CHE680
Advanced Analytical Chemistry
Lecture 4

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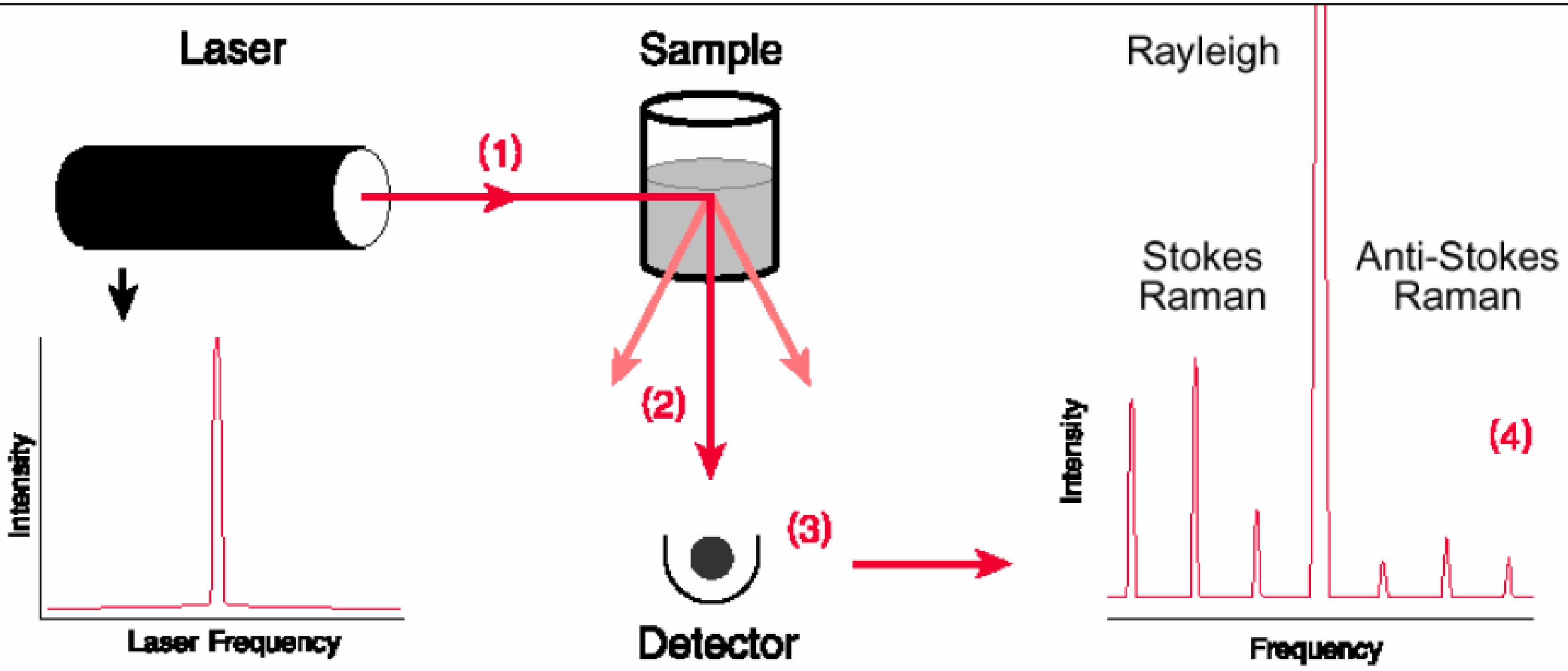
Overview of Raman Spectroscopy

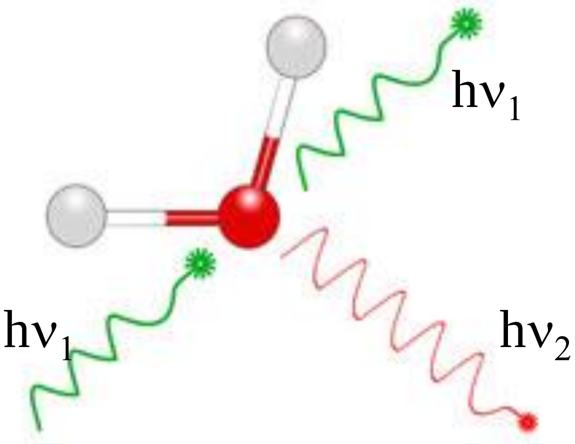


(1) Laser light excites the sample.
(2) This light is scattered in all directions.
(3) Some of this scattered light is directed to the detector which records the Raman spectrum.
(4) This spectrum shows both light at the original laser (or Rayleigh) frequency and the Raman spectral features unique to the sample.

Raman Spectroscopy

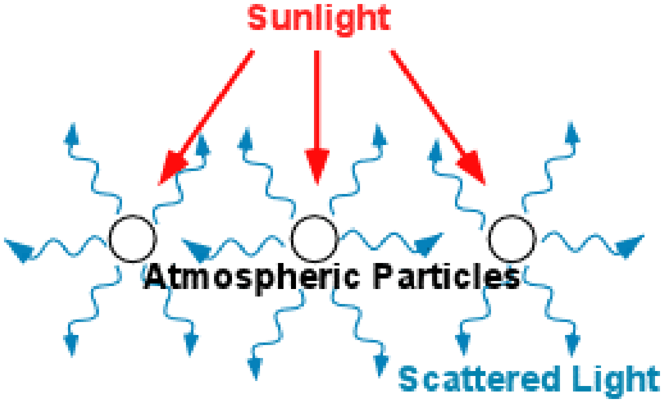
- Theory
- Chemical Information
- Instrumentation
- Comparison with IR
- Various Modes

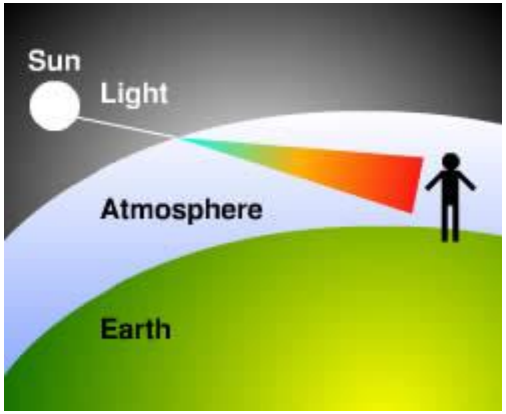
Sir C.V.Raman (1888-1970)



http://www.jobinyvon.com/usadivisions/Raman/raman_resource.htm
http://carbon.cudenver.edu/public/chemistry/classes/chem4538/raman.htm
http://www.chemsoc.org/ExemplarChem/entries/2004/birmingham_jones/raman.html
http://www.kosi.com/raman/resources/tutorial/index.html

Rayleigh (Elastic) Scattering



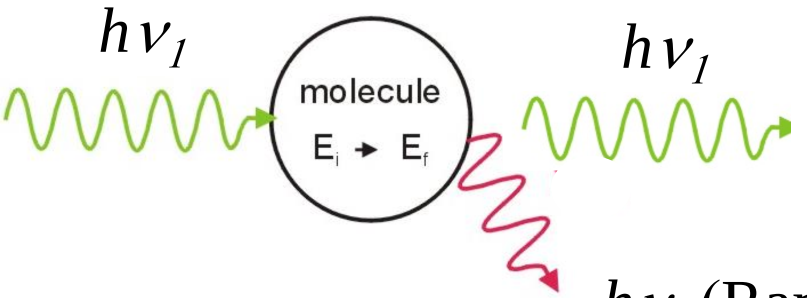


Sunlight comes into the atmosphere and can be scattered in any direction as it passes through a medium. This diffuses the light, spreading it out in all directions so it is not just a single, straight beam.

Blue skies are produced as shorter wavelengths of the incoming visible light (violet and blue) are selectively scattered by small molecules of oxygen and nitrogen. The violet and blue light has been scattered over and over by the molecules, so our eyes register it as blue light coming from all directions, giving the sky its blue appearance.

At dusk, when the sun is low on the horizon, sunlight passes through more atmosphere to reach us than during the day. By the time the light reaches us, more of the colors have been scattered. The last color to be scattered is red. If there are many particles in the air (due to pollution, dust or smoke), the sun and sky can appear red in the middle of the day.

Raman (Inelastic) Scattering



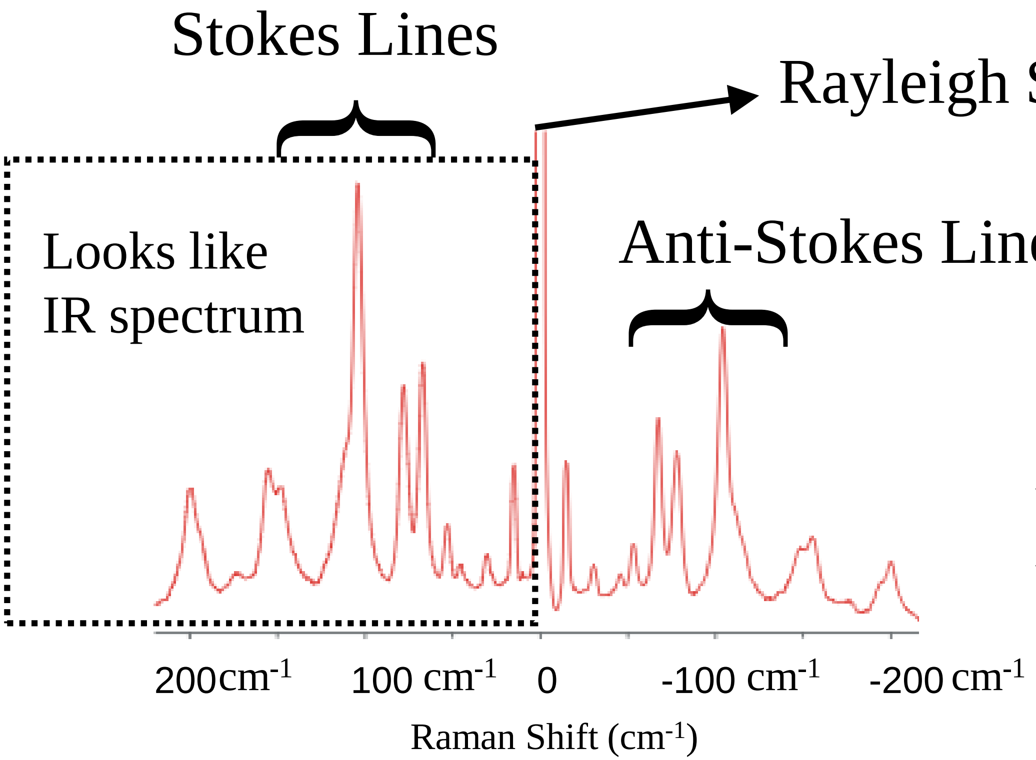
$h\nu_1$

$h\nu_1$ 99.999% (Rayleigh, all directions)

$h\nu_2$(Raman scattering, all directions)

- Rayleigh scattering: same energy (frequency)
- Raman scattering: 0.001% of scattered light has a different frequency by vibrational energy of molecules in the sample.
- One portion of Raman scattering, energy was decreased (Stokes), the other exhibit increased energy (Anti-Stokes)
- Indian physicist Raman observed it (Novel Prize in 1931)

Stokes and Anti-Stokes Lines



Stokes Lines

Rayleigh Scattering

Looks like
IR spectrum

Anti-Stokes Lines

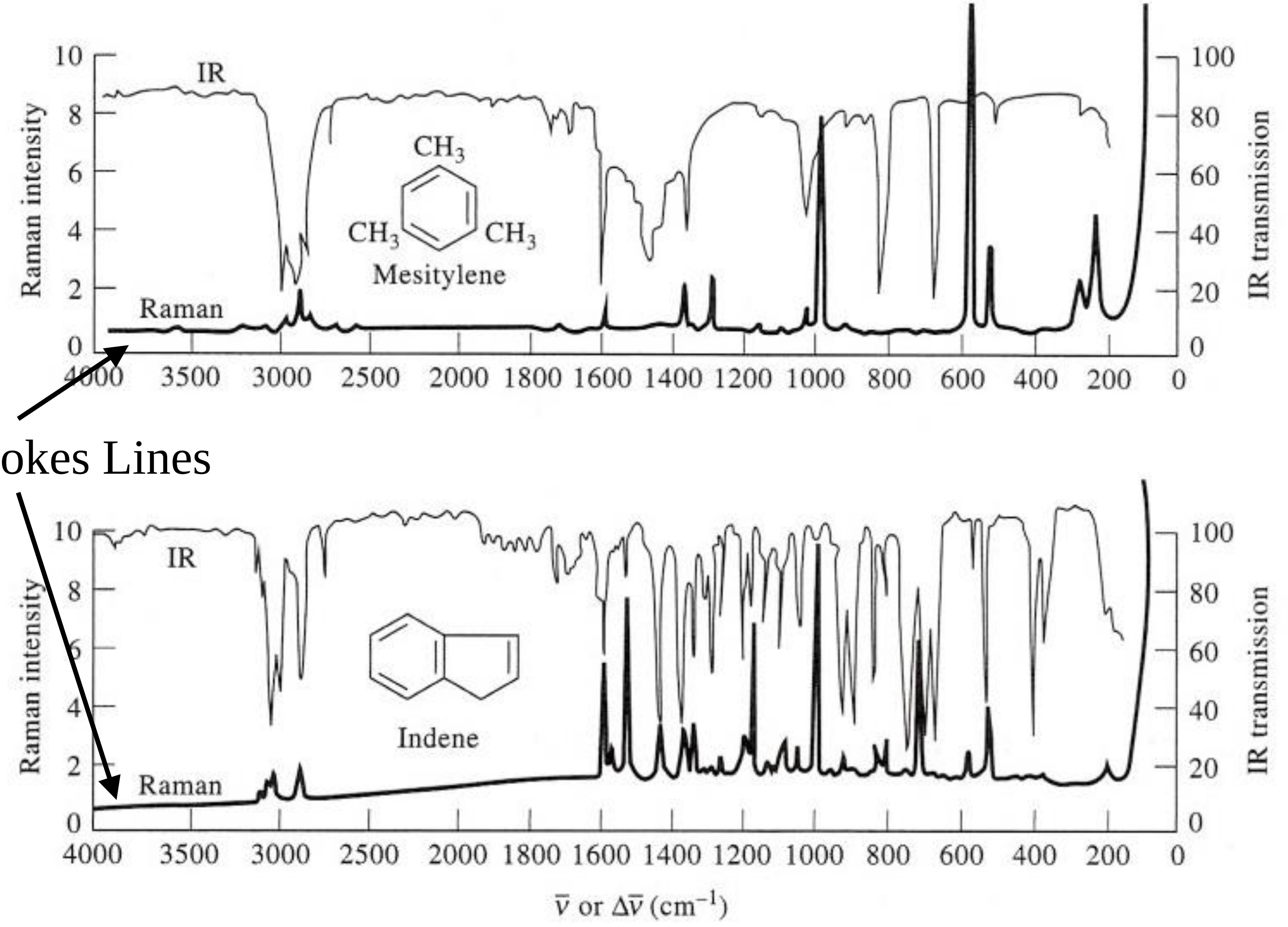
Raman Shift $(\Delta\nu) = \nu_0 - \nu_1$

ν_0 = input frequency

ν_1 = output frequency

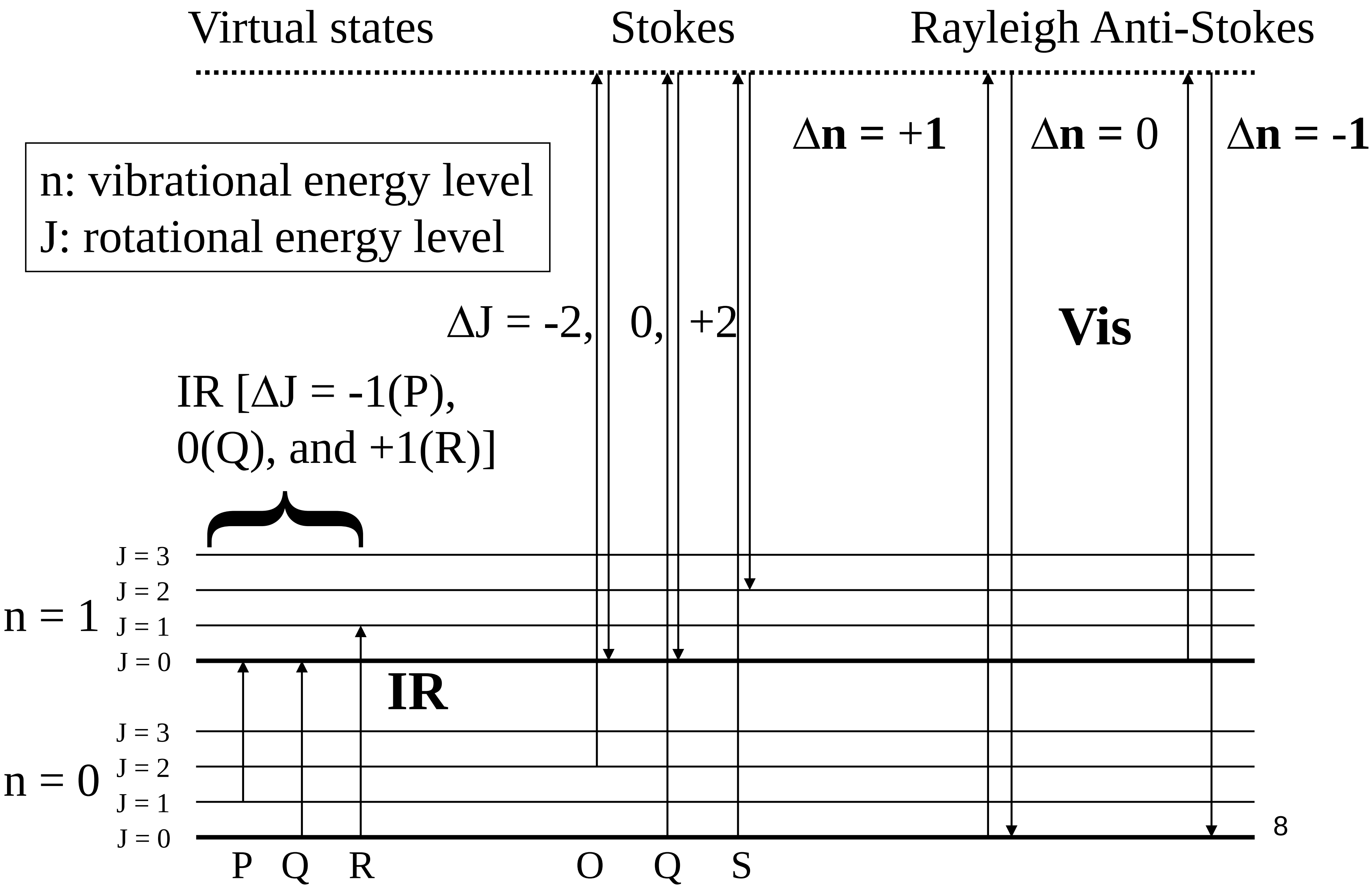
- Raman shifts for Stokes and anti-Stokes lines are identical
- Peak intensities for Stokes Lines are greater than those for Anti-Stokes Lines
- Raman shift is independent of input source (energy)
- Relative Raman shifts in Stokes Lines produce spectra like IR

IR vs Raman Spectroscopy



Stokes Lines

IR vs Raman Spectroscopy



Virtual states

Stokes

Rayleigh Anti-Stokes

Δn = +1

Δn = 0

Δn = -1

n: vibrational energy level
J: rotational energy level

ΔJ = -2, 0, +2

Vis

IR [ΔJ = -1(P), 0(Q), and +1(R)]

n = 1

J = 3
J = 2
J = 1
J = 0

IR

n = 0

J = 3
J = 2
J = 1
J = 0

P Q R

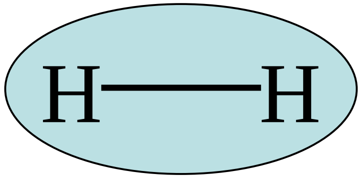
O Q S

Raman Selection Rule

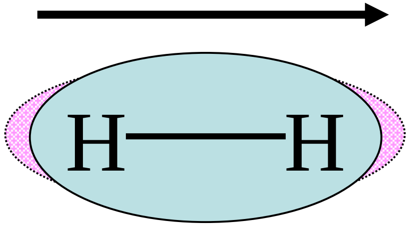
- Vibrational energy levels
  - **$\Delta n = \pm 1$**
  - Polarizability (α) must *change* during particular vibration
- What's the polarizability?

Polarizability

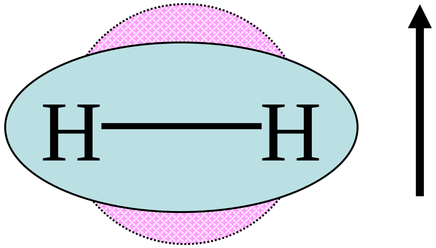
The polarizability (α) is the relative tendency of the electron cloud of an atom (or molecule) to be distorted from its original shape by the presence of an external electric field.



no electric field

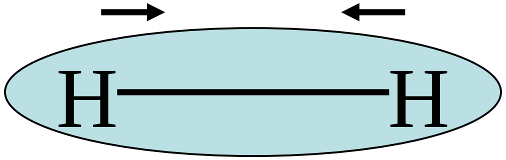


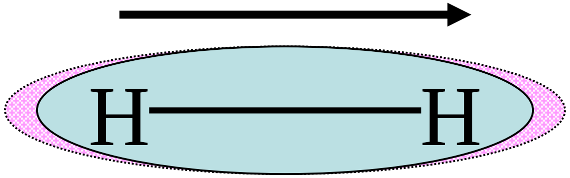
electric field (E_x)



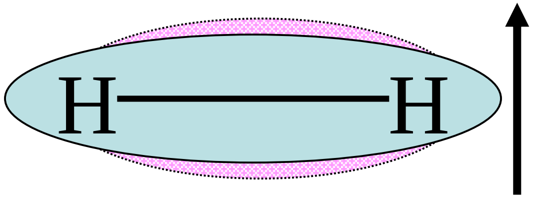
electric field (E_z)

During vibrational motion, a redistribution of electron density occurs, therefore, response to the electric field (polarizability) changed.





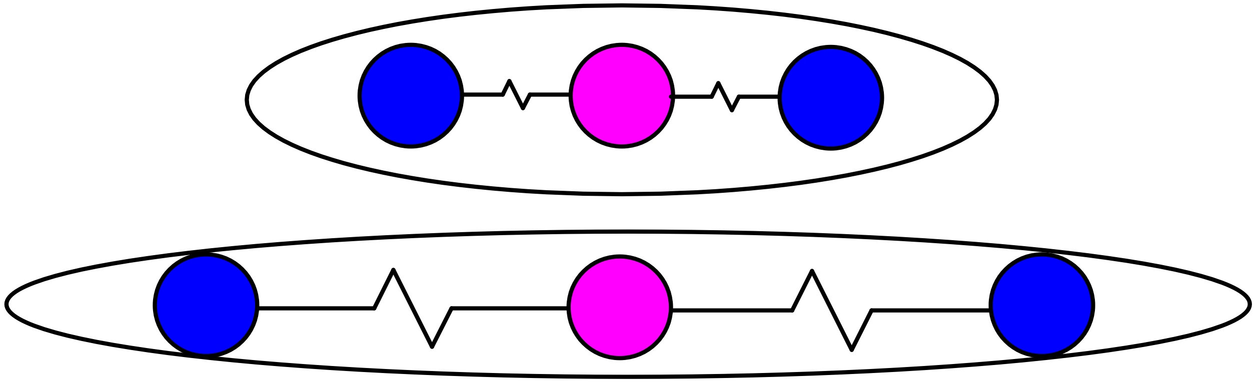
electric field (E_x)



electric field (E_z)

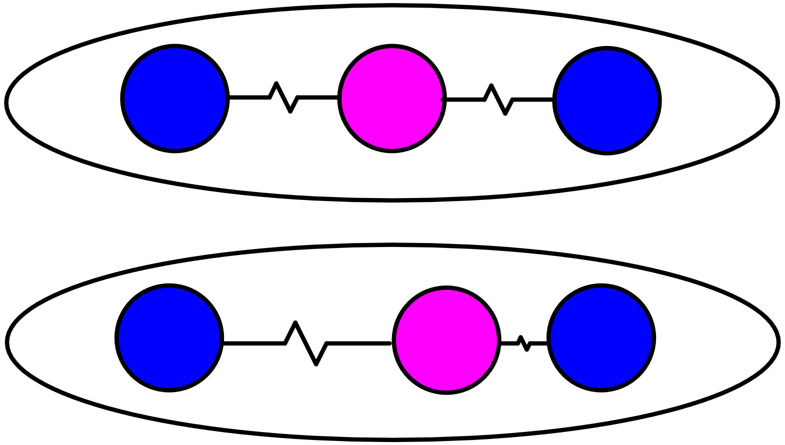
In any cases, there is no changes in net dipole moment

Vibrational Raman for CO_2



- Symmetric stretching vibration of CO_2
- Polarizability changes
  - therefore Raman band at 1,340 cm^{-1}
- Dipole moment does *not* change
  - no absorption at 1,340 cm^{-1} in IR

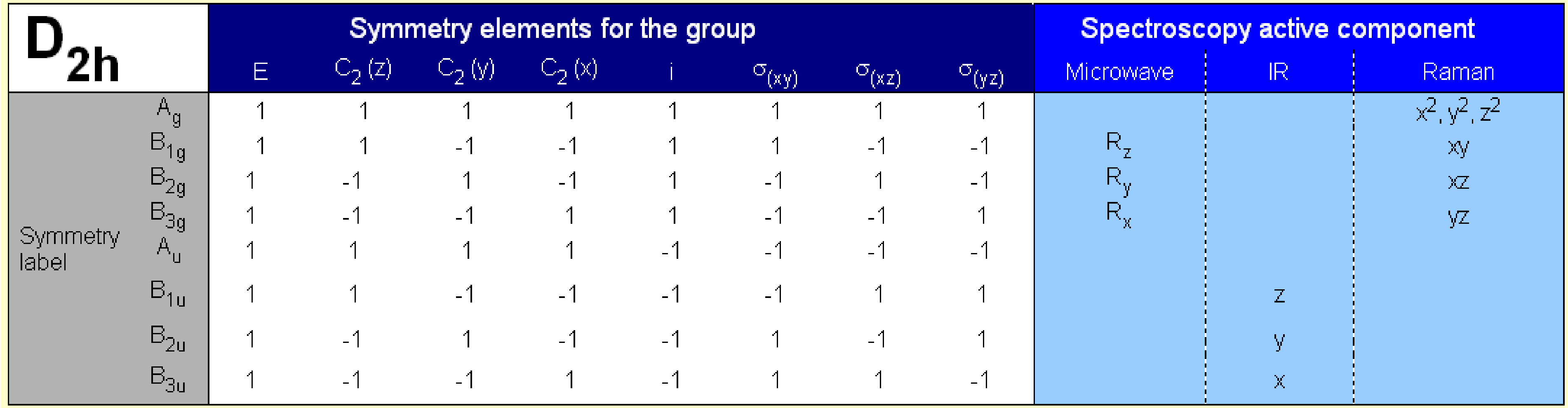
Vibrational Raman for CO_2



- Asymmetric stretching vibration of CO_2
- Polarizability does *not* change during vibration
  - No Raman band near 2,350 cm^{-1}
- Dipole moment does change
  - CO_2 absorbs at 2,349 cm^{-1} in the IR

Exclusion Rule

- For molecules with inversion symmetry, any vibrational modes can not be active in both IR and Raman
- If any modes are IR active, they are Raman inactive (or *vice versa*)
- H_2, CO_2, C_2H_2, Benzene, C_2H_4, etc



D_{2h}		Symmetry elements for the group								Spectroscopy active component		
		E	C_2 (z)	C_2 (y)	C_2 (x)	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$	Microwave	IR	Raman
Symmetry label	A_g	1	1	1	1	1	1	1	1			x^2, y^2, z^2
	B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z		xy
	B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y		xz
	B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x		yz
	A_u	1	1	1	1	-1	-1	-1	-1			
	B_{1u}	1	1	-1	-1	-1	-1	1	1		z	
	B_{2u}	1	-1	1	-1	-1	1	-1	1		y	
	B_{3u}	1	-1	-1	1	-1	1	1	-1		x	

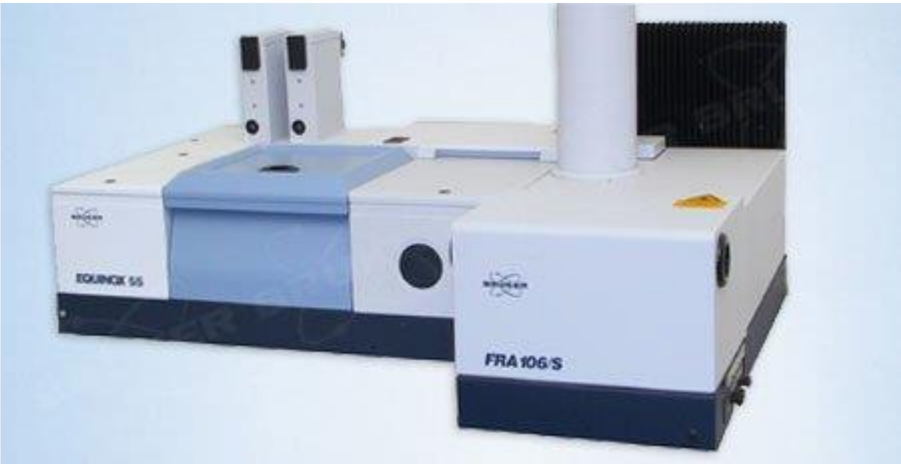
IR vs Raman Spectroscopy

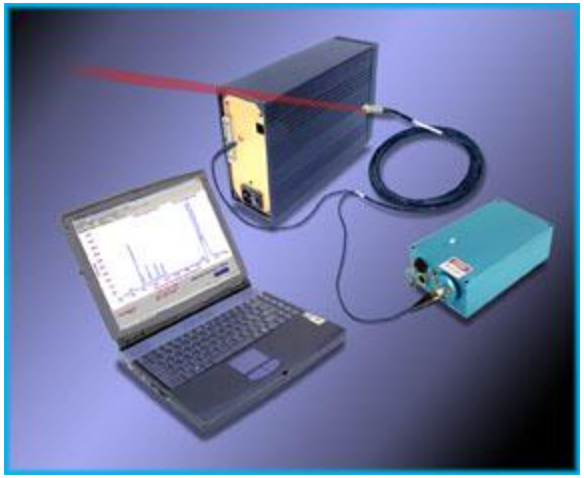
Raman		**Infrared**
scattering	mechanism	absorption
a monochromatic strong radiation (visible laser)	source	all infrared frequencies within scan range
$\nu_i - \nu_a$ (input – absorption)	probing	ν_a, absorption frequency
polarizability (α) change	selection rule	dipole moment (μ) change
no absorption	H_2O	absorption
active, active	HCl, N_2	active, inactive

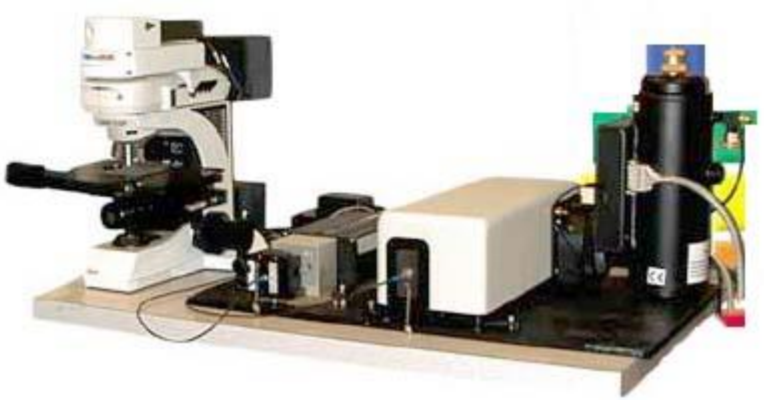
Advantages of Raman Spectroscopy

- Minimal or no sample preparation
- Sampling directly through glass containers
- Non-destructive analysis, so the same sample can be used in other analyses
- Non-intrusive analysis, permitting study of more labile sample features, such as crystal structure
- Minimal water interference
- No interference from atmospheric CO_2 or H_2O

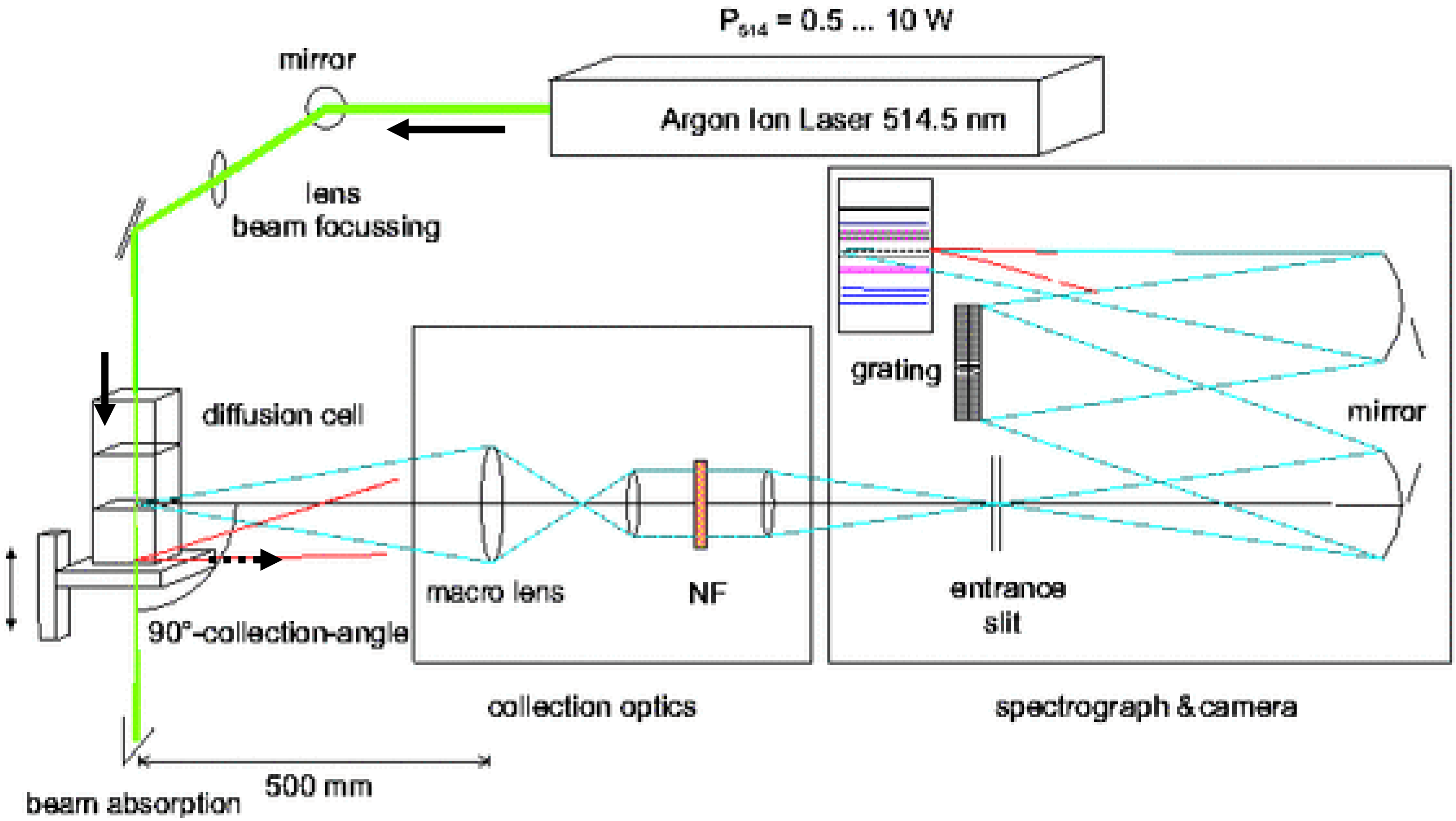
Instrumentation







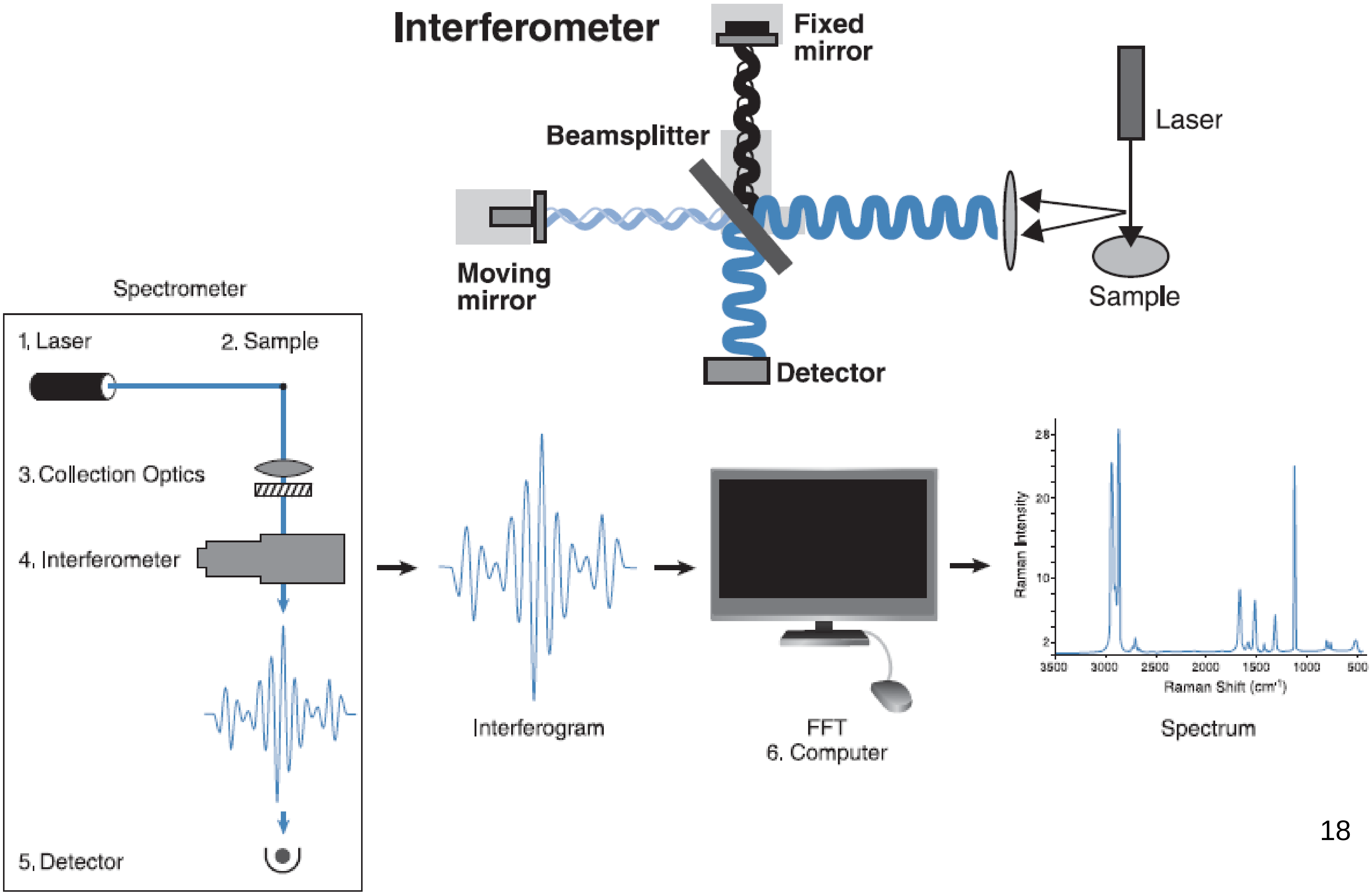
Instrumentation (Dispersive)



Nd-YAG (1064 nm), He/Ne (632.8), Diode Laser (782 or 830 nm), Semiconductor (976 nm)

The shorter, the stronger Raman signal.

Instrumentation (FT)



Detectors

1. Dispersive: Si charged-coupled device (CCD), photomultiplier
2. FT Mode
    a) The InGaAs detector offers the most benefits for:
        - Samples with intense Raman scattering, e.g., neat organic liquids and white powders
        - Samples that can tolerate high laser power
        - Routine lab work and QC sampling
    b) The Ge detector offers the most benefits for:
        - Samples with weak Raman scattering, such as aqueous solutions
        - Samples requiring low laser power, for example when sample burning is a problem
        - Instrument settings that reduce optical throughput, such as high spectral resolution
        - High-speed applications, such as high-throughput screening or chemical mapping

Modified Raman Spectroscopy

As the typical intensity of Raman scattering is 0.001% of that of input light, signal is very weak. Thus, it was not popular due to the low sensitivity (detection limit, ~0.1 M).

- Resonance Raman Spectroscopy (~10^{-8} M)
- Surface Enhanced Raman Spectroscopy (SERS, ~10^{-9} – 10^{-12} M)
- Coherent Anti-Stokes Raman Spectroscopy (CARS, 10^4–10^5 times)

Surface Enhanced Raman Spectroscopy (SERS)

The Raman scattering from a compound (or ion) adsorbed on or even within a few Angstroms of a structured metal surface can be 10^3-10^6 times greater than in solution. This surface-enhanced Raman scattering is strongest on silver, but is observable on gold and copper as well. SERS is employed to study the solution phase vibrational structure of molecules adsorbed on gold and silver colloids. SERS is also used to study monolayers of materials adsorbed on metals, including electrodes.