Spectrum

Photon energy (J)

Wavelength (m)

- Gamma rays
- X rays
- Ultraviolet (UV) radiation
- Infrared (IR) radiation
- Microwaves
- Radio waves

Visible light

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Key equation in spectroscopy is \[ \hbar \omega \equiv h \nu = \left| E_2 - E_1 \right| \]

<table>
<thead>
<tr>
<th>Spectral Range</th>
<th>( \lambda ) (nm)</th>
<th>( \nu \times 10^{14} ) / (Hz)</th>
<th>Wave number/ (cm(^{-1}))</th>
<th>Energy/ (kJ/mol)</th>
<th>Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio</td>
<td>( \sim 1 \times 10^9 )</td>
<td>( \sim 10^{-6} )</td>
<td>( \sim 0.01 )</td>
<td>( \sim 1 \times 10^{-4} )</td>
<td>NMR</td>
</tr>
<tr>
<td>Microwave</td>
<td>( &gt;100,000 )</td>
<td>( &lt; 10^{-2} )</td>
<td>( &lt; 30 )</td>
<td>( &lt; 0.1 )</td>
<td>Rotational</td>
</tr>
<tr>
<td>Infrared</td>
<td>( &gt;1000 )</td>
<td>( &lt; 3.0 )</td>
<td>( &lt; 10,000 )</td>
<td>( &lt; 120 )</td>
<td>Vibrational</td>
</tr>
<tr>
<td>Visible (red)</td>
<td>( \sim 700 )</td>
<td>( \sim 4 )</td>
<td>( \sim 13,000 )</td>
<td>( \sim 160 )</td>
<td>Electronic</td>
</tr>
<tr>
<td>Visible (blue)</td>
<td>( \sim 450 )</td>
<td>( \sim 6 )</td>
<td>( \sim 20,000 )</td>
<td>( \sim 250 )</td>
<td>Electronic</td>
</tr>
<tr>
<td>Ultraviolet</td>
<td>( &lt;300 )</td>
<td>( &gt; 10 )</td>
<td>( &gt;30,000 )</td>
<td>( &gt; 400 )</td>
<td>Electronic</td>
</tr>
</tbody>
</table>
Energy transfer is between EM field and molecule

As the electric field oscillates it points one way at one time and the other way at a later time. The Field interacts with the charges. The energy of the interaction is:

\[ V(t, x) = \sum q_i r_i E(r, t) = \mu \cdot E \]
Basic concepts in spectroscopy

- The electric field of the light will interact with the charges of the electrons.
- When the energy of the photon matches the energy of the transition, absorption or emission of light can happen.
- Wave number, $\tilde{\nu} = \frac{1}{\lambda}$ generally used to describe transition. (units cm$^{-1}$)
- Selection rules restrict possible transitions.
- Molecule must have permanent or dynamic dipole to couple to EM field in dipole description.
- Raman spectroscopy can be used if no permanent or dynamic dipole
3 possible processes: absorption, spontaneous emission and stimulated emission

There is a spontaneous rate constant (A) that can only relax the system. The stimulated rates are driven by the strength of the light field, and the stimulated rate constants (B) for the up and down transfers are the same and proportional to the spontaneous rate constant, so they are driven by the same processes.

\[ B_{12} \rho(\nu) N_1 = B_{21} \rho(\nu) N_2 + A_{21} N_2 \]

\[ B_{12} = B_{21} \text{ and } B_{21} \left( \frac{16\pi^2 \hbar \nu^3}{c^3} \right) = A_{21} \]
Vibrational spectroscopy transitions

- Transition probability zero unless transition dipole moment not zero
- At 300K, usually only $n=0$ (ground vibrational) state occupied.

\[
\mu_{xn}^{mn} = \int_{-\infty}^{\infty} \psi_m^*(x) \mu_x(x) \psi_n(x) \, d\tau \neq 0
\]

In a molecule
3n-5 (linear) or
3n-6 (nonlinear) vibrational modes;
Each mode acts as its own harmonic oscillator

Allowed transitions:
$\Delta n = \pm 1$
n=0 to $n=1$
dominant transition
Anharmonicity allows $\Delta n = \pm 2, \pm 3$ (very weak).

$\Delta E$ between adjacent levels not all the same.

The Morse potential is a realistic potential and allows dissociation.

Different level spacings don’t give rise to multiple peaks; level spacings are not the same.

Anharmonicity allows $\Delta n = \pm 2, \pm 3$ (very weak).

$\Delta E$ between adjacent levels not all the same.
IR Light Drives Vibrations

Adsorption of IR light excites normal modes, not individual bonds

Neither mode is simple O-H bond stretch because all three atoms coupled through bonds.
IR absorption spectroscopy

Beer-Lambert law: The intensity of the light drops incrementally as the light moves incrementally through the solution:

$$dI(\lambda) = -\epsilon(\lambda) M I(\lambda) dl$$

$$\frac{I(\lambda)}{I_0(\lambda)} = e^{-\epsilon(\lambda) M l}$$

Characteristic group frequencies

<table>
<thead>
<tr>
<th>Group</th>
<th>Frequency (cm⁻¹)</th>
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<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretch</td>
<td>3400</td>
<td>C=O stretch</td>
<td>1700</td>
</tr>
<tr>
<td>N-H stretch</td>
<td>3350</td>
<td>C=C stretch</td>
<td>1650</td>
</tr>
<tr>
<td>C-H stretch</td>
<td>2900</td>
<td>C-C stretch</td>
<td>1200</td>
</tr>
<tr>
<td>C-H bend</td>
<td>1400</td>
<td>C-Cl stretch</td>
<td>700</td>
</tr>
</tbody>
</table>
Experimental setup and spectra

3n-6 = 9 for CH₄ and
3n-5 = 1 for CO. Why is number of observed peaks different?
Rotational spectroscopy selection rule

for diatomic molecules is $\Delta J = \pm 1$

Permanent dipole needed to couple molecular rotations to EM field.

\[
B = \frac{\hbar}{2\pi I}
\]

\[
I = \mu r_0^2
\]
Rotational Energy levels

\[ E = \frac{\hbar^2}{2I} J(J+1) = \hbar BJ(J+1) \]

\[ \Delta E \] for transitions starting at \( J \) given by

\[ \Delta E = E(J_{\text{final}}) - E(J_{\text{initial}}) \quad \text{for } \Delta J = +1 \]

\[ \Delta E_+ = \hbar B \left\{ (J+1)(J+2) - J(J+1) \right\} = 2\hbar BJ(J+1) \]

and for \( \Delta J = -1 \)

\[ \Delta E_- = \hbar B \left\{ (J-1)(J) - J(J+1) \right\} = -2\hbar BJ \]
Unlike vibrational spectroscopy, energy difference between adjacent energy levels not the same.
Because rotational levels more closely spaced than vibrational levels, vibrational excitation will also lead to rotational excitation.
Rotational-vibrational spectroscopy

\[ \nu_{\text{light}} = \frac{1}{2\pi} \omega_{\text{HO}} + B \left\{ -\frac{J}{J+1} \right\} \]

\[ \Delta \nu_{\text{light}} = B \]

Peak frequencies (equally spaced!) determined by energy level spacing.

Peak intensities determined by number of molecules of originating level.
$J$ value of highest intensity depends sensitively on $T$

$$\frac{n_J}{n_0} = \frac{g_J}{g_0} e^{-(\varepsilon_J - \varepsilon_0)/kT} = (2J + 1) e^{-\hbar^2 J(J+1)/2I kT}$$

Reconsider IR spectra for CO and CH$_4$
High Resolution IR Rot-Vib Spectrum of CO
Why does the light field drive a transition?

• Simplified and adapted from section 19.9 (or 8.9)
• This method will be used to explain molecular structure, so it is very useful.
• The light field interacts with the electrons in the molecule (nuclei too, but they move more slowly). This perturbs the molecule.
• To a first order we can construct the wave function as a sum of the one describing the present state, and the one describing the state to which we might go.
• Then we solve the time dependent Schrodinger Equation.

\[
i\hbar \frac{d\Psi}{dt} = (H_o + H_{lf})\Psi
\]

\[
\Psi = a_1 \Psi_1 + a_2 \Psi_2 \quad \text{(ansatz or guess)}
\]

\[
i\hbar \frac{d\Psi_m}{dt} = H_o \Psi_m = E_m \Psi_m \quad \text{and} \quad \Psi_j = e^{-i\omega_j t}\phi_j
\]

The two eigenfunction of the molecular Hamiltonian act as basis function

The coefficients (a1 and a2) are time dependent (only) and are linked by the normalization condition.

The light field is the perturbation on the molecule.
A light driven process

• The light field Hamiltonian is (in the semi-classical approach); the kx spatial part of the light field has been dropped: k is very small, compared to the size of a molecule
  \[ H_{LF} = \mu E_o \cos(\omega t) \quad \text{and} \quad \mu = \sum_i q_i r_i \]

• Substitution in for the trial or guessed wave function gives an equation for the coefficients:
  \[ \begin{array}{c}
i\hbar \left( \frac{da_1}{dt} \Psi_1 + \frac{da_2}{dt} \Psi_2 \right) = H_{lf} (a_1 \Psi_1 + a_2 \Psi_2) \\
\end{array} \]

• We take advantage of the orthonormality of the basis functions (eigenstate) to integrate and get rid of those functions
  \[ i\hbar \frac{da_1}{dt} = a_2 e^{i(\omega_1 - \omega_2)t} \cos \omega t E_o \mu_{21} \]
  \[ i\hbar \frac{da_2}{dt} = a_1 e^{-i(\omega_1 - \omega_2)t} \cos \omega t E_o \mu_{12} \]

• We simplify the problem assuming:
  \[ 0 = \int \Psi_1^* H_{lf} \Psi_1 dx = \int \Psi_2^* H_{lf} \Psi_2 dx \]
  \[ \int \Psi_2^* H_{lf} \Psi_1 dx = e^{-i(\omega_1 - \omega_2)t} \cos \omega t \mu_{21} E_o \]
  \[ \mu_{21} = \int \phi_2^* \mu \phi_1 dx \]
How does the light induce a transition?

• The problem is still pretty complicated, but if we match the light field to the energy difference then the time dependence drops out of the problem.

• The resulting problem can be solved for the coefficients.

• If we assume that the molecule is in state one at time zero then we have a boundary condition on $a_2(t=0)=0$

• The second order differential equation for $a_2$ is the same as that for the $X(t)$ for the Harmonic Oscillator, so we know the answer, $a_2$ just oscillates. The frequency of oscillation is driven by the light field.

• To induce a transition then, we need to have $\mu_{12}$ be non-vanishing. This is called a transition dipole moment (matrix element). It is this term that is fundamental to allowing transitions even when the energy matches. This term leads to the selection rules.

• The text gives a more detailed treatment, but this simplified form demonstrates how population can be moved from one level to another.

$$\omega = \pm (\omega_1 - \omega_2)$$

$$\hbar \omega = \pm \Delta E_{1,2}$$

$$i\hbar \frac{da_1}{dt} = a_2 \frac{1}{2} E_o \mu_{21}$$

$$i\hbar \frac{da_2}{dt} = a_1 \frac{1}{2} E_o \mu_{12}$$

$$(i\hbar)^2 \frac{d^2 a_2}{dt^2} = \frac{1}{4} E_o \mu_{12} E_o \mu_{21} a_2$$

$$\frac{d^2 a_2}{dt^2} = -\left( \frac{|E_o \mu_{12}|}{2\hbar} \right)^2 a_2$$

$$\frac{d^2 a_2}{dt^2} = - (\omega_{oscil})^2 a_2$$

$$\frac{|E_o \mu_{12}|}{2} = \hbar \omega_{oscil}$$

$$a_2(t) = \sin \omega_{oscil} t$$

$$a_1(t) = \cos \omega_{oscil} t$$