

Raman Spectroscopy

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A New Type of Secondary Radiation

The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments, a beam of sunlight was converged successively by a telescope objective of 18 cm. aperture and 230 cm. focal length, and by a second lens of 5 cm. focal length. At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation *in vacuo*) or its dust-free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with the ordinary scattering, and secondly by its polarisation, which is in many cases quite strong and comparable with the polarisation of the ordinary scattering. The

Quantum mechanical model of a diatomic molecule

For a molecule approximated by two balls connected with a spring, added with a potential that accounts for:

- repulsion between electronic clouds when the atomic nuclei approach
- variable behaviour of the bond force when the atoms move apart from one another

the energy spectrum is:

- discrete
- when written as an increasing function of vibrational quantum number ν , the difference between two adjacent energy levels decreases with ν
- allows occurrence of transitions with $\Delta\nu \geq 2$

Further if bond rupturing for over-displacement is accounted, the energy spectrum would look like figure B in the following:

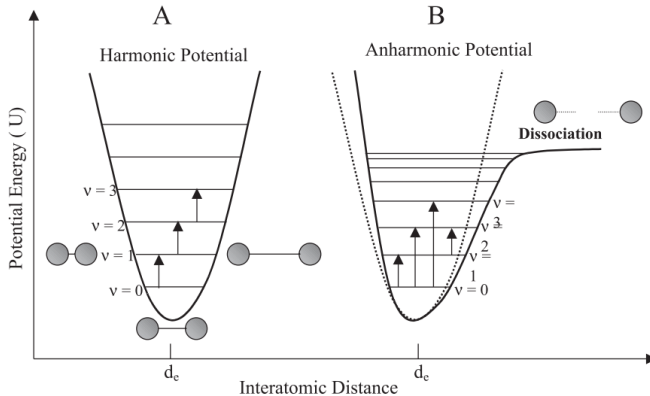


Figure: Schematic representation of the harmonic (A) and anharmonic (B) models for the potential energy of a diatomic molecule. d_e = equilibrium distance (U = minimum).

Possible transitions for different wavenumbers of incident light

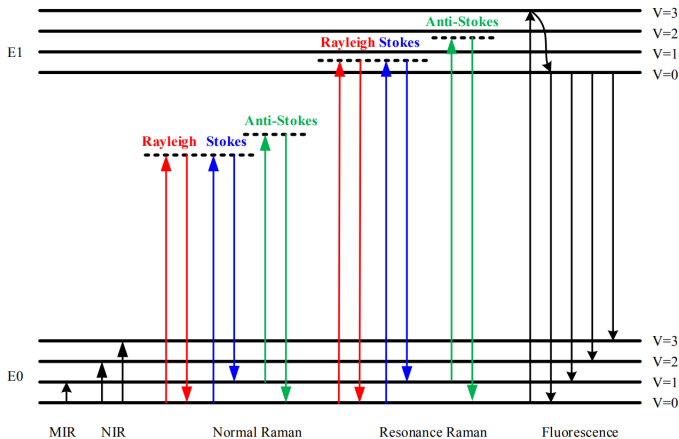


Figure: Energy level diagram related to IR absorption, Raman scattering and fluorescence emission

Raman Scattering

- As seen in previous slide, a given molecule at one of its ground vibrational states, when irradiated with a monochromatic light of wavenumber within a certain range (dependent on the molecule), say $\bar{\nu}_s$, it gets excited to a virtual state and within $10^{-14}s$, it returns to one of the ground vibrational state emitting a photon of the same energy it lost. Light due to such photons is called scattered light. This phenomenon is called Scattering of light.
- The scattered light is predominantly of the same wavenumber $\bar{\nu}_s$, and for some set of $\bar{\nu}_0$ s, there is a very small intensity of light with wavenumber $\bar{\nu}_s + \bar{\nu}_0$ and of even less intensity with wavenumber $\bar{\nu}_s - \bar{\nu}_0$.

Inference/Reason?

- Defining raman shift for a scattered light of wavenumber $\bar{\nu}_0$ as $\bar{\nu}_s - \bar{\nu}_0$ where $\bar{\nu}_s$ is the wavenumber of source light, let's see an example of raman spectrum for a molecule.

Raman Spectra of CCl₄

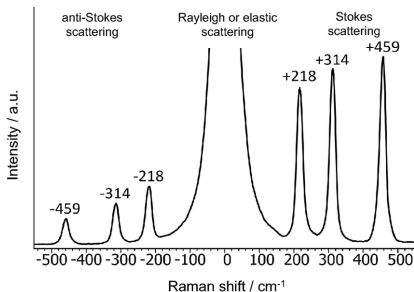


Figure: Both anti-Stokes and Stokes lines (532nm source)

Where peaks corresponding to:

- Positive Raman-Shifts: Stokes lines
- Negative Raman-Shifts: Anti-Stokes lines
- 0 Raman-Shift: Rayleigh lines

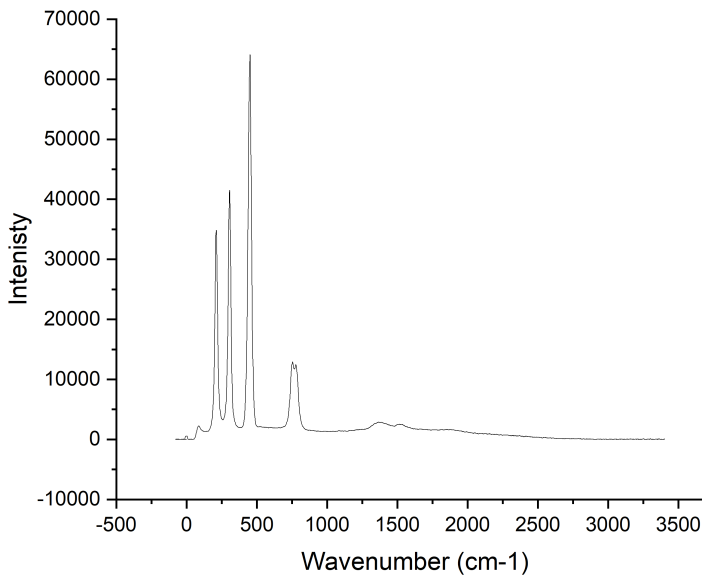


Figure: Stokes lines for CCl₄ as obtained by our group in lab

Classical theory

Raman scattering originates from the interaction between incident electromagnetic radiation and molecular vibration. According to classical theory, when a molecule is placed in an electric field $E = E_s \cos(2\pi\nu_s t)$, an electric dipole moment P is induced,

$$P = \alpha E \quad (1)$$

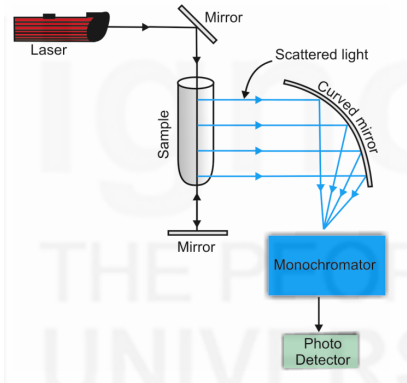
where α is the polarizability. Considering only lower order Raman scattering, then since molecular vibrations are composed of several normal modes, it can be written as,

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q_i} \right) Q_i + \dots \quad (2)$$

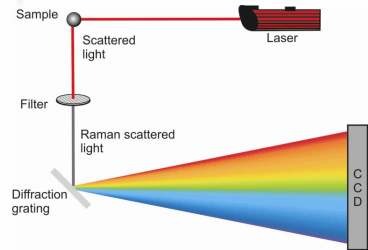
where Q is the normal coordinates of the various vibration modes and can be expressed as, $Q_i = Q_{i0} \cos(2\pi\nu_i t)$. Substituting (2) into the dipole moment P gives

$$P = \alpha_0 E_s \cos(2\pi\nu_s t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial Q_i} \right) Q_{i0} E_s [\cos(2\pi t(\nu_s + \nu_i)) + \cos(2\pi t(\nu_s - \nu_i))] \quad (3)$$

Instrument setup



(a) Dispersion Raman Spectrometer



(b) FT-Raman Spectrometer

Figure: Schematic representations of experimental setups

Instrumentation

There are two main issues in Raman spectroscopy that need to be addressed by suitable instrumentation:

- Inherent weakness of the Raman scattering signal as compared to the intense Rayleigh scattering
- Spectral resolution

Five basic components for a Raman spectrometer:

- An intense laser source
- Sample handling unit
- Monochromator or interferometer
- Detector
- Signal processing and output device

Instrumentation

Radiation Sources for Raman Spectroscopy

- Laser: high intensity, single wavelength and coherence
- The intensity of Raman scattering is dependent on the fourth power of the frequency of the exciting radiation

Sample Handling Devices

- Glass cuvettes can be used
- Water is not as much of a problem as in IR spectroscopy

Transducers or Detectors

- Initially eyes were the detectors followed by photographic plates
- Photomultiplier tubes, FT instruments
- Nowadays, including the ones in lab use charge-coupled devices (CCDs)
- Filtering devices like holographic grating or interference filters kept before the detector to filter Rayleigh component

Instrumentation

Fibre-optic probes

- Laser beam from source is focused onto a fine bundle of optical fibres called input fibres that transport it to the sample
- These input fibres are enclosed by a set of optical fibres called collection fibres
- Collection fibres collect the scattered radiation from the sample and send it back to the instrument
- Directed to a suitable monochromator

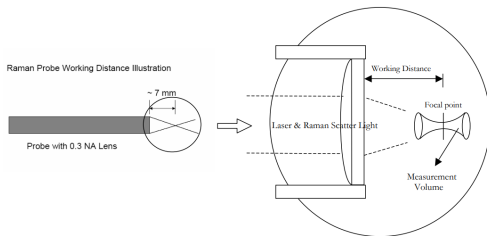


Figure: Optical path and measurement volume of Raman probe

Bibliography

- IGNOU Self-Learning material (Unit-6 Raman spectroscopy)
- Near Infrared Spectroscopy: fundamentals, practical aspects and analytical applications - Celio Pasquini
- Raman Spectroscopy for In-Line Water Quality Monitoring - Instrumentation and Potential - Zhiyun, Deen M.J., Selvaganapathy