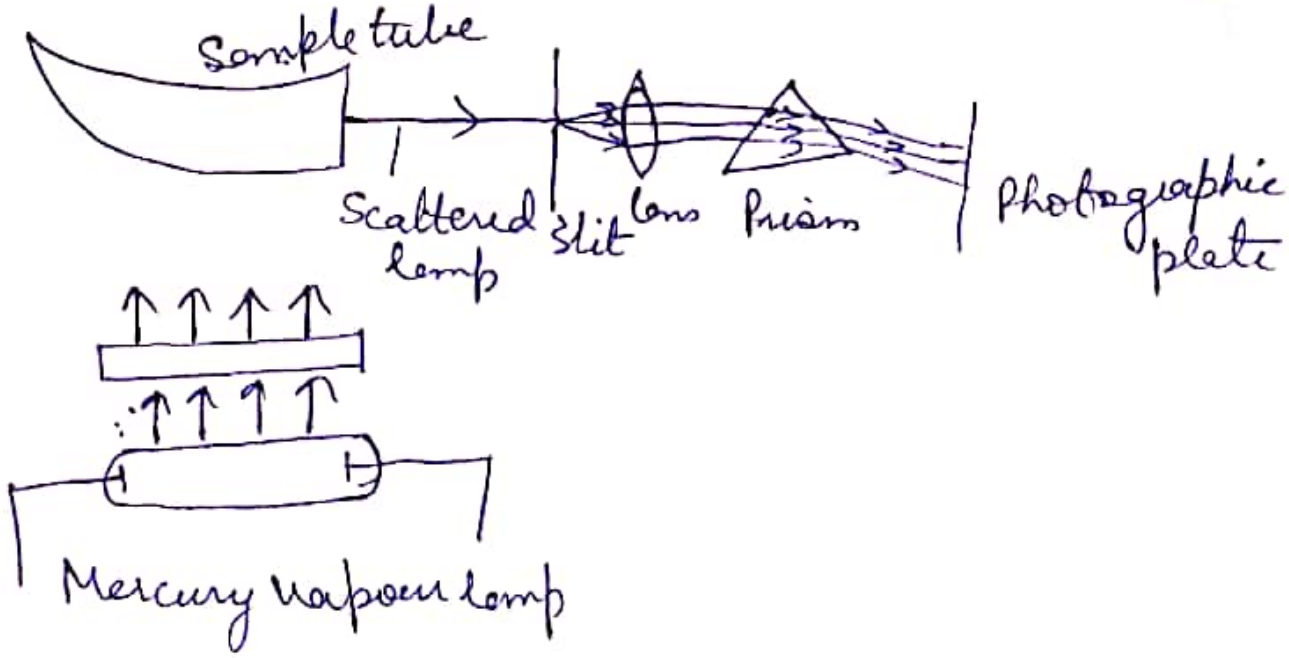
Type of molecules that give rotation vibration Raman Spectra

To be a molecule be raman active, the polarization of the molecule must change as the molecule vibrates. Molecule homonuclear as heteromolecule when vibrates the control of the nuclei over elections varies and there is change in polarization.

- Both types of molecules show rotation - vibration spectra, they are vibrational Raman active.
- Homonuclear molecule donot give pure vibrational or rotational spectra because they donot possess a permanent dipole moment.

Advantage of Raman over IR spectroscopy:

- Raman ~~acts~~ spectra is for liquid, gases & solid & Infra red spectra is for gases, for liquid and solid it is diffused.
- Raman frequency is independent of the frequency of incident radiation.
- Raman spectra is for O_2 N_2 Cl_2 also although they donot have permanent dipole moment. But not for IR spectroscopy.



Classical theory of Raman effect:

- The electric moment of the oscillator at any time is given by $aE_0 \cos 2\pi \nu_{ex} t \cos(2\pi\nu t + \delta)$

$$= \frac{1}{2} a E_0 [\cos(2\pi(\nu_{ex} + \nu)t + \delta)] + \cos[2\pi(\nu_{ex} - \nu)t - \delta]]$$

The emitted light consist of two frequencies $\nu_{ex} + \nu$ and $\nu_{ex} - \nu$

ν_{ex} is frequency of parent line

$\nu_{ex} + \nu$ for anti stoke's line

$\nu_{ex} - \nu$ for stoke's line.

Quantum theory of Raman Effect:

- A beam of monochromatic radiation of frequency ν_0 has its energy distributed in quanta each of energy $h\nu_0$ what happens.

* The molecule might deviate the photon without absorbing its energy which result in modified line
* The molecule might absorb part of the incident photon, give rise to Stokes line, frequency less than that of incident radiation.
* Molecule are in excited state impart energy to incident photon this produce anti Stokes line whose frequency is greater than incident radiation

Law of mutual Exclusion: If a molecule has a centre of symmetry then Raman active vibrations are infrared inactive and vice versa If there is no centre of symmetry then some vibrations may both be Raman and IR active

Coherent Anti Stokes Raman Spectroscopy

CARS:

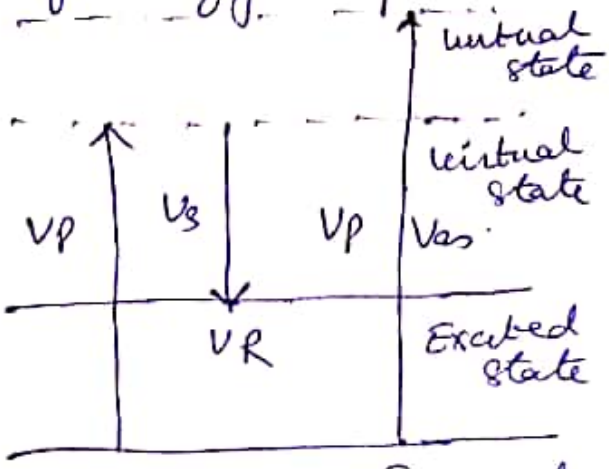
- In this a Raman transition is coherently driven by two laser fields called laser and stokes and the third laser field - Probe generating an anti stokes signal field.

The coherent nature of technique allows efficient coupling of the laser field to a particular vibrational mode. and the signal increases by many orders of magnitude.

- This technique is useful for biological application as there is no net transfer of energy to specimen.

-CARS theory is a high resolution, chemically specific non linear imaging technique

The beam of frequencies V_p & V_s are focused on sample.



The stoke pulse & pump interact with sample through third order to generate blue shift. anti stokes signal $V_{as} = 2V_p - V_s$.

The radiation V_{as} is anti stokes Raman radiation relative to V_p and is very intense and is also coherent as is CARS.

Two laser pulse (pump & stoke pulses) populate a vibrational level of a molecule and third pulse known as probe pulse, scatters off it to generate the CARS signal