

AB_3 type molecules \rightarrow require more discussion.

In general, we expect $3N - 6 = 6$ fundamental vibrations for these four-atom molecules.

If the molecular shape has some symmetry this number will be reduced by degeneracy.

In particular, for the symmetric planar and symmetric pyramidal shapes, one stretching and one angle deformation mode are each doubly degenerate \rightarrow only four different fundamental frequencies should be observed.

Both molecular shapes are in fact symmetric tops with the main (threefold) axis A passing through atom A perpendicular to the B_3 plane. With respect to this axis the vibrations can be described as \parallel or \perp .

The symmetric modes of vibration are parallel and Raman polarized while the asymmetric are perpendicular and depolarized.

All the vibrations of the pyramidal molecule change both the dipole moment and the polarizability, hence all are both infrared and Raman active.

The symmetric stretching mode (ν_1) of the planar molecule, leaves the dipole moment unchanged (it remains zero) and so is infrared inactive. Symmetric bending mode does not change the polarizability \rightarrow so ν_2 is Raman active for planar AB_3 .

The overall pattern of the spectra;

- Planar AB_3 :
- 1 vibrates Raman active only (ν_1)
 - 1 Infra-red active only (ν_2)
 - 2 vibrates both Raman and infra-red active (ν_3, ν_4)

Pyramidal AB_3 : All four vibrates both Raman and infra-red active

Non-symmetric AB_3 : possibly more than four different fundamental frequencies.

We consider spectra of NO_3^- and ClO_3^- . The Nitrate ion fits the expected pattern for a planar system, while the chlorate ion is pyramidal.

Infra-red and Raman spectra of NO_3^- and ClO_3^-

Nitrate ion (NO_3^-)			Chlorate ion (ClO_3^-)		
Raman (cm^{-1})	Infra-red (cm^{-1})	Assignment	Raman (cm^{-1})	Infra-red (cm^{-1})	Assignment
690	680 \perp	ν_4	450 (depol.)	424 \perp	ν_4
—	830 \parallel	ν_2	610 (pol.)	624 \parallel	ν_2
1049	—	ν_1	940 (depol.)	930 \perp	ν_3
1355	1350 \perp	ν_3	982 (pol.)	994 \parallel	ν_1

Finally ClF_3 have no less than six strong infra-red absorptions some of which also occur in Raman. The molecule is neither symmetric planar nor pyramidal. A complete analysis not possible from the Raman and infra-red spectra alone. Use of microwave spectroscopy is required.

Techniques and Instrumentation

Raman Spectrometer → Raman spectroscopy →

emission spectroscopy and the bulk of the instrumentation is simply a typical visible-region spectrometer.

The distinguishing characteristic of Raman work → is the exciting source.

The advent of accessible and relatively inexpensive laser sources → useful in Raman techniques.

Exciters → Traditional mercury discharge lamp as an exciting source.

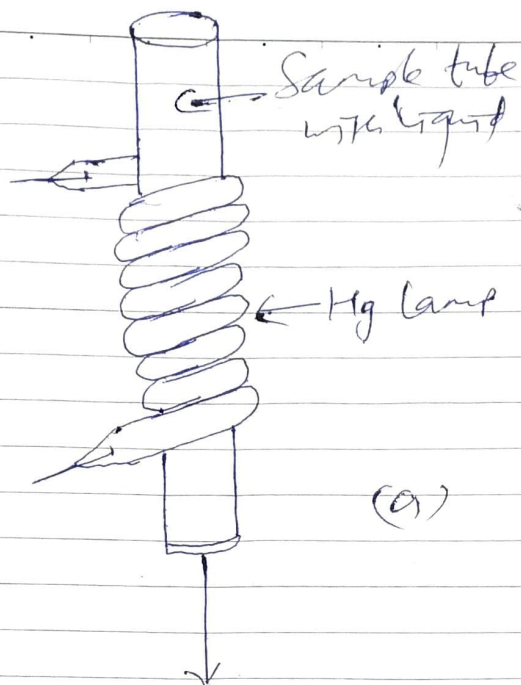
Required 10-20 ml of sample and often very time consuming

Now Raman spectra → of virtually all samples can be run on a completely rolling basis using one ml or less sample and taking a few minutes only.

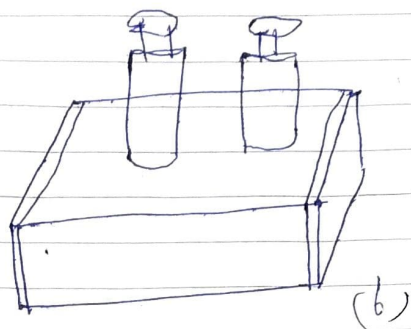
Laser → almost ideal as a Raman source; it gives a very narrow, highly monochromatic beam of radiation → may be focused very finely into a small sample and packs a relatively large power. from several milliwatts to a few watts.

We compare two excitation techniques.

(a) mercury lamp in the form of a spiral around sample



(a)



(b)

Sample container for excitation by a laser

excitation of a sample with a spiral mercury lamp

Scattered radiation to spectrometer

(a) type of excitation pumps a good deal of energy into the sample, but it spreads over the many emission lines of the mercury vapour - notably 435.8 and 253.6nm. It suffers from three main disadvantages.

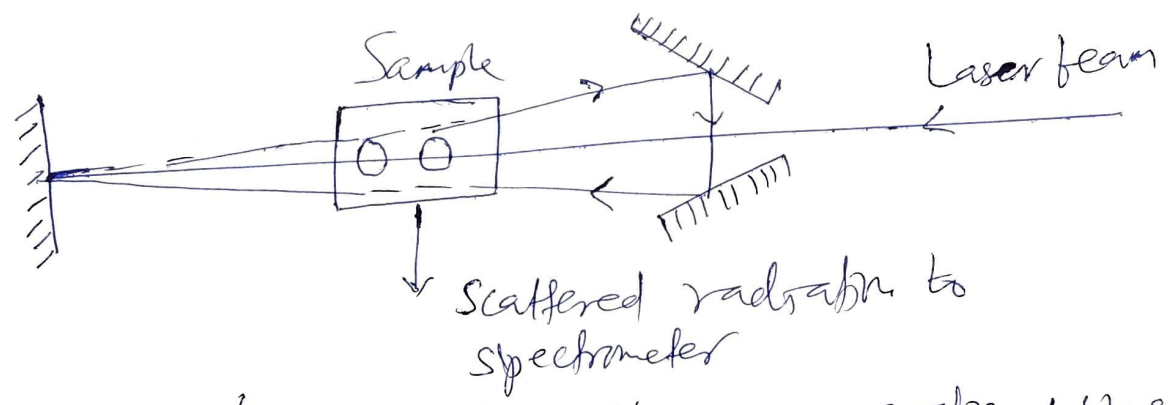
(1) The extended source allows a good deal of the exciting radiation to be scattered directly into the spectrometer where it masks all the Raman lines less than some 100 cm⁻¹ from the exciting frequency.

(2) The sample tube needs to be about 10-20 cm long and 1-2 cm in diameter so that large quantities of sample are required.

(3) The relatively high frequency of Hg radiation

often causes the sample to fluoresce and the resulting fluorescence spectrum swamps the very weak Raman spectrum.

Mercury lamp is often still preferred for gaseous samples, where a large sample tube can have a carefully tailored mercury lamp built round it, and thus collect the exciting radiation with maximum efficiency.



(c) Plan view of multi-pass operation using a Laser beam.

Laser beam is directed through a sample and by means of mirrors, caused to undergo multiple passes, (three are shown) but by careful alignment of mirrors up to 10 passes may be achieved, thus enhancing the Raman signal.

The sample container is a 'box' of quartz about 2 cm long and 0.5 cm² in cross-section, provided with filling ports, its capacity is thus 1 ml.

The quantity of sample required can be reduced considerably, by using a km capillary tube.