

Near I.R. - F.T. Raman Spectroscopy

(28)

Near-I.R. excited Raman spectroscopy developed in 1986. FT Raman is so successful compared to conventional Raman spectroscopy \rightarrow for most ~~spectra~~ (Visible laser excitation)

Samples, spectra are free of fluorescence, so applicable to many samples that could not be examined by conventional Raman spectroscopy and spectra can be acquired rapidly.

Both conventional and FT Raman spectroscopies are based on the same principle. FT Raman differs from conventional Raman in two important ways:

- (1) The laser wavelength used to excite samples lies in the near I.R.
- (2) Instead of using dispersive gratings a Michelson interferometer is used to analyse scattered light.

An FT Raman instrument consists of the following components

- (1) a laser for sample excitation (often a 1064 nm Nd:YAG laser)
- (2) one or more filters to effectively block the Rayleigh scattering
- (3) An efficient interferometer
- (4) a highly sensitive detector
- (5) A capability to do a fast Fourier transform on an acquired interferogram

Laser chosen \rightarrow usually a near-IR laser to avoid any sample fluorescence that may arise. An FT instrument is built around an interferometer. Such an instrument has several advantages.

* Simultaneous detection of all the wavelengths of light \rightarrow FT ~~spectroscopy~~ instrument records a spectrum in a shorter time than a grating instrument. \rightarrow Felgett advantage

* High throughput \rightarrow Jacquinot advantage

Use of longer wavelength excitation laser ($\approx 1 \mu\text{m}$) \rightarrow lesser energy supplied, so the virtual state is lower and less likely to overlap an upper electronic state. This greatly reduces fluorescence interferences.

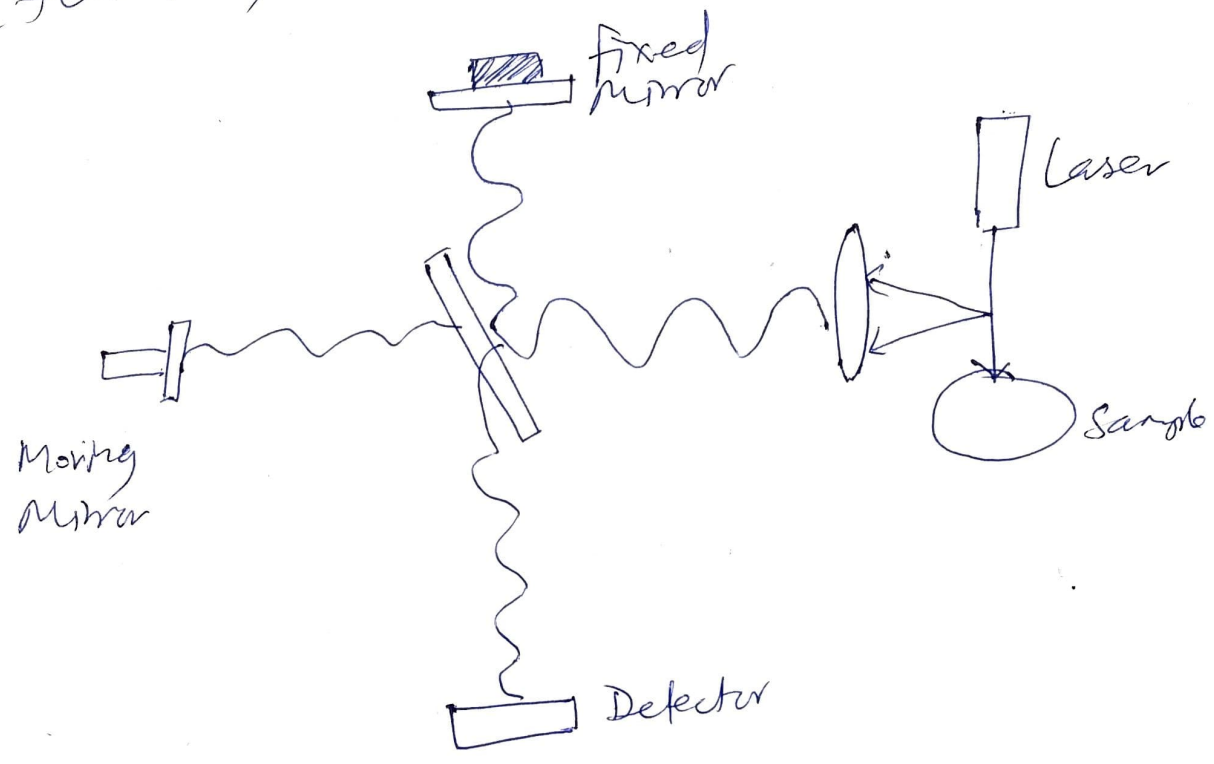
In CuAs or liquid nitrogen-cooled Ge detectors are typically used for ~~RT~~ Raman spectroscopy.

FT-Raman spectroscopy uses an interferometer to produce an interferogram which "encodes" the unique frequencies of the Raman scattering into a single signal. This signal is measured very quickly (usually in one second) making signal averaging fast and ~~and~~ accurate.

The interferometer employs a beamsplitter optimized for near-infrared radiation, which divides the incoming Raman scatter into two optical beams, one transmitted and one reflected.

Reflected beam travels to and reflects off a flat mirror that is fixed in place.

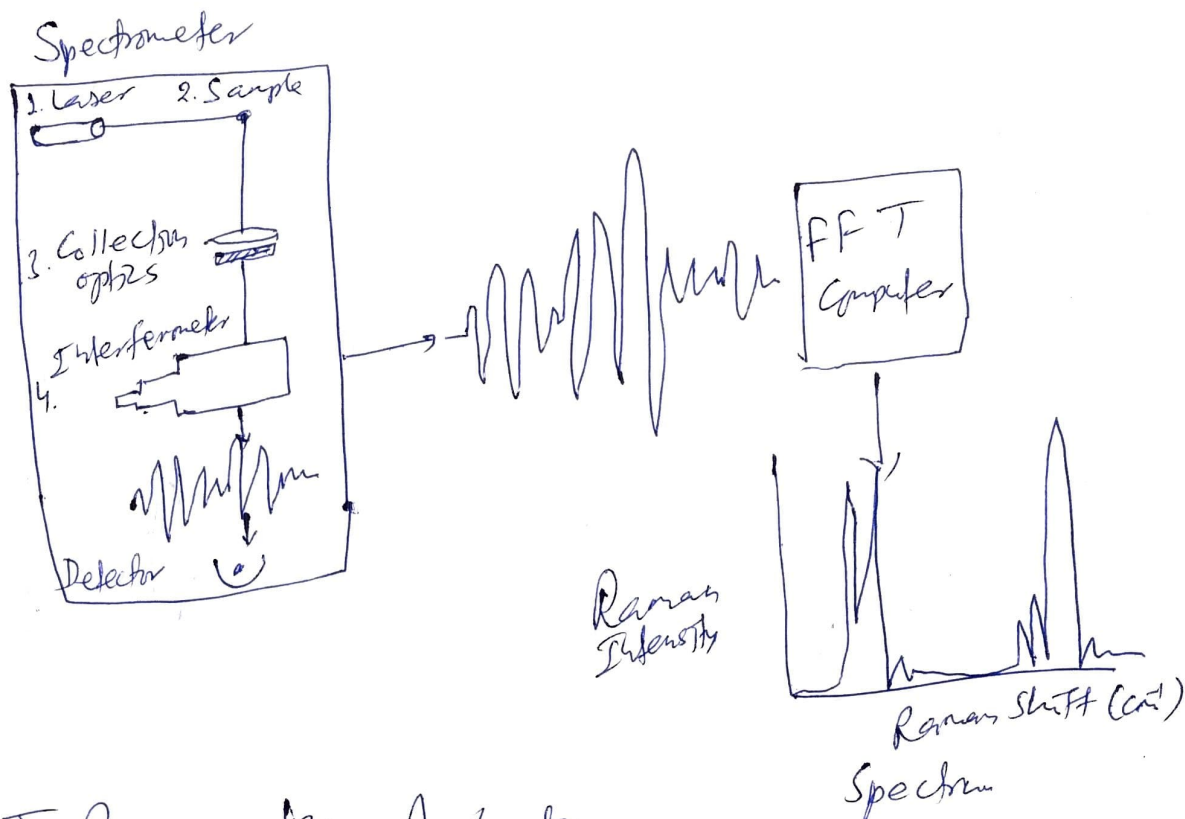
The transmitted beam travels to and reflects off a flat mirror attached to a mechanism that allows the mirror to move a short distance (few nm) away from the beam splitter



The two beams recombine at the beam splitter, they constructively and destructively interfere with each other. The moving mirror has a constant frequency and fixed motion, so the interference is modulated. The resulting interference pattern has the unique property that every data point (a function of the moving mirror position) has information about every frequency of the Raman scatter

(25)

Vibrational spectra are typically presented as frequency spectra (plot of intensity at each individual frequency). The individual frequencies are decoded using the well known mathematical technique called Fourier transformation. The computer performs this transformation and the desired spectral information is processed.



FT-Raman Key Applications

FT-Raman best choice in situations where sample fluoresce or are likely to contain minor impurities that may fluoresce. Significant success has been realized in the pharmaceutical industry for unknown identification, incoming raw material characterization, final product quality and quantitative analysis using FT-Raman. Also useful for forensic analyses, pulp and paper, textiles, petrochemicals etc.

Pr. The exciting line in an experiment is 5460 \AA and the Stokes line is at 5520 \AA . Find the wavelength of the anti-Stokes line.

Soln Raman shift $\Delta\nu = \nu_i - \nu_s$

for Stokes line $\nu_s < \nu_i$

$$\nu_i = \frac{1}{5460 \text{ \AA}} = \frac{1}{5460 \times 10^8} = 18315 \text{ cm}^{-1}$$

$$\nu_s = \frac{1}{5520 \text{ \AA}} = \frac{1}{5520 \times 10^8} = 18116 \text{ cm}^{-1}$$

$$\Delta\nu = \nu_i - \nu_s = 199 \text{ cm}^{-1}$$

(as $\nu_s < \nu_i$ Stokes lines)

Stokes and anti-stokes lines have the same number displacement w.r.t the exciting line ν_i and for anti-stokes lines $\nu_s < \nu_i$, we write

$$\begin{aligned} (\nu_s) \text{ anti-stokes line} &= \nu_i + \Delta\nu \\ &= 18315 + 199 \\ &= 18514 \text{ cm}^{-1} \end{aligned}$$

So wavelength $\lambda = \frac{1}{18514 \text{ cm}^{-1}} = 5401 \text{ \AA}$

Pr. In the Rotational Raman Spectra of HCl the displacements from the exciting line are presented by

$$\Delta\nu = \pm (62.4 + 41.6J) \text{ cm}^{-1}$$

Calculate the moment of inertia of HCl molecule

Soln

$$\Delta\nu = 2B(2J+1)$$

$$2B(2J+1) = (62.4 + 41.6J)$$

$$\Rightarrow B = 10.4 \text{ cm}^{-1}$$

$$B = \frac{h}{8\pi^2 I C}$$

$$I = \frac{h}{8\pi^2 B C}$$

$$I = 2.7 \times 10^{-40} \text{ gm-cm}^2$$