depth of focus or confocal parameter



$$2z_0 = \frac{2\pi W_0^2}{\lambda} = 2f$$

The depth of focus of a Gaussian beam.

Phase of Gaussian beam

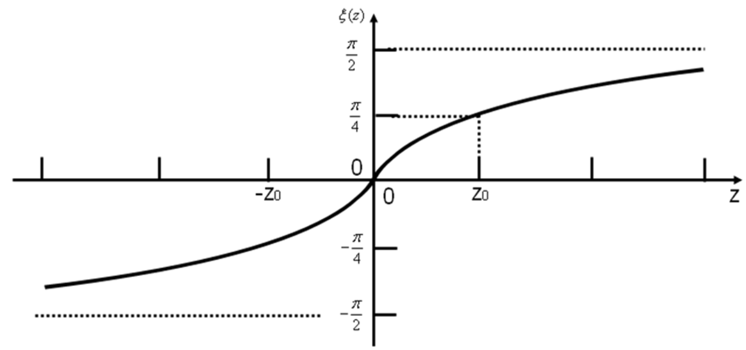
$$\xi(z) = \arctan\frac{\lambda z}{\pi W_0^2} = tg^{-1}\frac{z}{z_0}$$

The phase of the Gaussian beam is,

$$\varphi(\rho, z) = kz - \xi(z) + \frac{k\rho^2}{2R(z)}$$

On the beam axis (p = 0) the phase

$$\varphi(0, z) = kz - \xi(z)$$



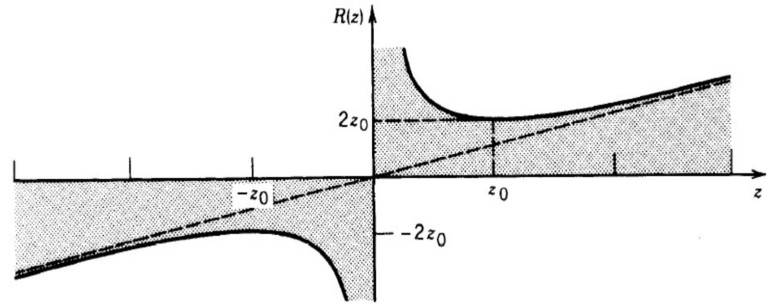
kz Phase of plan wave

$\xi(z)$ an excess delay of the wavefront in comparison with a plane wave or a spherical wave

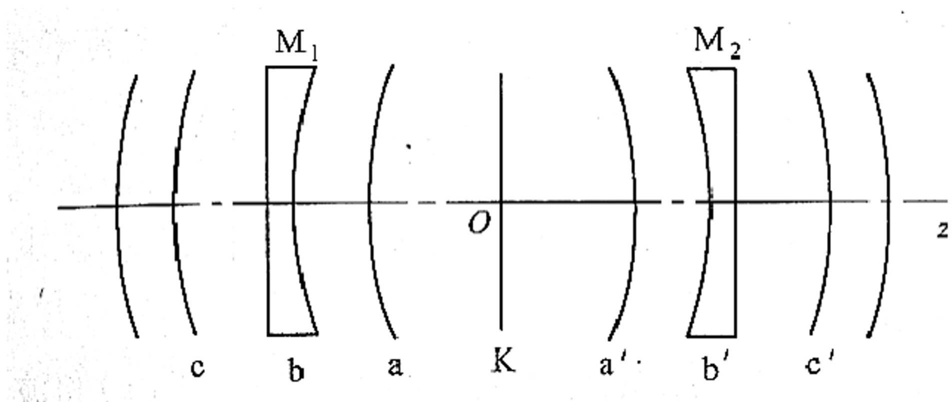
The excess delay is $-\pi/2$ at z=-∞, and $\pi/2$ at z= ∞

The total accumulated excess retardation as the wave travels from z = -∞ to z =∞is π. This phenomenon is known as the ***Guoy effect***.

Wavefront



$$R(z) = z[1 + (\frac{\pi W_0^2}{\lambda z})^2] = \left| z + \frac{f^2}{z} \right|$$



Confocal field and its equal phase front

Parameters Required to Characterize a Gaussian Beam

How many parameters are required to describe a plane wave, a spherical wave, and a Gaussian beam?

- The plane wave is completely specified by its complex amplitude and direction.
- The spherical wave is specified by its amplitude and the location of its origin.
- The Gaussian beam is characterized by more parameters- its peak amplitude the parameter A, its direction (the beam axis), the location of its waist, and one additional parameter: the waist radius W_0 or the Rayleigh range z_o,

Parameter used to describe a Gaussian beam

- ***q-parameter*** is sufficient for characterizing a Gaussian beam of known peak amplitude and beam axis

$$\frac{1}{q(z)} = \frac{1}{R(z)} - i\frac{\lambda}{\pi W^2(z)} \quad \rightarrow \quad \frac{1}{q(z)} = \frac{1}{z + iz_0}$$

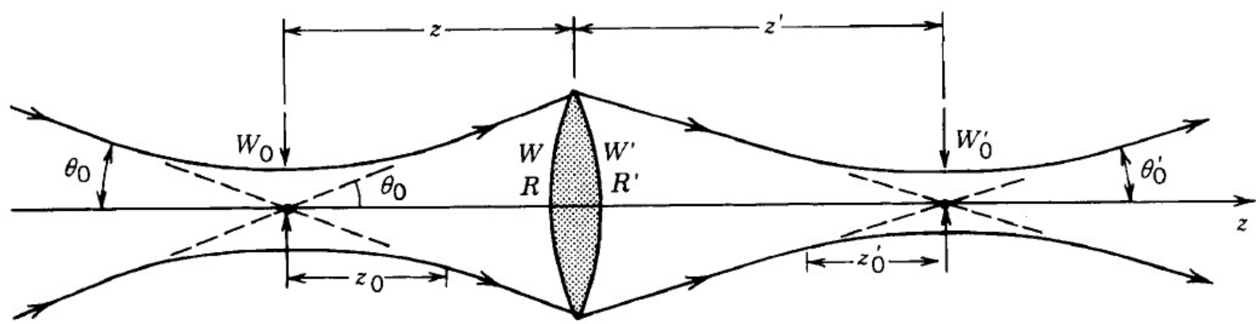
$\Rightarrow$ $q(z) = z + iz_0$

If the complex number $q(z) = z + iz_0$, is known, the distance z to the beam waist and the Rayleigh range z_0. are readily identified as the real and imaginary parts of $q(z)$.

the real part of $q(z)$ z is the beam waist place
the imaginary parts of $q(z)$ z_0 is the Rayleigh range

C. TRANSMISSION THROUGH OPTICAL COMPONENTS

a). Transmission Through a Thin Lens



Phase +phase induce by lens must equal to the back phase

$$\boxed{kz + k\frac{\rho^2}{2R} - \zeta} - k\frac{\rho^2}{2f} = kz + k\frac{\rho^2}{2R'} - \zeta \Rightarrow \frac{1}{R'} = \frac{1}{R} - \frac{1}{f} \Rightarrow \frac{1}{R} - \frac{1}{R'} = \frac{1}{f}$$

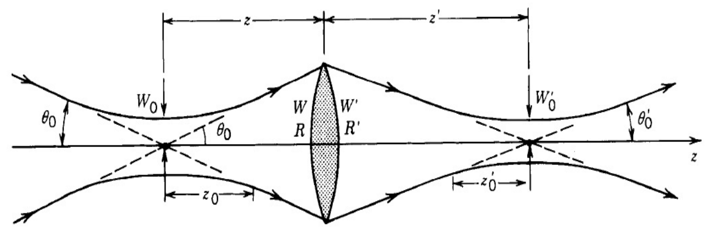
Notes:

R is positive since the wavefront of the incident beam is diverging and R' is negative since the wavefront of the transmitted beam is converging.

In the thin lens transform, we have

$$W = W'$$

$$\frac{1}{R'} = \frac{1}{R} - \frac{1}{f}$$



If we know W_0, z_1, f we can get

$$W_0'^2 = W^2[1+(\frac{\pi W^2}{\lambda R'})^2]^{-1}$$

$$-z' = R'[1+(\frac{\lambda R'}{\pi W^2})^2]^{-1}$$

The minus sign is due to the waist lies to the right of the lens.

$$W_0' = \frac{W}{[1+(\pi W^2/\lambda R')^2]^{1/2}} \qquad -z' = \frac{R'}{1+(\pi R'/\lambda W^2)^2}$$

because $R = z[1+(z_0/z)^2]$ *and* $W = W_0[1+(z/z_0)^2]^{1/2}$

Waist radius $$W_0' = MW_0$$

Waist location $$(z'-f) = M^2(z-f)$$

Depth of focus $$2z_0' = M^2(2z_0)$$

Divergence angle $$2\theta_0' = M^2(2\theta_0)$$

The beam waist is magnified by M, the beam depth of focus is magnified by M^2, and the angular divergence is minified by the factor M.

magnification $$M = \frac{M_r}{(1+r^2)^{1/2}}$$ where $$r = \frac{z_0}{z-f}$$

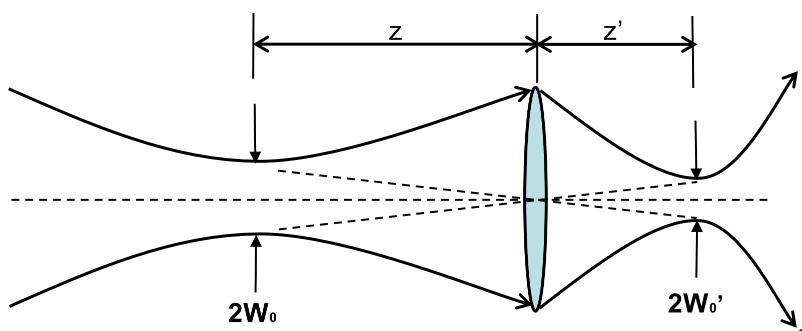
$$M_r = \left|\frac{f}{z-f}\right|$$

The formulas for lens transformation

Limit of Ray Optics

Consider the limiting case in which *(z - f)* >>z_o, so that the lens is well outside the depth of focus of the incident beam, The beam may then be approximated by a spherical wave, thus

$$r = \frac{z_0}{z-f} \to 0 \qquad and \qquad M \approx M_r$$



$$W_0' \approx M W_0$$

$$\frac{1}{z'} + \frac{1}{z} \approx \frac{1}{f}$$

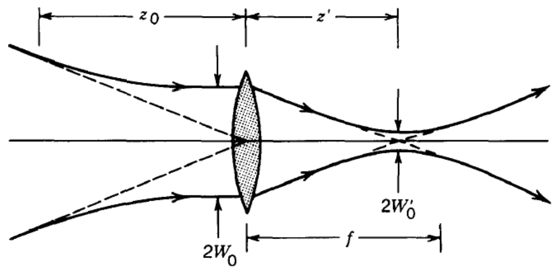
Imaging relation

$$M \approx M_r = \left| \frac{f}{z-f} \right|$$

The magnification factor Mr is that based on ray optics. provides that *M* < *Mr,* the maximum magnification attainable is the ray-optics magnification Mr.

b). Beam Shaping

Beam Focusing



If a lens is placed at the waist of a Gaussian beam, so $z=0$, then

$\because$

$$M = \frac{1}{[1+(z_0/f)^2]^{1/2}}$$

$$W_0' = \frac{W_0}{[1+(z_0/f)^2]^{1/2}}$$

$$z' = \frac{f}{1+(f/z_0)^2}$$

If the depth of focus of the incident beam $2z_0$, is much longer than the focal length f of the lens, then $W_0' = (f/z_o)W_o$. Using $z_0 = \pi W_0^2/\lambda$, we obtain

$$W_0' \approx \frac{\lambda}{\pi W_0} f = \theta_0 f \qquad\qquad z' \approx f$$

The transmitted beam is then focused at the lens' focal plane as would be expected for parallel rays incident on a lens. This occurs because the incident Gaussian beam is well approximated by a plane wave at its waist. The spot size expected from ray optics is zero

Focus of Gaussian beam

$$W'^2_0 = \frac{W_0^2}{(1-\frac{z_1}{f}) + (\frac{W_0^2}{\lambda f})^2}$$

- For given f, W'^2_0 changes as

when $z_1 < f$ W'^2_0 decreases as z decreases

$z_1 = 0$ W_0' reaches minimum, and M<1, for f>0, it is focal effect

when $z_1 > f$, W_0' increases as z increases

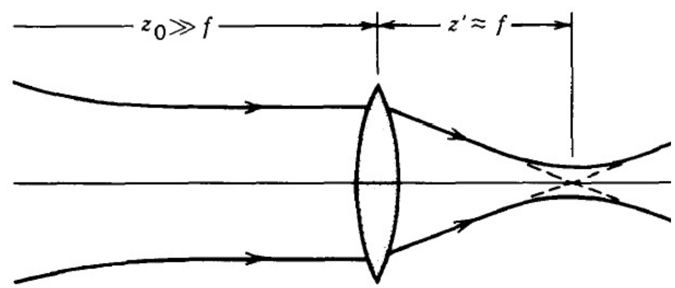
when $z_1 >> f$ the bigger z, smaller f, better focus

when $z = f$ W'_0 reaches maximum, when $\frac{\pi W_0^2}{\lambda} > f$, it will be focus

In laser scanning, laser printing, and laser fusion, it is desirable to generate the smallest possible spot size, this may be achieved by use of the shortest possible wavelength, the thickest incident beam, and the shortest focal length. Since the lens should intercept the incident beam, its diameter D must be at least $2W_0$. Assuming that $D = 2W_o$, the diameter of the focused spot is given by

$$2W_0' \approx \frac{4}{\pi}\lambda F_{\#} \qquad F_{\#} = \frac{f}{D}$$

where F# is the F-number of the lens. A microscope objective with small F-number is often used.



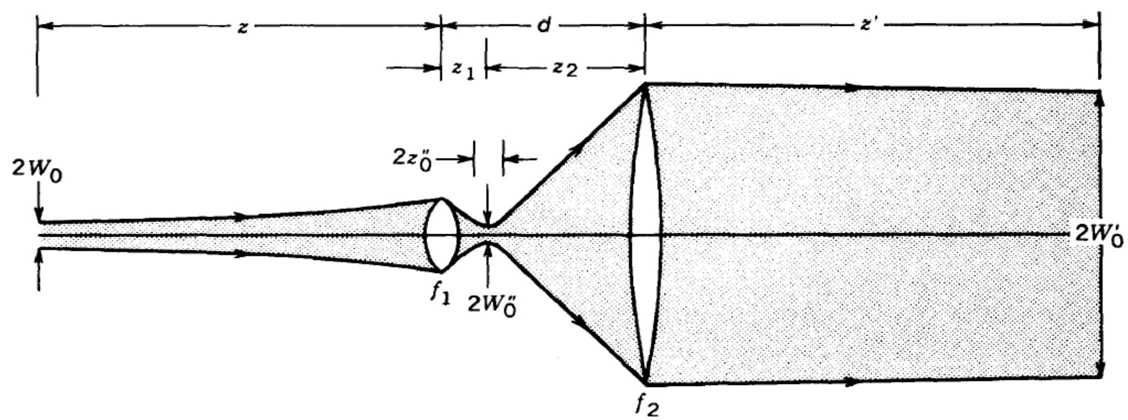
Beam collimate

locations of the waists of the incident and transmitted beams, z and z' are

$$\frac{z'}{f} - 1 = \frac{z/f - 1}{(z/f - 1)^2 + (z_0/f)^2}$$

The beam is collimated by making the location of the new waist z' as distant as possible from the lens. This is achieved by using the smallest ratio z_0/f (short depth of focus and long focal length).

Beam expanding



A Gaussian beam is expanded and collimated using two lenses of focal lengths fi and f2,

Assuming that $f_1 << z$ and $z - f_1 >> z_0$, determine the optimal distance *d* between the lenses such that the distance z' to the waist of the final beam is as large as possible.

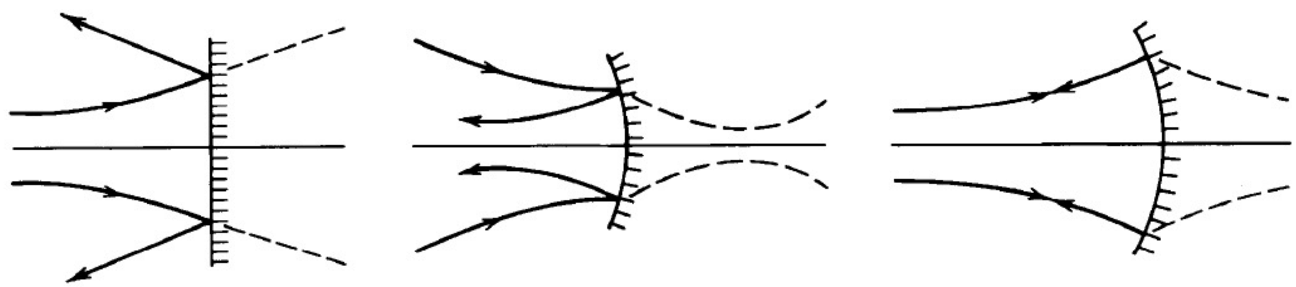
overall magnification $M = W_0'/W_o$

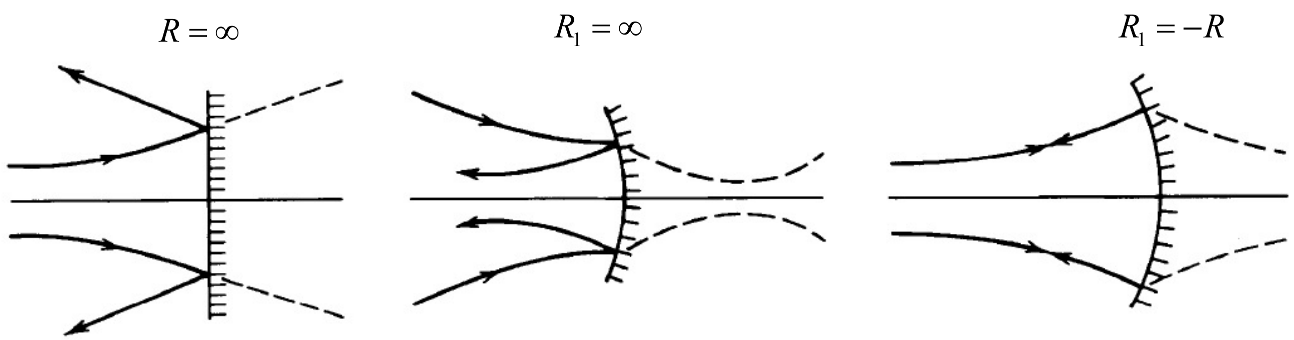
C). Reflection from a Spherical Mirror

Reflection of a Gaussian beam of curvature R_1 from a mirror of curvature R:

$$W_2 = W_1 \qquad \frac{1}{R_2} = \frac{1}{R_1} + \frac{2}{R} \qquad f = -R/2.$$

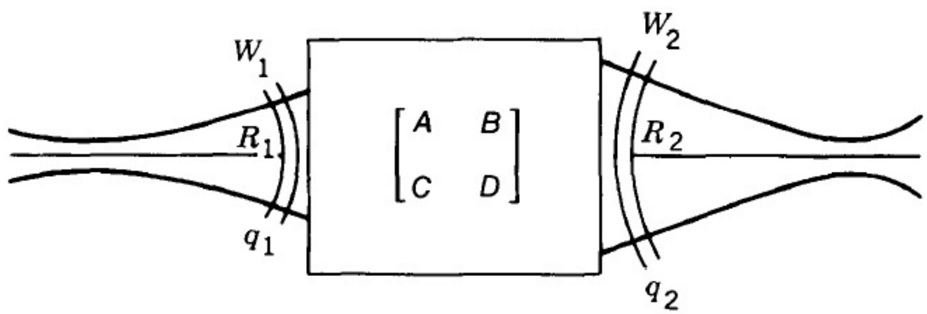
R > 0 for convex mirrors and R < 0 for concave mirrors,





- If the mirror is planar, i.e., R =∞, then R_2= R_1, so that the mirror reverses the direction of the beam without altering its curvature
- If R_1= ∞, i.e., the beam waist lies on the mirror, then R_2= R/2. If the mirror is concave (R < 0), R_2 < 0, so that the reflected beam acquires a negative curvature and the wavefronts converge. The mirror then focuses the beam to a smaller spot size.
- If R_1= -R, i.e., the incident beam has the same curvature as the mirror, then R_2= R. The wavefronts of both the incident and reflected waves coincide with the mirror and the wave retraces its path. This is expected since the wavefront normals are also normal to the mirror, so that the mirror reflects the wave back onto itself. the mirror is concave (R < 0); the incident wave is diverging (R_1 > 0) and the reflected wave is converging (R_2< 0).

d). Transmission Through an Arbitrary Optical System



An optical system is completely characterized by the matrix M of elements (A, B, C, D) ray-transfer matrix relating the position and inclination of the transmitted ray to those of the incident ray

The q-parameters, q_1 and q_2, of the incident and transmitted Gaussian beams at the input and output planes of a paraxial optical system described by the (A, B, C, D) matrix are related by

ABCD law

The q-parameters, q_1 and q_2, of the incident and transmitted Gaussian beams at the input and output planes of a par-axial optical system described by the (A, B, C, D) matrix are related by

$$\boxed{q_2 = \frac{Aq_1 + B}{Cq_1 + D}}$$

Because the q parameter identifies the width W and curvature R of the Gaussian beam, this simple law, called the ABCD law

Invariance of the ABCD Law to Cascading

If the ABCD law is applicable to each of two optical systems with matrices $M_i = (A_i, B_i, C_i, D_i)$, i = 1,2,…, it must also apply to a system comprising their cascade (a system with matrix $M = M_1M_2$).

C. HERMITE - GAUSSIAN BEAMS

The self-reproducing waves exist in the resonator, and resonating inside of spherical mirrors, plan mirror or some other form paraboloidal wavefront mirror, are called the modes of the resonator

Hermite - Gaussian Beam Complex Amplitude

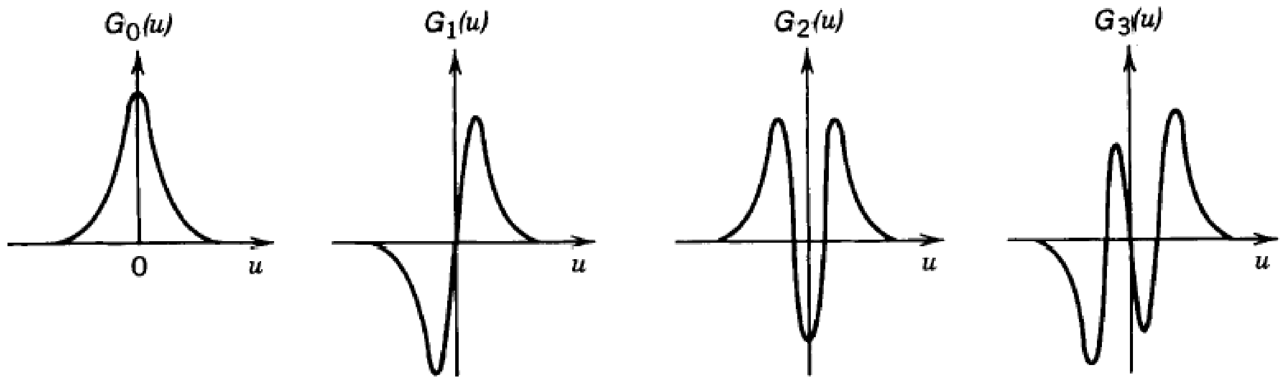
$$U_{l,m}(x,y,z) = A_{l,m}[\frac{W_0}{W(z)}]G_l[\frac{\sqrt{2}x}{W(z)}]G_m[\frac{\sqrt{2}y}{W(z)}]\times\exp[-jkz - jk\frac{x^2+y^2}{2R(z)} + j(l+m+1)\zeta(z)]$$

where $$G_l(u) = H_l(u)\exp(\frac{-u^2}{2}), \qquad l = 0,1,2,...,$$

is known as the **Hermite-Gaussian function** of order *l*, and $A_{l,m}$ is a constant

Hermite-Gaussian beam of order *(l, m).*

The Hermite-Gaussian beam of order (0, 0) is the Gaussian beam.

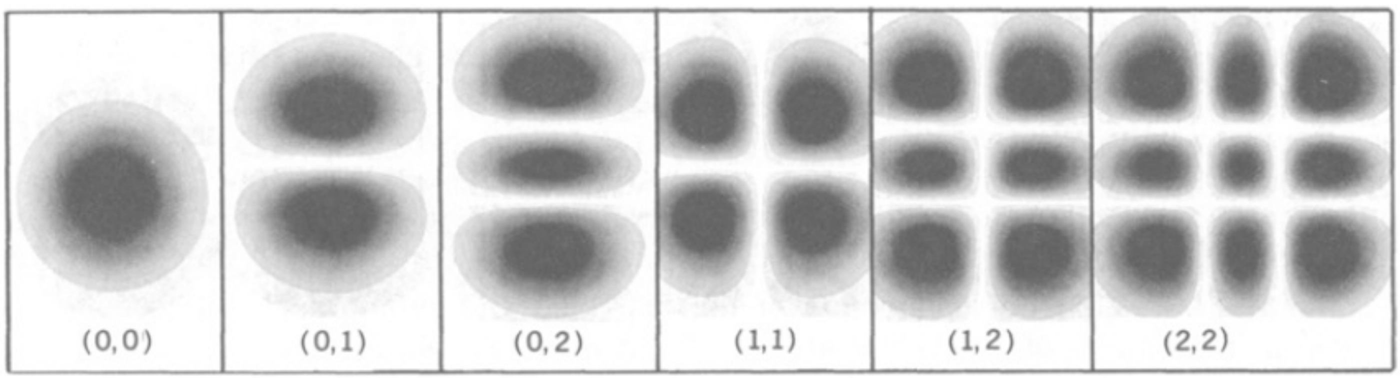


$H_0(u) = 1$, the Hermite-Gaussian function of order O, the Gaussian function.
$G_1(u) = 2u\ exp(\ -u^2/2)$ is an odd function,
$G_2(u) = (4u^2 - 2)\ exp(\ -u^2/2)$ is even,
$G_3(u) = (8u^3 - 12u)exp(\ -u^2/2)$ is odd,

Intensity Distribution

The optical intensity of the *(l, m)* Hermite-Gaussian beam is

$$I_{l,m}(x,y,z) = \left|A_{l,m}\right|^2 [\frac{W_0}{W(z)}]^2 G_l^2[\frac{\sqrt{2}x}{W(z)}] G_m^2[\frac{\sqrt{2}y}{W(z)}]$$



Light Scattering

- Particle counters
- Nephelometry

Particle Sensors

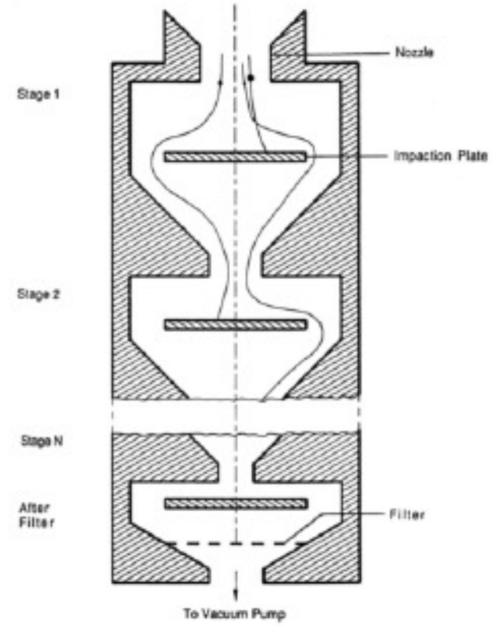
- Inexpensive (relatively)
  - Gravimetric for particle mass
  - Light scattering for large particle mass
  - Condensation nucleus counter (CNC) for counting small particles
  - Cascade impactor for size-resolved mass
- Mid-range
  - Optical particle counters
- Expensive
  - Aerodynamic particle sizing for large particles
  - Differential mobility analyzer for small particles

Measuring particle size, amount

Most basic approach:
Particle collection, gravimetry (weighing)

- Cascade impactors: size cuts
    - MOUDI

- Size cuts depend on Stokes' number

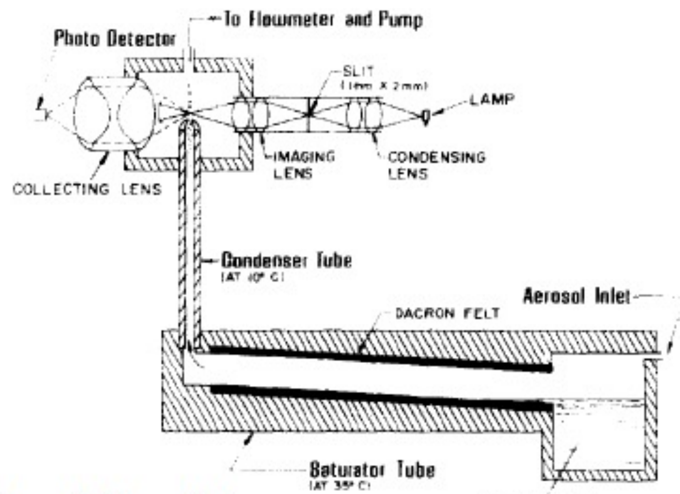


Cascade impactor

Condensation particle counter (CPC, CNC)

Standard TSI CPC
(e.g. Model 3775)

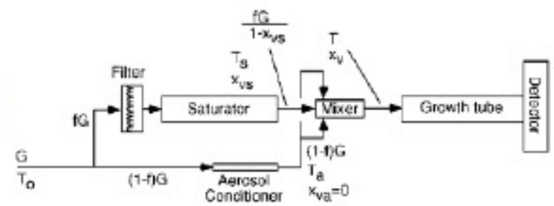
- $D_p > 4$ nm
- Working fluid: Butanol
- Response time several seconds
  → SMPS spectra
  acquisition takes minutes



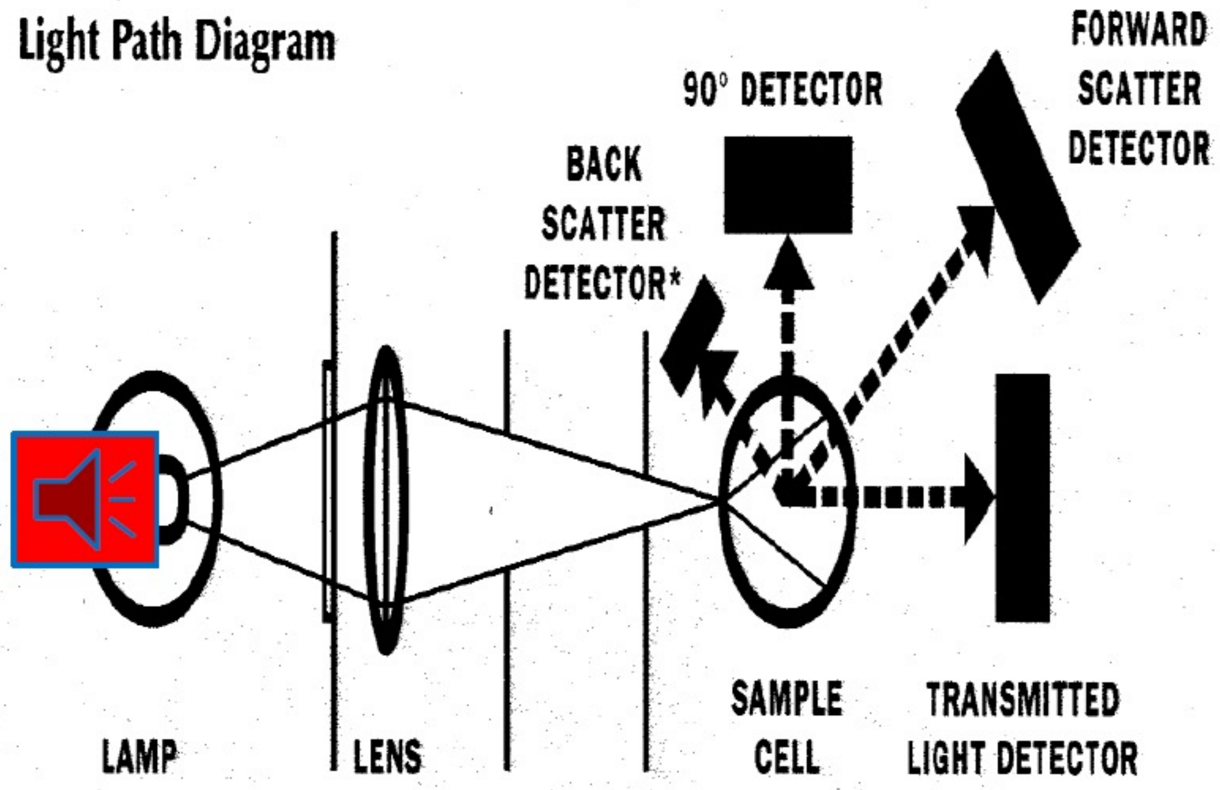
Agarwal & Sem, 1980

<u>Fast mixing: < 1 sec time response</u>

"Fast mixing condensation nucleus counter: Application to rapid scanning differential mobility analyzer measurements," J Wang, VF McNeill, DR Collins, RC Flagan, *Aerosol Sci. Tech.* 36 (6). 678-689 (2002)

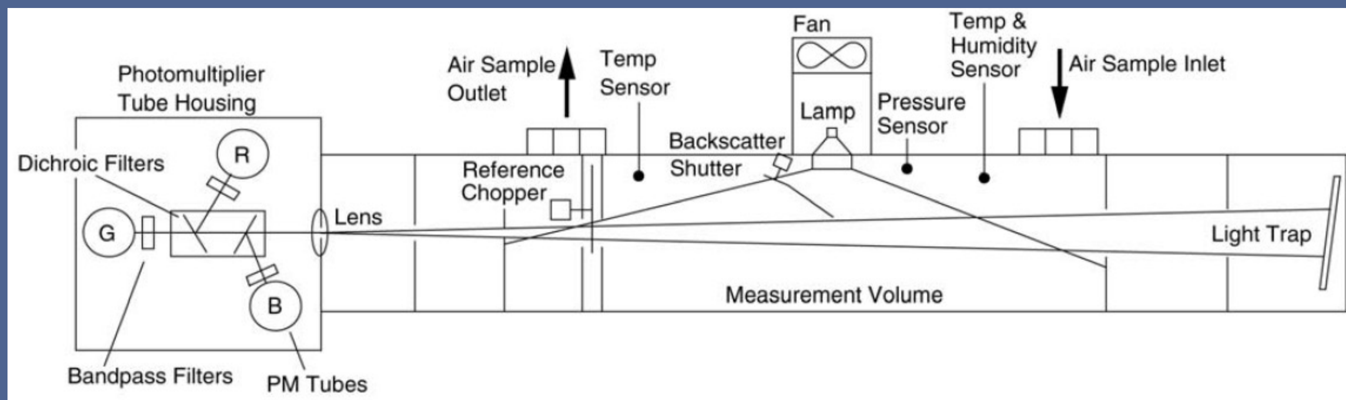


NEPHELOMETER



Concentration of particles :Nephelometry

- **In Nephelometry an equation that describe the relation between the intensity of scattered radiation , intensity of incident radiation , and concentration of particles Is= Ks x IO x C**
- ***Where ;***
- ***IO= Intensity of incident light***
- ***Is=Intensity of scattered radiation***
- ***Ks= It is constant which depend on suspended particle and suspension medium.***
- ***C=Concentration of solution***

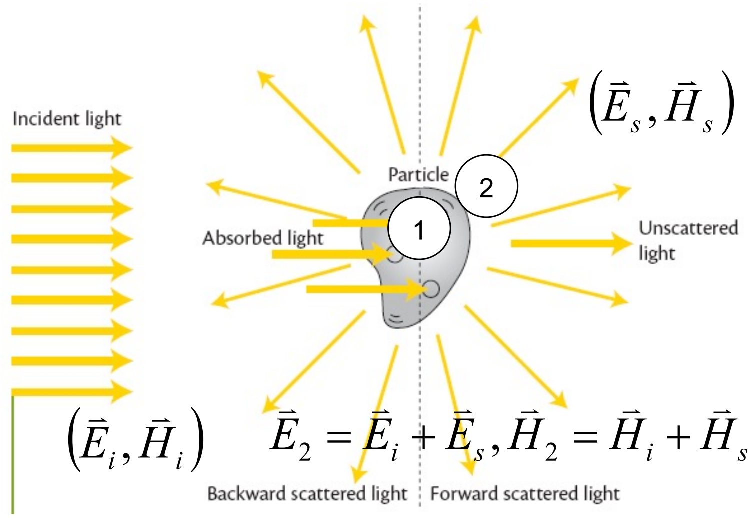


Scattering is measured at 453, 554 and 698 nm

Scattering of light by spherical particles (Mie scattering).

The problem (Bohren and Huffman, 1983):
Given a particle of a specified size, shape and optical properties that is illuminated by an arbitrarily polarized monochromatic wave, determine the electromagnetic field at all points in the particles and at all points of the homogeneous medium in which it is embedded.

$$\left(\vec{E}_1, \vec{H}_1\right), \left(\vec{E}_2, \vec{H}_2\right), \left(\vec{E}_i, \vec{H}_i\right), \left(\vec{E}_s, \vec{H}_s\right)$$



$$\left(\vec{E}_s, \vec{H}_s\right)$$

$$\left(\vec{E}_i, \vec{H}_i\right) \quad \vec{E}_2 = \vec{E}_i + \vec{E}_s, \vec{H}_2 = \vec{H}_i + \vec{H}_s$$

We will assume that the wave is plane harmonic wave and a spherical particles.

Plane parallel harmonic wave:

$$\vec{E}_i = \vec{E}_0 \exp\left(i\left(\vec{k}\cdot x - \omega t\right)\right)$$

$$\vec{H}_i = \vec{H}_0 \exp\left(i\left(\vec{k}\cdot x - \omega t\right)\right)$$

Must satisfy Maxwell's equation where material properties are constant:

$$\nabla\cdot\vec{E} = 0$$

$$\nabla\cdot\vec{H} = 0$$

$$\nabla\times\vec{E} = i\omega\mu\vec{H}\ldots\ldots\ldots1$$

$$\nabla\times\vec{H} = -i\omega\varepsilon\vec{E}\ldots\ldots\ldots2$$

$$k^2 = \varepsilon\mu\omega^2$$

ε is the *permittivity*
εμ is the *permeability*.

The vector equation reduce to after taking the curl of both sides of equations a1 and 2

$$\nabla\times(\nabla\times E) = i\omega\mu\nabla\times H = \omega^2\varepsilon\mu E$$

$$\nabla\times(\nabla\times H) = -i\omega\varepsilon\nabla\times E = \omega^2\varepsilon\mu$$

$$\Downarrow$$

$$\nabla^2\vec{E} + k^2\vec{E} = 0$$

$$\nabla^2\vec{H} + k^2\vec{H} = 0$$

Subject to Boundary conditions

$$\left[\vec{E}_2 - \vec{E}_1\right]\times\hat{n} = 0$$

$$\left[\vec{H}_2 - \vec{H}_1\right]\times\hat{n} = 0$$

An exact scattering solution for homogeneous spherical particles. Derivation not too difficult but very long…

- Based on wave equation in spherical polar co-ordinates, origin center of particle….Most of the mathematical complexity in this theory is due to expressing a plane wave as an expansion in spherical polar functions

- Scalar solutions to the wave equation are

$$r\psi(r,\theta,\phi) = \sum_{n=0}^{\infty}\sum_{l=-n}^{n} P_n^l(\cos\theta)[c_n\psi_n(kmr) + d_n\chi_n(kmr)]\{a_l\cos l\phi + b_l\sin l\phi\}$$

Legendre Bessel Neumann

- Related to vector solutions

$$E = M_v + iN_u$$

$$H = m(-M_u + iN_v$$

$$M = \nabla\times(r\psi)$$

- Series expansion for E and H

$$N = \frac{\nabla\times M}{k}$$

- The desired expansion of plane waves in spherical harmonics are

$$E_i = E_o \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (M_{o1n}^{(1)} - iN_{e1n}^{(1)}) \qquad H_i = \frac{-k}{\omega\mu} E_o \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (M_{e1n}^{(1)} + iN_{o1n}^{(1)})$$

Consider particle sphere radius r, refractive index m, surrounded by vacuum, m=1. To find the coefficients defining the scattered wave, use boundary condition at surface of sphere

$$(\mathbf{E}_i + \mathbf{E}_s - \mathbf{E}_1) \times \hat{\mathbf{e}}_r = (\mathbf{H}_i + \mathbf{H}_s - \mathbf{H}_1) \times \hat{\mathbf{e}}_r = 0$$

Inside the sphere

$$\mathbf{E}_1 = \sum_{n=1}^{\infty} E_n \left(c_n \mathbf{M}_{o1n}^{(1)} - i d_n \mathbf{N}_{e1n}^{(1)} \right),$$

$$\mathbf{H}_1 = \frac{-\mathrm{k}_1}{\omega\mu_1} \sum_{n=1}^{\infty} E_n \left(d_n \mathbf{M}_{e1n}^{(1)} + i c_n \mathbf{N}_{o1n}^{(1)} \right)$$

Field expressed by incoming wave, Bessel function j_n $(k_1 r)$- Finite at the origin

Scattered field

$$\mathbf{E}_s = \sum_{n=1}^{\infty} E_n \left(i a_n \mathbf{N}_{e1n}^{(3)} - b_n \mathbf{M}_{o1n}^{(3)} \right),$$

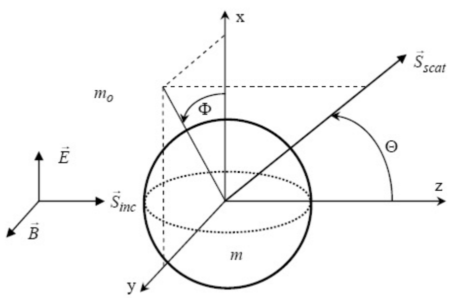
$$\mathbf{H}_s = \frac{\mathrm{k}}{\omega\mu} \sum_{n=1}^{\infty} E_n \left(i b_n \mathbf{N}_{o1n}^{(3)} + a_n \mathbf{M}_{e1n}^{(3)} \right)$$

Field expressed by superposition of incoming and outgoing waves expresses in spherical Hankel functions

More interested in the rate W at which electromagnetic energy crosses the boundary of a closed surface A which encloses a volume V is

$$W_a = -\int_A S.\hat{n}\,dA$$

For a non absorbing medium, W_a is the rate at which energy is absorbed by the sphere. This is equal to the Extinction Rate (sum of energy absorption rate and energy scattering Rate) – Scattering rate



$$W_{ext} = W_a + W_s$$

$$W_{ext} = -\int_A \hat{S}_{ext} \bullet \hat{e}_r dA$$

$$W_s = \int_A \hat{S}_s \bullet \hat{e}_r dA$$

For example

$$W_s = -\frac{1}{2}\mathrm{Re}\int_0^{2\pi}\int_0^{\pi}(E_{s\theta}H^*_{s\phi} - E_{s\phi}H^*_{s\theta})r^2 \sin\theta d\theta d\phi$$

$$E_{s\theta} = \frac{\cos\phi}{\rho}\sum_{n=1}^{\infty} E_n (ia_n \xi'_n \tau_n - b_n \pi_n)$$

$$E_{s\phi} = \frac{\sin\phi}{\rho}\sum_{n=1}^{\infty} E_n (b_n \xi_n \tau_n - ia_n \xi'_n \pi_n)$$

$$H_{s\theta} = \frac{k}{\mu\omega}\frac{\sin\phi}{\rho}\sum_{n=1}^{\infty} E_n (ib_n \xi'_n \tau_n - a_n \xi_n \pi_n)$$

$$H_{s\phi} = \frac{k}{\mu\omega}\frac{\cos\phi}{\rho}\sum_{n=1}^{\infty} E_n (ib_n \xi'_n \pi_n - a_n \xi_n \tau_n)$$

where

$$\pi_n = \frac{P'_n}{\sin\theta}$$

$$\tau_n = \frac{dP'_n}{d\theta}$$

Are angle dependent functions

Key parameters are Scattering and extinction cross sections,

σ_{ext} and σ_s such that $\sigma_{ext} = \sigma_s + \sigma_a$

These cross sections are the ratios of the rate at which energy is scattered or absorbed (W_a ; W_s) divided by the incident Irradiance

$$\sigma_s = \frac{W_a}{I_i}$$

$$\sigma_a = \frac{W_s}{I_i}$$

$$\sigma_{ext} = \frac{W_{ext}}{I_i}$$

$$\sigma_{sca} = \frac{W_{sca}}{I_i} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\,\mathrm{Re}(a_n + b_n)$$

$$\sigma_{ext} = \frac{W_{ext}}{I_i} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)(|\,a_n\,|^2 + |\,b_n\,|^2)$$

The coefficients a_n,b_n, obtained from the boundary conditions

$$E_{i\theta} + E_{s\theta} = E_{1\theta}$$
$$E_{i\phi} + H_{s\phi} = E_{1\phi}$$
$$H_{i\theta} + H_{s\theta} = H_{1\theta}; r = a$$
$$H_{i\phi} + H_{s\phi} = H_{1\phi}$$

X is the size parameter = $\frac{2\pi Na}{\lambda}$ and *m* is the relative refractive index = N_1/N= ration of the refractive index of the particle and the medium

$$a_n = \frac{m\psi_n(mx)\psi'_n(x) - \psi_n(x)\psi'_n(mx)}{m\psi_n(mx)\xi'_n(x) - \xi_n(x)\psi_n'(mx)}$$

$$b_n = \frac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi'_n(x) - m\xi_n(x)\psi'_n(mx)}$$

$$\psi_n(mx) = mxj_n(mx)$$
$$\xi_n(mx) = mxh_n^{(1)}(mx)$$

ψ and ξ Are the Riccati- Bessel Functions, j are the Bessel functions and h are Hankel functions

Introduction (T-matrix approach)

- Incident and scattered electromagnetic fields are expanded in vector spherical functions M_{mn} and N_{mn} .

$$\boldsymbol{E}^{\mathrm{inc}}(\boldsymbol{R}) = \sum_{n=1} \sum_{m=-n} [a_{mn}\mathrm{Rg}\boldsymbol{M}_{mn}(k\boldsymbol{R}) + b_{mn}\mathrm{Rg}\boldsymbol{N}_{mn}(k\boldsymbol{R})],$$

$$\boldsymbol{E}^{\mathrm{sca}}(\boldsymbol{R}) = \sum_{n=1}^{n_{\max}} \sum_{m=-n}^{n} [p_{mn}\boldsymbol{M}_{mn}(k\boldsymbol{R}) + q_{mn}\boldsymbol{N}_{mn}(k\boldsymbol{R})], \quad |\boldsymbol{R}| > r_0,$$

k is the wave number in the surrounding medium r_o is the radius of circumscribing sphere of the scattering particles a_{mn} and b_{mn} are the incident field coefficients and p_{mn} and q_{mn} are scattered field coefficients RgM_{mn}, RgN_{mn} indicates that they are regular at origin

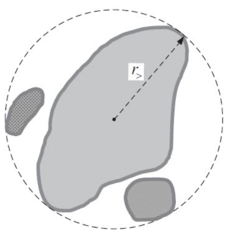


Fig. Cross section of any arbitrarily scattering object (Mischenko et al. 2000)

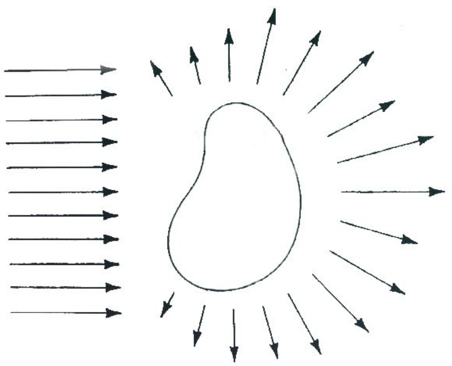


Fig. Incident field (E^{inc}, H^{inc}) gives rise to field inside particle (E^1, H^1) and scattered field (E^{sca}, H^{sca}). (*Craig F. Bohren, Donald R. Huffman 1983*)

T-matrix approach

❖ Linearity of Maxwell's equations contributes to develop relation between scattered field coefficients p_{mn} & q_{mn} and incident field coefficients a_{mn} & b_{mn}.

❖ Linear relation is given by a T-matrix (T) as :

$$p_{mn} = \sum_{n'=1}^{n_{\max}} \sum_{m'=-n'}^{n'} [T^{11}_{mnm'n'} a_{m'n'} + T^{12}_{mnm'n'} b_{m'n'}],$$

$$q_{mn} = \sum_{n'=1}^{n_{\max}} \sum_{m'=-n'}^{n'} [T^{21}_{mnm'n'} a_{m'n'} + T^{22}_{mnm'n'} b_{m'n'}].$$

❖ Writing same equation in compact matrix notation yields :

$$\begin{bmatrix} p \\ q \end{bmatrix} = T \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} T^{11} & T^{12} \\ T^{21} & T^{22} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix}.$$

❖ This equation is the basis of the T-matrix approach.

T-matrix approach

$$\left\{\begin{aligned} C_{ext} &= -\frac{2\pi}{k^2}\mathrm{Re}\sum_{n=1}^{n_{\max}}\sum_{m=-n}^{n}[T^{11}_{mnmn} + T^{12}_{mnmn}], \\ C_{sca} &= \frac{2\pi}{k^2}\sum_{n=1}^{n_{\max}}\sum_{n'=1}^{n_{\max}}\sum_{m=-n}^{n}\sum_{m'=-n'}^{n'}\sum_{i=1}^{2}\sum_{j=1}^{2}\left|T^{ij}_{mnm'n'}\right|^2 \end{aligned}\right\}.$$

- Higher the absorption cross section of particle lower will be the value of SSA

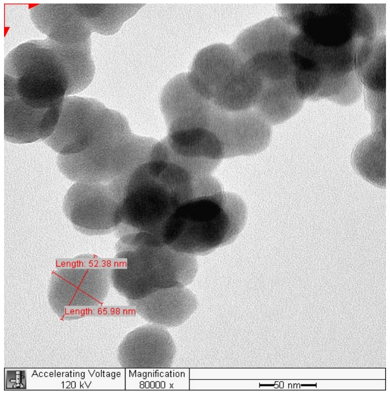
$$C_{abs} = C_{ext} - C_{sca}$$

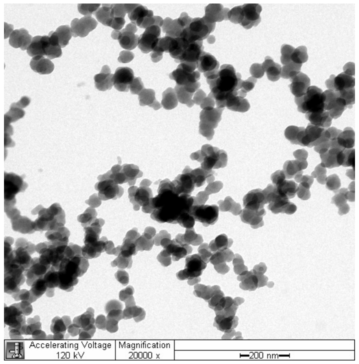
$$\text{Single scattering albedo}\,(\omega_0) = \frac{C_{sca}}{C_{ext}}.$$

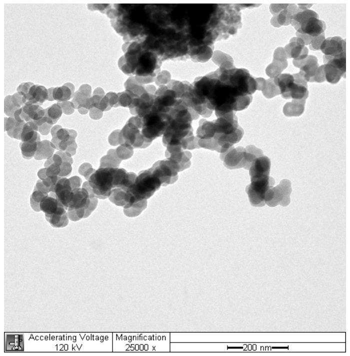
Theoretical Methods and Approximations

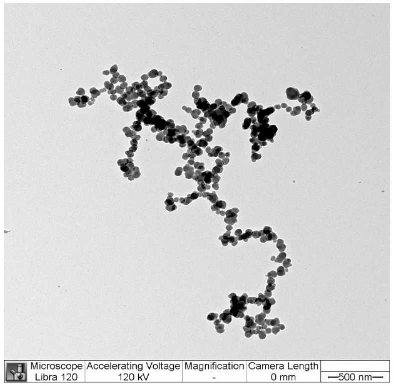
Imaging

- Filter samples of freshly emitted aerosols were collected on TEM grids.
- Images of the samples were taken using Transmission Electron Microscope (TEM)









RDG Approximations

Conditions for RDG

#1: $2x_p|m-1| \ll 1$ **where** $x_p = k \times a$

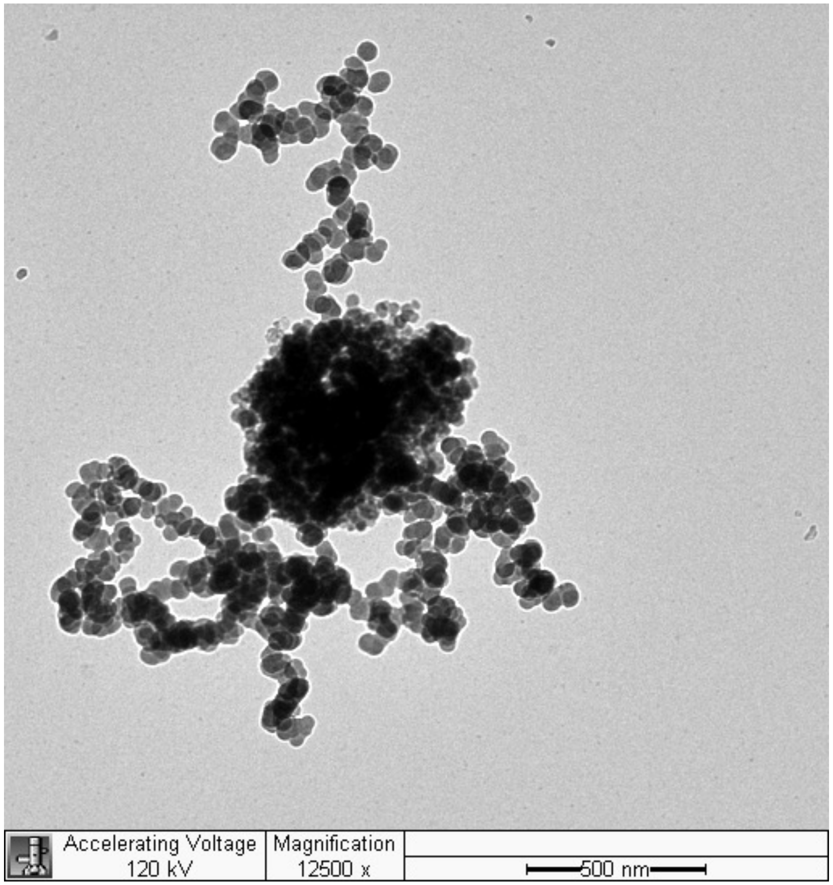
#2: $|m-1| \ll 1$ **and** $m = n + ik$

Flaming BB aerosol from eucalyptus has x_p values between 0.29 and 0.34 for incident light having wavelengths between 580 and 500 nm.

RDG Approximations

Assumptions

- The effects of multiple scattering induced by other particles in the aggregate are negligible.
- Self-interaction of the primary particle itself is negligible.
- The primary particles are spherical and of the same diameter.
- Primary particles are in point-contact.



RDG Approximations

The Absorption Cross Section for a monomer is given as:

$$C_{abs}^{p} = [4\boldsymbol{\pi} x_p^3 Im((m^2-1)/(m^2+2))]/k^2$$

The Scattering Cross Section for a monomer is given as:

$$C_{sca}^{p} = [x_p^6 \left|(m^2-1)/(m^2+2)\right|^2]/k^2$$

RDG Approximations

The absorption cross section for the aggregate is given by:

$$C_{abs}^{agg} = N_p C_{abs}^{p}$$

The total scattering cross section for the aggregate is given by:

$$C_{sca}^{agg} = N_p^2\ C_{sca}^{p} 2\boldsymbol{\pi} \int_0^{\boldsymbol{\pi}} S(qR_g)\frac{1}{2}\left(1 + cos^2\theta\right)sin\theta d\theta$$

$S\left(qR_g\right)$ **is called the Structure or form factor.**

RDG Approximations

The structure factor is given by:

$$S(qR_g) = [1 + 8(qR_g)^2/(3D_f) + (qR_g)^8]^{-D_f/8}$$

The modulus of the scattering wave vector

$$q = 2k\sin(\theta/2)$$

$qR_g < 1$ **implies Guinier regime (Small Scattering Regime)**

$qR_g > 1$ **implies power-law regime (Large Scattering Regime)**

The structure factor of Yang and Koylu (2005) gives a unified expression connecting the two regimes with a single expression, which gives a broadened transition between the two regimes.