Atomic and Molecular Physics

Course Code: PHYS4009

Lecture Topic

Raman Spectroscopy

By

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Outline

- *Raman Scattering*

- *Description of Raman Effect*

- *Semiclassical Theory of Raman Scattering*

- *Quantum Description of Raman Effect*

- *Selection Rule for Vibrational Transition*

- *Raman-Active and Inactive vibrations of H_2O and CO_2*

- *Mutual Exclusion Principle*

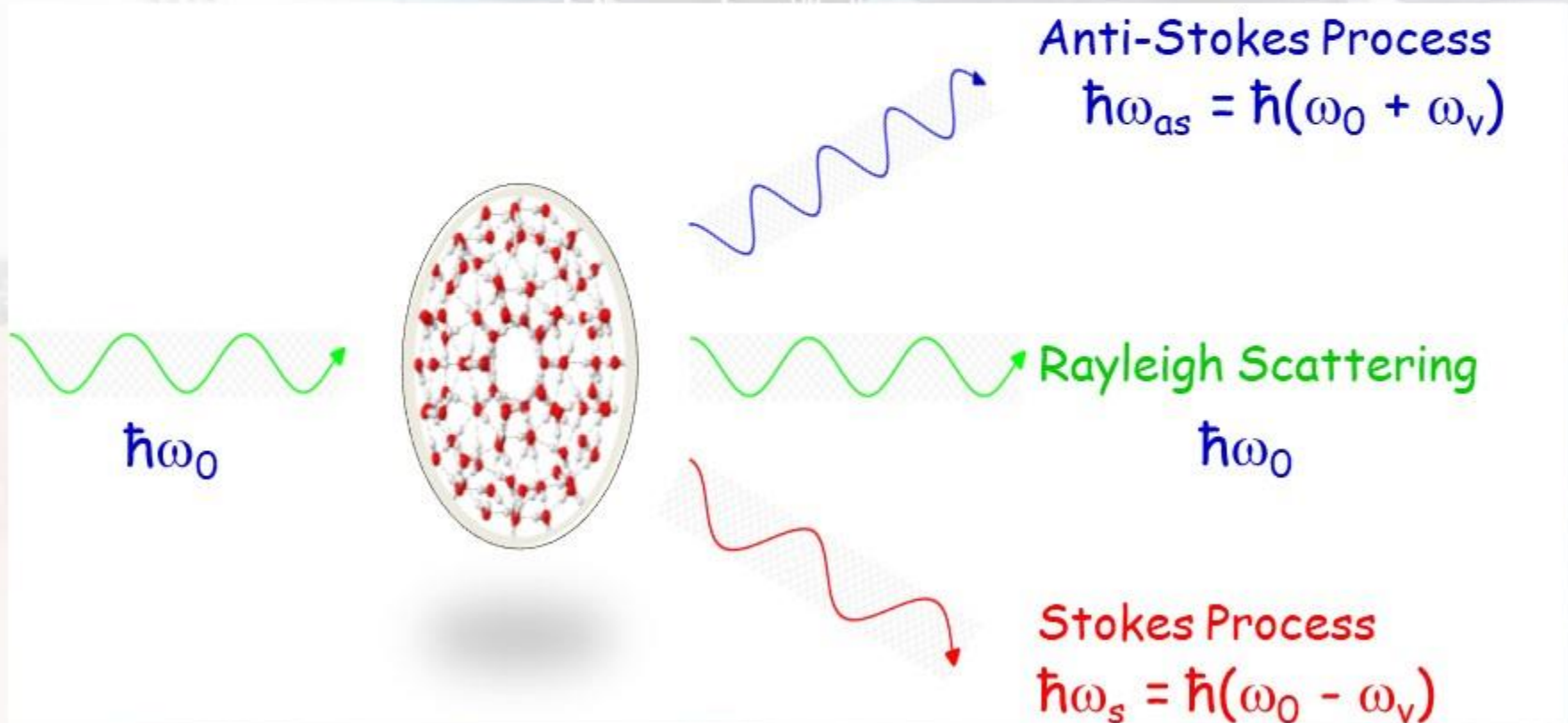- *Advantages and Disadvantages of Raman Spectroscopy*

Raman Scattering

When a beam of light is passed through a transparent substance, a small amount of the radiation energy is scattered. If monochromatic radiation such as laser, or radiation of a very narrow frequency band, is used, the scattered energy will consist almost entirely of radiation of the incident frequency (the so-called Rayleigh scattering) but, in addition, certain discrete frequencies above and below that of the incident beam will be scattered; it is this which is referred to as **Raman scattering**.

Raman scattering is **inelastic scattering of light**. The scattered radiation with a frequency lower than that of the incident beam is referred to as **'Stokes'** radiation, while that at higher frequency is called **'anti-Stokes'** radiation. Raman scattering is a very weak process, only one out of few lakh scattered radiation is Raman scattered radiation. Therefore, sensitive apparatus is required for Raman study.

Raman Effect

Raman scattering is an inelastic scattering of light or photon by a molecule, therefore, it contains the information about the molecular systems.

Anti-Stokes Process

$$\hbar\omega_{as} = \hbar(\omega_0 + \omega_v)$$

Rayleigh Scattering

$$\hbar\omega_0$$

$$\hbar\omega_0$$

Stokes Process

$$\hbar\omega_s = \hbar(\omega_0 - \omega_v)$$

Semiclassical Theory of Raman Scattering

When a molecule is irradiated by an electromagnetic radiation, the incident radiation field, E induces an electric dipole such that the induced dipole moment is p. The magnitude of the induced dipole moment is given by:

$$p = \alpha E_0$$

where
$$\alpha = \alpha_e + \left(\frac{\partial \alpha}{\partial Q}\right)_e Q + \frac{1}{2!}\left(\frac{d^2\alpha}{dQ^2}\right)_e Q^2 + \cdots \qquad Q = r - r_e$$

and
$$E = E_0 \cos(\omega_0 t)$$

Also Q oscillates at the natural vibrational frequency,

$$Q = Q_0 \cos(\omega_v t)$$

The dipole moment induced by a field of frequency ω_o is given by:

$$\vec{p} = \left[\alpha_e + \left(\frac{\partial \alpha}{\partial Q} \right)_e Q_0 \cos(\omega_v t) \right] \vec{E}_0 \cos(\omega_0 t) =$$

$$\alpha_e \vec{E}_0 \cos(\omega_0 t) + \frac{\vec{E}_0 Q_0}{2} \left(\frac{\partial \alpha}{\partial Q} \right)_e \{ \cos[(\omega_0 + \omega_v)t] + \cos[(\omega_0 - \omega_v)t] \}$$

The induced dipole moment has frequency components at ω_0 (Rayleigh), at $[\omega_o + \omega_v]$ (anti-Stokes) and at $[\omega_o - \omega_v]$ (Stokes).
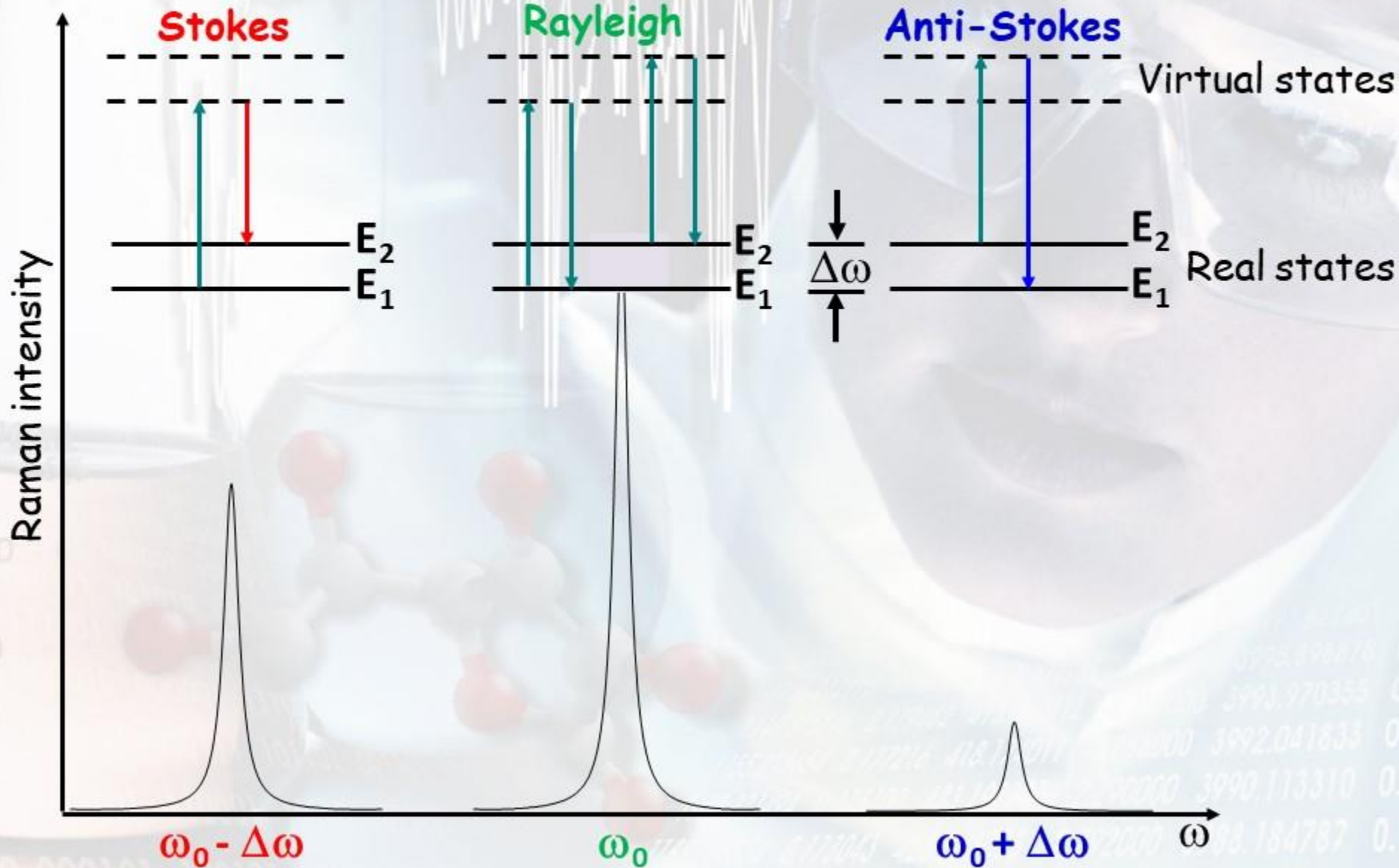
Here the coefficients of the $\cos(\omega_o + \omega_v)t$ and $\cos(\omega_o - \omega_v)t$

TERMS ARE EQUAL

THIS MEANS THAT Stokes and Anti-Stokes SHOULD HAVE

EQUAL INTENSITY

Quantum Description of Raman Effect

The semi-classical description of the Raman effect could explain only the Rayleigh, Stokes and anti-Stokes lines but unable to explain the different intensity of the Stokes and anti-Stokes. According to quantum description of Raman effect, where quantized vibrational energy levels are considered, and when intense monochromatic radiation incident on the molecule, it may take the molecule from the ground state E_1 to any virtual state, then it may return to ground state E_1 in a **Rayleigh scattering process** or to excited state E_2 in a **Stokes Raman transition**. Alternatively, it may go from the excited state E_2 to any virtual state and return to excited state E_2 **(Rayleigh)** or to ground state E_1 **(Raman anti-Stokes)**. However, in many molecules at normal temperatures the initial population of the excited state E_2 is so low that anti-Stokes transitions may be too weak to be observed. Whereas, at normal temperatures the population of the ground state E_1 is quite high and therefore, the intensity of the Stokes lines is high compared to anti-Stokes lines.

Selection Rule for Vibrational Raman Transition

In analogy to the vibrational IR transition, the vibrational Raman transition moment $R_{v'v''}$ is given by

$$R_{v'v''} = \left(\frac{d\alpha}{dQ}\right)_e A \int \psi_{v'}^* Q \psi_{v''} dQ + \ldots \ldots \ldots$$

For the Raman active transition, the $R_{v'v''}$ should be non-zero. The above equation has two term; $\left(\frac{d\alpha}{dQ}\right)_e$ and an integral $\int \psi_{v'}^* Q \psi_{v''} dQ$. In order to have $R_{v'v''}$ non-zero, both term should be non-zero. Therefore, for Raman active transition, following condition should meet:

$\left(\frac{d\alpha}{dQ}\right)_e \neq 0$ i.e. there must be **change of polarizability at equilibrium inter-nuclear separation during vibration** and $\int \psi_{v'}^* Q \psi_{v''} dQ \neq 0$, the integral is non-zero only when, $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$ which constitute the vibration selection rule for Raman transition.

The transition intensities are proportional to $|R_{v'v''}|^2$ and therefore to $\left(\frac{d\alpha}{dQ}\right)_e^2$. Since, α is tensor quantity given as:

$$\alpha = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix}$$

we cannot illustrate easily its variation with internuclear coordinate Q, instead we use the mean polarizability $\bar{\alpha}$, where

$$\bar{\alpha} = \frac{1}{3}\left[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right]$$
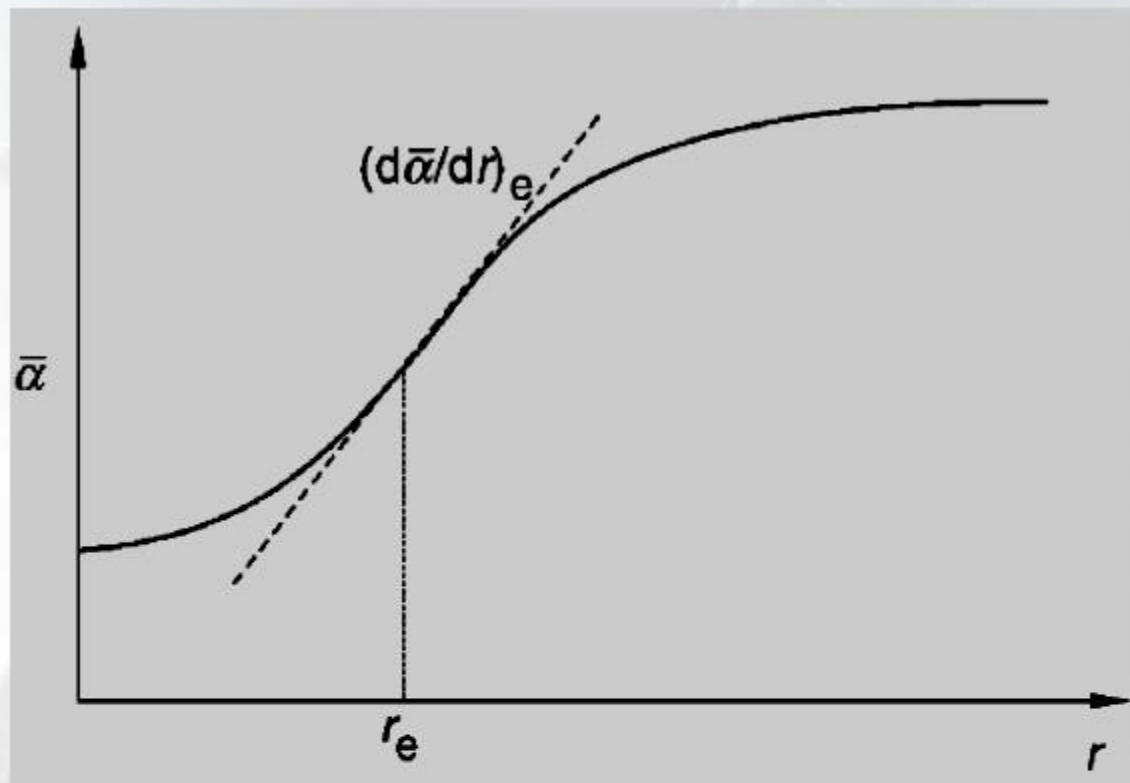
Figure shows the variation of the mean polarizability $\bar{\alpha}$ with internuclear distance r in a diatomic molecule, typically how $\bar{\alpha}$ varies with r; $d\bar{\alpha}/dr$ is usually positive and, unlike $d\mu/dr$ in Figure varies little with r. For this reason vibrational Raman intensities are less sensitive than are infrared intensities to the environment of the molecule, such as the solvent in a solution spectrum.
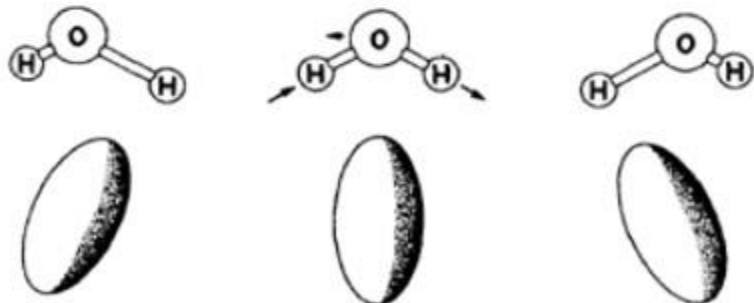
Raman Active and Inactive Vibrations of H$_2$O
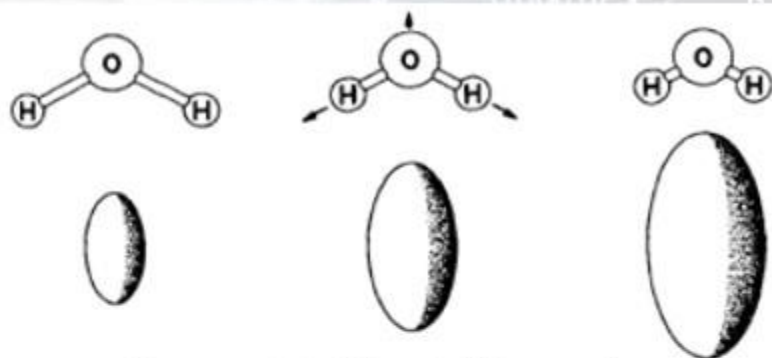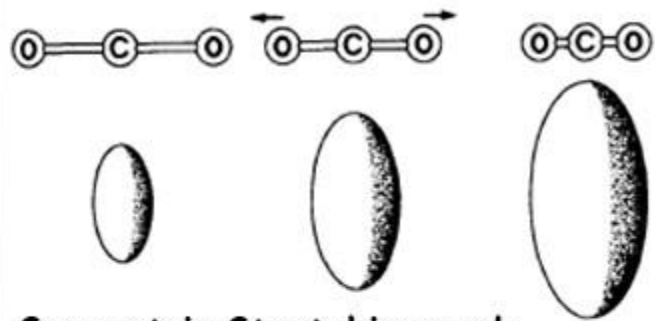

Symmetric Stretching mode
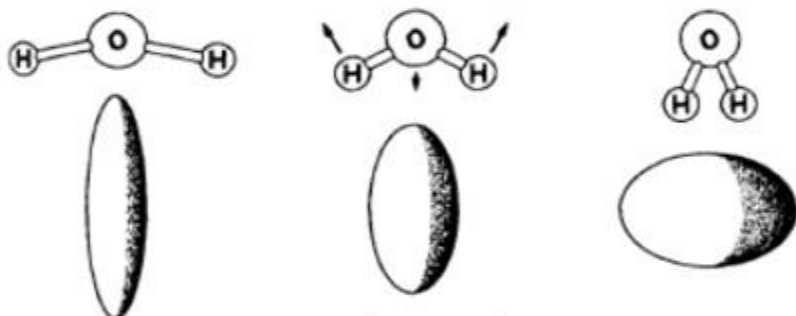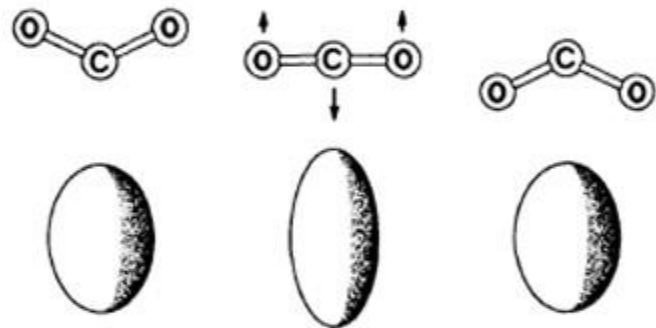
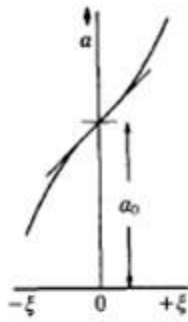Bending mode

Anti-symmetric Stretching mode

$$\left(\frac{d\alpha}{dQ}\right)_e \neq 0$$

Since, **all three vibrations** of H$_2$O involve obvious changes in at least one aspect (size, shape or direction) of the polarizability ellipsoid, and all are **Raman active**.
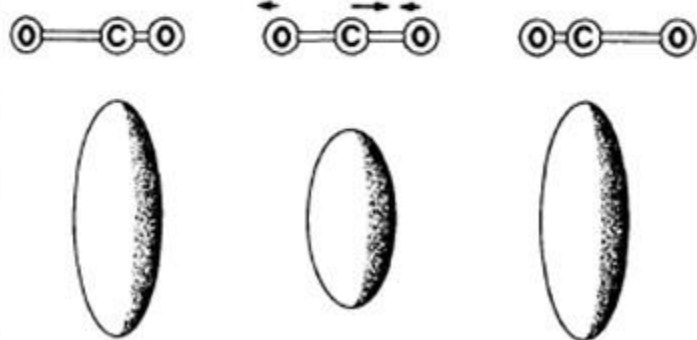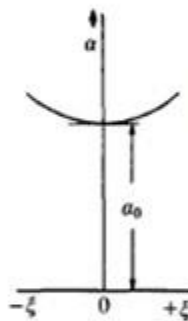
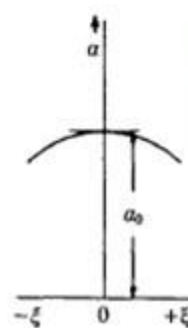# Raman Active and Inactive Vibrations of CO_2

Symmetric Stretching mode

Bending mode

Anti-symmetric Stretching mode

Consider the linear triatomic molecule CO_2, whose three fundamental vibrational modes have been shown; the extreme and equilibrium configurations of the molecule and their approximate polarizability ellipsoids are also shown. In **symmetric stretching** mode, during the motion the molecule changes size, and so there is a corresponding fluctuation in the size of the ellipsoid; the motion is thus **Raman active**.

It might be thought that the **other two vibrational modes** are also Raman active, because the molecule changes shape during each vibration and hence, presumably, so does the ellipsoid; however, both these modes are observed to be **Raman inactive**.

In **symmetric stretching vibration of CO_2** when the bonds stretch (Q positive), α increases, while when the bonds contract (negative Q) α decreases. since we are concerned only with small displacements; it is plain that near the equilibrium position ($Q = 0$) the curve has a distinct slope, i.e. $d\alpha/dQ \neq 0$ at $Q = 0$. Thus for small displacements the motion produces a change in polarizability and is therefore **Raman active**.

In the **bending motion of CO_2**, considering a downwards displacement of the oxygen atoms as negative Q and an upwards displacement as positive. For small displacements we evidently have $d\alpha/dQ = 0$ and hence for small displacements there is effectively no change in the polarizability and the motion is **Raman inactive**.

The same argument applies to the **asymmetric stretch vibration of CO_2**, the polarizability decreases equally for positive and negative Q, so the plot of polarizability against Q has the appearance shown. Again $d\alpha/dQ = 0$ for small displacements and the motion is **Raman inactive**.

Since we have seen that the Raman spectrum is forbidden for $d\alpha/dQ = 0$ but allowed for $d\alpha/dQ \neq 0$, we can imagine that the 'degree of allowedness' varies with $d\alpha/dQ$. Thus if the polarizability curve has a large slope at Q = 0 the Raman line will be strong; if the slope is small it will be weak; and if zero, not allowed at all. From this stems the following very useful general rule:

Symmetric vibrations give rise to intense Raman lines; non-symmetric ones are usually weak and sometimes unobservable.

In particular, a bending motion usually yields only a very weak Raman line; e.g. the bending motion of H_2O, although allowed in the Raman, has not been observed, nor has anti-symmetric vibration, for which $d\alpha/dQ$ is also small.

Mutual Exclusion Principle

Summery of Raman and IR active and inactive vibration of CO_2

Mode of vibration of CO_2	Raman	Infra-red
Symmetric stretch	Active	Inactive
Bending	Inactive	Active
Asymmetric stretch	Inactive	Active

From the above observation an extremely important general rule has been established whose operation may be exemplified by CO_2. We see that, for CO_2 molecule, no vibration is simultaneously active in both Raman and IR. The corresponding general rule is: *Rule of mutual exclusion*.

If a molecule has a *centre of symmetry* then Raman active vibrations are infra-red inactive, and vice versa. If there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and infra-red active.

Advantages and Disadvantages of Raman Spectroscopy

Advantages

- It is a non-destructive technique. It can be used for solids, liquids, polymers or vapors.

- No sample preparation is required.

- No interference of water.

- Very small amount of sample is required.

Disadvantages

- The Raman effect is very weak. The detection requires a very sensitive and optimized instruments.

- Presence of impurities causes fluorescence which usually masks the Raman signal.

- Intense laser radiation can burn the sample.

Books for Further Reading

1. Fundamentals of Molecular Spectroscopy by C. N. Banwell (McGraw Hill)

2. Basic Atomic & Molecular Spectroscopy by J. M. Hollas (Royal Society of Chemistry)

Thank you