

**21.06.12 lecture PCIII**

**Chemische Bindung und  
Molekulare Spektroskopie  
(Lehramt)**

**Raman-Spektroskopie**

# RAMAN Spectroscopy



Sir C.V.Raman (1788-1970)

- Discovered the *inelastic scattering phenomenon* in 1928,
- Was awarded the Nobel Prize for Physics for his work on the scattering of light and for the discovery of the effect named after him in 1930.

[http://nobelprize.org/nobel\\_prizes/physics/laureates/1930/raman-lecture.pdf](http://nobelprize.org/nobel_prizes/physics/laureates/1930/raman-lecture.pdf)

*Nature* 121, 501-502 (31 March 1928)  
A New Type of Secondary Radiation  
C. V. RAMAN & K. S. KRISHNAN

*Nature* 121, 619-619 (21 April 1928)  
A Change of Wave-length in Light Scattering  
C. V. RAMAN

FURTHER observations by Mr. Krishnan and myself on the new kind of light-scattering discovered by us have been made and have led to some very surprising and interesting results.  
In order to convince ourselves that the secondary radiation observed by us was a true scattering and not a fluorescence, we proceeded to examine the effect in greater detail. The principal difficulty in observing the effect with gases and vapours was its excessive feebleness. In the case of substances of sufficient light-scattering power, this difficulty was overcome by using an enclosed bulb and heating it up so as to secure an adequate density of vapour. Using a blue-violet filter in the track of the incident radiation was complementary green-yellow scattered radiation was observed with a number of organic vapours, and it was even possible to determine its state of polarisation. It was found that in certain cases, for example pentane, it was strongly polarised, while in others, for example naphthalene, it was unpolarised. Liquid carbon disulphide was studied, and a note was published in the *Proceedings of the Royal Society* in 1928.



Was ist Lichtstreuung?

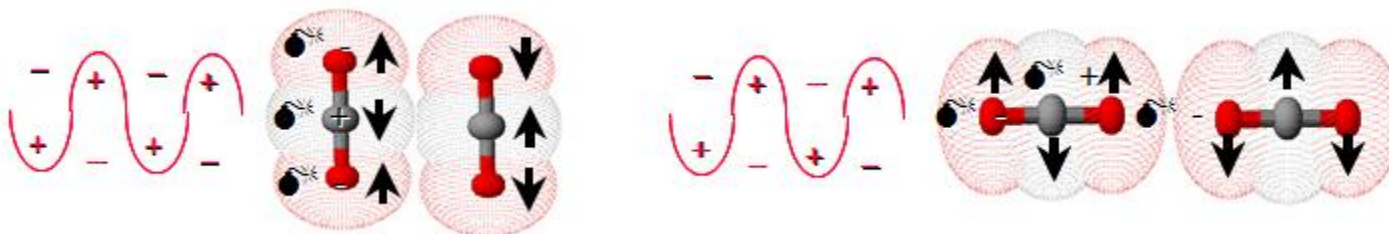
Raman-Streuung und Rayleigh-Streuung

# IR and RAMAN spectroscopies-I

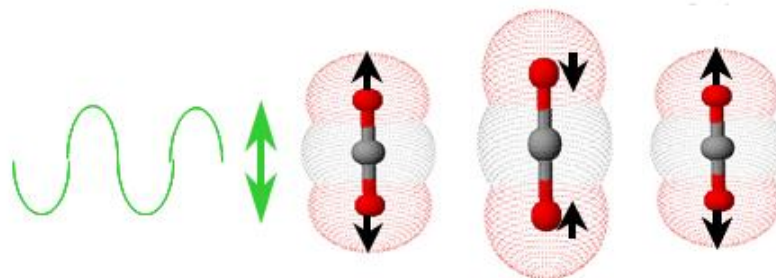
- Raman spectroscopy probes the vibration modes of materials, much like infrared (IR) spectroscopy.
- They both results from the same type of quantized vibrational changes. Thus, the difference in wavelength between the incident and scattered visible radiation corresponds to wavelengths in the mid-infrared region.
- However, whereas **IR** bands arise from a **change in the dipole moment**, **Raman** bands arise from a **change in the polarizability**.
- In many cases, transitions that are allowed in Raman are forbidden in IR, so these techniques are often complementary.

# How is Raman Different from IR?

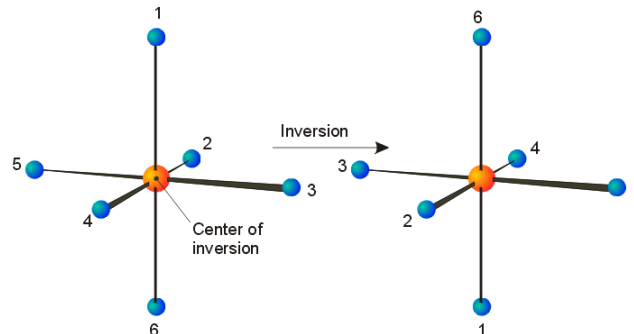
**IR-Change in Dipole Moment :  $\Delta\mu \neq 0$**



**Raman-Change in Polarizability:  $\Delta\alpha \neq 0$**

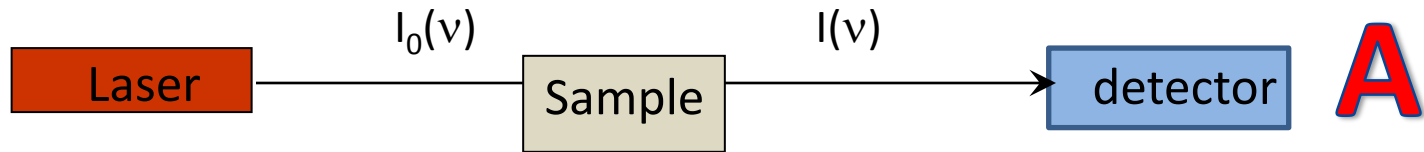


Selection rules are therefore different and can be exclusive for **centrosymmetric** molecules.

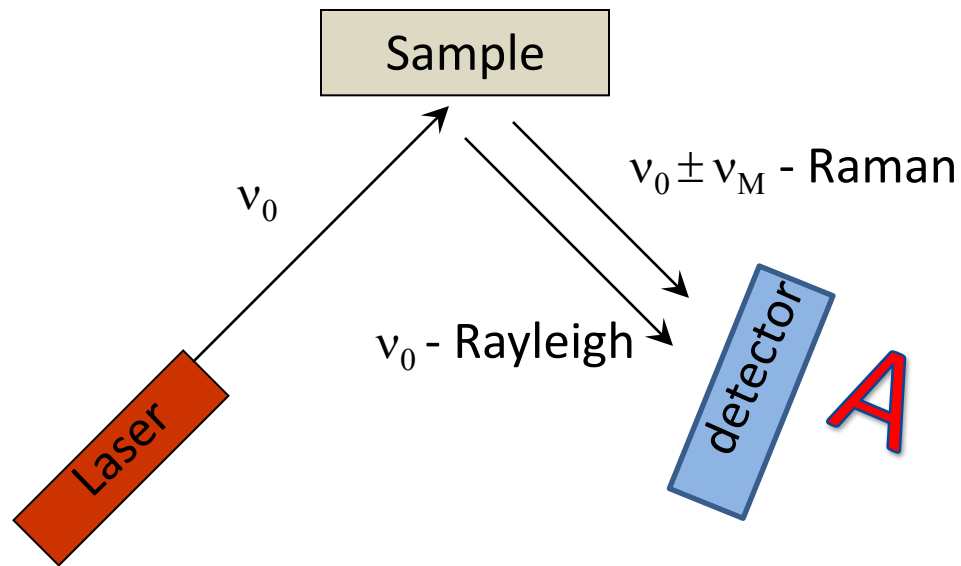


**Rule of mutual exclusion  
(Ausschlußregel)**

# IR Spectrography - Absorption



# Raman Spectrography - Scattering

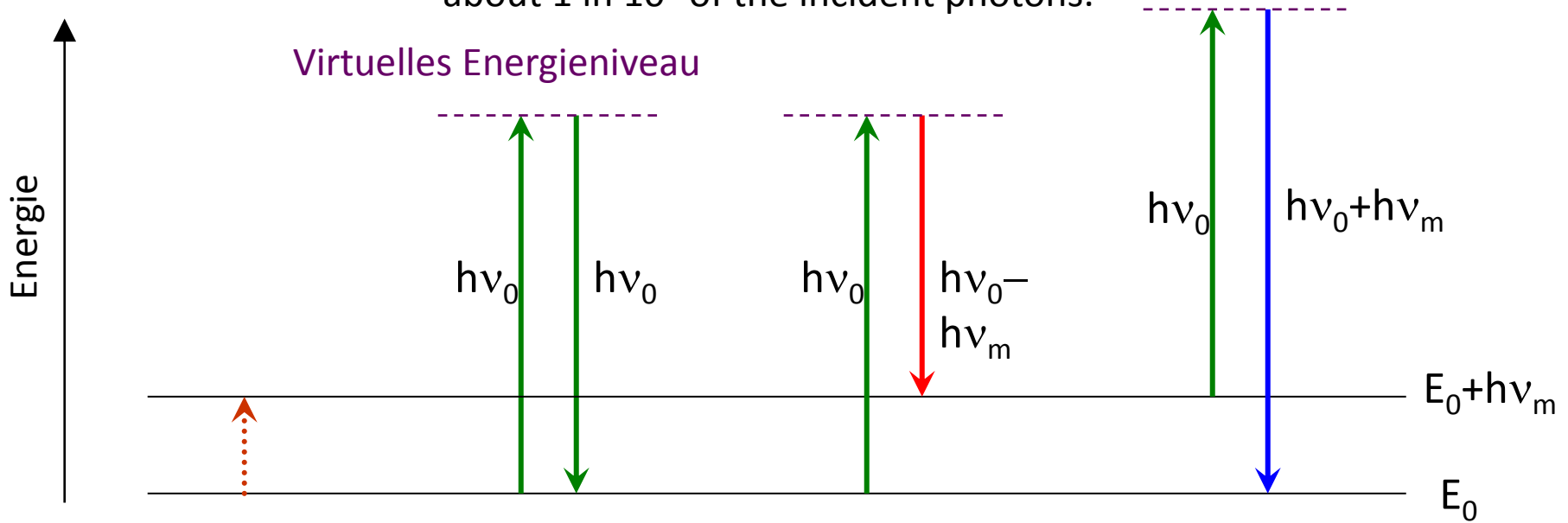


**Elastic scattering (Rayleigh): original frequency shift:  $\nu_0$**

**Inelastic scattering (Raman): with frequency shift:  $\nu_0 \pm \nu_M$**

# Photon scattering energy scheme

The Raman effect comprises a very small fraction, about 1 in  $10^7$  of the incident photons.



**IR Absorption**  
 $\Delta E_{vib} = h\nu_{vib}$

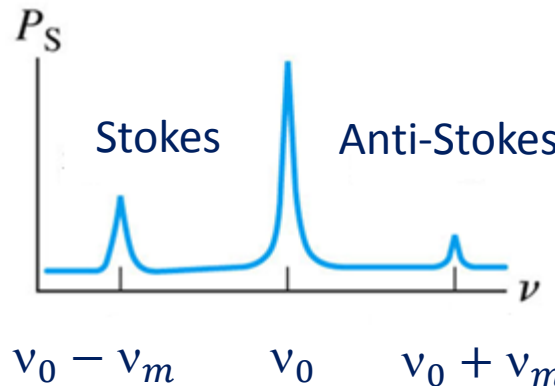
**Rayleigh Streuung (elastic)**

**Stokes Streuung**

**Anti-Stokes Streuung**

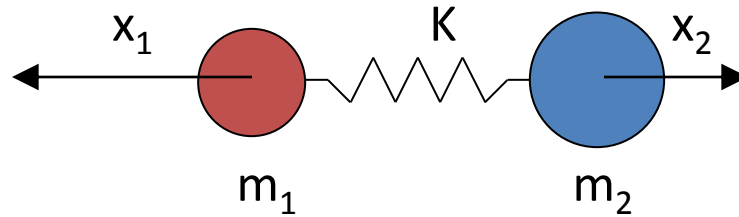
**Raman (inelastic)**

Grundzustand:  $E_0$   
 erster angeregter  
 zustand:  $E_0 + h\nu_m$



Notice: Stokes line is stronger

# Scattering of radiation by diatomic molecule



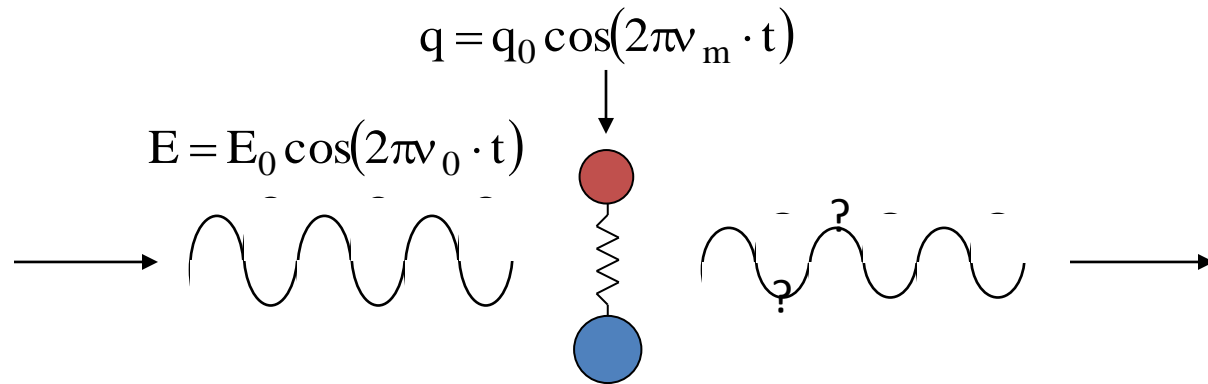
$$\frac{m_1 m_2}{m_1 + m_2} \left( \frac{d^2 x_1}{dt^2} + \frac{d^2 x_2}{dt^2} \right) = -K(x_1 + x_2)$$

Just like  
Hooke's law:  
 $F = kX$

Reduced mass  $\mu$   $\frac{d^2 q}{dt^2} = -K \cdot q$  displacement

$$\Rightarrow q = q_0 \cos(2\pi \nu_m \cdot t)$$

Where:  $\nu_m = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$

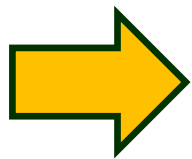


Induced dipole moment:

$$\mu = \alpha \cdot E = \alpha \cdot E_0 \cos(2\pi\nu_0 \cdot t)$$

For a small amplitude of vibration, the polarizability  $\alpha$  is a linear function of  $q$ :

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} \cdot q + \dots$$



$$\mu = \alpha_0 E_0 \cos(2\pi\nu_0 \cdot t) + \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} \cdot q_0 \cos(2\pi\nu_m \cdot t) \cdot E_0 \cos(2\pi\nu_0 \cdot t) =$$

$$= \alpha_0 E_0 \cos(2\pi\nu_0 \cdot t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} q_0 E_0 [\cos(2\pi\{\nu_0 - \nu_m\} \cdot t) + \cos(2\pi\{\nu_0 + \nu_m\} \cdot t)]$$

Rayleigh  
scattering

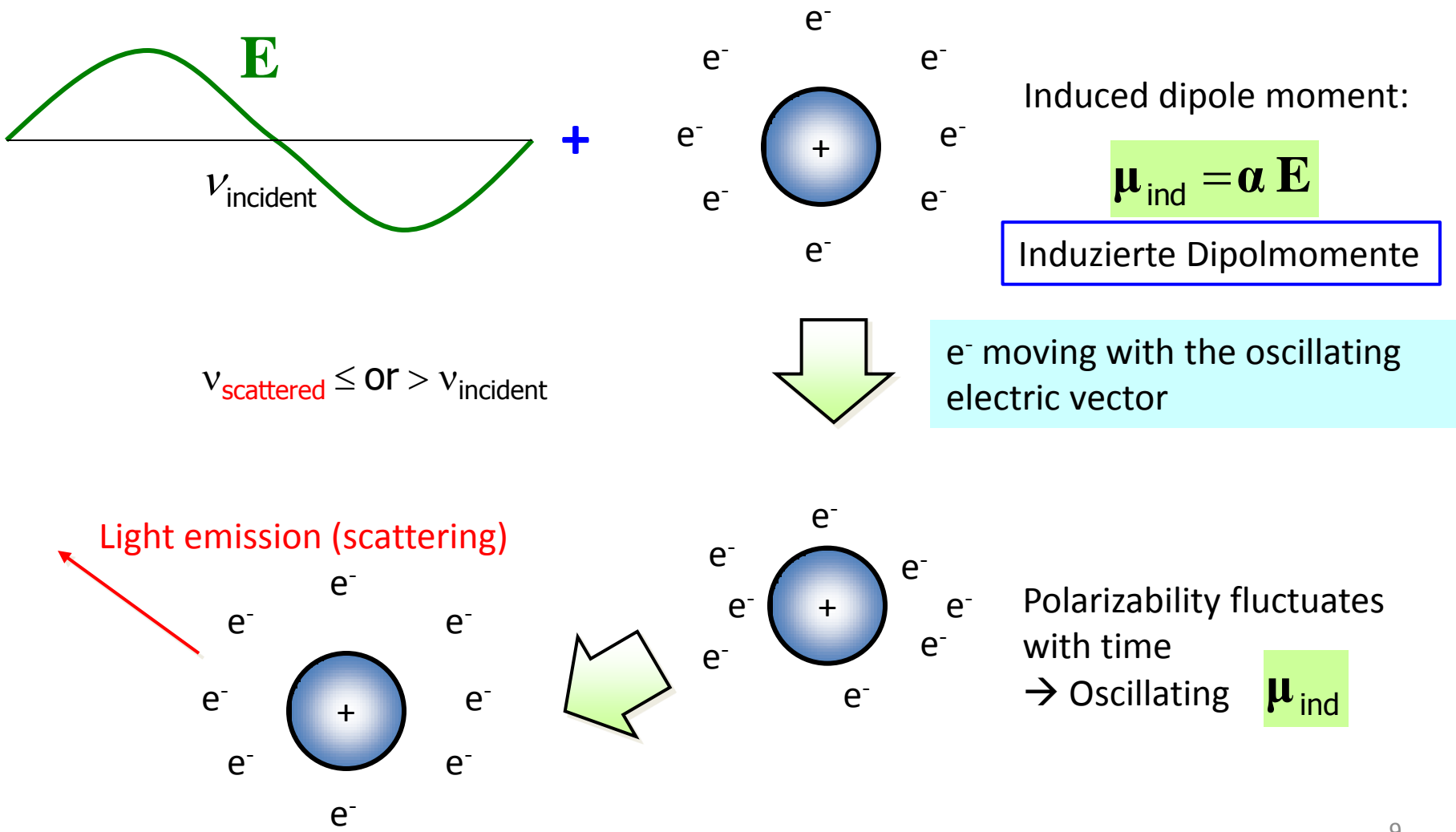
Stokes  
scattering

Anti-Stokes  
scattering

$$\cos A \cdot \cos B = 1/2 [\cos(A + B) + \cos(A - B)]$$

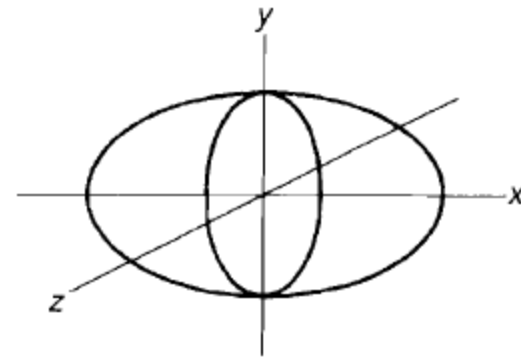


- A **Change in Polarizability** of the Molecules upon Interaction with the Incident Light



$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

The polarizability tensor



The polarizability ellipsoid

**Polarizability is affected by**

1- Atomic number Z:

$\mu \propto$  the amount of electrons,  
Electrons become less control by nuclear charge.

2- Bond Length:

$\mu \propto$  Bond Length

3- Atomic or Molecular Size:

$\mu \propto$  Size,

4- Molecular orientation with respect to an electric field

Parallel or perpendicular (Exp: Parallel has more effect)

5- Bond Strength (Bond order):

$\mu \propto$  1/strength of bond C=C, and C≡C, C≡N bonds are strong scatterers, bonds undergo polarization.

6- Electronegativity difference:

$\mu \propto$  1/ difference in electronegativity

7- Covalent bonds more polarizable than ionic bonds.

# Example 1: the vibration modes of CO<sub>2</sub>

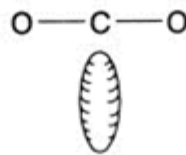
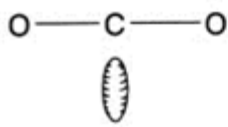
Ausschlußregel !!!

+ q

q = 0

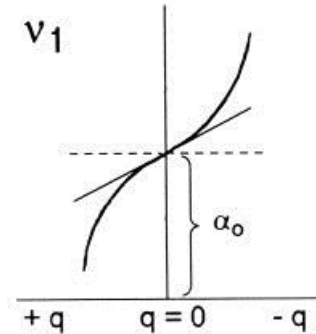
- q

v<sub>1</sub>

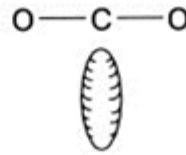
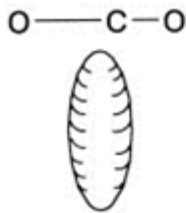


Symmetrische-Streckschwingung

Raman Active



v<sub>3</sub>

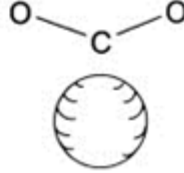
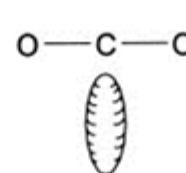
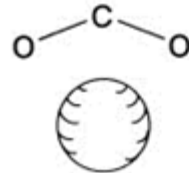


Asymmetrische-Streckschwingung

IR Active

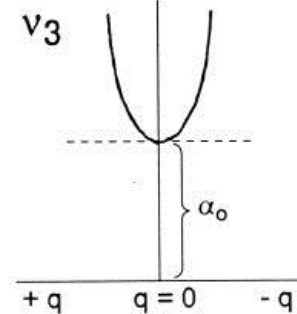
$(d\alpha/dq)_0 \neq 0$

v<sub>2</sub>



Biegeschwingung

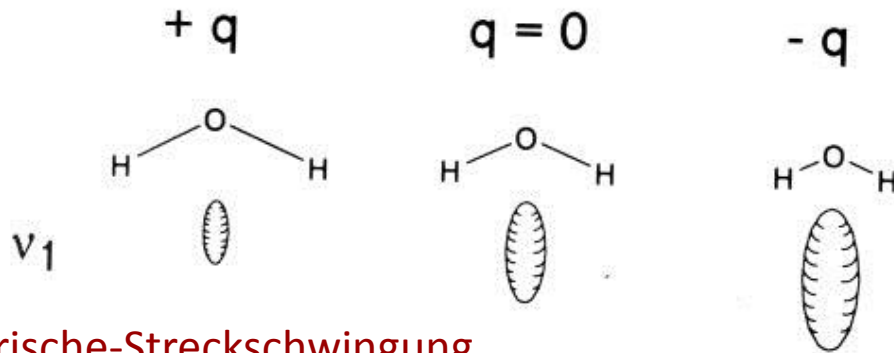
IR Active



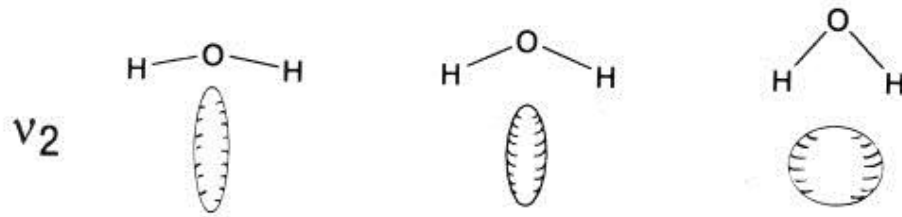
$(d\alpha/dq)_0 = 0$

$$P = \alpha_0 E_0 \cos(2\pi\nu_0 \cdot t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} q_0 E_0 [\cos(2\pi\{\nu_0 - \nu_m\} \cdot t) + \cos(2\pi\{\nu_0 + \nu_m\} \cdot t)] \quad 11$$

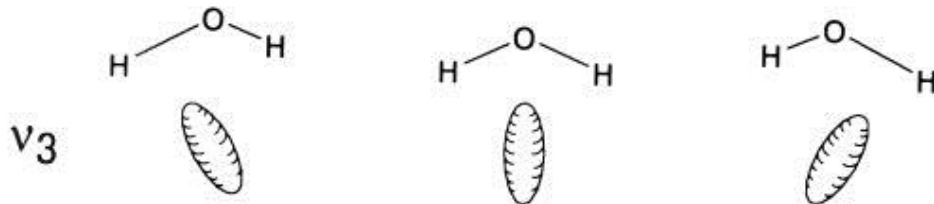
# Example 2: the vibration modes of H<sub>2</sub>O



Symmetrische-Streckschwingung



Biegeschwingung



Asymmetrische-Streckschwingung

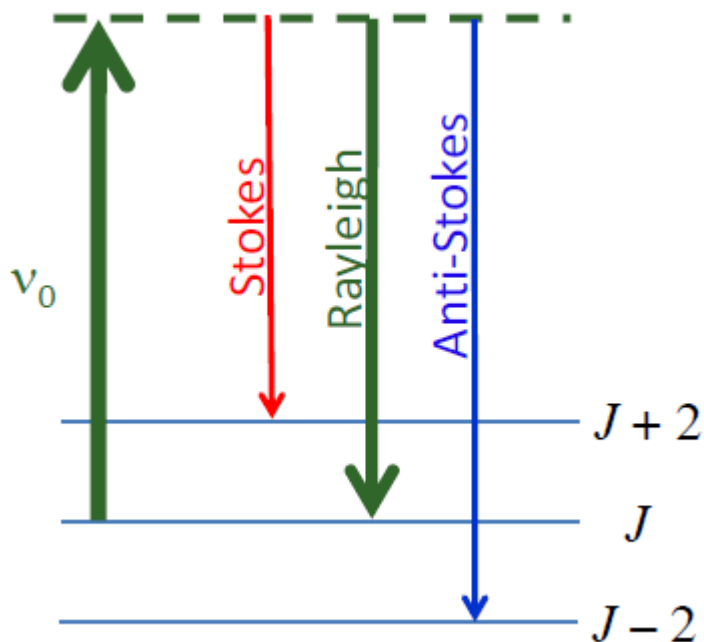
No inversion center!

All the modes are both  
Raman & IR Active

# Selection rules (Auswahlregel)

As a molecule rotates, the polarizability presented to the electric field changes:

- the induced dipole is modulated by rotation,
- results in rotational transitions.



$$\Delta J = 0, \mp 2$$

$\Delta J = 0$  : Rayleigh  
 $\Delta J = +2$  : stokes line  
 $\Delta J = -2$  : Anti-stokes line

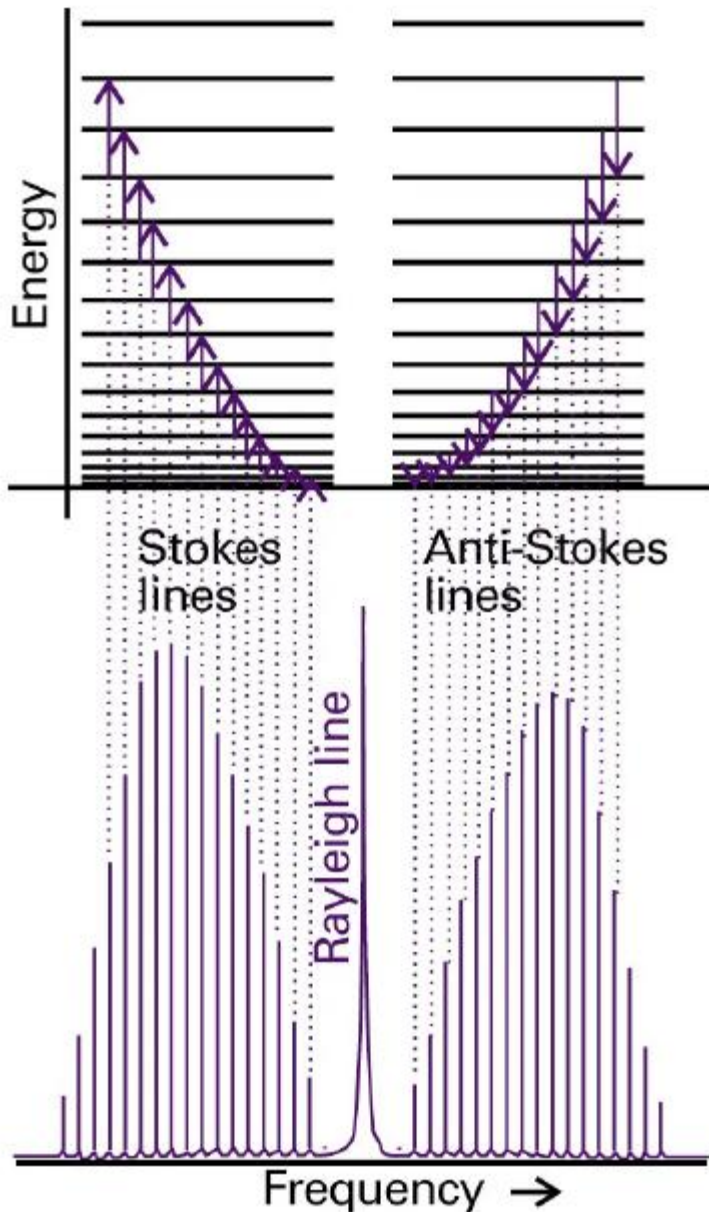
## Example: Rigid rotor

$$E_J = BJ(J + 1), \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots)$$

Stokes and Anti-Stokes lines are observable at

$$\Delta E = \{(E_{J+2}) - E_J\} = B(4J + 6), \text{ cm}^{-1}$$

$$\bar{\nu} = \nu_0 \mp B(4J + 6), \text{ cm}^{-1}$$



- a gap of  $6B$  between  $\nu_0$  and 1st lines of each branch

- lines in each branch of equal spacing =  $4B$

# IR and RAMAN spectroscopies-II

- Advantages
  - detects vibration motions for symmetric structures,
  - Raman is more sensitive in some cases (like rough surfaces),
  - useful for studying the catalyst itself (crystalline phases, low frequency vibrations whereas IR is more useful for molecules and adsorbates,
  - needs a small sample volume (laser spot)
  - Can be used for aqueous samples (biological applications)
  - Glass /quartz cell (no NaCl tablet!)
  - Few intense overtone/combination bands , so few spectral overlaps
  - Single shot/scan between 4000-50cm<sup>-1</sup> without setup modifications
- Problems:
  - Laser source/ heating or decomposition of sample,
  - Can cause fluorescence,
  - Expensive apparatus,
  - Obtaining high res RO/RO-Vib spectra is difficult .