- **Problem:**

  Calculate the frequency (ν) of light with a wavelength (λ) of 500 nm. The speed of light (c) is 3×10^{8} m/s.

- **Solution:**

  Frequency is calculated using the formula:

$$\text{Frequency } (\nu) = \frac{\text{Speed of Light } (c)}{\text{Wavelength } (\lambda)}$$

  Substituting the values:

$$\nu = \frac{3 \times 10^{8}\,\mathrm{m/s}}{500 \times 10^{-9}\,\mathrm{m}}$$

$$\nu = 6 \times 10^{14}\,\mathrm{Hz}$$

  So, the frequency is 6×10^{14} Hz.

- **Problem:**

  Calculate the energy of a photon with a frequency of 4×10^{14} Hz. Planck's constant (h) is 6.626×10^{-34} J·s.

- **Solution:**

  Energy is calculated using the formula:

$$E = h \times \nu$$

  Substituting the values:

$$E = 6.626 \times 10^{-34}\,\mathrm{J\,s} \times 4 \times 10^{14}\,\mathrm{Hz}$$

$$E = 2.6504 \times 10^{-19}\,\mathrm{J}$$

  So, the energy of the photon is 2.6504×10^{-19} J.

- **Problem:**

  A solution has a molar absorptivity (ε) of $2000\,\mathrm{L/mol\cdot cm}$ and a path length (l) of 1 cm. If the concentration (c) is $0.01\,\mathrm{M}$, calculate the absorbance (A).

- **Solution:**

  Absorbance is calculated using the formula:

$$A = \varepsilon \times c \times l$$

  Substituting the values:

$$A = 2000\,\mathrm{L/mol\cdot cm} \times 0.01\,\mathrm{mol/L} \times 1\,\mathrm{cm}$$

$$A = 0.02$$

  So, the absorbance is 0.02.

NMR Chemical Shift

- **Problem:**

  In a ^{1}H NMR spectrum, the resonance frequency of a proton is observed at 300.5 MHz. The reference frequency is 300 MHz. Calculate the chemical shift in ppm.

- **Solution:**

  Chemical shift is calculated using the formula:

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\nu_{\text{reference}}} \times 10^6\,\text{ppm}$$

  Substituting the values:

$$\delta = \frac{300.5\,\mathrm{MHz} - 300\,\mathrm{MHz}}{300\,\mathrm{MHz}} \times 10^6\,\text{ppm}$$

$$\delta = \frac{0.5}{300} \times 10^6\,\text{ppm}$$

$$\delta = 1.67\,\text{ppm}$$

  So, the chemical shift is 1.67 ppm.

- **Problem:** Calculate the chemical shift in ppm (δ) for a proton that has resonance at 150 Hz downfield from TMS on an NMR spectrophotometer that operates at 60 MHz.
- **Solution:** The chemical shift (δ) is calculated using the formula:

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{Operating Frequency (in MHz)}}$$

  Where:

  - $\nu_{\text{sample}} - \nu_{\text{TMS}}$ is the difference in frequency (Δν).
  - The operating frequency is given in MHz.

  Substituting the given values:

$$\delta = \frac{150\,\text{Hz}}{60\,\text{MHz}}$$

  Convert the operating frequency from MHz to Hz by multiplying by 10^6:

$$\delta = \frac{150\,\text{Hz}}{60 \times 10^6\,\text{Hz}} \times 10^6\,\text{ppm}$$

Simplifying:

$$\delta = \frac{150}{60}\,\text{ppm}$$

$$\delta = 2.5\,\text{ppm}$$

So, the chemical shift is 2.5 ppm.

- **Problem:** If the observed shift from TMS is 300 Hz and the operating frequency is 100 MHz, calculate the chemical shift (δ) in ppm.
- **Solution:** The chemical shift (δ) is calculated using the formula:

$$\delta = \frac{\Delta\nu}{\text{Operating Frequency}}$$

  Where:

  - $\Delta\nu$ is the observed shift from TMS.
  - The operating frequency is given in MHz.

  Substituting the given values:

$$\delta = \frac{300\,\text{Hz}}{100\,\text{MHz}}$$

  Convert the operating frequency from MHz to Hz by multiplying by 10^6:

$$\delta = \frac{300\,\text{Hz}}{100 \times 10^6\,\text{Hz}} \times 10^6\,\text{ppm}$$

Simplifying:

$$\delta = \frac{300}{100}\,\text{ppm}$$

$$\delta = 3\,\text{ppm}$$

So, the chemical shift is 3 ppm.

1. X-ray Spectroscopy Example: Calculating the Diffraction Angle

Problem: Calculate the angle θ for the first-order diffraction ($n = 1$) from a crystal plane with spacing $d = 2\,\text{Å}$ using X-rays with $\lambda = 1.54\,\text{Å}$.

Solution:

We use **Bragg's Law** for X-ray diffraction:

$$n\lambda = 2d\sin\theta$$

Given:

- $n = 1$ (first-order diffraction)
- $d = 2\,\text{Å}$
- $\lambda = 1.54\,\text{Å}$

Substitute the values into Bragg's Law:

$$1 \times 1.54 = 2 \times 2 \times \sin\theta$$

$$1.54 = 4\sin\theta$$

Solve for $\sin\theta$:

$$\sin\theta = \frac{1.54}{4} = 0.385$$

Now, calculate θ:

$$\theta = \arcsin(0.385) \approx 22.6^\circ$$

Answer: The diffraction angle θ is approximately **22.6°**.

Question:

A crystal is analyzed using X-ray diffraction with a wavelength of $1.54\,\text{Å}$. The first-order diffraction peak is observed at an angle of 20°. If the crystal is replaced with another crystal that has double the interplanar spacing, what will be the new diffraction angle for the first-order peak? Assume the same X-ray source is used.

- **Hint:** Use Bragg's Law to calculate the new angle.

Given:

- First-order diffraction ($n = 1$)
- Original interplanar spacing $d_1 = d = 2\,\text{Å}$
- New interplanar spacing $d_2 = 2d = 4\,\text{Å}$
- Wavelength of X-rays $\lambda = 1.54\,\text{Å}$
- Original diffraction angle $\theta_1 = 20^\circ$

Using Bragg's Law:

$$n\lambda = 2d \sin\theta$$

For the original crystal, we have:

$$1.54 = 2 \times 2 \times \sin 20^\circ$$

Now, for the new crystal with $d = 4\,\text{Å}$:

$$1.54 = 2 \times 4 \times \sin\theta_2$$

Solving for $\sin\theta_2$:

$$\sin\theta_2 = \frac{1.54}{8} = 0.1925$$

$$\theta_2 = \arcsin(0.1925) \approx 11.1^\circ$$

Question:

A sample of a crystal gives its first-order diffraction peak at 15° using X-rays of wavelength $1.54\,\text{Å}$. Calculate the interplanar spacing d. If the same crystal is analyzed with X-rays of wavelength $2.5\,\text{Å}$, at what angle would you expect the first-order diffraction peak to occur?

- **Hint**: First, use Bragg's Law to find d for the first set of conditions, then use it again to find the new angle with the different wavelength.

Given:

- $\theta_1 = 15^\circ$
- $\lambda_1 = 1.54\,\text{Å}$
- New wavelength $\lambda_2 = 2.5\,\text{Å}$

First, calculate the interplanar spacing d using Bragg's Law:

$$1 \times 1.54 = 2d \sin 15^\circ$$

$$d = \frac{1.54}{2 \times \sin 15^\circ}$$

$$d \approx \frac{1.54}{0.5176} = 2.975\,\text{Å}$$

Now, calculate the new diffraction angle θ_2 for $\lambda_2 = 2.5\,\text{Å}$:

$$1 \times 2.5 = 2 \times 2.975 \times \sin \theta_2$$

$$\sin \theta_2 = \frac{2.5}{5.95} \approx 0.4202$$

$$\theta_2 = \arcsin(0.4202) \approx 24.9^\circ$$

Answer: The new diffraction angle θ_2 is approximately **24.9°**.

Question:

A crystal with interplanar spacing $d = 3\,\text{Å}$ shows a first-order diffraction peak at an angle of 30° when irradiated with X-rays of a certain wavelength. What is the wavelength of the X-rays used? If this wavelength is decreased by 30%, what will be the new diffraction angle for the same order and plane?

- **Hint:** Use Bragg's Law to solve for the wavelength, then determine the new angle after adjusting the wavelength.

Given:

- $d = 3\,\text{Å}$
- $\theta_1 = 30^\circ$
- Wavelength λ_1 is unknown

Using Bragg's Law:

$$1 \times \lambda_1 = 2 \times 3 \times \sin 30^\circ$$

$$\lambda_1 = 6 \times 0.5 = 3\,\text{Å}$$

If the wavelength is decreased by 30%, the new wavelength λ_2 is:

$$\lambda_2 = 3 \times (1 - 0.3) = 2.1\,\text{Å}$$

Calculate the new diffraction angle θ_2:

$$1 \times 2.1 = 2 \times 3 \times \sin \theta_2$$

$$\sin \theta_2 = \frac{2.1}{6} = 0.35$$

$$\theta_2 = \arcsin(0.35) \approx 20.5^\circ$$

Answer: The new diffraction angle θ_2 is approximately **20.5°**.

2. IR Spectroscopy Example: Calculating the Wavenumber

Problem: Calculate the wavenumber of IR radiation with a wavelength of 5 μm.

Solution:

Wavenumber ($\tilde{\nu}$) is defined as the reciprocal of the wavelength in centimeters:

$$\tilde{\nu} = \frac{1}{\lambda}\,(\mathrm{cm}^{-1})$$

Given:

- $\lambda = 5\,\mu\mathrm{m} = 5 \times 10^{-4}\,\mathrm{cm}$

Substitute the value of λ:

$$\tilde{\nu} = \frac{1}{5 \times 10^{-4}}$$

$$\tilde{\nu} = 2000\,\mathrm{cm}^{-1}$$

Answer: The wavenumber of IR radiation is **2000 cm**$^{-1}$.

Question:
A molecule absorbs infrared radiation at a wavenumber of $1600\,\mathrm{cm}^{-1}$. Calculate the corresponding wavelength in micrometers. If the same molecule absorbs another IR radiation with a wavelength that is half of the previous wavelength, what is the new wavenumber?

- **Hint:** Convert wavenumber to wavelength and use the inverse relationship to find the new wavenumber.

Given:

- Wavenumber $\tilde{\nu}_1 = 1600\,\mathrm{cm}^{-1}$

Convert to wavelength (λ_1):

$$\lambda_1 = \frac{1}{1600}\,\mathrm{cm} = 6.25 \times 10^{-4}\,\mathrm{cm} = 6.25\,\mu\mathrm{m}$$

If the new wavelength is half, $\lambda_2 = \frac{\lambda_1}{2} = 3.125\,\mu\mathrm{m}$.

Calculate the new wavenumber ($\tilde{\nu}_2$):

$$\tilde{\nu}_2 = \frac{1}{\lambda_2} = \frac{1}{3.125 \times 10^{-4}}\,\mathrm{cm}^{-1} = 3200\,\mathrm{cm}^{-1}$$

Answer: The new wavenumber is **3200 cm**$^{-1}$.

An IR spectrometer is calibrated to measure absorbance in the range of $2\,\mu\mathrm{m}$ to $10\,\mu\mathrm{m}$. Calculate the range of wavenumbers this spectrometer can measure. If a sample shows an absorption band at $5\,\mu\mathrm{m}$, what would be the absorbance band's corresponding wavenumber in cm^{-1}?

- **Hint:** Use the conversion between wavelength and wavenumber to find the range and specific values.

Given:

- Range of wavelength $\lambda = 2\,\mu\mathrm{m}$ to $10\,\mu\mathrm{m}$

Wavenumber range:

$$\tilde{\nu}_{\min} = \frac{1}{10 \times 10^{-4}} = 1000\,\mathrm{cm}^{-1}$$

$$\tilde{\nu}_{\max} = \frac{1}{2 \times 10^{-4}} = 5000\,\mathrm{cm}^{-1}$$

For $\lambda = 5\,\mu\mathrm{m}$:

$$\tilde{\nu} = \frac{1}{5 \times 10^{-4}} = 2000\,\mathrm{cm}^{-1}$$

Answer: The wavenumber range is **1000 to 5000 cm**$^{-1}$, and the specific wavenumber is **2000 cm**$^{-1}$.

An unknown compound shows strong IR absorption peaks at $3000\,\mathrm{cm}^{-1}$ and $1500\,\mathrm{cm}^{-1}$. Calculate the respective wavelengths in micrometers. If the peaks are related by the fundamental vibrational mode and its first overtone, explain how you would identify which peak corresponds to which mode.

- **Hint:** The first overtone is approximately double the wavenumber of the fundamental mode.

Given:

- Peaks at $3000\,\mathrm{cm}^{-1}$ and $1500\,\mathrm{cm}^{-1}$

Convert to wavelengths:

$$\lambda_1 = \frac{1}{3000}\,\mathrm{cm} = 3.33\,\mu\mathrm{m}$$

$$\lambda_2 = \frac{1}{1500}\,\mathrm{cm} = 6.67\,\mu\mathrm{m}$$

The peak at $1500\,\mathrm{cm}^{-1}$ is likely the fundamental mode, and $3000\,\mathrm{cm}^{-1}$ is its first overtone.

Answer: Wavelengths are **3.33 μm** and **6.67 μm**.

3. Raman Spectroscopy Example: Calculating the Raman Shift

Problem: A laser with a wavelength of 532 nm is used in a Raman experiment. The scattered light has a wavelength of 550 nm. Calculate the Raman shift in cm^{-1}.

Solution:

The Raman shift ($\Delta\tilde{\nu}$) is given by the difference in wavenumbers of the incident and scattered light:

$$\Delta\tilde{\nu} = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_s}\right) \times 10^7\,\text{cm}^{-1}$$

Where:

- $\lambda_0 = 532\,\text{nm} = 532 \times 10^{-7}\,\text{cm}$
- $\lambda_s = 550\,\text{nm} = 550 \times 10^{-7}\,\text{cm}$

Substitute these values into the formula:

$$\Delta\tilde{\nu} = \left(\frac{1}{532 \times 10^{-7}} - \frac{1}{550 \times 10^{-7}}\right) \times 10^7$$

Calculate the wavenumbers:

$$\Delta\tilde{\nu} = \left(\frac{1}{532} - \frac{1}{550}\right) \times 10^7$$

$$\Delta\tilde{\nu} = (0.001880 - 0.001818) \times 10^7$$

$$\Delta\tilde{\nu} = (0.000062) \times 10^7$$

$$\Delta\tilde{\nu} = 620\,\text{cm}^{-1}$$

Answer: The Raman shift is **620 cm**$^{-1}$.

Question:

A Raman spectrum is obtained using a laser source of wavelength $488\,\mathrm{nm}$. The scattered light shows a Raman shift of $1200\,\mathrm{cm}^{-1}$. Calculate the wavelength of the scattered light. If the laser wavelength is changed to $514\,\mathrm{nm}$, what will be the new wavelength of the scattered light for the same Raman shift?

- **Hint:** Use the Raman shift formula and remember to convert wavelengths appropriately.

Given:

- Laser $\lambda_0 = 488\,\mathrm{nm}$
- Raman shift $\Delta\tilde{\nu} = 1200\,\mathrm{cm}^{-1}$

Wavelength of scattered light (λ_s):

$$\Delta\tilde{\nu} = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_s}\right) \times 10^7$$

Rearranging:

$$\frac{1}{\lambda_s} = \frac{1}{\lambda_0} - \frac{\Delta\tilde{\nu}}{10^7}$$

Substitute values:

$$\frac{1}{\lambda_s} = \frac{1}{488} - \frac{1200}{10^7}$$

$$\lambda_s \approx 516.7\,\mathrm{nm}$$

For new laser $\lambda_0 = 514\,\mathrm{nm}$:

$$\frac{1}{\lambda_s} = \frac{1}{514} - \frac{1200}{10^7}$$

$$\lambda_s \approx 543.2\,\mathrm{nm}$$

Answer: Scattered wavelengths are **516.7 nm** and **543.2 nm**.

Question:

In a Raman experiment, the laser source has a wavelength of $785\,\mathrm{nm}$. If the Stokes shift is observed at $3000\,\mathrm{cm}^{-1}$, calculate the wavelength of the Raman-scattered light. If an anti-Stokes shift of the same magnitude is observed, what would be the wavelength of the anti-Stokes scattered light?

- **Hint:** Use both Stokes and anti-Stokes shift calculations to find the two different scattered wavelengths.

Given:

- $\lambda_0 = 785\,\mathrm{nm}$
- Stokes shift $\Delta\tilde{\nu} = 3000\,\mathrm{cm}^{-1}$

Stokes-shifted wavelength (λ_s):

$$\frac{1}{\lambda_s} = \frac{1}{785} - \frac{3000}{10^7}$$

$$\lambda_s \approx 876.2\,\mathrm{nm}$$

Anti-Stokes wavelength:

$$\frac{1}{\lambda_{as}} = \frac{1}{785} + \frac{3000}{10^7}$$

$$\lambda_{as} \approx 707.2\,\mathrm{nm}$$

Answer: Stokes and anti-Stokes wavelengths are **876.2 nm** and **707.2 nm**.

Question:

A Raman experiment uses a laser with a wavelength of $532\,\mathrm{nm}$. The scattered light has wavelengths of both $540\,\mathrm{nm}$ and $520\,\mathrm{nm}$. Calculate the Raman shifts for both the Stokes and anti-Stokes scattering. Why are the Stokes and anti-Stokes intensities different, and what does this tell you about the population of vibrational states?

- **Hint:** Use the Raman shift formula for both calculations and discuss the Boltzmann distribution effect on Stokes and anti-Stokes intensities.

Given:

- $\lambda_0 = 532\,\mathrm{nm}$
- Scattered wavelengths: $\lambda_s = 540\,\mathrm{nm}$ (Stokes), $\lambda_{as} = 520\,\mathrm{nm}$ (anti-Stokes)

Calculate Raman shifts:

$$\text{Stokes shift: } \Delta\tilde{\nu} = \left(\frac{1}{532} - \frac{1}{540}\right) \times 10^7 \approx 287\,\mathrm{cm}^{-1}$$

$$\text{Anti-Stokes shift: } \Delta\tilde{\nu} = \left(\frac{1}{520} - \frac{1}{532}\right) \times 10^7 \approx 443\,\mathrm{cm}^{-1}$$

Answer: Stokes and anti-Stokes shifts are **287 cm**$^{-1}$ and **443 cm**$^{-1}$.