CARS & PARS

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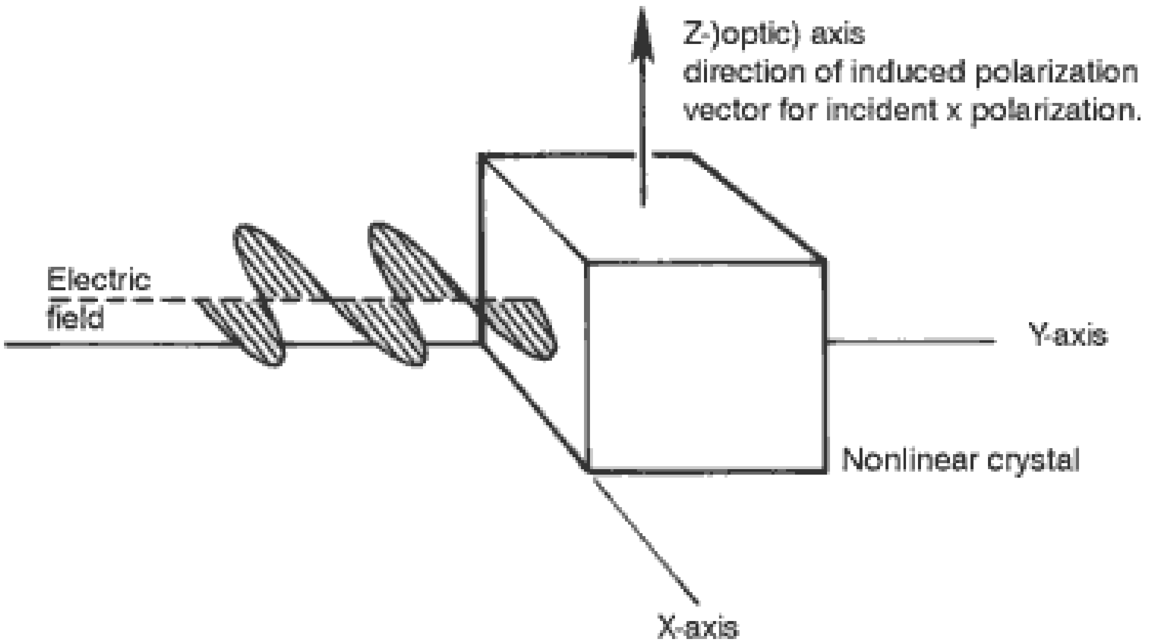
Nonlinear optical effects



$$P = \alpha E$$

At extremely high intensities

$$P(t) = \chi^{(1)} E(t) + \chi^{(2)} E(t)^2 + \chi^{(3)} E(t)^3 + \ldots$$

Nonlinear optical effects

Nonlinear Raman methods

a) Stimulated Raman scattering (SRS)
b) Hyper Raman effect (HRE)
c) Stimulated Raman gain (SRG)
d) Inverse Raman spectroscopy (IRS)
e) Coherent anti-stokes Raman scattering (CARS)
f) Coherent stokes Raman scattering (CSRS)
g) Photo acoustic Raman scattering (PARS)

Coherent anti-stokes Raman scattering (CARS)

- A nonlinear analogue of SRS
- 3rd order nonlinear optical process involving 3 laser beams

CARS is a third order nonlinear optical process, requiring high intensity laser pulses

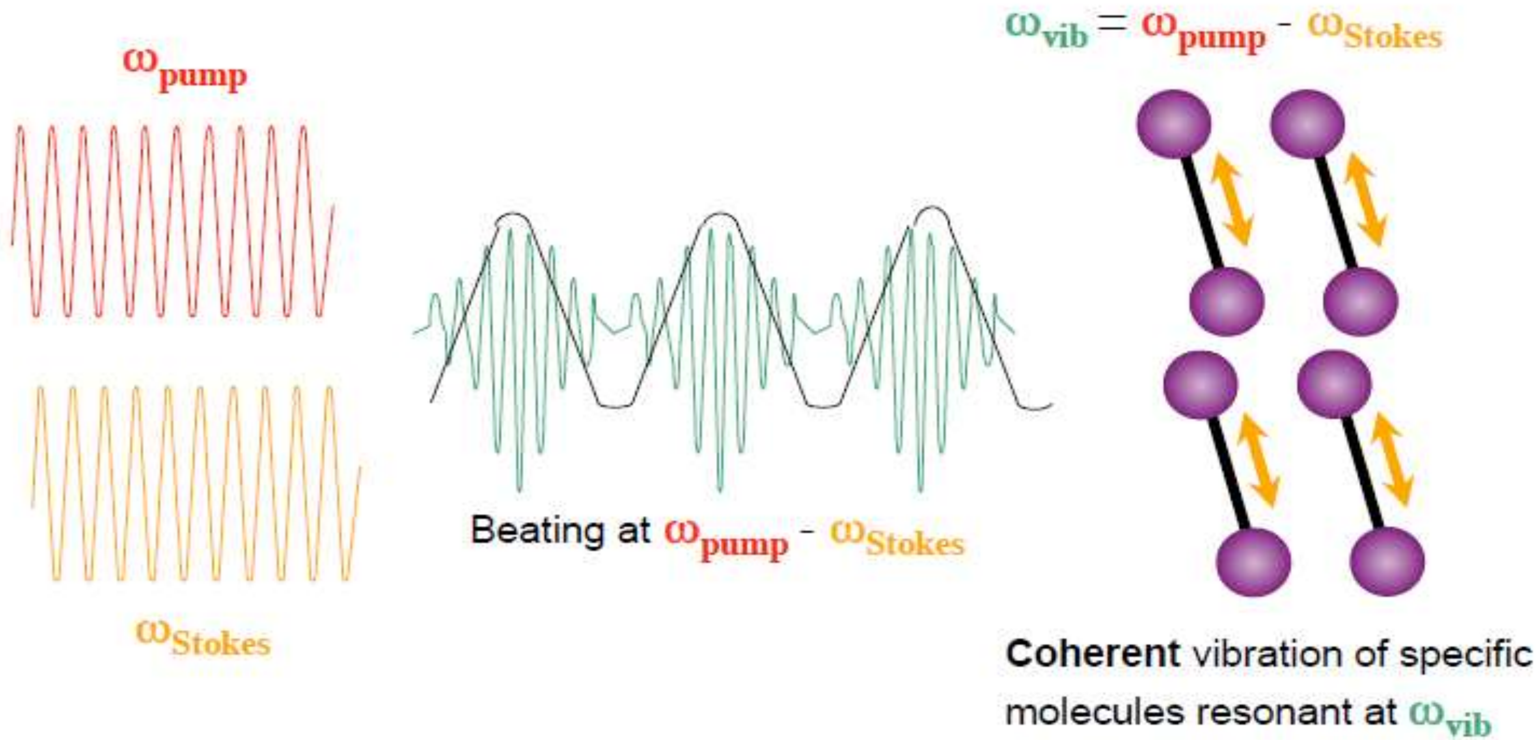
Polarization

$$P(t) = \chi^{(1)} E(t) + \chi^{(2)} E(t)^2 + \chi^{(3)} E(t)^3 + \dots$$

Higher order terms becomes important when peak powers are high

For CARS, $P_{AS} = \chi^{(3)} E_p^2 E_s$

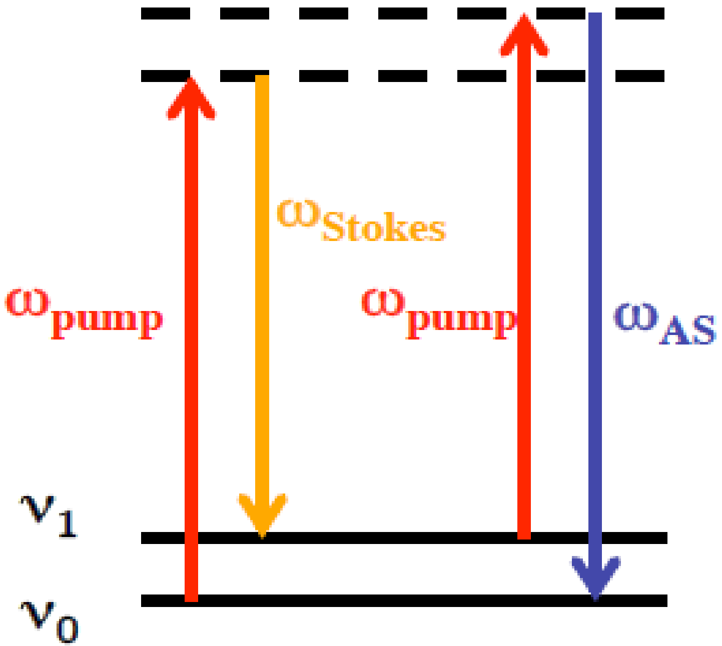
CARS uses two laser frequencies to interact resonantly with a specific molecular vibration



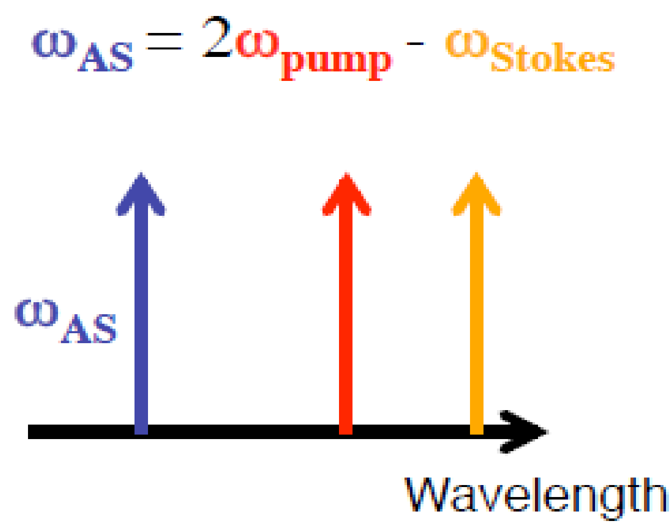
When (ωp-ωs) matches the molecular vibrational frequency ωvib, the antistokes signal is produced with frequency $\omega_{as} = 2\omega_p - \omega_s$ such that $(\omega_p > \omega_s)$

Coherent radiation frequency $\omega_{as} = 2\omega_p - \omega_s = \omega_p + (\omega_p - \omega_s)$

CARS signals are generated at wavelengths shorter than the excitation wavelengths (anti-Stokes)



Energy diagram



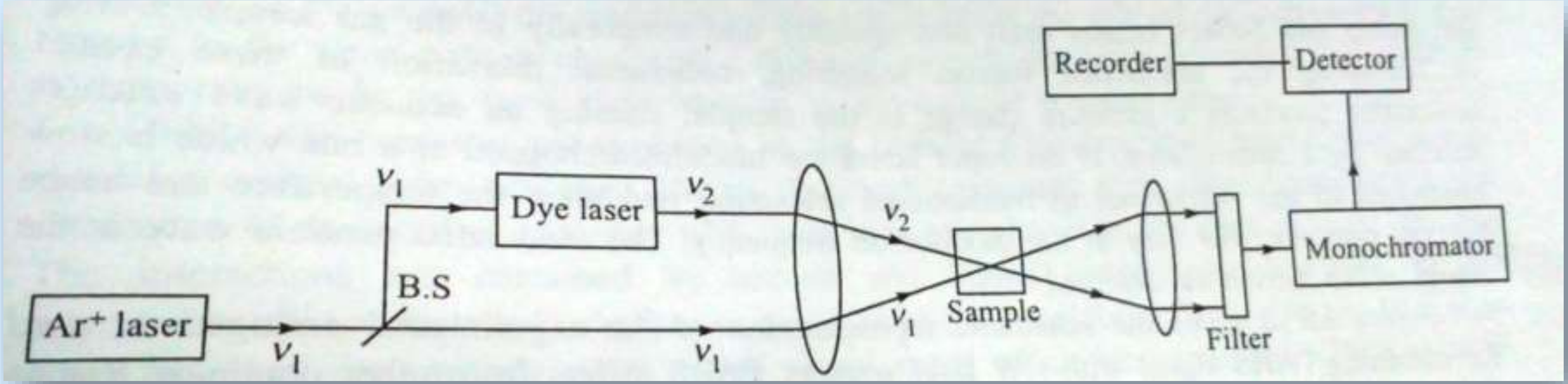
Anti-Stokes

If ωp is fixed and ωs is varied so $\omega p - \omega s = \omega m$, Raman active, then

$\omega as = \omega p + \omega m$, an anti-stokes Raman frequency.

Experimental setup of CARS

- 1[st] developed by Maker & Terhune (1963)



- Conversion efficiency to $\omega as = \omega p + \omega m$ is greater than the conversion efficiency in normal Raman scattering

- No fluorescence effect & thermal radiation.

Observations.......

- Coherent & non linear beam
- Highly intense
- Highly directional
- Beam is blue shifted

Advantages of CARS

- 4 or 5 orders of magnitude more intense than normal signal.
- Easily detected.
- No fluorescence and thermal emission problem.
- CARS microscopy is mild, non disruptive imaging technique for biological application.
- Increase in scattering intensity.
- Well suited for temperature measurements.
- Used for low concentration determination (µg).
- High conversion efficiency.

Disadvantage of CARS

- Complicated setup with difficult adjustments.
- At high pressure band shape get distorted.
- Samples may get damaged by high power laser.
- Fluctuations in output signal due to frequency instability of laser.

Comparison

Normal Raman scattering	CARS
Can be done using single CW laser source	Require at least two pulsed laser source
Detected on the red side of incoming radiation	Detected on the blue side
Less conversion efficiency	High conversion efficiency

APPLICATIONS...

- Important technique for studying molecular structure
- Used for studying biological samples
- For studying rotational spectra of gases
- For temperature measurements

Applications…

Plant cell imaging

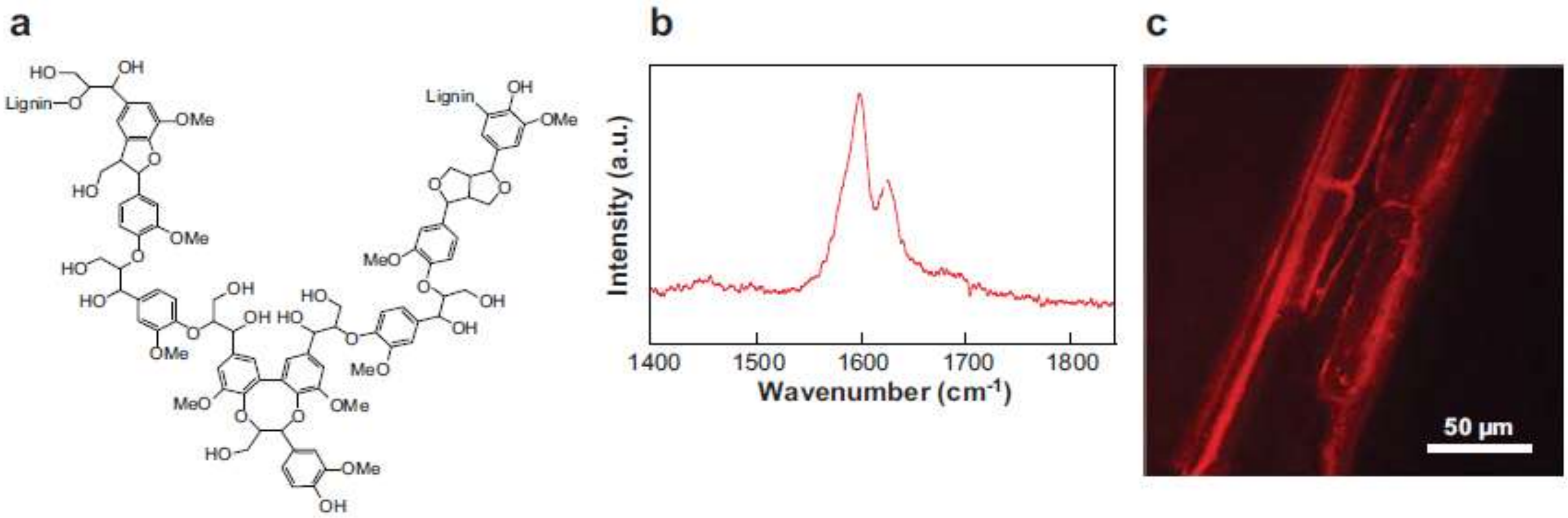


Figure 7

(*a*) Chemical structure of the lignin polymer. (*b*) Raman spectrum of lignin, with prominent bands near 1600 cm^{-1} arising from the aryl ring stretching vibrations. (*c*) Coherent anti-Stokes Raman scattering microscope image at 1600 cm^{-1} showing the distribution of lignin in the cell walls surrounding the plant cells in corn stover.

Applications

Biomedical Imaging

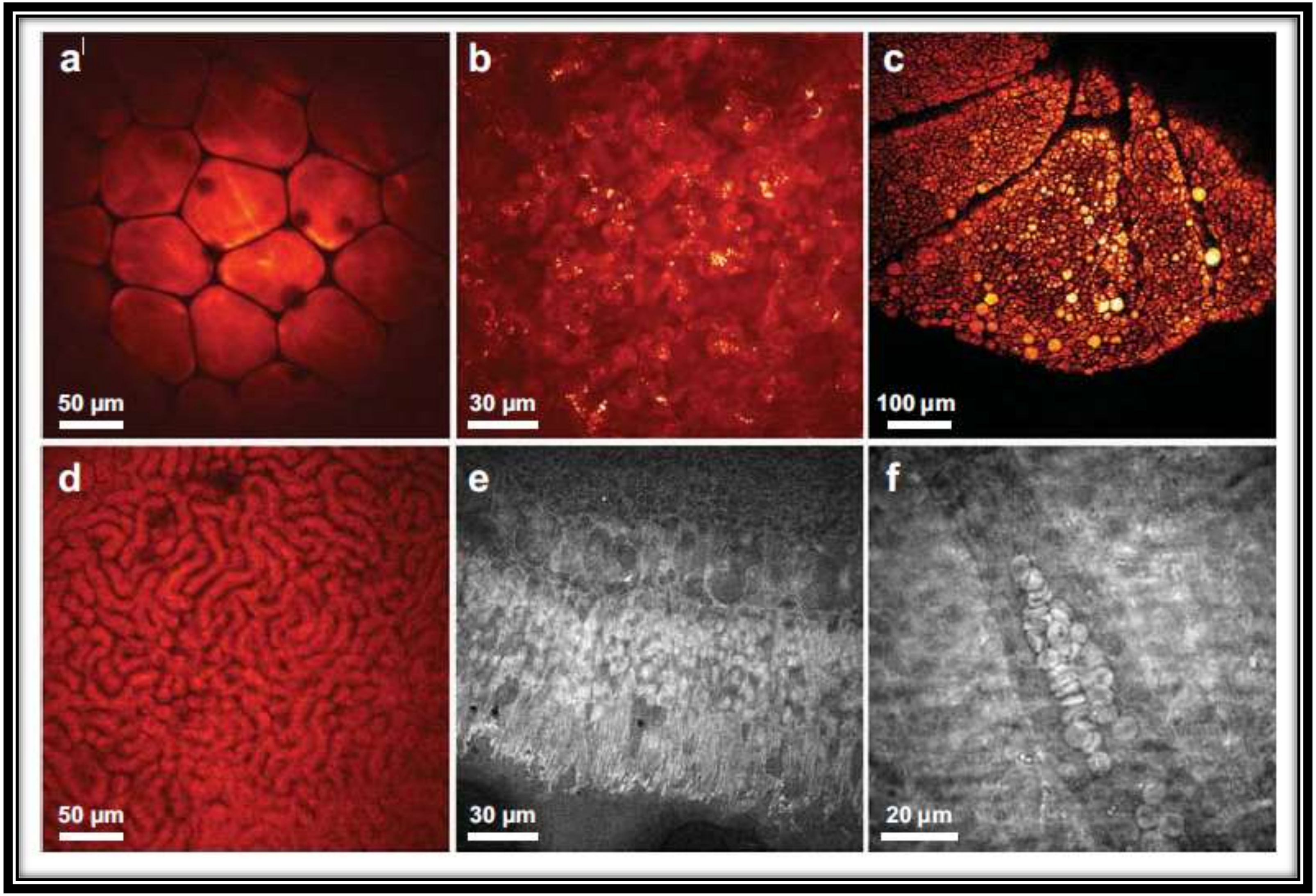
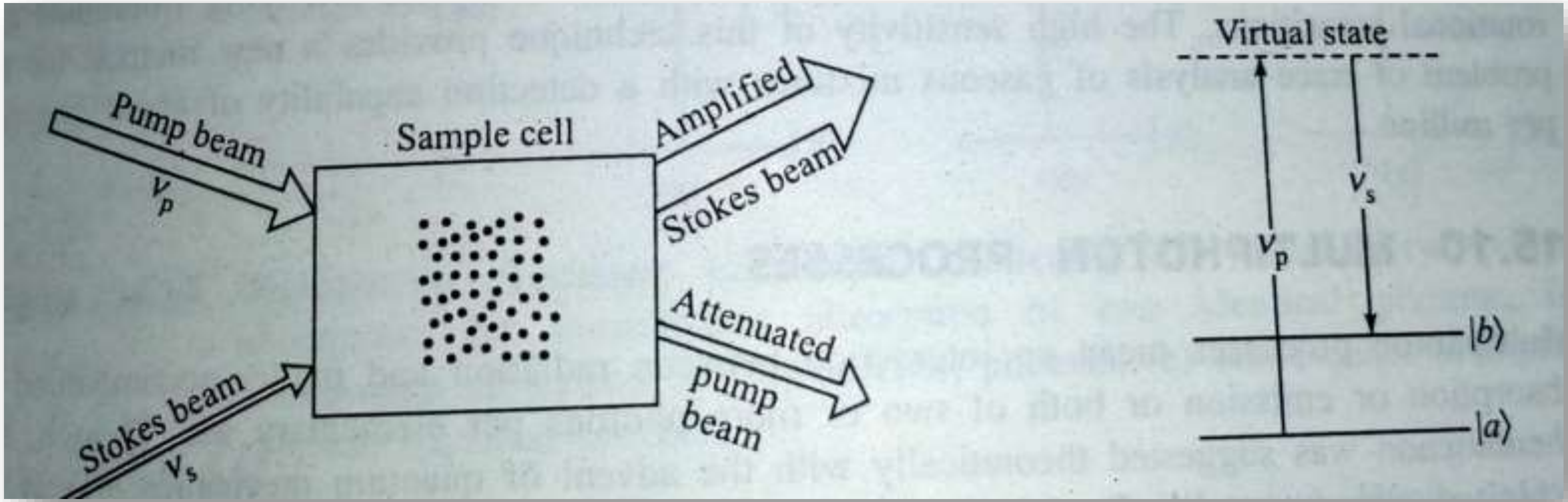


Photo acoustic Raman scattering (PARS)

- Associated with 3rd order nonlinear polarizability

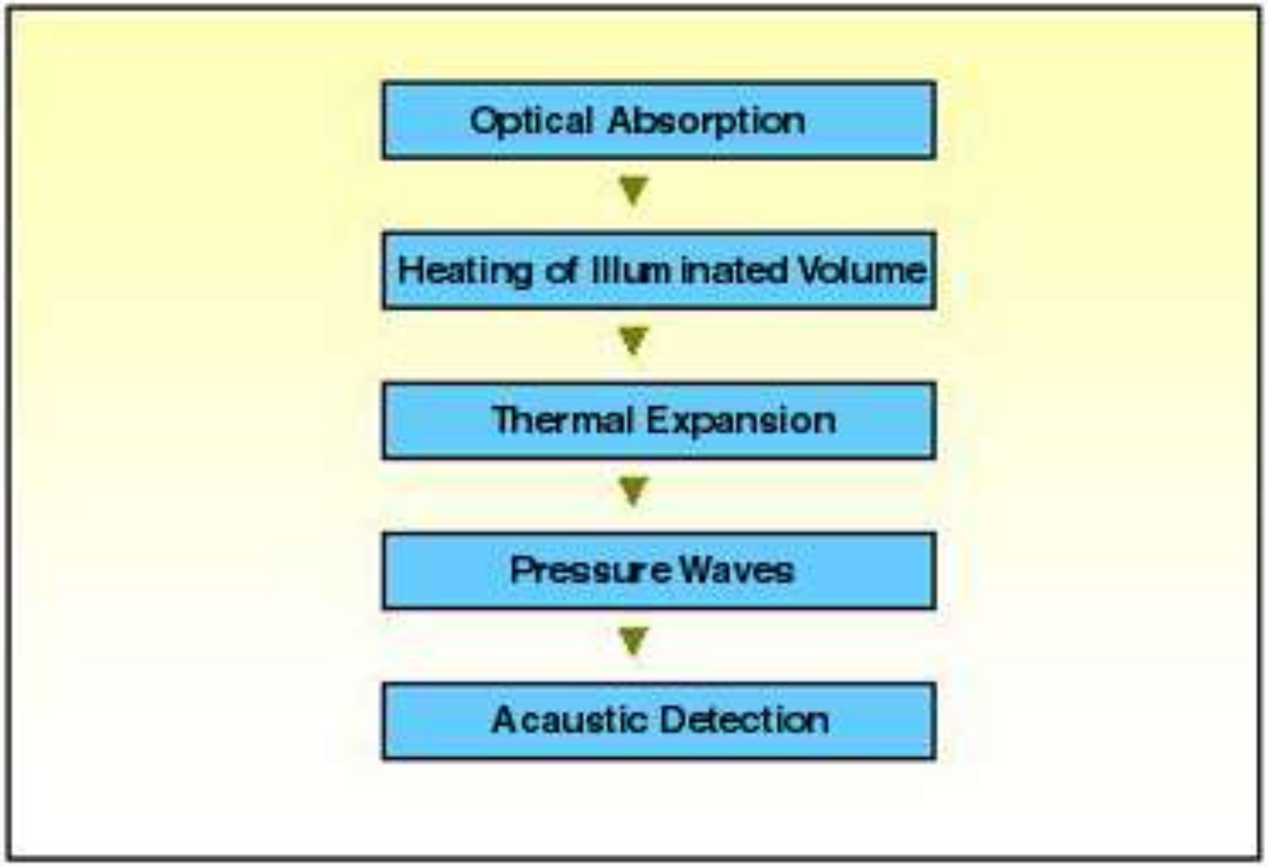
Also requires ωp and ωs such that ωp – ωs = ωm, Raman active

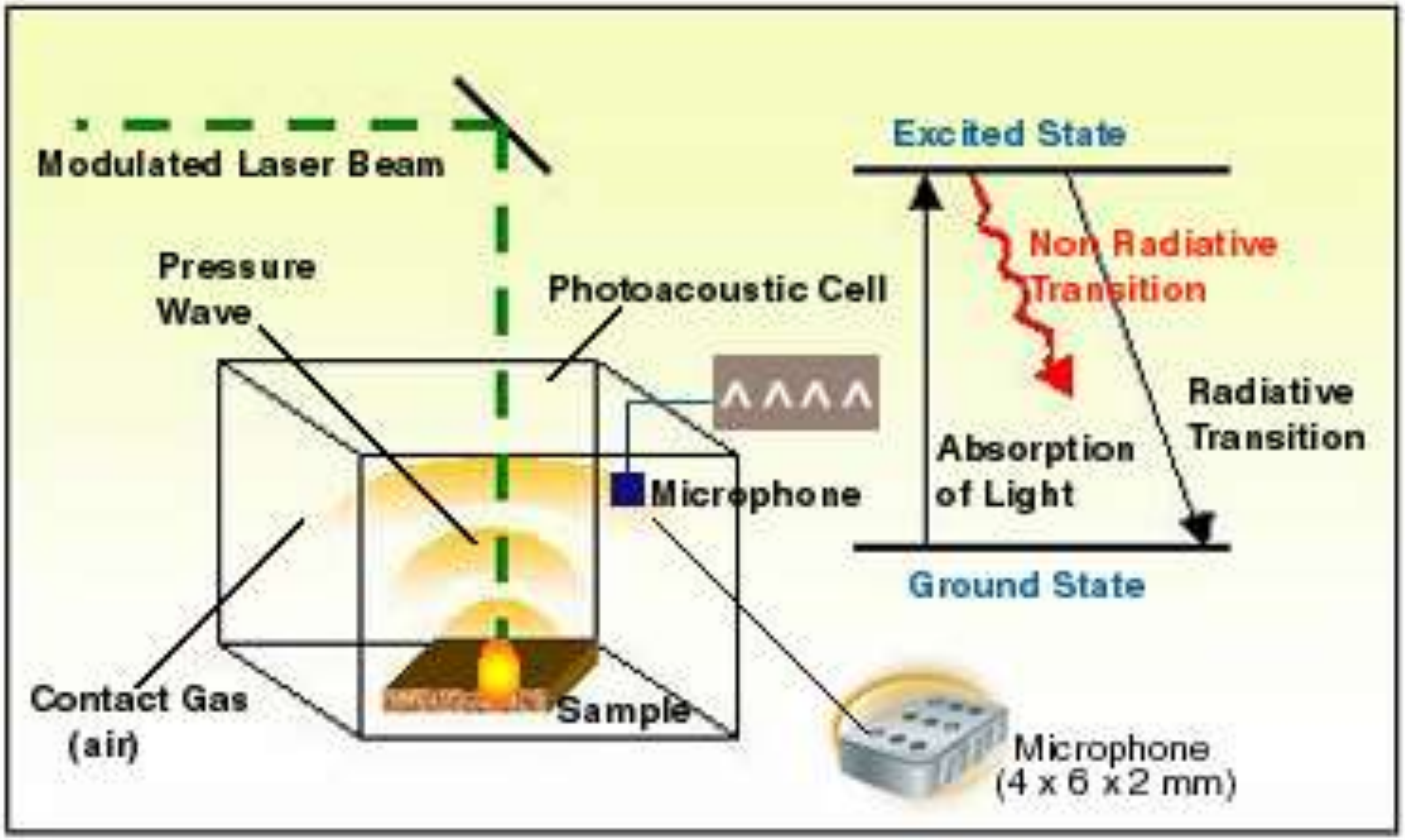


PARS process

Photo acoustic effect

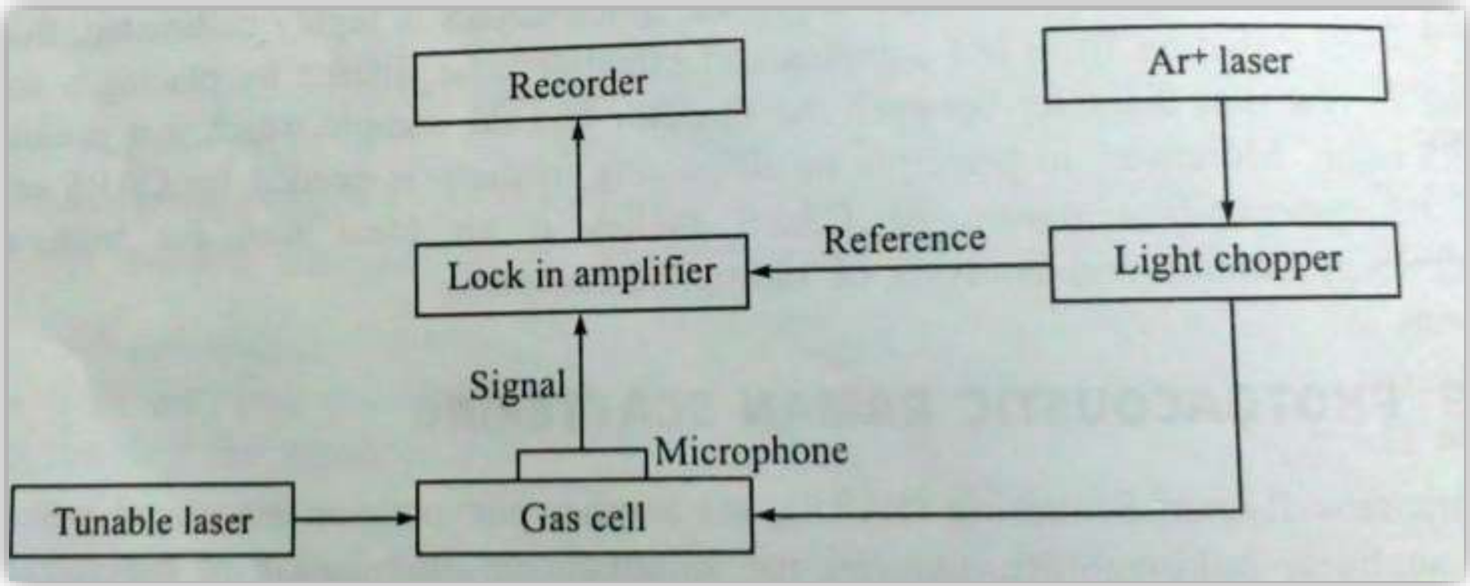
- Observed & investigated by Alexander Graham Bell & others in 1980s





Basic principle: photo acoustic effect

Energy absorbed by the sample produces sound waves which are detected by sensitive microphone.



Schematic diagram of the experiment

Chopper – modulates the radiation

Lock in amplifier – reduce background noise

Conventional Spectroscopy

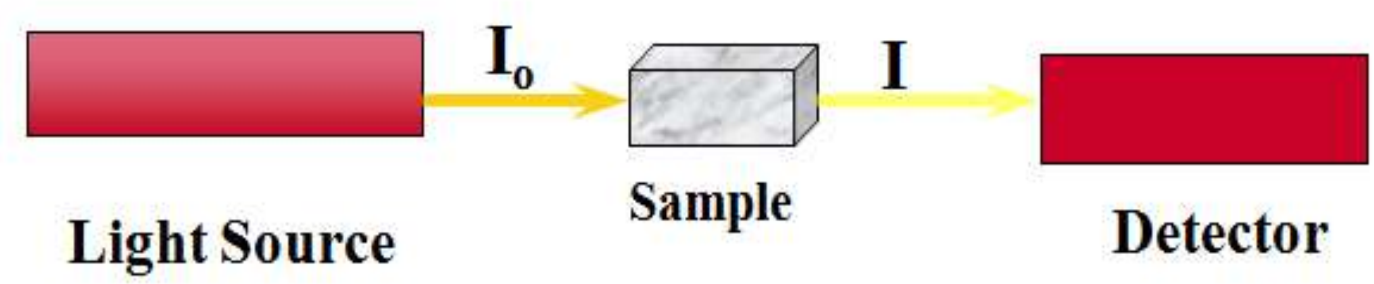
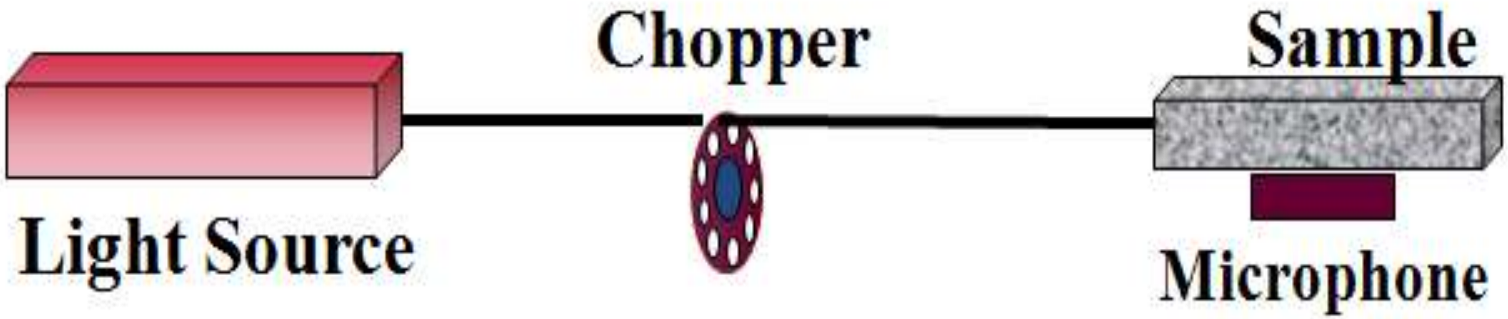


Photo acoustic spectroscopy



Advantages

- Provide accurate way of determining spectra of opaque samples
- Highly sensitive
- Only detect the radiation that is observed

Disadvantage

- Can identify only one wavelength at a time

Applications…

- New method in trace analysis of gaseous samples
- Most significant in biological & biochemical systems
- Used for identification of compounds
- Identifies inorganic & organic solids and commercial polymers


Thank you