Molecular spectra

\[ E = E_{\text{trans}} + E_{\text{el}} + E_{\text{ vib}} + E_{\text{ rot}} \]

- **\( E_{\text{trans}} \)**: motion of a molecule as a whole. Not quantized, in most cases can be treated classically.

- **\( E_{\text{el}} \)**: electron configuration (usually involves complicated calculations).
  - In many cases a molecule is in its ground electronic state.

- **\( E_{\text{ vib}} \)**: energy of vibration

- **\( E_{\text{ rot}} \)**: rotation

\[ B = U(R_0) \]  
- minimum energy (binding energy)

\[ R_0 \] - average distance b/w atoms

Near the stable minimum we can approximate potential as a harmonic potential

\[ U = U(R_0) + \frac{1}{2} K x^2 \]

\[ K = \left. \frac{\partial^2 U}{\partial R^2} \right|_{R=R_0} \]

\( x = x_1 - x_2 \)

Relative displacement of two atoms depending on the electronic state
Schrödinger equation

\(-\frac{\hbar^2}{2m_1} \frac{d^2\psi}{dx^2} - \frac{\hbar^2}{2m_2} \frac{d^2\psi}{dx^2} + \frac{1}{2} Kx^2\psi(x) = E_{vib}\psi(x)\)

kinetic energy of atom 1
kinetic energy of atom 2

\(\frac{1}{\mu} \frac{1}{2}\hbar^2 \frac{d^2\psi}{dx^2} + \frac{1}{2} Kx^2\psi = E_{vib}\psi(x)\)

\(\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}\) - reduced mass

same equation for multi-atom molecules

We know this solution! (SHO) simple harmonic oscillator

\(E_{vib} = (\nu + \frac{1}{2}) \hbar \omega\)

\(\omega = \sqrt{\frac{K}{\mu}}\) \(\nu\) - vibrational quantum number

Equidistant spectrum

\(\Delta E = \hbar \omega \approx 0.1 - 0.3 \text{eV}\)

\(\Delta E = \frac{3}{2} \hbar \omega\) larger than thermal energy \((kT \approx 0.03 \text{eV})\)

Thus, typically molecules are in ground vibrational state.
More realistic description of molecular vibration - Morse potential

\[ U_{\text{Morse}}(R) = D \left( 1 - e^{-\alpha(R-R_0)} \right)^2 \]

For small \( R - R_0 \)

\[ U_{\text{Morse}}(R) \approx D a^2 (R-R_0)^2 \]

Can take into account higher order effect

\[ U_{\text{Morse}}(R) \approx D a^2 (R-R_0)^2 - D a^3 (R-R_0)^3 \]

we can use wave functions describing simple harmonic oscillator to find correction due to anharmonicity

\[ E_{\text{vib}} = \hbar \omega \left( \nu + \frac{1}{2} \right) - \frac{\hbar^2 \omega^2}{4D} \left( \nu + \frac{1}{2} \right)^2 \]

As \( \nu \) increases, the separation between levels decreases

\( \nu \)

Higher \( \nu \) – larger vibration amplitude – move farther away from equilibrium, and atoms are weaker bound, and it becomes easier to move them apart.
Rotational energy

Assume rigid molecule (valid approximation)
Molecule can rotate around one, two or three axes

Kinetic energy associated with this rotation
\[ K_{\text{rot}} = \frac{1}{2} I_z \omega^2 \]

\( I_z \) - moment of inertia w/respect to z axis (w/respect to center of mass)

We can express kinetic energy in terms of angular momentum
\[ K_{\text{rot}} = \frac{\dot{z}^2}{2I} \Rightarrow E_{\text{rot}} = \frac{\hbar^2 l(l+1)}{2I} \]

\( l \) - rotational quantum number

\[ \Delta E_{l+1} - \Delta E_l = \frac{\hbar^2 (l+1)(l+2)}{2I} \]

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

Minimum energy separation
\[ \Delta E = \hbar \omega_0 = \frac{\hbar^2}{I} \]

Higher harmonics
2\( \hbar \omega_0 \), 3\( \hbar \omega_0 \), ...

\( \hbar \omega_0 \approx 0.001 \text{ eV} \)

Finest energy splitting
Molecular spectra

Molecules are usually in a ground electronic state.
Internal energy = rotational & vibrational

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

Optical transitions - molecule changes its state and a photon is emitted or absorbed.

\[ E_{\text{photon}} = E_i - E_f \quad \text{energy conservation} \]

Photon \( S = 1 \) \( \Rightarrow \) has angular momentum

Angular momentum conservation
\[ \Delta l = \pm 1 \]

Due to the properties of SHO wavefunctions
\[ \Delta V = \pm 1 \] (breaks for high \( V \), where SHO approximation stops working)
Normally, molecules are in ground vibrational state $v=0$

$\Delta l = \pm 1$

$\Delta E_+ = \hbar \omega + \frac{\hbar^2}{I} (l+1)$

$\Delta E_- = \hbar \omega + \frac{\hbar^2}{I} l$

Equidistant spectrum of photons with $\hbar \omega$ are absorbed!

Strength of the transition depends on spatial charge distribution of initial and final stages, light polarization, etc.

Transition probability

$$P_{if} \propto \left| \int \psi_i^*(\vec{r},t) (-e\vec{E}\vec{r}) \psi_f(\vec{r},t) \, d^3\vec{r} \right|^2$$

$$P_{if} \propto \left| \int \psi_i^*(\vec{r}) (-e\vec{E}_{light}) \psi_f(\vec{r}) \, d^3\vec{r} \right|^2$$

depends on spatial dependence of wave functions

dipole matrix elements
Carbon-Monoxide Spectrum

Absorption

Energy (eV)

\[ E_0 \] \[ E_+ \]

\[ \hbar \omega \]