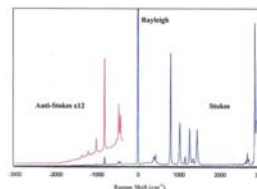
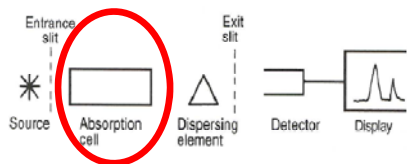


Raman Spectroscopy

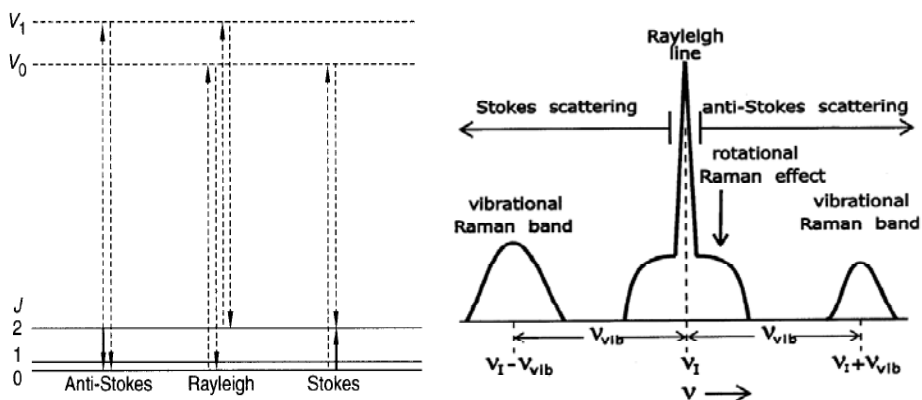


- Hollas Chapters 5.3 + 6.1 + Bernath Chapter 8
- Raman effect
- Polarizability vs induced dipole moment
- Stokes vs Anti-Stokes
- Raman shift
- Symmetry

11 Sept 2008

CHEM 5161

Selection rules, Stokes vs Anti-Stokes



Raman Selection Rules in linear molecules:

Rotational Raman: $\Delta J = 0, \pm 2$

Ro-vibrational Raman: $\Delta v = 1$ and $\Delta J = 0, \pm 2$

Polarizability tensor

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

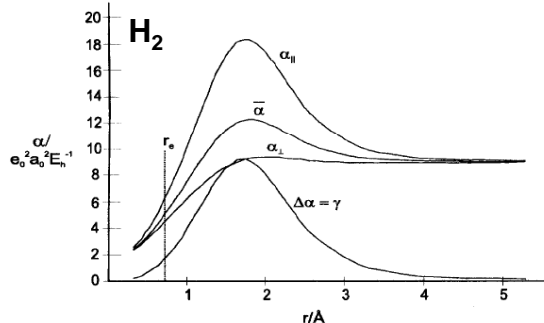
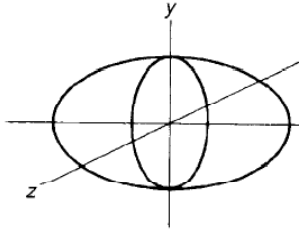
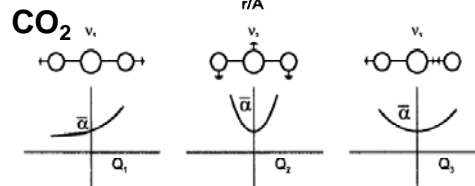


Figure 5.14 The polarizability ellipsoid



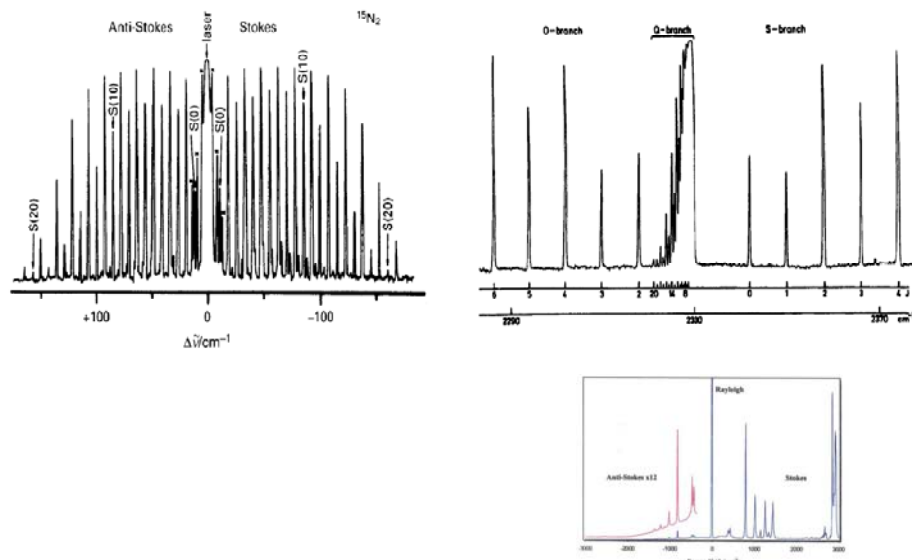
SI-Units: $1 \text{ C m}^2 \text{ V}^{-1} = 1.11265 \cdot 10^{-16} \text{ cm}^3 = 1.11265 \cdot 10^{-40} \text{ \AA}^3$
 Cgs units: $\text{\AA}^3 \Leftrightarrow \text{cm}^3$

Raman vs dipole allowed spectroscopy

- Raman: less restrictive than normal dipole-allowed spectroscopy
- homonuclear molecules (H₂, O₂, N₂ etc.) and heteronuclear molecules (HCl etc.) give signal
- induced dipole moment changes as a result of the change of the polarizability ellipsoid as the molecule vibrates/rotates
- Also electronic transitions can be observed
- **Rule of mutual exclusion: there is no stretch that will be both IR AND Raman active !!**

$$\frac{\partial \mu}{\partial r}$$

Stokes vs Anti-Stokes intensities in Rotational vs Ro-vibrational RS



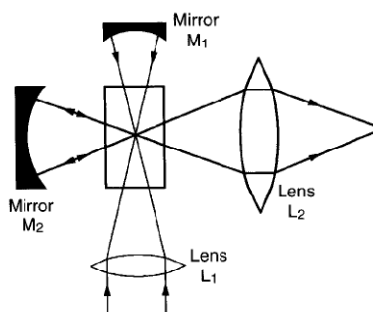
Experimental setup

- Raman Intensity:

$$I'_{\parallel} = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \left(\frac{45\bar{\alpha}^2 + 4\gamma^2}{45} \right) N_0 V_S I_0$$

$$I'_{\perp} = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \left(\frac{\gamma^2}{15} \right) N_0 V_S I_0,$$

$$I' = \frac{\pi^2}{\epsilon_0^2 \lambda^4} \left(\frac{45\bar{\alpha}^2 + 7\gamma^2}{45} \right) N_0 V_S I_0.$$



- I' ca. 10^{-6} of Rayleigh intensity

- $$\frac{\text{Anti-Stokes intensity}}{\text{Stokes intensity}} = \frac{(\nu_1 + \nu_{\text{vib}})^4 e^{-h\nu_{\text{vib}}/kT}}{(\nu_1 - \nu_{\text{vib}})^4}$$

Raman	IR
+ H ₂ O is ok	H ₂ O strongly absorbs
+ Cheap materials	Salt plates, expensive
(-) Inherently weak proc	More intense proc
- Sample degradation	Soft on sample
+ 1 inst. for vib + rot	2 instruments needed
+ Fast detector resp.	Slow detector resp.
- More expensive	Cheaper
- Hard to compare	Spectral libraries
+ Simpler spectra	More complex spectra

Raman spectra provide ...

- A chemical fingerprint of chemical structure (normal modes of vibration, rotation). Note: group frequencies differ in the Raman and infrared spectra
- Identification of phases (mineral inclusions, daughter minerals in fluid inclusions, composition of the gas phase in inclusions)
- Anions in the fluid phase (CO₃²⁻, HCO₃⁻, PO₄³⁻, BO₄³⁻, SO₄²⁻, HS⁻, OH⁻)
- Identification of crystalline polymorphs (sillimanite, kyanite, andalusite and others)
- Measurement of mid-range order in solids
- Measurement of orientation
- Measurement of stress
- High-pressure and high-temperature in situ studies
- Phase transition and order-disorder transitions in minerals (a-b phase transition in quartz, graphite)
- Water content of silicate glasses and minerals
- Speciation of water in glasses