Recitation #3
Modern Physics

Problem #4: Electron Energy Loss Spectroscopy

Discussion: Helium atomic gas.

Kinetic energy of incident electrons: \( K_i = 26 \text{ eV} \)

\[ K = \frac{1}{2} m v^2 \]

\[ v = \sqrt{\frac{2K}{m_e}} \]

\[ F_e = q \vec{v} \times \vec{B} = -e vB \]

\[ F_c = \frac{m v^2}{r} \]

\[ F_c = F_e \Rightarrow e vB = \frac{m v^2}{r} \Rightarrow r = \sqrt{\frac{mv}{eB}} \]
Problem # 2.

Discuss the rotation-vibration spectrum of HCl molecule. (or any general molecule).

Discussion.

Energy of molecule \[\rightarrow\] Electronic
\[\rightarrow\] Vibrational
\[\rightarrow\] Rotational.

Electronic energy levels:

quantized energies \[\rightarrow\] n quantum number

Vibrational energy levels:
approximation of a diatomic molecule
\[k \quad m_1 \quad \sigma \quad m_2\]
spring denotes a `bond` where `k` represents the strength of the bond.

For simple harmonic oscillator (SHO):

\[\omega = \sqrt{\frac{k}{m}}\]  
\[f = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}\]

\[\omega = \sqrt{\frac{k}{\mu}}\]  
where \(\mu = \frac{m_1 m_2}{m_1 + m_2}\)
is the reduced mass.

Reduced mass \(\mu\) is used to convert a two body problem to a single body problem.
Quantized vibrational energy levels:

$$E_{\text{vib}} = \left(n_v + \frac{1}{2}\right)hf.$$  \hfill (3)

$$n_v = \text{vibrational quantum number}$$

$$n_v = 0, \frac{1}{2}, 1, \ldots$$

Transition energy between any neighboring vibrational energy levels $n$ and $n-1$:

$$\Delta E_{\text{vib}} = \left(n + \frac{1}{2}\right)hf - \left(n-1 + \frac{1}{2}\right)hf.$$  

$$= \left(n + \frac{1}{2} - n + 1 - \frac{1}{2}\right)hf = hf = \text{constant.}$$

Vibrational energy levels are equidistant in energy.

Rotational energy levels

Rotational kinetic energy

$$E_{\text{rot}} = \frac{1}{2} I \omega^2.$$  

$I = \text{moment of inertia}$.

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = m_1 r^2.$$  

$$E_{\text{rot}} = \frac{1}{2I} (I \omega)^2.$$  

$L = I \omega = \text{angular momentum}.$

$$E_{\text{rot}} = \frac{1}{2I} L^2.$$
Angular momentum is quantized in quantum mechanics:

\[ L = \sqrt{I (I+1)} \hbar \quad \text{where} \quad \hbar = \frac{\hbar}{2\pi} \]

\( I \) = rotational quantum number
\( I = 0, 1, 2, \ldots \)

\[ E_{\text{rot}} = \frac{l (l+1) \hbar^2}{2I} \]

Transition energy between two neighboring rotational energy levels:

\( l = n \) and \( l = n-1 \) is

\[ \Delta E_{\text{rot}} = E_{\text{rot}, n} - E_{\text{rot}, n-1} = \frac{n (n+1) \hbar^2}{2I} - \frac{(n-1)n \hbar^2}{2I} = \frac{n^2 - n^2 + n}{2I} \frac{\hbar^2}{2I} = \frac{\hbar^2}{2I} \cdot (2n) \]

\[ \Delta E_{\text{rot}} = \frac{\hbar^2}{2I} \cdot l \]

\( \Rightarrow \) the difference between neighboring energy levels increases linearly with \( l \).

The energy difference between two neighboring transitions is then constant and is \( \frac{\hbar^2}{I} \).
Rotation-vibrational transitions

transition between neighboring vibrational energy levels also involve change in rotational energy levels.

Selection rule for transition \( \Delta l = \pm 1 \).

The peak at \( hf \) is missing as that transition requires \( \Delta l = 0 \) which is not possible.

Rotatio-vibrational Spectrum
What informations can we extract from rotation-vibrational spectrum of HCl?

The central missing peak lies at $\nu f = 8.65 \times 10^{13}$ Hz. Therefore,

$$h \nu = 6.63 \times 10^{-34} \text{ m}^2 \text{kg/s} \times 8.65 \times 10^{13} \text{ Hz}.$$  

Hence,

$$J = 5.73 \times 10^{-20} \text{ J} = 0.36 \text{ eV}.$$  

As $f = \frac{1}{2\pi\sqrt{K \mu}}$,

$$K = \frac{(2\pi f)^2 \mu}{h^2} \quad \mu = \frac{m_H m_C}{m_H + m_C},$$

with $m_H = 1 \times 1.66 \times 10^{-27} \text{ kg}$ and $m_C = 35 \times 1.66 \times 10^{-27} \text{ kg}$.

$$K' = 2.865 \text{ N/m},$$

a measure of bond strength.

The difference between two consecutive peaks is approximately $0.06 \times 10^{13} \text{ Hz} = \Delta \nu$.

$$\frac{h^2}{I} = h \Delta \nu \Rightarrow \frac{h^2}{4\pi^2 I} = h \Delta \nu$$

Hence,

$$I = \frac{h}{4\pi^2 \Delta \nu} = 8.8 \times 10^{-47} \text{ kg m}^2.$$
\[ I = \mu r^2 \], where \( r \) is the bond length.

\[ r = \sqrt{\frac{I}{\mu}} = 0.23 \text{ nm}. \]

**Question:** Why does the intensity of the lines drop towards outer frequencies?

The inner lines result due to transitions between rotational states of small \('l'\) value, while the outer lines are caused by transitions between high \('l'\) value states.

**The population distr.**

Consider that the HCl is in thermal equilibrium with the surroundings, then the population distribution of the rotational energy levels is governed by Boltzmann distribution.

\[ P(n) = e^{-\frac{E_{rot}}{k_B T}} = e^{-\frac{\ell(\ell+1) \hbar^2}{I k_B T}} \]

Rotational states with high \('l'\) values are less occupied than as compared to the states with smaller \('l'\), therefore the outer transitions have low probability.