

Raman Effect

Submitted by
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INTRODUCTION

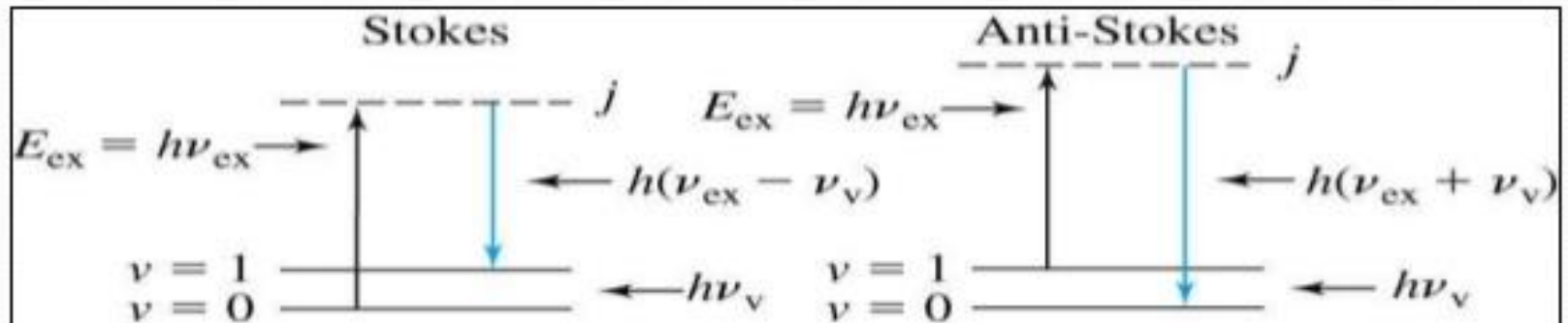
- Raman spectroscopy was discovered by C. V. Raman in 1928
- It is a spectroscopic technique used to observe vibration, rotational, and other low-frequency modes in a system.
- Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified.
- When the radiation passes through the transparent medium the species present scatter a fraction of the beam in all directions
- Raman scattering results from the same type of quantities vibration changed associated with IR spectra
- The difference in wavelength between the incident and scattered visible radiation corresponds to wavelength in the mid IR region

PRINCIPLE

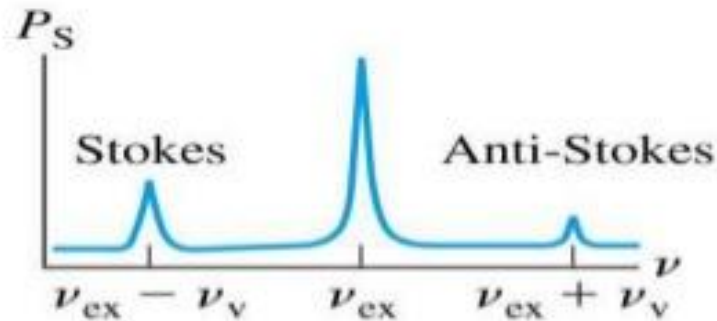
- When monochromatic radiation is incident upon a sample then this light will interact with the sample in some fashion. It may be reflected, absorbed or scattered in some manner. It is the scattering of the radiation that occurs which gives information about molecular structure
- Raman is based on scattering. The sample is irradiated with a coherent source, typically a laser. Most of the radiation is elastically scattered (called the Rayleigh scatter).
- A small portion is inelastically scattered (Raman scatter, composed of Stokes and anti-Stokes portions). This latter portion is what we are particularly interested in because it contains the information in which we are interested.

- The spectrum is measured with the laser line as a reference. Hence, the peaks are measured as the shift from the laser line.
- The peak positions are determined by the vibrational energies associated with the bonds in the molecule(s) of which the sample is composed. Because of this, the spectrum ends up looking very similar to an IR spectrum and is interpreted similarly.
- There is a footnote to this however, as the principle of mutual exclusion applies. That is, peaks that are emphasized in IR (polar bonds with high dipole moments) are de-emphasized somewhat in Raman.
- The bands that are emphasized in a Raman spectrum are those that are due to highly polarizable bonds such as those with π electrons.

- The emitted radiation is of three types:
 1. **Stokes** scattering
 2. **Anti-stokes** scattering
 3. **Rayleigh** scattering

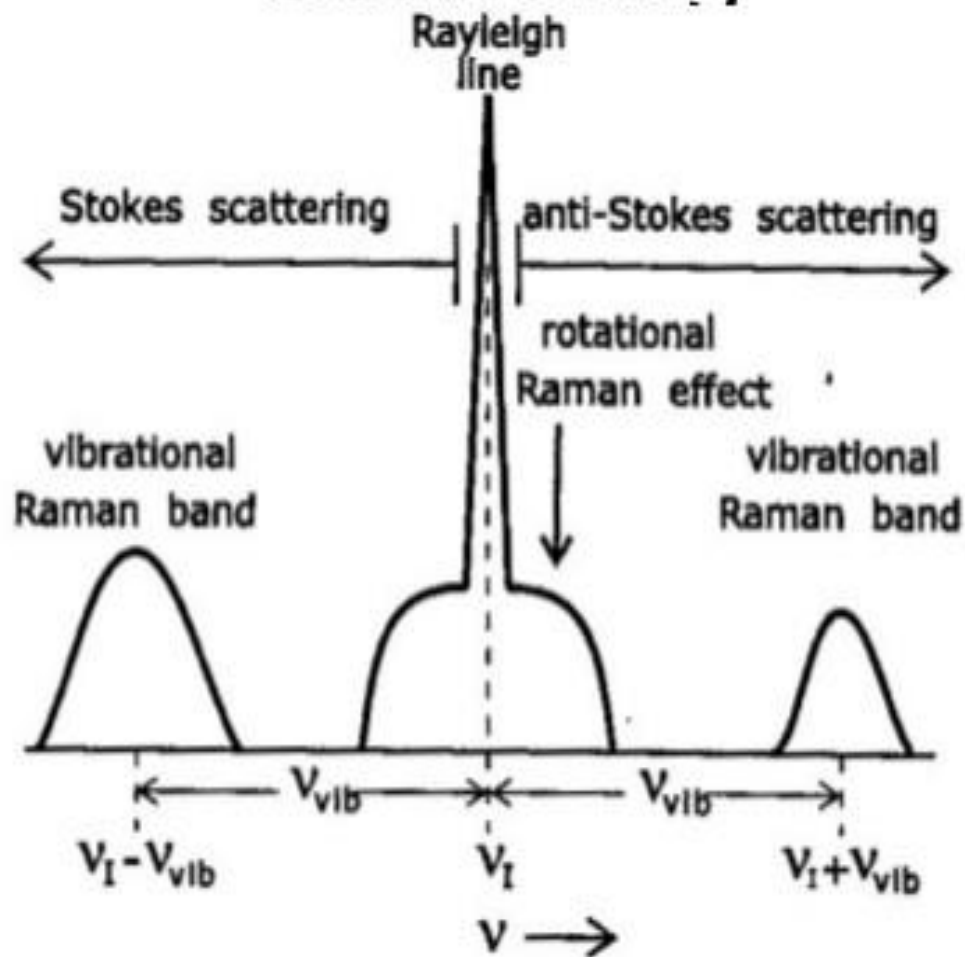


(a)



(b)

Stokes and Anti-Stokes Scattering



Why Raman spectroscopy?

- Information on rotational and **vibrational** levels
- Raman effect small but accessible by use of **lasers**
- **Complementary** information **to IR** spectroscopy
 - homonuclear diatomic molecules, low frequency range
- **In situ analysis** of organic and inorganic compounds
- Analysis of **aqueous solutions and solids** (powders)
- Using resonance and surface enhancement effects $\sim 10^{10}$
 - **Trace gas/single molecule analysis** - molecular structure

Classical Theory

- Spatial charge separation under influence of electric field E

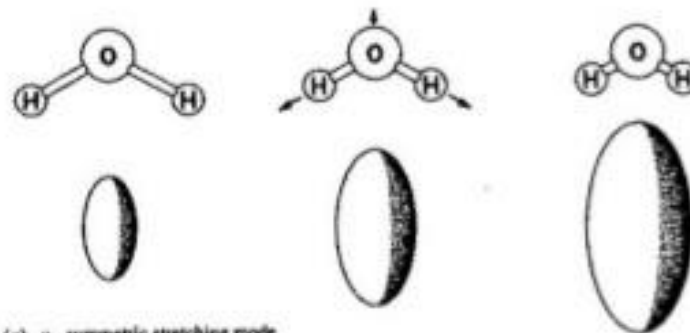
→ induced dipole moment μ :

$$\mu = \alpha E$$

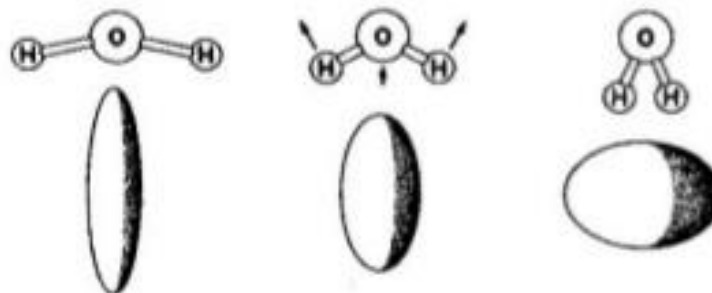
α : polarizability

→ *Example: polarizability changes during CO₂ vibrations*

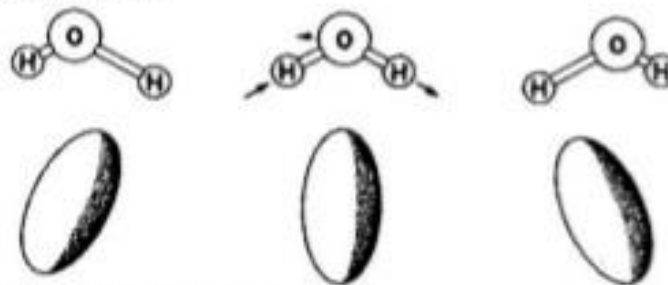
Raman Activity of H_2O Vibrations



(a) ν_1 , symmetric stretching mode



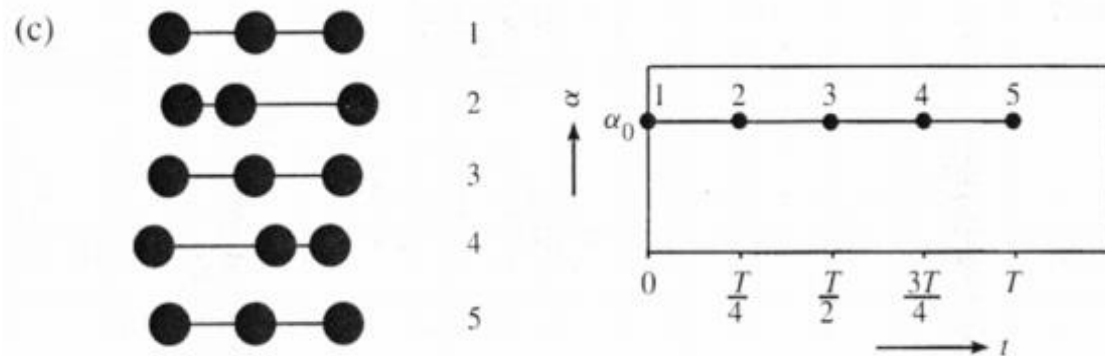
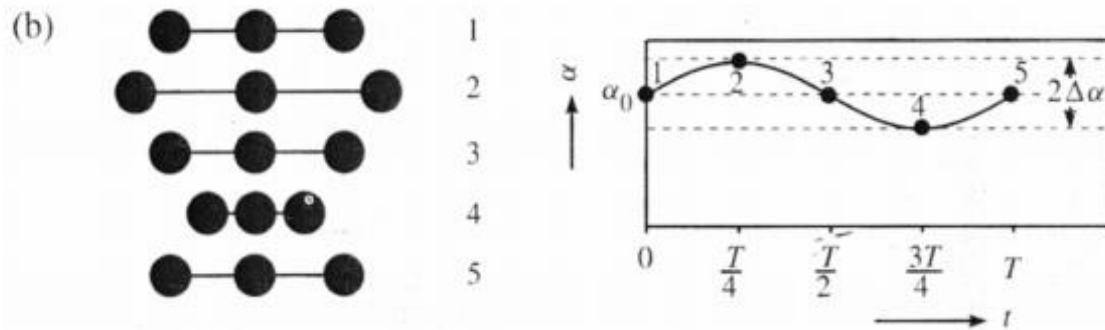
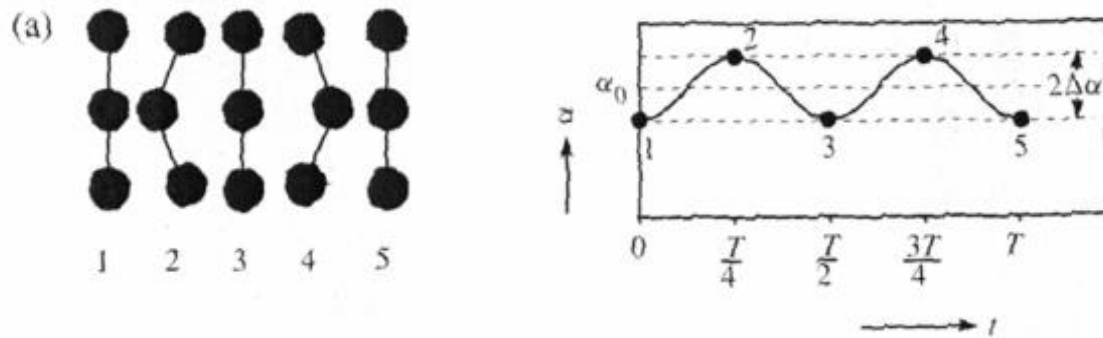
(b) ν_2 , bending mode



(c) ν_3 , asymmetric stretching mode

Figures 4.6 The change in size, shape, or direction of the polarizability ellipsoid of the water molecule during each of its three vibrational modes. The centre column shows the equilibrium position of the molecule, while to right and left are the (exaggerated) extremes of each vibration.

Vibrational modes of CO₂



- Spatial charge separation under influence of electric field \mathbf{E}
→ induced dipole moment $\boldsymbol{\mu}$:

$$\boldsymbol{\mu} = \alpha \mathbf{E}$$

α : polarizability

- Electric field \mathbf{E} due to electromagn. wave with frequency ν_0

$$\mathbf{E} = \mathbf{E}_0 \cos 2\pi \nu_0 t$$

$$\rightarrow \boldsymbol{\mu} = \alpha \mathbf{E}_0 \cos 2\pi \nu_0 t$$

→ emission of light at same frequency ν_0

- Internal vibrational motion with Eigenfrequency ν_M

$$q = q_0 \cos 2\pi \nu_M t$$

- Polarizability $\alpha \rightarrow$ develop in series

$$\alpha = \alpha_{q=0} + (\partial\alpha/\partial q)_{q=0} q + \text{higher order terms}$$

$$\rightarrow \mu = \alpha E$$

$$= (\alpha_{q=0} + (\partial\alpha/\partial q)_{q=0} q_0 \cos 2\pi \nu_M t) E_0 \cos 2\pi \nu_0 t$$

$$= \underbrace{\alpha_{q=0} E_0 \cos 2\pi \nu_0 t}_{\text{Rayleigh}} + \frac{1}{2} (\partial\alpha/\partial q)_{q=0} q_0 E_0 [\cos 2\pi (\nu_0 - \nu_M)t + \cos 2\pi (\nu_0 + \nu_M)t]_{\text{Stokes/Anti-Stokes}}$$

Rayleigh

Stokes/Anti-Stokes

Quantum Mechanical Explanation

→ harmonic oscillator: $\Delta v = \pm 1$

inelastic impact	elastic impact	inelastic impact
$\Delta E_M > 0$	$\Delta E_M = 0$	$\Delta E_M < 0$
$v = v_0 - v_{\text{vib}} < v_0$	$v = v_0$	$v' = v_0 + v_{\text{vib}} > v_0$
<p>Energy level diagram for Stokes scattering. The ground state is $v=0$ and the first excited state is $v=1$. An upward arrow from $v=0$ to $v=1$ is labeled $h\nu_0$. A downward arrow from $v=1$ to $v=0$ is labeled $h(\nu_0 - \nu_{\text{vib}})$.</p>	<p>Energy level diagram for Rayleigh scattering. The ground state is $v=0$ and the first excited state is $v=1$. Two upward arrows from $v=0$ to $v=1$ are labeled $h\nu_0$. Two downward arrows from $v=1$ to $v=0$ are labeled $h\nu_0$.</p>	<p>Energy level diagram for Anti-Stokes scattering. The ground state is $v=0$ and the first excited state is $v=1$. An upward arrow from $v=0$ to $v=1$ is labeled $h\nu_0$. A downward arrow from $v=1$ to $v=0$ is labeled $h(\nu_0 + \nu_{\text{vib}})$.</p>
Stokes	Rayleigh	Anti-Stokes

First Report of Raman Observation

Nature 121, 501-502 (31 March 1928)

A New Type of Secondary Radiation

C. V. RAMAN & K. S. KRISHNAN

Abstract

If we assume that the X-ray scattering of the 'unmodified' type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wave-length corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wave-length as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

First Report of Raman Observation

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A New Type of Secondary Radiation

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Continue

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 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.

The Nobel Prize in Physics

1930

Professor Sir C.V. Raman

SIR CHANDRASEKHARA V. RAMAN

The molecular scattering of light

Nobel Lecture, December 11, 1930

The colour of the sea

In the history of science, we often find that the study of some natural phenomenon has been the starting-point in the development of a new branch of knowledge. We have an instance of this in the colour of skylight, which has inspired numerous optical investigations, and the explanation of which, proposed by the late Lord Rayleigh, and subsequently verified by observation, forms the beginning of our knowledge of the subject of this lecture. Even more striking, though not so familiar to all, is the colour exhibited by oceanic waters. A voyage to Europe in the summer of 1921 gave me the first opportunity of observing the wonderful blue opalescence of the Mediterranean Sea. It seemed not unlikely that the phenomenon owed its origin to

http://nobelprize.org/nobel_prizes/physics/laureates/1930/raman-lecture.pdf



1888-1970

"for his work on the scattering of light and for the discovery of the effect named after him"

EXPERIMENTAL STUDY



Raman with his spectrometer

MODERN SPECTROMETER



Thank You