6. Molecular structure and spectroscopy I

1 molecular spectroscopy – introduction

2 light-matter interaction
Molecular energy domains

Born-Oppenheimer approximation ⇒

\[
\hat{H} \approx \hat{H}_e + \hat{H}_n \Leftrightarrow \begin{cases} 
\Psi \approx \psi \Phi \equiv \psi_e \Phi \\
E \approx V + E_n \equiv E_e + E_n 
\end{cases}
\]

Ignoring nuclear spin and transforming to centre-of-mass system

\[
\hat{H}_n \approx \hat{H}_v + \hat{H}_r + \hat{H}_t \xrightarrow{\text{CM transf}} \hat{H}_v + \hat{H}_r \Rightarrow \\
\hat{H} \approx \hat{H}_e + \hat{H}_v + \hat{H}_r \Leftrightarrow \begin{cases} 
\Psi \approx \psi_e \psi_v \psi_r \\
E \approx E_e + E_v + E_r 
\end{cases}
\]

For EM transition between molecular states

\[
h\nu = \Delta E = \Delta E_e + \Delta E_v + \Delta E_r
\]

\[
\Delta E_e \gg \Delta E_v \gg \Delta E_r
\]
Molecular spectral domains – overview
Molecular spectra – physical origin

Spectra are associated with primarily *varying electric or magnetic dipole moments*.

**Radiowave region** Flipping of nuclear or electron spin magnetic moments interacting with the magnetic component of the EM field.

**Microwave region** Rotational motion – requires *permanent molecular electric dipole moment*.
Molecular spectra – physical origin

Infrared region  Vibrational motion – requires *varying molecular electric dipole moment*

![Diagram of molecular structures showing vibrational motion and dipole moments](image)

- **O** represents oxygen, **C** represents carbon, **δ⁻** and **δ⁺** represent dipole moments.
- **Stretching** and **bending** motions are illustrated with arrows indicating the movement of the dipole moment.
- The diagram shows different configurations of the molecule under stretching and bending vibrations, highlighting how the dipole moment varies in each case.
Visible and ultraviolet Rearrangement of valence electronic charge density in the interaction with the electric component of the EM field
Molecular spectra – physical origin

**Raman spectra** are different – caused by *varying molecular polarisability*.

The total radiated energy from an oscillating dipole, ignoring permanent dipoles,

\[ I = \frac{2}{3c^2} \left( \frac{d^2P}{dt^2} \right)^2 \; ; \; P = \alpha \mathcal{E}_0 \sin(\omega t) \equiv \mu_{\text{ind}} \]

There are two main contributions

\[
\begin{align*}
\text{vibration} & \quad \alpha \approx \alpha_0 + \alpha_{1v} \sin(\omega_v t) \\
\text{rotation} & \quad \alpha \approx \alpha_0 + \alpha_{1r} \sin(2\omega_r t) \\
\text{(anisotropic } \alpha) &
\end{align*}
\]

\[
(\text{Product} - \text{to} - \text{sum} : \sin(a) \sin(b) = \frac{1}{2} \{ \cos(a - b) - \cos(a + b) \})
\]

\[ P = \]

\[
\begin{array}{ccc}
\uparrow & \uparrow & \uparrow \\
\text{Rayleigh} & \text{Stokes} & \text{anti-Stokes}
\end{array}
\]
6.1 molecular spectroscopy – introduction

Molecular properties from spectroscopy

<table>
<thead>
<tr>
<th>Type of spectroscopy</th>
<th>Type of molecular energy</th>
<th>Information extracted</th>
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<td>Microwave</td>
<td>Rotation of heavy molecules</td>
<td>Interatomic distances, dipole moments, bond angles</td>
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<tr>
<td>Far infrared</td>
<td>Rotation of light molecules, vibrations of heavy molecules</td>
<td>Interatomic distances, bond force constants</td>
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<tr>
<td>Infrared</td>
<td>Vibrations of light molecules; vibration-rotation</td>
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<tr>
<td>Raman</td>
<td>Rotation, vibrations</td>
<td>Interatomic distances, bond force constants, charge distributions (for energy changes not observable with infrared)</td>
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<td>Visible, ultraviolet</td>
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<td>Electron spin resonance (ESR)</td>
<td>Energy required to reverse the direction of electron spin in magnetic field</td>
<td>Position of spectrum, shape of spectral lines, hyperfine structure</td>
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<td>Nuclear magnetic resonance (NMR) (radio frequency)</td>
<td>Transition between different energy states of nuclei</td>
<td>Chemical shifts, chemical identification</td>
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*Adapted from L. Hollenberg (1970).
6. Molecular structure and spectroscopy I

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Basic processes

“single”-photon

multiphoton

The lifetime of these virtual states in multi-photon processes is important
Einstein coefficients

For non-degenerate two-level (N=2,1) system at thermal equilibrium (\(\tilde{\nu} \equiv \nu/c\)) noting that absorption (\(\propto B_{12}\)) and stimulated emission (\(\propto B_{21}\)) depend on the radiation density, \(\rho(\tilde{\nu})\), while spontaneous emission (\(\propto A_{21}\)) does not, the rate of change of particles in state \(N_2\) is:

\[
\dot{N}_2 = N_1 B_{12} \rho(\tilde{\nu}) - N_2 B_{21} \rho(\tilde{\nu}) - N_2 A_{21} \equiv 0 \iff
\]

\[
\rho(\tilde{\nu}) = \frac{A_{21}}{N_1 B_{12} - B_{21}}
\]

\[
\frac{N_1}{N_2} = \frac{e^{-E_1/k_B T}}{e^{-E_2/k_B T}} = e^{(E_2-E_1)/k_B T} = e^{\hbar \nu/k_B T}
\]

\[
\text{Planck}
\]

\[
B_{12} = B_{21}
\]

\[
A_{21} = 8\pi \hbar \tilde{\nu}^3 B_{12}
\]
Beer-Lambert law

For a system of $N_1$ molecules/m$^3$ in $N_1$ and $N_2$ molecules/m$^3$ in $N_2$. A flux of photons, $F = I_0 / h\nu$ (photons/m$^2$ s) from left enters the system, and can be absorbed or stimulate emission only. What is $F$ after a distance $l$?

$$\rho(\tilde{\nu}) = I_0 / c = h\tilde{\nu}F \Rightarrow \dot{N}_2 = -B_{21}h\tilde{\nu}FN_2 + B_{12}h\tilde{\nu}FN_1 \equiv \sigma FN \Delta N ; \Delta N = N_1 - N_2$$

Change in $F$ in passing element $dx$

$$I = I_0e^{-\sigma \Delta N l}$$
**Time-dependent perturbation theory**

\[ i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \]

Semiclassically – quantum two-level system interacting with classical EM field

Split \( \hat{H} \) in time dependent \( \hat{H}' \) and independent \( \hat{H} \) parts

\[ \hat{H} = \hat{H} + \hat{H}' \Leftrightarrow i\hbar \frac{\partial}{\partial t} \Psi = [\hat{H} + \hat{H}'] \Psi \]

then, without \( \hat{H}' \)

\[ i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \Leftrightarrow \Psi = \sum_n \psi_n e^{-iE_n t/\hbar} = \sum_n \psi_n e^{-i\omega_n t} \]

where

\[ \hat{H}\psi_n = E_n \psi_n \]

For the perturbed system, soln. is a linear combination:

\[ \Psi(t) = \sum_n a_n(t) \psi_n e^{-i\omega_n t} = \sum_n a_n \psi_n e^{-i\omega_n t} \]

Plug this into the TDSE:

\[ i\hbar \sum_n \dot{a}_n \psi_n e^{-i\omega_n t} = \hat{H}' \sum_n a_n \psi_n e^{-i\omega_n t} \]

And multiply by \( \sum_n \psi_n^* e^{i\omega_n t} \) as appropriate and integrate over all space, for a two-state system \( (\psi_{0,1}) \)

where \( \langle \psi_0 \mid \hat{H}' \mid \psi_0 \rangle = \int \psi_0 \hat{H}' \psi_0 d\tau \)
TDPT – electric dipole approximation

In the **electric dipole approximation** $\lambda \gg l_{\text{system}}$

$$\hat{H}' = -\mu_z \mathcal{E}_z \cos \omega t \equiv -ezE_z \cos \omega t$$

$\hat{H}'$ is an odd function, since $\mu = ez$

$$|\psi_n|^2 \implies \text{even}, \quad \psi_n \hat{H}' \psi_n \implies \text{odd}, \quad \langle \psi_n | \hat{H}' | \psi_n \rangle = 0$$

The solutions reduce to:

$$\dot{a}_0 = \frac{ia_1}{\hbar} M_{01} \mathcal{E}_z e^{-i\omega_{10}t} \cos \omega t, \quad \dot{a}_1 = \frac{ia_0}{\hbar} M_{10} \mathcal{E}_z e^{i\omega_{10}t} \cos \omega t$$

$$M_{01} = M_{10} = \langle \psi_1 | \mu | \psi_0 \rangle$$

Weak field, so $a_1 \approx 0, a_0 \approx 1$.

$$\dot{a}_1 = i \mathcal{E}_z \frac{M_{10}}{\hbar} (\cos(\omega t)e^{i\omega_{10}t}) = \frac{i\mathcal{E}_z M_{10}}{2\hbar} \left( e^{i(\omega_{10}+\omega)t} + e^{i(\omega_{10}-\omega)t} \right)$$

Rotating Wave Approximation, terms in $\hat{H}$ which oscillate rapidly are neglected while slow oscillations kept. $(\omega_{10} + \omega) \gg (\omega_{10} - \omega)$:

$$\dot{a}_1 \approx \frac{i\mathcal{E}_z M_{10}}{2\hbar} e^{i(\omega_{10}-\omega)t} = \frac{i\mathcal{E}_z M_{10}}{2\hbar} e^{-i\Delta t}, \quad \Delta = \omega - \omega_{10}$$

$$a_1 = \int_0^t \dot{a}_1 dt = \frac{i\mathcal{E}_z M_{10}}{2\hbar} \int_0^t e^{-i\Delta t} dt$$

$$a_1 = \frac{\mathcal{E}_z M_{10}}{-2\hbar \Delta} (e^{-i\Delta t} - 1)$$

**transition dipole moment** $M_{mn} \Rightarrow \left\{ \begin{array}{l} \text{selection rules} \\ \text{line intensities} \end{array} \right.$
TDPT – Einstein coefficients

Transition probability is given by $|a_m(t)|$, in principle.

$$P_{mn} = |a_m(t)|^2 = \frac{\mathcal{E}_z^2}{4\hbar^2 \Delta^2} |M_{mn}|^2 |e^{-i\Delta t} - 1|^2$$

$$P_{mn} =$$

However, monochromatic \( \neq \) short times. Remember $\Delta E \Delta t \geq \hbar \Rightarrow \Delta \omega \Delta t \geq 1 \Rightarrow \text{integration over } \omega \text{ required.}$ With broadband radiation density $\rho = \varepsilon_0 \mathcal{E}_z^2/2$

$$P_{mn} = \int |a_m(t)|^2 d\omega$$

$$= \int \varepsilon_0 \mathcal{E}_z^2/2$$

$$= \int \rho(\omega_{mn})$$

$$= \int \varepsilon_0 \mathcal{E}_z^2/2$$

The absorption rate per molecule is then

$$\frac{dP_{mn}}{dt} = \frac{\pi}{\varepsilon_0 \hbar^2} |M_{mn}|^2 \rho(\omega_{mn}) = \frac{1}{3} \frac{d(N_m/N)}{dt} = \frac{2\pi}{3} B_{mn} \rho(\omega_{mn}) \Leftrightarrow$$

$$B_{mn} = \frac{2\pi^2}{3\varepsilon_0 \hbar^2} |M_{mn}|^2$$

$$A_{mn} = \frac{16\pi^3 \nu^3}{3\varepsilon_0 \hbar c^3} |M_{mn}|^2$$