Principles of Raman Spectroscopy

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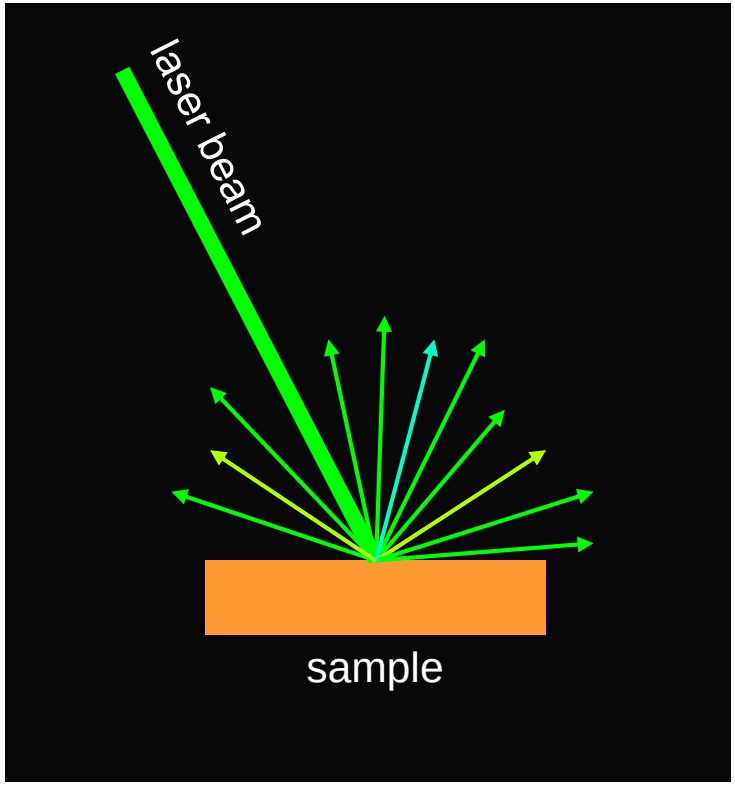
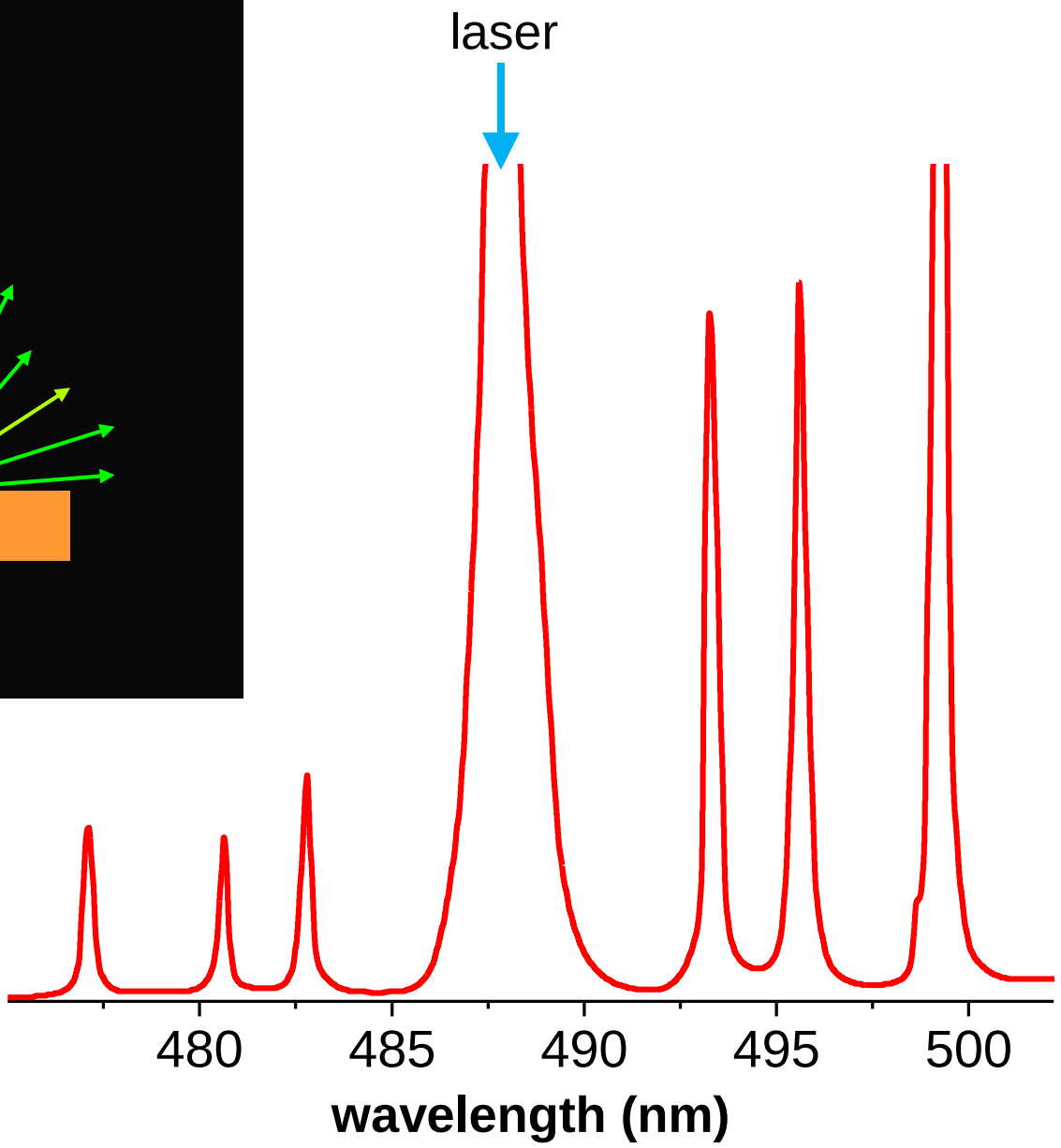
The phenomenon of Raman scattering





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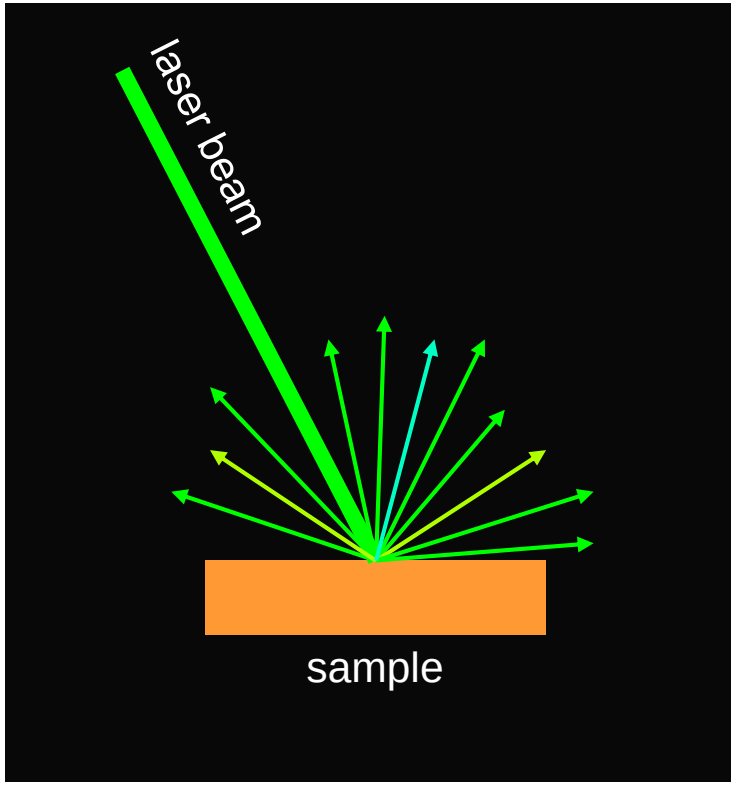

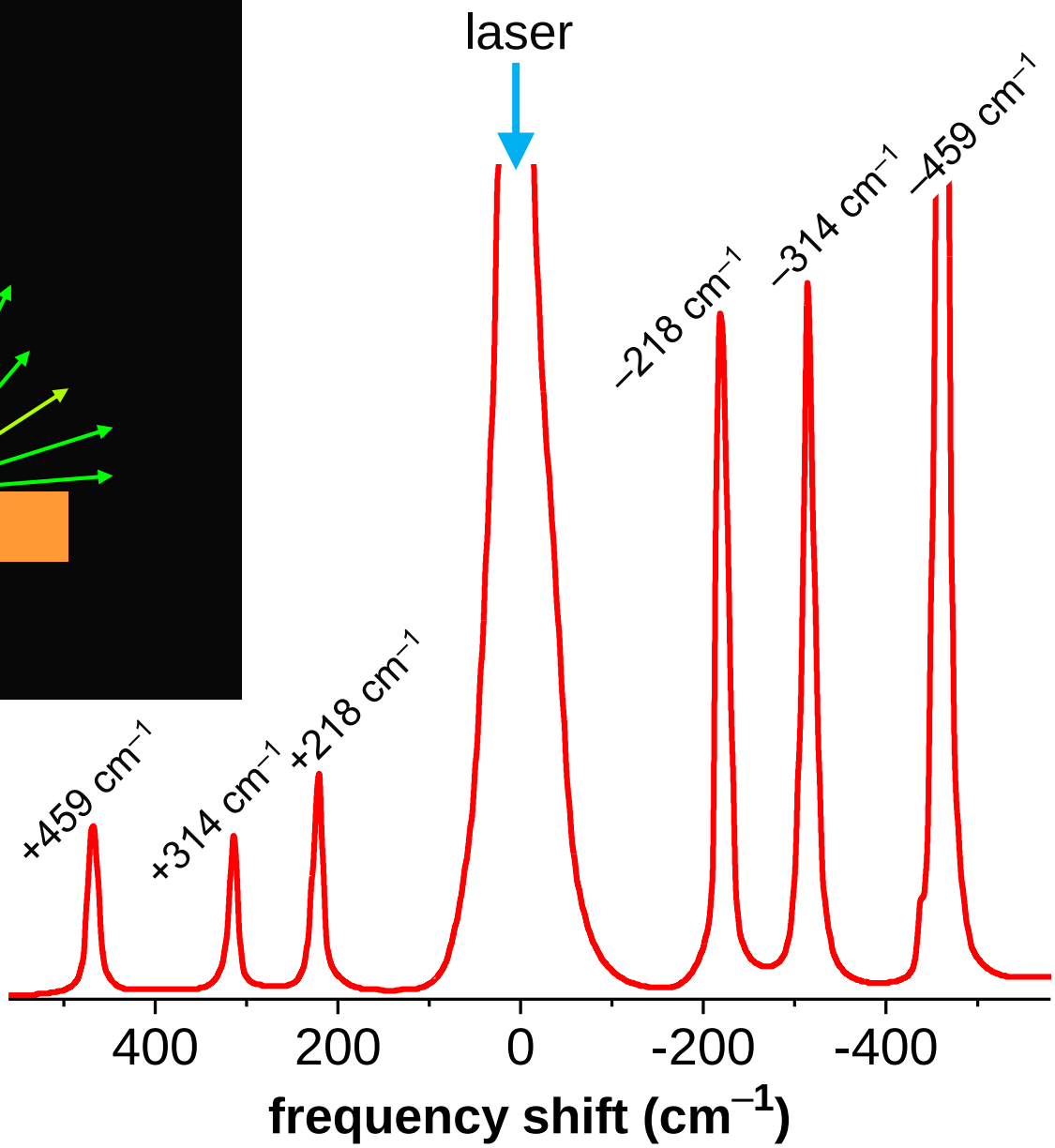

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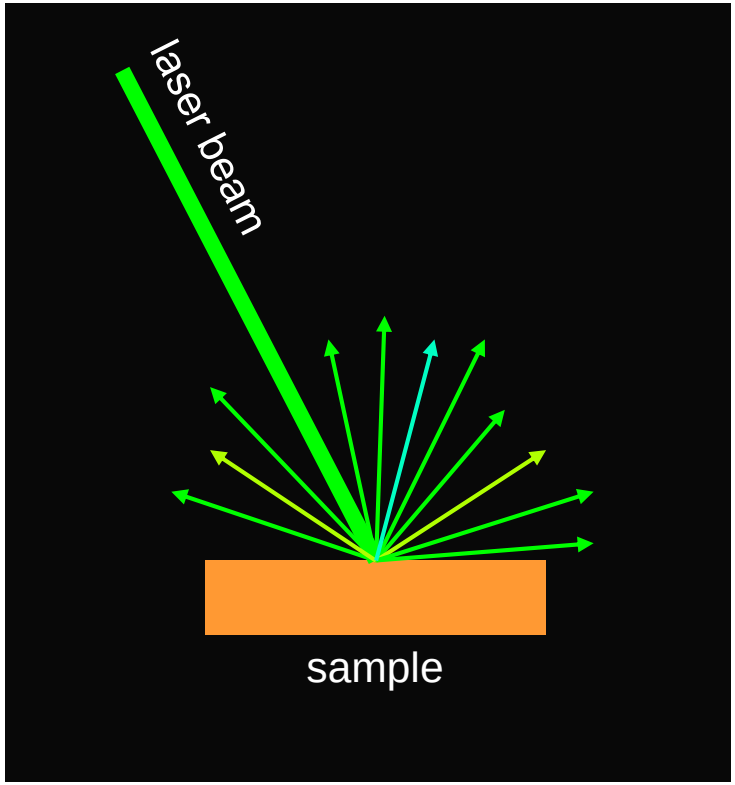
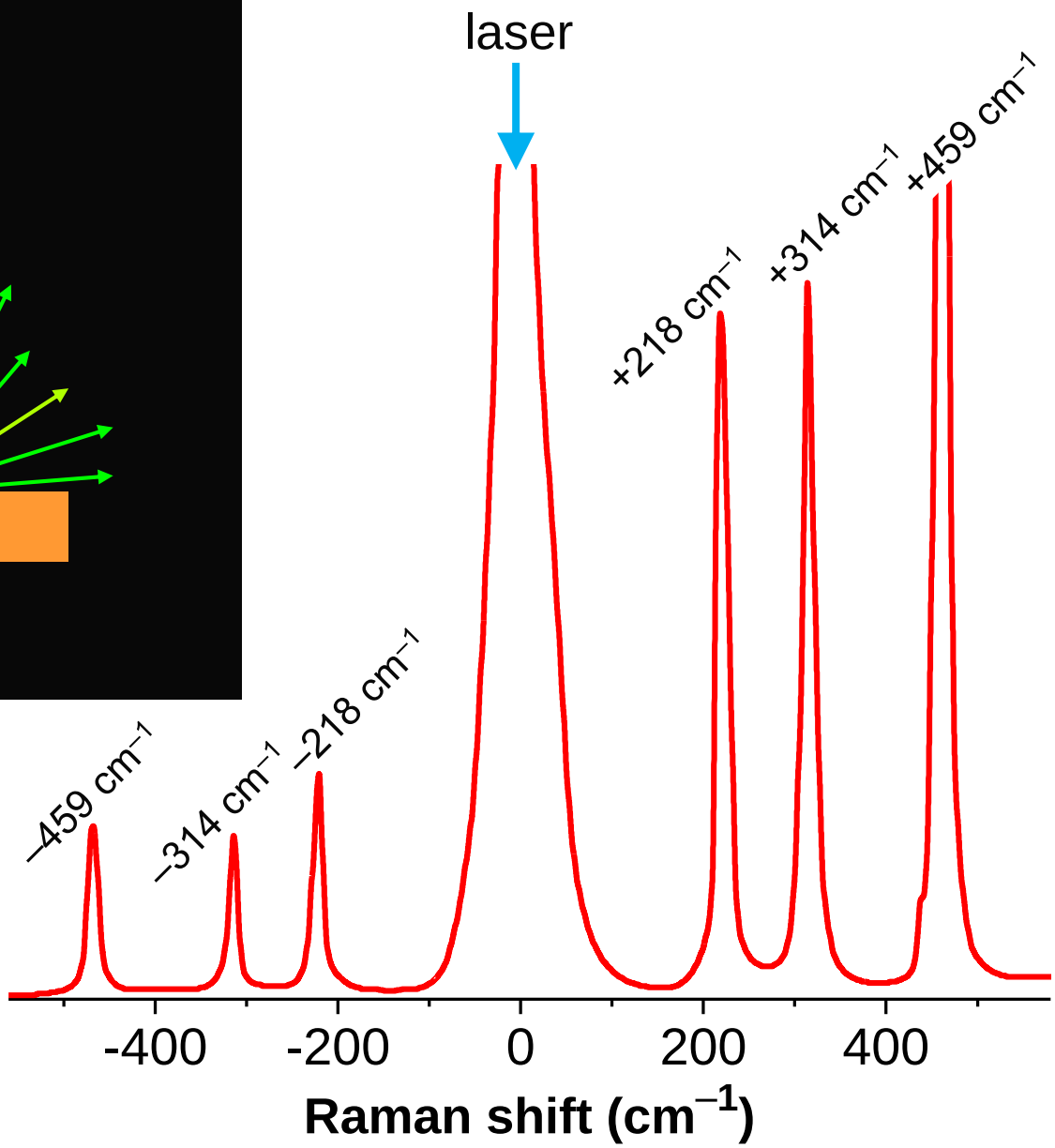
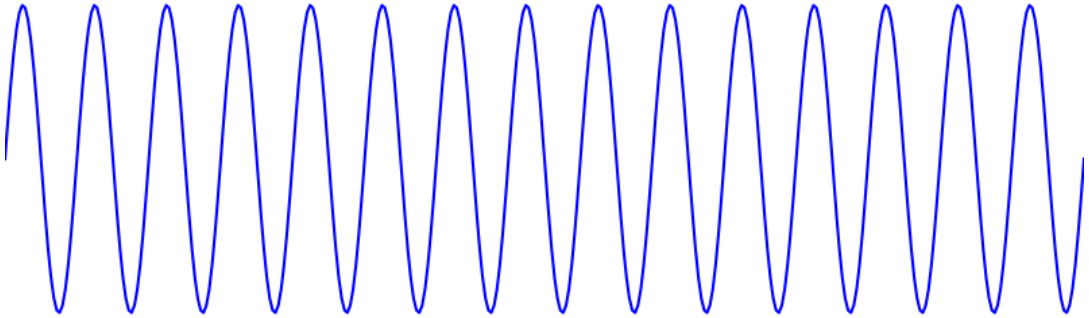




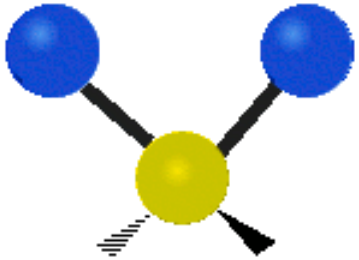
Classical interpretation of Raman scattering

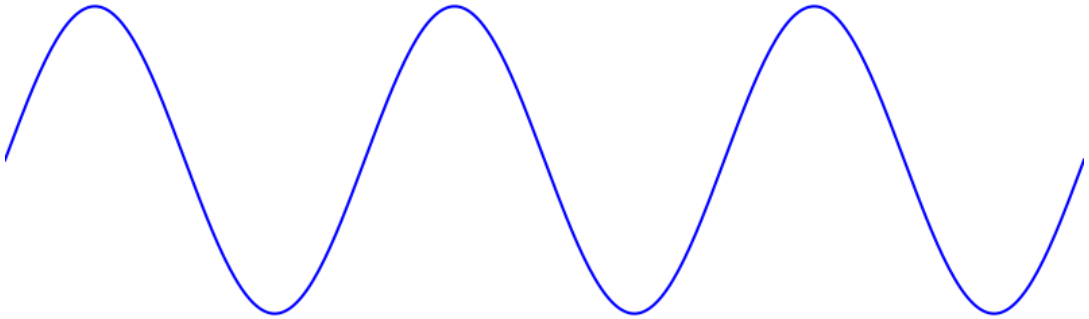
incident light wave

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



molecular vibration

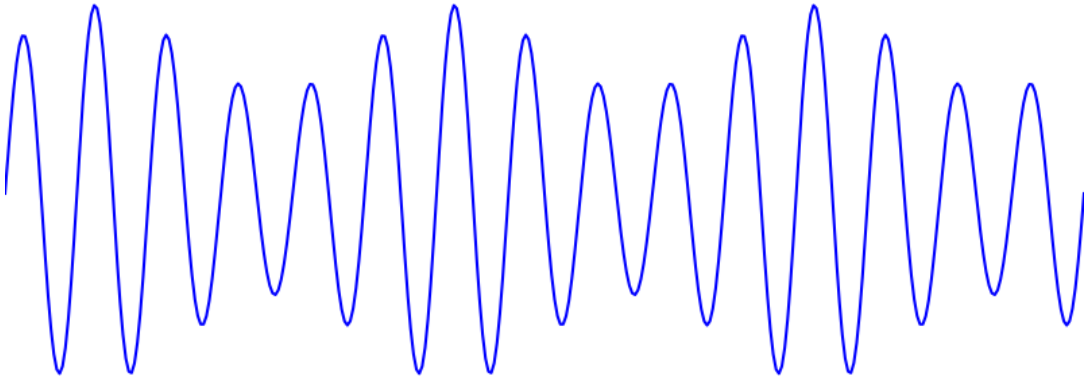




$$q(t) = q_0 \cos \Omega t$$

induced dipole moment

$$p(t) = \alpha(q)E(t)$$



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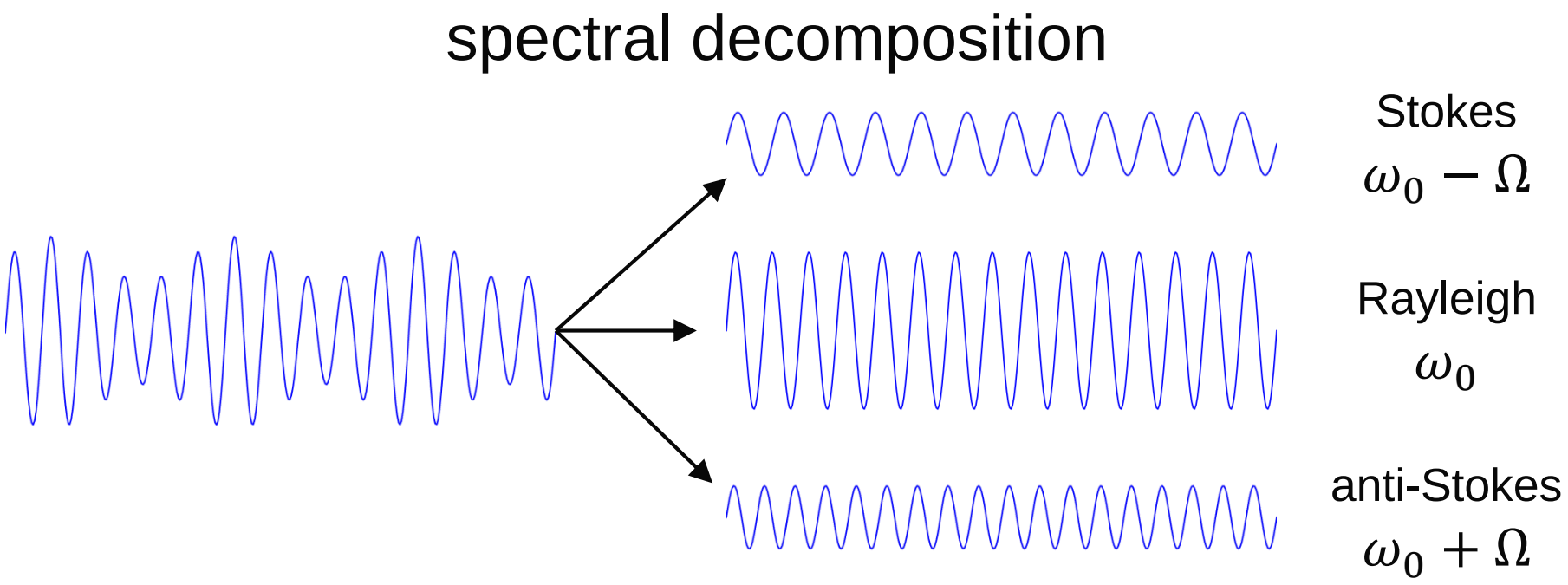
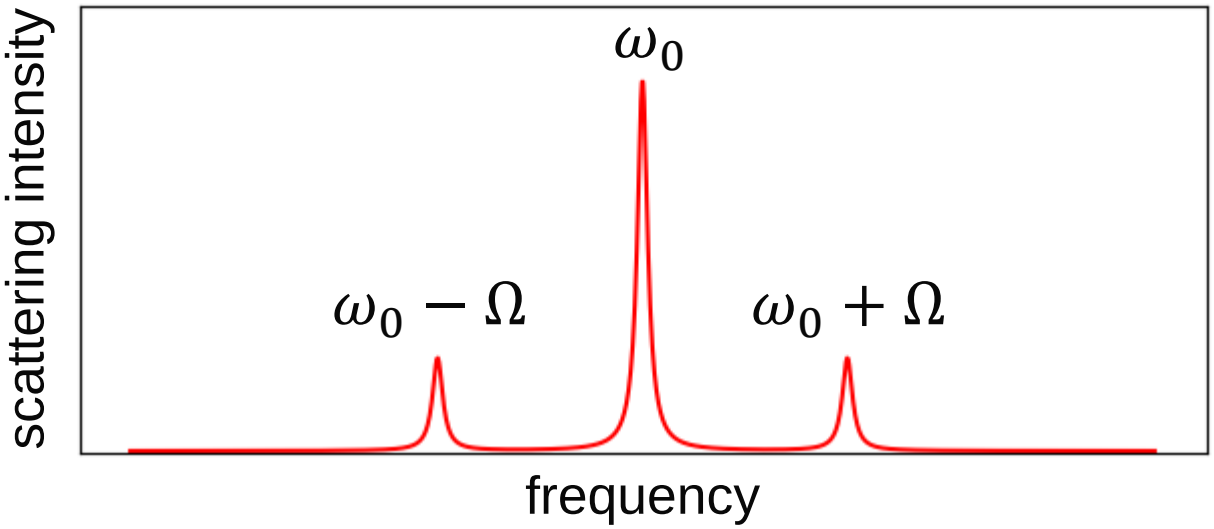
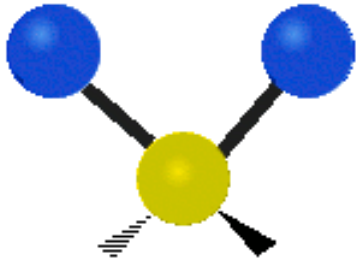
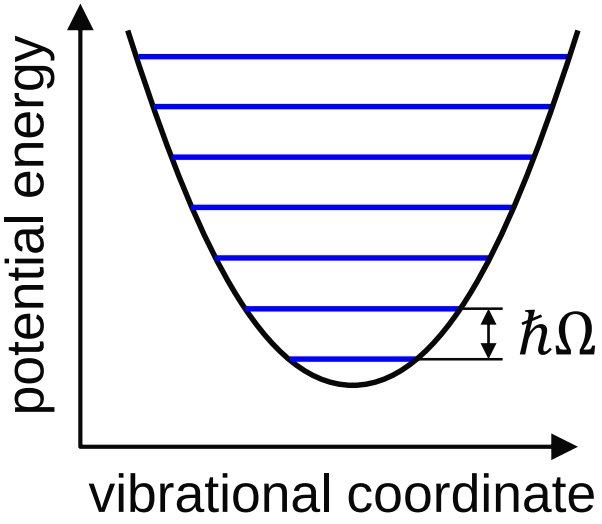




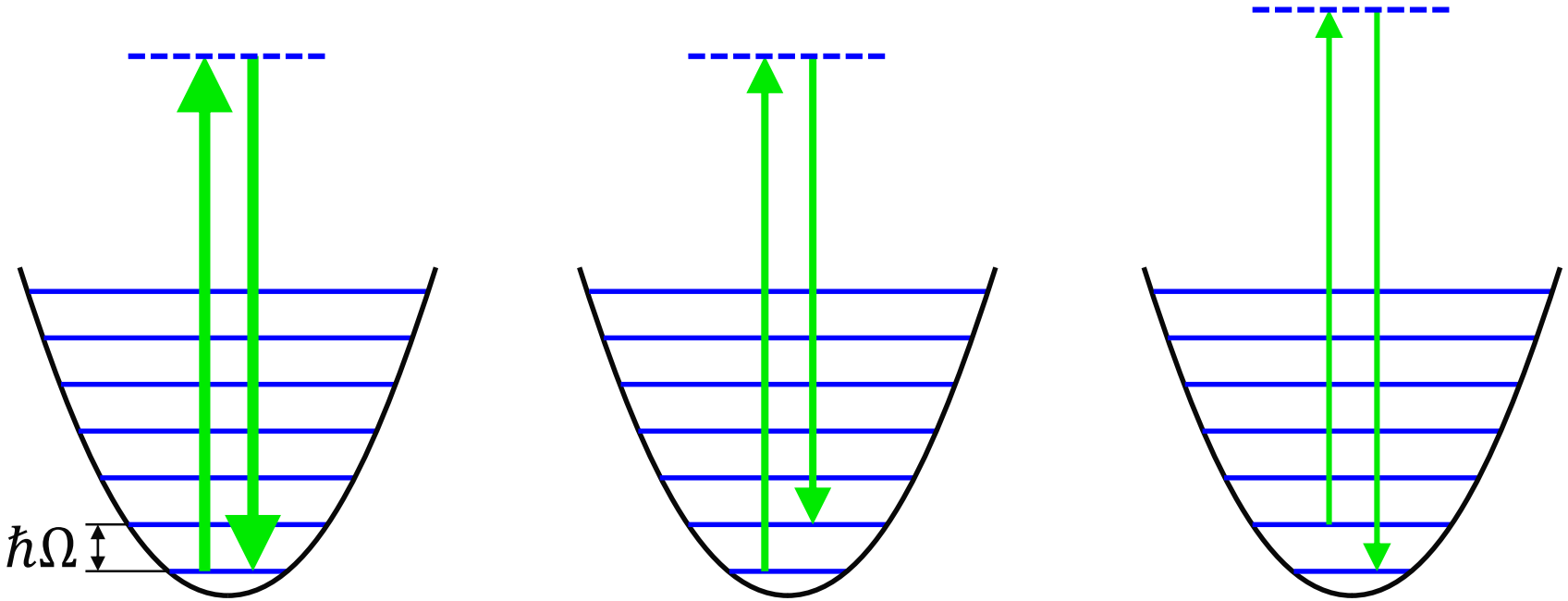
Quantum interpretation of Raman scattering



$$q(t) = q_0 \cos \Omega t$$



Quantum interpretation of Raman scattering



Rayleigh

Stokes

$$\hbar\omega = \hbar\omega_0 - \hbar\Omega$$

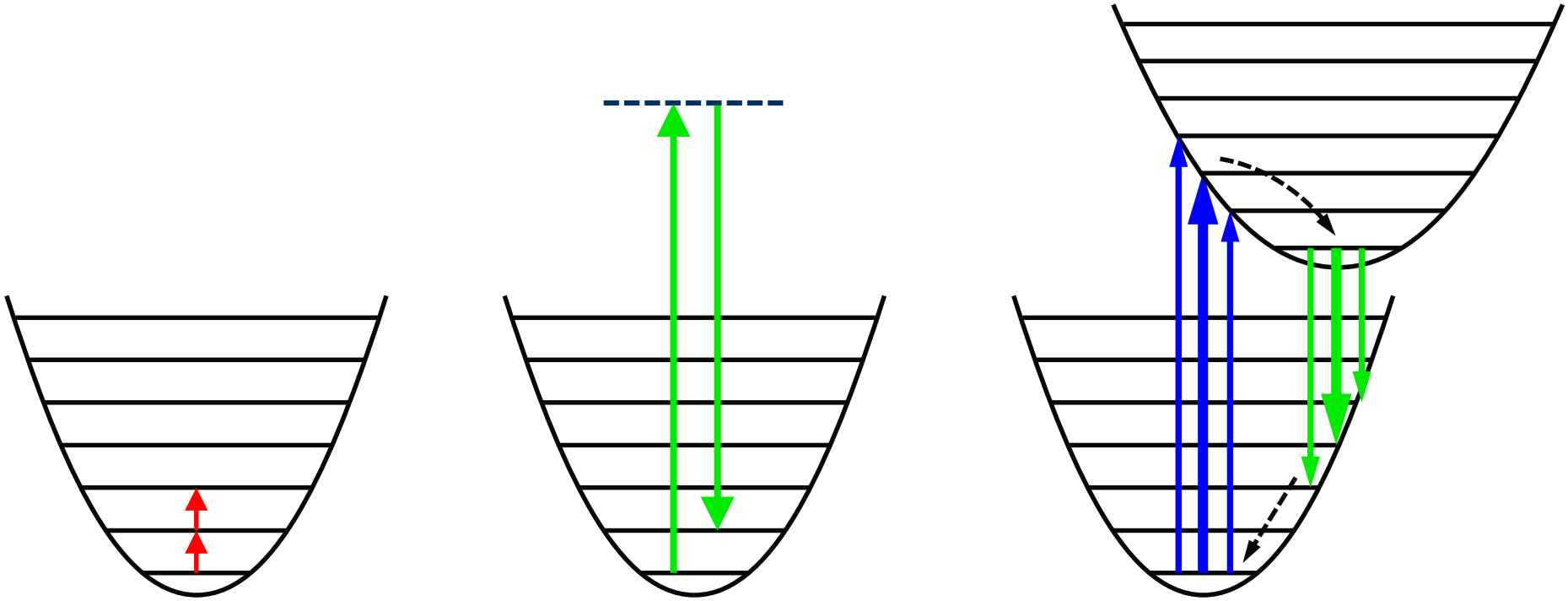
$$\omega = \omega_0 - \Omega$$

anti-Stokes

$$\hbar\omega = \hbar\omega_0 + \hbar\Omega$$

$$\omega = \omega_0 + \Omega$$

Relation to other molecular spectroscopies

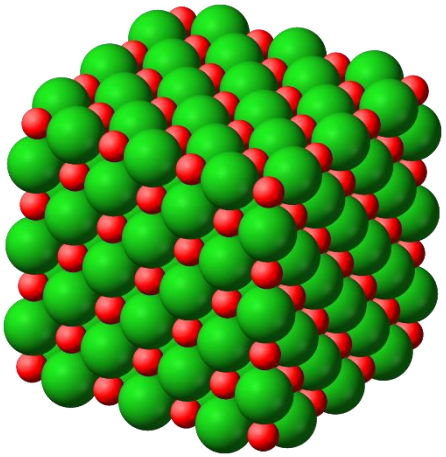


IR-absorption

Raman scattering

UV-VIS absorption
and fluorescence

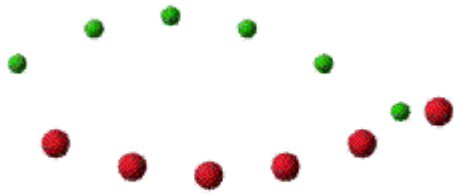
Raman spectroscopy of crystals



regularly packed
array of atoms

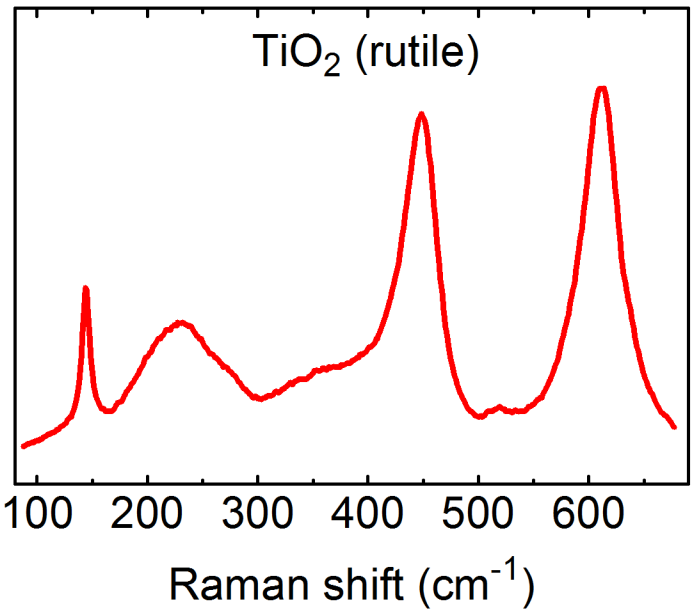
acoustic vibrations
(low frequencies)

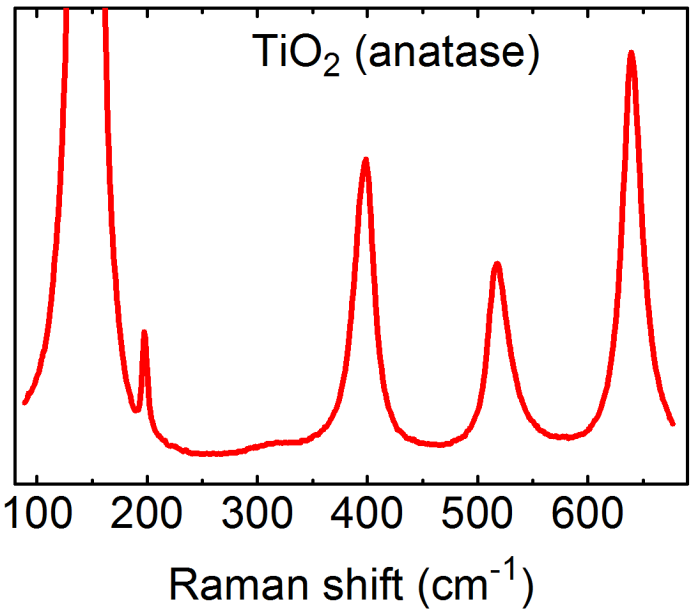
optical vibrations
(high frequencies)

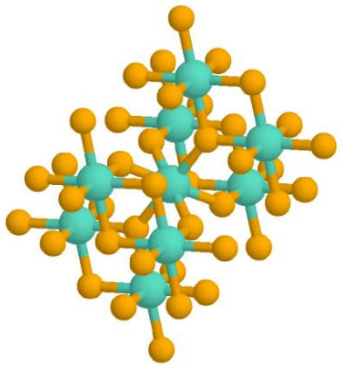


Raman spectroscopy of crystals

same chemical substance, different crystalline structures







https://en.wikipedia.org/wiki/Rutile
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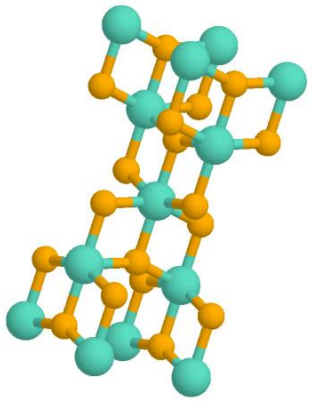

https://en.wikipedia.org/wiki/Anatase
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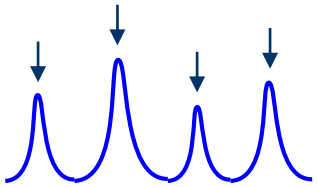
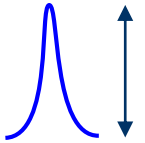
Information from Raman spectra

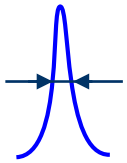


peak positions → molecular frequencies, chemical and phase content

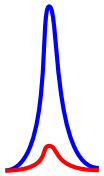


intensities → amount of substance (film thickness, crystalline/amorphous ratio, …)

peak shifts → mechanical stresses



linewidths → crystal quality (crystallinity, defects, impurities)

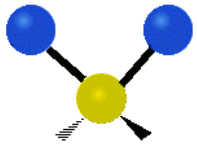
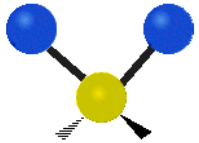
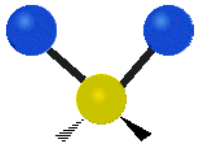
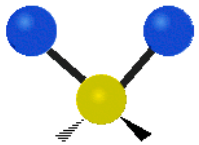
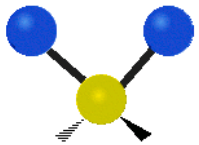
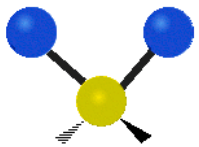


polarization → symmetry and orientation

Comparison of Raman and IR spectroscopies

	Raman	Infrared absorption
Detected vibrations		
- **vibrational modes**	symmetric (e.g., homo-nuclear)	asymmetric (e.g., hetero-nuclear)
- **frequencies**	relative	absolute
- **low frequency modes**	excellent	difficult
Sample preparation		
- **liquids**	very simple	very simple
- **powders**	very simple	simple
- **polymers**	very simple	simple
- **gases**	simple	very simple
Aqueous solutions	very good	very difficult
Fluorescence	may strongly interfere	no impact
Possibility of non-destructive analysis	good	very good

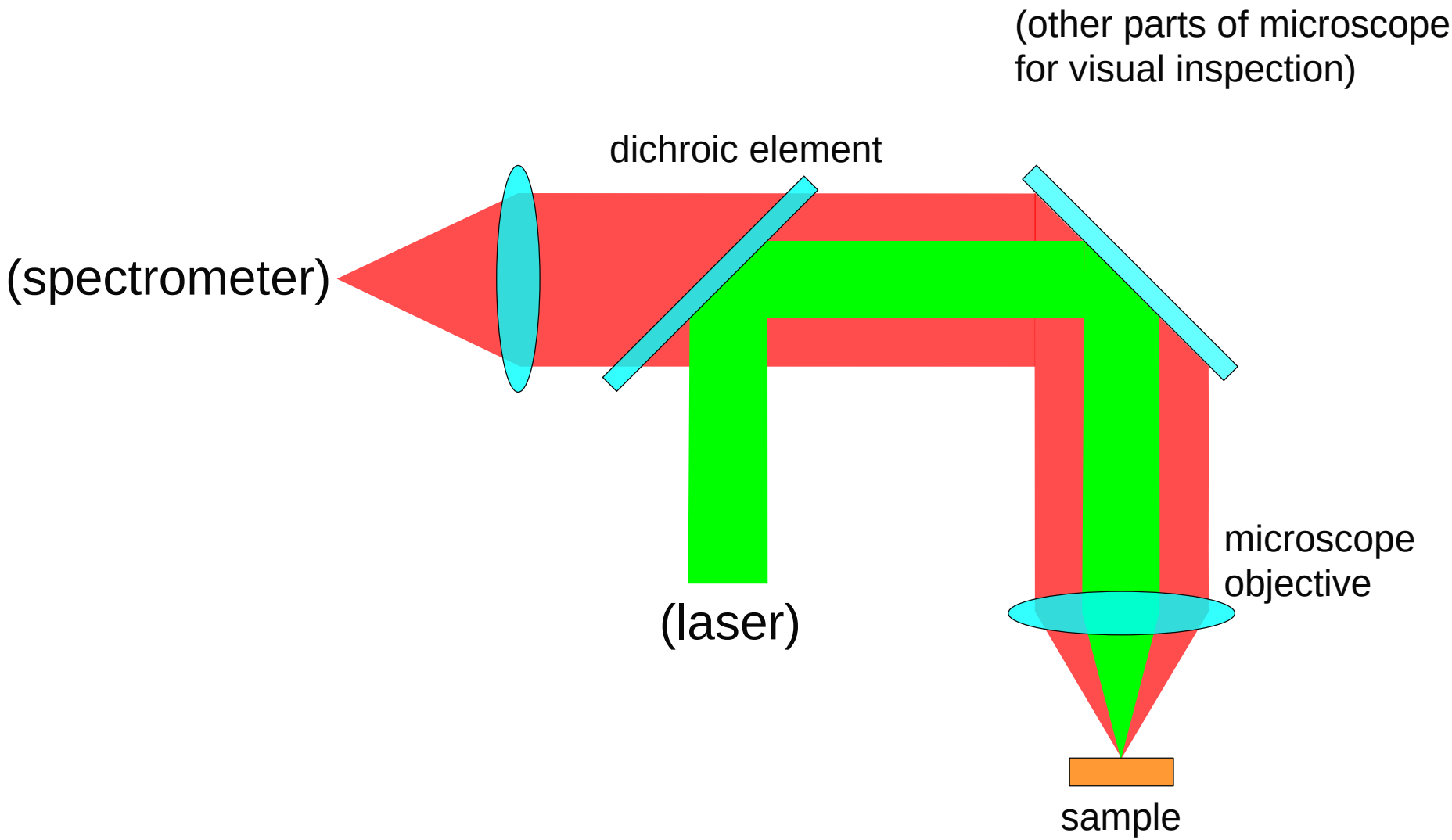
Comparison of Raman and IR spectroscopies

symmetrical stretching		Raman
anti-symmetrical stretching		infrared
scissoring		Raman
rocking		infrared
twisting		Raman
wagging		infrared

Raman micro-spectrometer

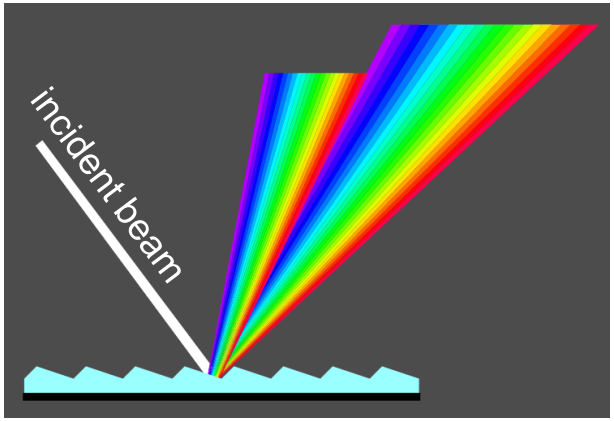
- ✓ sensitivity
- ✓ spectral resolution
- ✓ spatial resolution

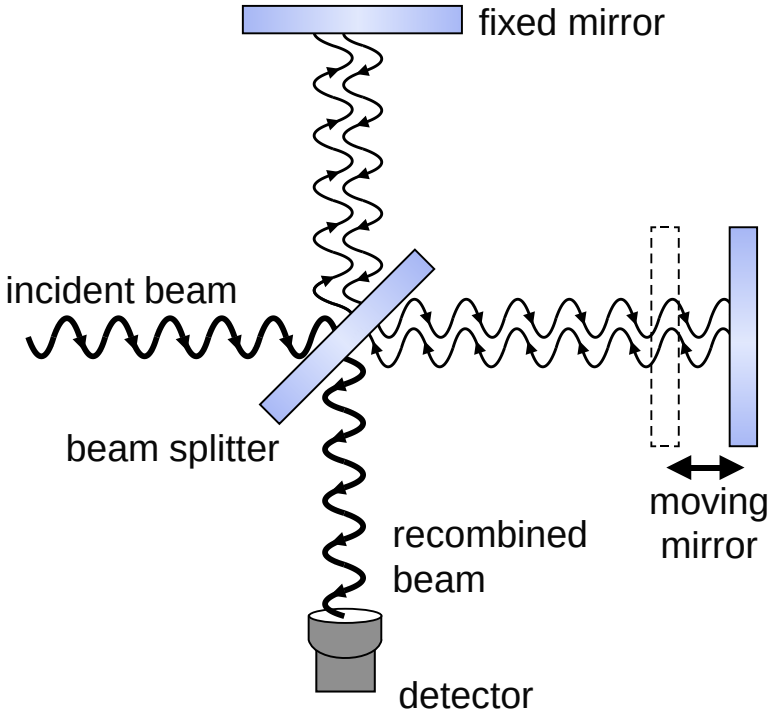
Raman micro-spectrometer



Spectrometer

- Dispersive
  - spatial separation of wavelengths (by diffraction grating)
  - usually CCD array detector is used
  - excellent removal of the Rayleigh line
  - optimal in visible region
- Interferometric (FT-Raman)
  - modulation of spectral components (due to interference)
  - the spectrum is recovered by Fourier transform of the interferogram
  - uses a point detector
  - excellent wavelength precision
  - optimal in NIR region (and for strongly fluorescing samples)
  - can combine IR absorption and Raman





https://en.wikipedia.org/wiki/Fourier-transform_infrared_spectroscopy, Petergans [Public domain, license CC-by-SA 3.0]

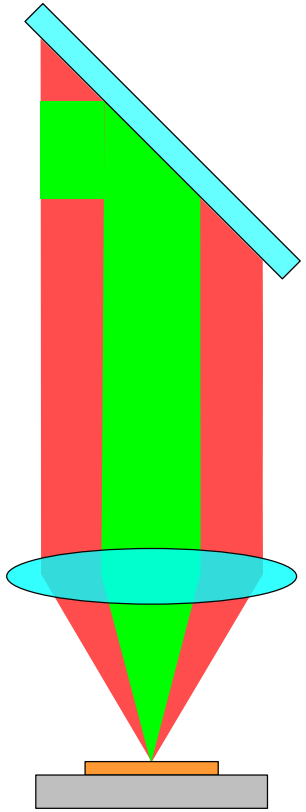
Challenges

⚠ Presence of fluorescence
- optimize excitation wavelength

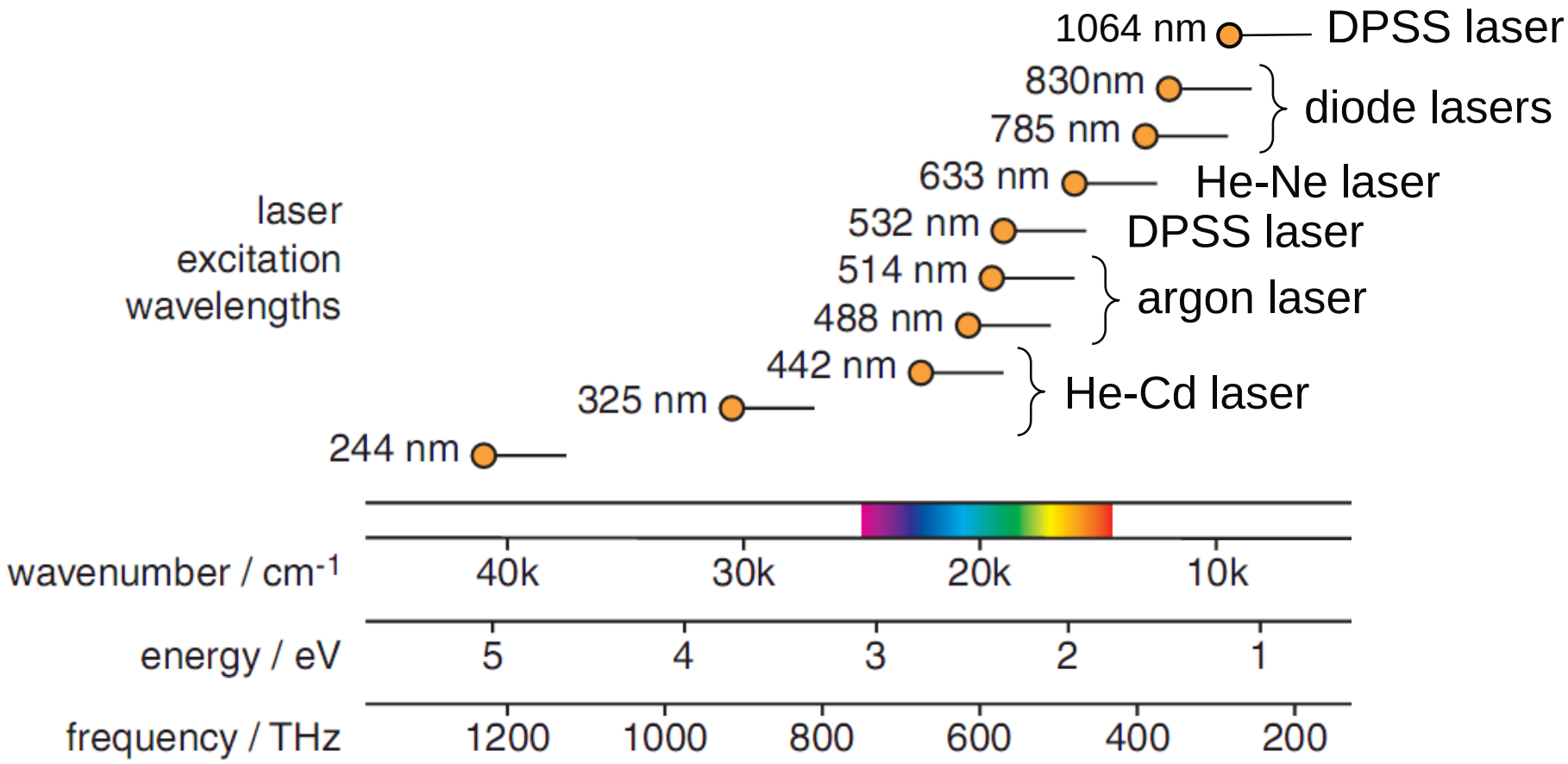
⚠ Heating/damaging of sample under a high irradiance (~10 mW/μm^2)
- attenuate or defocus laser
- optimize excitation wavelength

⚠ Short working distance (~0.2 mm) of the objective lens
- special LWD objectives available

⚠ Strong signal from substrate
- use another substrate
- prepare a thicker layer
- correct for the substrate spectrum



Typical excitation sources



Choosing excitation wavelength

Visible lasers:

- ✓ strong Raman lines (Raman cross section $\propto \lambda^{-4}$)
- ✓ may allow measurement of strongly absorbing (dark) samples
- ✗ may induce a strong fluorescence background

NIR lasers:

- ✓ low photon energy cannot excite fluorescence
- ✗ less effective Raman excitation
- ✗ more powerful laser beam required, may heat up or damage the sample

Summary

- The Raman effect reveals molecular vibrations in visible or NIR spectral range
- Complementary to IR absorption
  - a vibration is usually observed only in one of the spectra
  - technical issues
- It is necessary to choose appropriate excitation wavelength and laser power to
  - reveal the inherently weak Raman lines
  - avoid strong background fluorescence
  - avoid heating/damaging of the sample in the focused laser beam