

Chemistry 2

Lecture 9 Raman Spectroscopy



Assumed knowledge

Only vibrations that give rise to a change in the dipole moment are IR active. A harmonic oscillator gives rise to a single peak in the IR spectrum as $\Delta v = \pm 1$. For a real molecule, bands with $\Delta v = \pm 1, 2, 3$ are also possible but become increasingly weak.

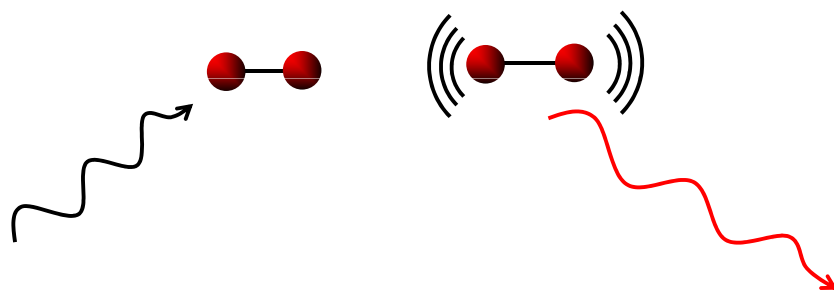
Learning outcomes



- Be able to qualitatively explain the origin of the Stokes and anti-Stokes line in the Raman experiment
- Be able to predict the Raman activity of normal modes by working out whether the polarizability changes along the vibration
- Be able to use the rule of mutual exclusion to identify molecules with a centre of inversion (centre of symmetry)

Scattering (particle nature of light)

- Consider the collision between a photon and a molecule



- Molecule must be in a quantised vibrational state:

$$E_{\text{light, final}} = E_{\text{init}} - E_{\text{molecule}}$$

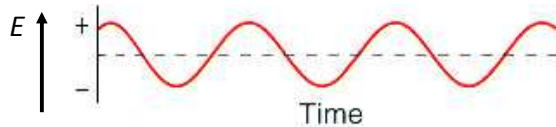
Polarizability

- Polarizability = how easily can electrons be moved in response to external field.
- Important in intermolecular forces:
 - dispersion force \propto polarizability
 - induced dipole, $\mu \equiv \alpha E$
 - where E is the electric field strength, and α is the *polarizability* of the molecule.
- Big atoms/molecules are more polarizable.

	He	N ₂	CH ₃ F	H ₂ C=CH ₂
α (Å ³)	0.20	1.72	3.84	4.5

Scattering (wave nature of light)

- Light has an oscillating electric field, E :
 - $E = E_0 \sin(2\pi\nu t)$
 - where ν is the frequency of the light (Hz or s^{-1})



- A polarizable molecule in an electric field will have an induced dipole that oscillates:
 - $\mu = \alpha [E_0 \sin(2\pi\nu t)]$ (1)
- An oscillating dipole will radiate light of frequency ν which gives rise to RAYLEIGH scattering of light (also called elastic scattering)

Scattering (wave nature of light)

- A vibrating molecule will change the polarizability (remember bigger molecules are more polarizable).
- Therefore the polarizability of the molecule will *oscillate* at the molecule's own characteristic frequency ν_{vib} :
 - $\alpha = \alpha_0 + \beta \sin(2\pi\nu_{\text{vib}} t)$ (2)

Scattering (wave nature of light)

- Combining (1) and (2)*:
 - $\mu = [\alpha_0 + \beta \sin(2\pi\nu_{\text{vib}} t)] \times [E_0 \sin(2\pi\nu t)]$
 - $= [\alpha_0 E_0 \sin(2\pi\nu t)] + [\beta E_0 \sin(2\pi\nu_{\text{vib}} t) \sin(2\pi\nu t)]$
 - $= [\alpha_0 E_0 \sin(2\pi\nu t)] + \frac{1}{2} \beta E_0 [\cos(2\pi(\nu - \nu_{\text{vib}}) t) - \cos(2\pi(\nu + \nu_{\text{vib}}) t)]$
- The oscillating dipole has frequency components:
 - $\nu + \nu_{\text{vib}}$ and $\nu - \nu_{\text{vib}}$
- It will *radiate*, albeit weakly, at these $\nu + \nu_{\text{vib}}$ and $\nu - \nu_{\text{vib}}$:
RAMAN scattering

* $\sin A \sin B = \frac{1}{2} [\cos(A-B) - \cos(A+B)]$

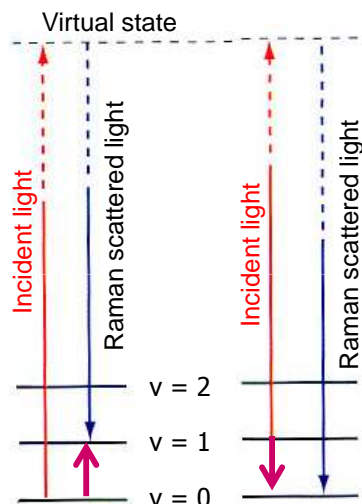
Rayleigh and Raman scattering

$$\mu = \underbrace{[\alpha_0 E_0 \sin(2\pi\nu t)]}_{\text{Rayleigh scattering}} + \frac{1}{2} \beta E_0 \underbrace{[\cos(2\pi(\nu - \nu_{\text{vib}}) t) - \cos(2\pi(\nu + \nu_{\text{vib}}) t)]}_{\text{Raman scattering}}$$

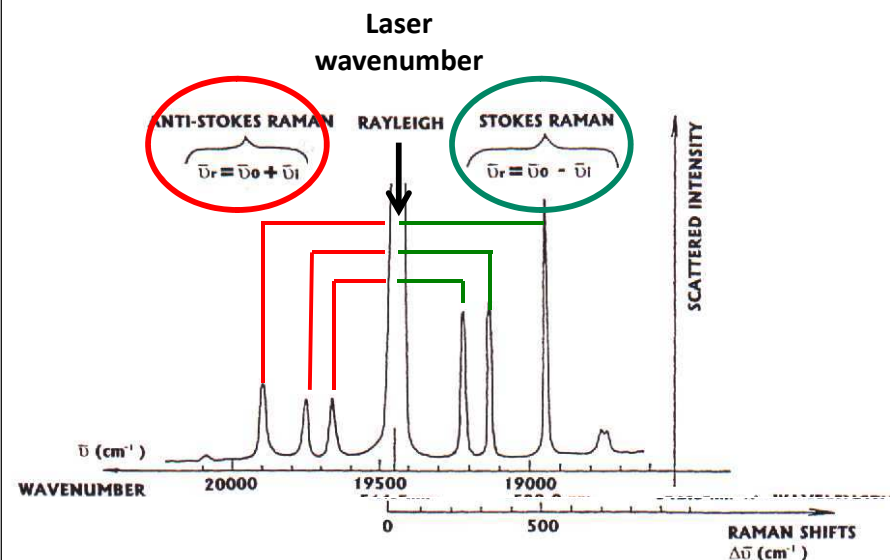
- Rayleigh scattering
 - Same λ or ν
 - Depends on E_0
 - Depends on α_0
- Raman scattering
 - $\nu_{\text{scattering}}$ *shifted* by vibrational frequency of molecule
 - Depends on E_0
 - Depends on β (change in polarizability)

Raman scattering

- A Raman spectrum arises when a photon *scatters* from a molecule.
- In the scattering of the photon from the molecule the molecule may be left in a *higher* vibrational state, and hence the photon must have *lost* the same amount of energy
- Alternatively, the molecule may be left in a *lower* vibrational state, and hence the photon must have *gained* the same amount of energy.

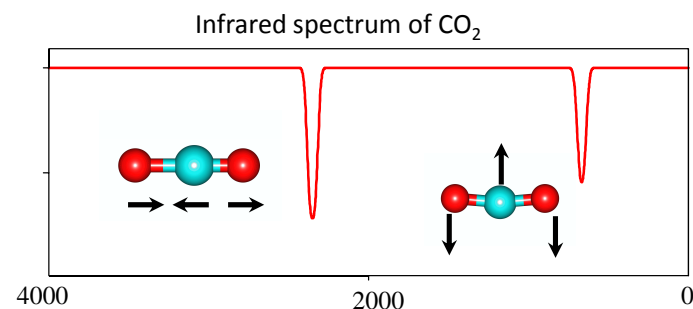


A Raman spectrum



Vibrational spectroscopy spectrum rules

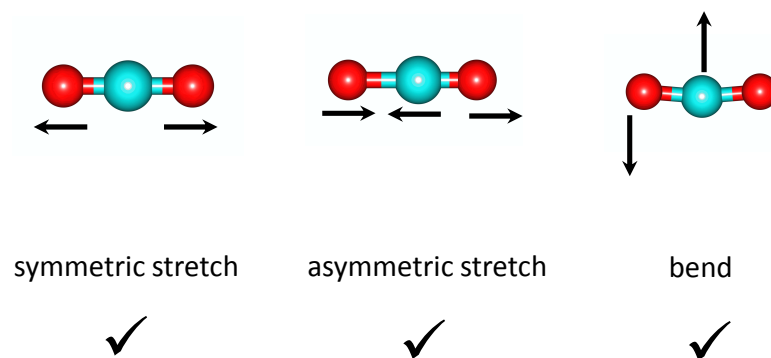
- Gross selection rule in IR spectroscopy: vibration must lead to an oscillating dipole



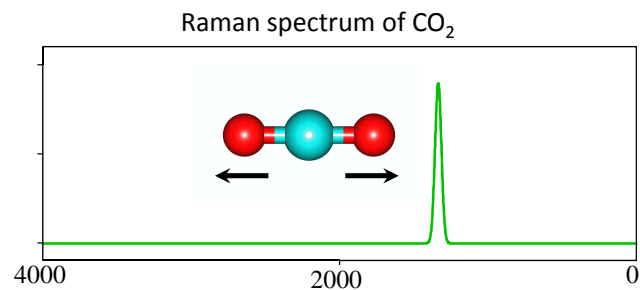
- Gross selection rule in Raman spectroscopy: vibration must lead to a change in polarizability

Vibrational spectroscopy spectrum rules

- Which modes will have a change in polarizability?



Vibrational spectroscopy spectrum rules

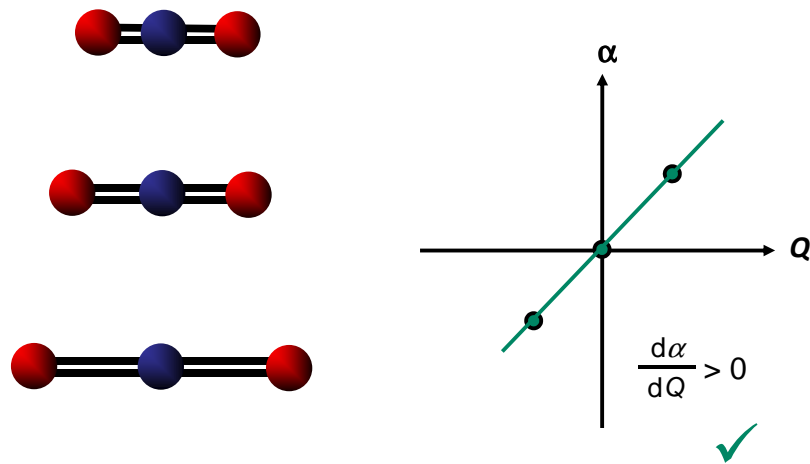


- Only the symmetric stretch is observed. What happened to the other two vibrations?

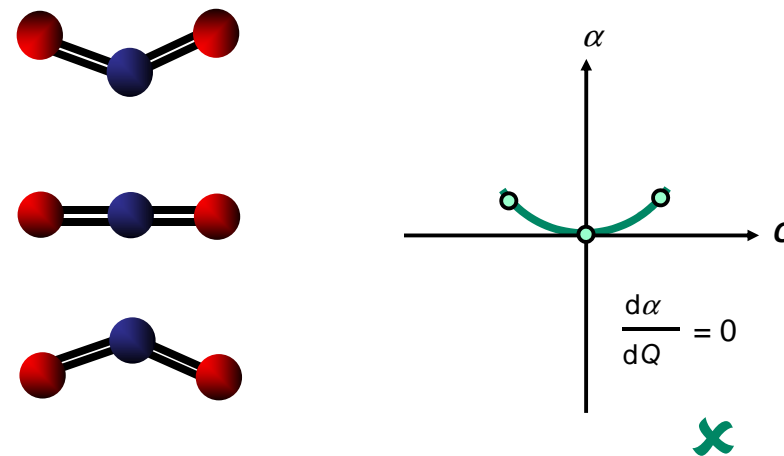
Change in polarizability = $d\alpha/dQ$

- α is the polarizability and Q is a generic vibrational coordinate (e.g. r for a stretch, θ for a bend, etc)
- Need to examine how α changes along the vibration for each mode

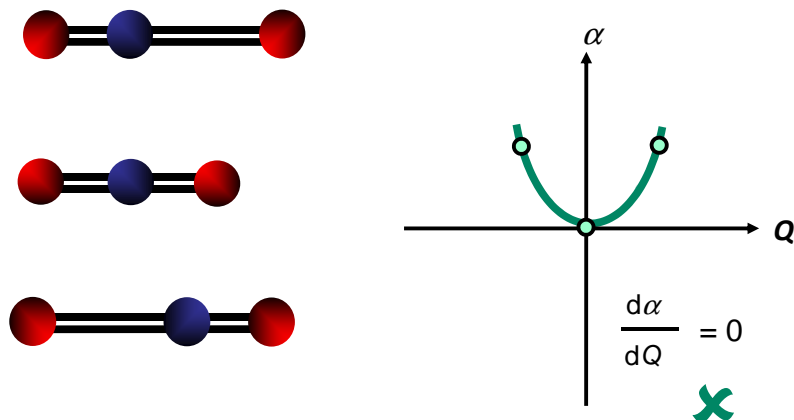
Symmetric stretch



Bend



Asymmetric stretch



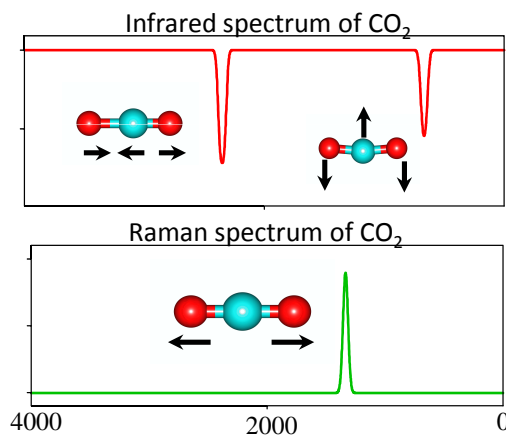
Raman selection rules

- Vibrations that have a *symmetric* polarizability change do not appear in Raman.
- Bending vibrations are not strong Raman modes.
- Symmetric stretches tend to be strong Raman modes.

Vibrational spectroscopy spectrum rules

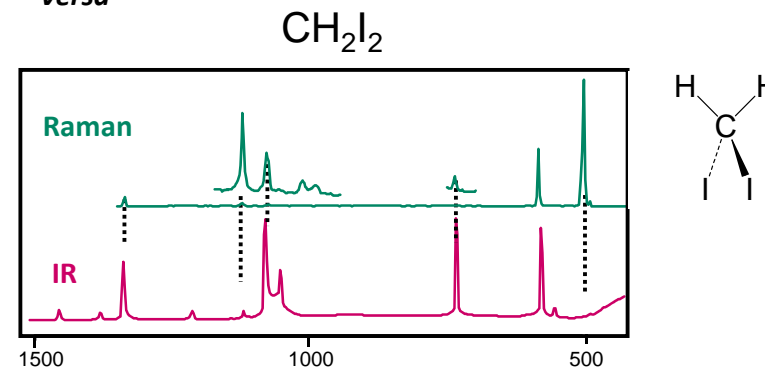
- IR: vibration must lead to an oscillating dipole
- Raman: vibration must lead to a change in polarizability

- Raman spectroscopy *complements* IR spectroscopy because the gross selection rule is different



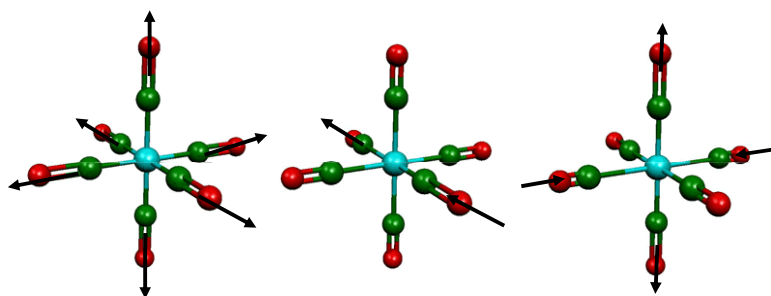
Combined use of IR and Raman to work out structure

- Bending vibrations are not strong Raman modes.
- In general, vibrations can be in both IR and Raman but those which are strong in IR tend to be weak in Raman, and *vice versa*



Metal Carbonyl Complexes: $M(CO)_6$

- Octahedral complex: see $C\equiv O$ stretches

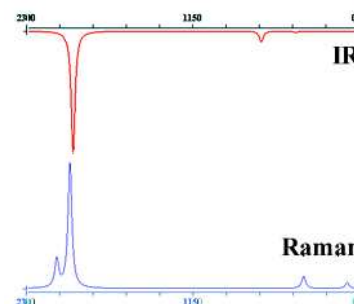


IR?
 Raman?



Metal Carbonyl Complexes: $M(CO)_6$

- Octahedral $M(CO)_6$



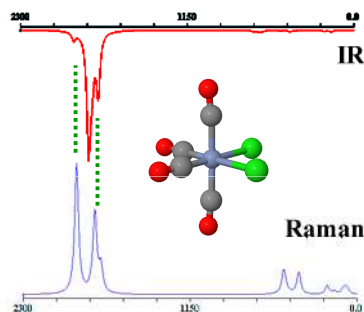
ν (CO stretches):
1 IR
2 Raman

rule of mutual exclusion: for molecules with a centre of inversion (symmetry), no vibrations are both IR and Raman active



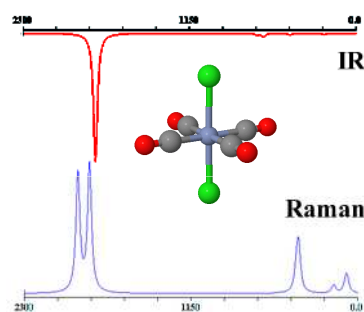
Metal Carbonyls: $[M(CO)_4X_2]$

- cis*- $[M(CO)_4X_2]$



ν (CO stretches):
4 IR (1 very weak)
4 Raman (1 very weak)
some *common* bands

- trans*- $[M(CO)_4X_2]$



ν (CO stretches):
1 IR
2 Raman
no common bands –
rule of mutual exclusion



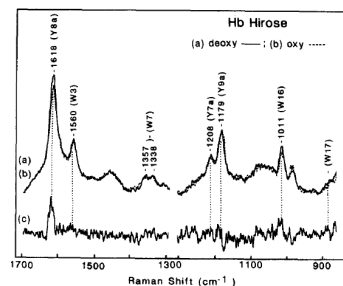
Applications of Raman Spectroscopy

- Although Raman can clearly be used to extract bond lengths, dissociation energies, etc, this is simply not the main use of the technique. Raman spectroscopy requires the use of high powered lasers and the same information is more readily obtained from normal IR spectroscopy.
- Advantages:
 - no absorption of light, therefore less damage to a specimen;
 - uses visible light, so can be used with imaging techniques (microscopes etc);
 - uses a laser so can have high spatial resolution;
 - highly specific for different compounds (good for fingerprinting)

Resonance Raman

- In the normal Raman experiment, visible laser light is chosen which does *not* correspond to an absorption
- In resonance Raman, the laser *matches* an absorption
 - this leads to enhancement of vibrations of bonds near absorbing centre
- Widely used in bioinorganic chemistry to probe metal centre in enzyme: provides information on active site in large molecule

Resonance Raman spectrum of deoxy- and oxyhaemoglobin showing vibrations of porphyrin ring



13th Century Illuminated Text



Raman Microscopy Of A 13th-Century Illuminated Text R. J. H. Clark and P. J. Gibbs.
Analytical Chemistry News & Features, February 1, 1998; pp. 99 A-104 A.
<http://pubs.acs.org/hotartcl/ac/98/feb/raman.html>

13th Century Illuminated Text



- Aim:
Identify palette,
Establish conservation problem,
Provide data for proposed treatment to reverse degradation.
- Sample:
Byzantine/Syriac Gospel lectionary dates from 1216-20 A.D.
Valued at > \$1 million USD
- Technique:
Raman Microscopy
× 50 or × 100 objective
 $\lambda_{\text{ex}} = 488, 514.5, 647.1 \text{ nm}$

Deterioration of the Illuminations

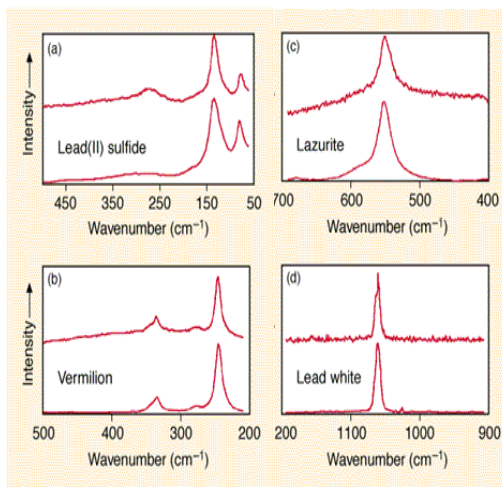


Deterioration has occurred mainly around the edges of the illuminations. The phenomenon is most striking on the figures faces.

Unaffected areas are used for comparison and assist in determination of the original colour scheme.



Analysis of the Pigments



- Analysis revealed seven pigments or compounds.
 lead white
 lead(II) sulfide
 vermilion,
 lapis lazuli,
 orpiment,
 realgar, and
 pararealgar

Summary

- In the Raman experiment, visible light is shined on a sample
- Most light is simply scattered with the same frequency (Rayleigh)
- Some light is scattered have lost (Stoke's) or gained (anti-Stoke's) energy corresponding to the vibrational frequencies of the molecule
- A vibration must lead to a change in polarizability to show the Raman effect
 - Vibrations that have a *symmetric* polarizability change do not appear in Raman.
 - Bending vibrations are not strong Raman modes.
 - Symmetric stretches tend to be strong Raman modes.
- Raman is complementary to IR
 - Peaks which are strong in IR tend to be weak in Raman, and *vice versa*
 - For molecules with a centre of inversion, no peaks are present in *both*

Next lecture

- Electronic spectroscopy

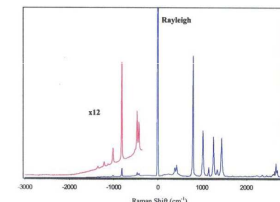
Week 12 homework

- Vibrational spectroscopy worksheet in tutorials
- Practice problems at the end of lecture notes
- Play with the "IR Tutor" in the 3rd floor computer lab and with the online simulations:

<http://assign3.chem.usyd.edu.au/spectroscopy/index.php>

Practice Questions

- The Raman spectrum of cyclohexane is shown below. The very intense peak in the middle of the spectrum is Rayleigh scattering from the laser.
 - Explain the difference between Rayleigh and Raman scattering
 - (i) What are the collective names given to the peaks in the spectrum at positive and at negative Raman shift?
 (ii) Explain how the peaks at positive and negative Raman shift arise.
 (iii) Why are the peaks at negative Raman shift weaker than that at positive Raman shift?



- Which of the molecules below will exhibit a Raman spectrum?
 (a) HBr (b) Cl₂ (c) CO₂ (d) HCO (e) CH₄
- Which vibrations of acetylene (C₂H₂) will show up in the Raman spectrum?
 (a) symmetric CH stretch (b) asymmetric CH stretch (c) C≡C stretch (d) symmetric bend (e) asymmetric bend
- Which vibrations of carbonyl sulfide (OCS) will show up in the Raman spectrum?
 (a) C=S str. (b) C=O str. (c) bend