**General Properties of Light and Matter** (VH 8; CS 7)

**Range of energy:** spectroscopies and molecular processes

<table>
<thead>
<tr>
<th>Energy (kcal/mol)</th>
<th>Wavelength (meters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>-13</td>
</tr>
<tr>
<td>7</td>
<td>-12</td>
</tr>
<tr>
<td>6</td>
<td>-11</td>
</tr>
<tr>
<td>5</td>
<td>-10</td>
</tr>
<tr>
<td>4</td>
<td>-9</td>
</tr>
<tr>
<td>3</td>
<td>-8</td>
</tr>
<tr>
<td>2</td>
<td>-7</td>
</tr>
<tr>
<td>1</td>
<td>-6</td>
</tr>
<tr>
<td>1</td>
<td>-5</td>
</tr>
<tr>
<td>0</td>
<td>-4</td>
</tr>
<tr>
<td>-1</td>
<td>-3</td>
</tr>
<tr>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>-3</td>
<td>-1</td>
</tr>
<tr>
<td>-4</td>
<td>0</td>
</tr>
<tr>
<td>-5</td>
<td>1</td>
</tr>
</tbody>
</table>

**Very high energies - electrons from inner to extreme outer shells or to continuum**

- X-rays: scattering from atomic centers
- UV: excitation of electrons from one orbital to another
- Visible: excitation of electrons from one “big” orbital to another
- IR: bond vibrations, bends
- Microwave: bond rotational modes, EPR
- RF: nuclear magnetic resonance

**“Light” and energy**

\[ E = h\nu = hc/\lambda \]
Electromagnetic radiation ("light") composed of electrical and magnetic components.

E and B components are perpendicular and vary in space with time. Light can be represented as a spatial "wave." Frequency of oscillation is $\nu$, and wavelength $\lambda$.

This is the classical representation and we will mostly stick with this kind of explanation, however, there are times when classical analogies fail, and only quantum mechanics will correctly predict nature.

Quantization of energy - only discrete states available

Quantum mechanics tells us that systems can only exist in discrete states. There is no classical analogy here.

In classical mechanics, a spring of a specified length, width, and physical makeup can vibrate at any of an infinite number of frequencies. In quantum mechanics only discrete states are available, which are defined by the physical properties of the spring.

Since states are discrete, energy gaps are discrete, and spectroscopic band widths would be very narrow, but heterogeneity in sample and environment broadens most bands significantly.
Each component in an ensemble has a discrete transition energy, but heterogeneity within the ensemble of microsystems results in a broad band associated with the macrosystem.

Later: Dynamics will also be seen to effect linewidths.
We will also see later that spin states of nuclei and electrons are also quantized (“up” and “down”).

**Brief summary of quantum mechanics**

The state of a system (atom, molecule) is described by a wave function

$$\psi(x,y,z,\text{spin},t)$$  
($$\psi$$ is, in general, a complex function - imaginary numbers...)

The probability of finding the system at a particular set of conditions of a state is given by the product of $$\psi$$ and its complex conjugate $$\psi^*$$.

$$P = \psi \psi^*$$

The probability of the system being “anywhere” in state $$\psi$$ is determined by averaging over all conditions of that state:  

$$P(t) = \int P \, dx \, dy \, dz \, d(\text{spin}) = \int \psi \psi^* \, d\tau.$$  
Because QM tells us that systems exist discretely in a given state, then $$\int \psi \psi^* \, d\tau = <\psi | \psi> = 1.$$ (d$$\tau$$ means “over all space - dx dy dz)

**Operators - The Result of a Measurement**

An observable quantity (e.g. energy, dipole moment, location in space) is governed by a mathematical device known as an operator.

The Hamiltonian $$H$$ is used to describe the energy of a state.

The result of a measurement on a state (e.g. measure the energy) can be calculated by taking the average value of the operator operating on that state: the expectation value.

$$\int \int \int \psi \, H \, \psi^* \, dx \, dy \, dz = \int \psi \, H \, \psi^* \, d\tau = E$$  
in other words,

$$<\psi | H | \psi> = E$$

**A transition between two states can be induced by a perturbation.**

The effectiveness of this induction is governed by the extent to which the perturbation can deform the initial state to make it resemble the final state (i.e., mix the states)

Assume a perturbation which can mix states, described as a potential $$V$$.

The expectation that it will induce a system in state $$\psi_1$$ to effect a transition to state $$\psi_2$$ is given by

$$P(\text{mixing}) = <\psi_2 | V | \psi_1>$$  
remember that as $$V | \psi_1 \rightarrow \psi_2$$, then this goes to $$<\psi_2 | \psi_2> = 1$$

**Light can be a perturbation**

The ability of light to induce transitions can be calculated by its ability to induce dipole moments that oscillate with the light.
The electric component of light can induce dipoles in electronic states. In this case, the probability of an electric vector $\mathbf{u}$ inducing a transition is $<\psi_2|\mathbf{u}|\psi_1>$

**Perturbations have a directionality**
The preferred directions for inducing dipole moments are determined by and fixed with respect to the geometry of the molecule. $\psi$ is a function of space (x,y,z), as is $\mathbf{u}$, therefore the ability of the electric dipole (vector) to induce transitions is dependent on their relative geometries.

**Light can induce transitions between states** (CS 7.1)

**Energy match is required**
Probability of light-induced transition is related to the matching of the light energy to the energy difference between levels
From quantum mechanics, the probability of a system initially in state $a$ being found in state $b$ (ie. $a \rightarrow b$) is given by the following:

$$P_b = \frac{|\langle \psi_b | \mathbf{u} | \psi_a \rangle \cdot E_o|^2}{\hbar^2} \cdot \frac{t^2 \cdot \sin^2 \left( \frac{E_b - E_a - \omega}{\hbar/2\pi} t \right)}{2 \left( \frac{E_b - E_a - \omega}{\hbar/2\pi} t \right)}$$

$$P_B = |C_b(t)|^2 = \frac{1}{\hbar^2} \frac{t^2 \cdot \sin^2 \left[ \left( \frac{E_b - E_a}{\hbar} - \omega \right) t \right]}{2 \left[ \left( \frac{E_b - E_a}{\hbar} - \omega \right) t \right]^2}$$

$\mathbf{u}$ induces a dipole in state $a$, perturbing it to "resemble" state $b$. This term reflects this ability.

where $\mathbf{u}$ is the electric dipole operator, $E_o$ is the electric field (a vector), and $E_b$ and $E_a$ are the energies of systems in states $\psi_b$ and $\psi_a$, respectively.

Note that since $\hbar \omega$ is the energy of the light, transitions from $a$ to $b$ will be most likely when the denominator ($(E_b - E_a)/\hbar - \omega$) is small, that is when $\hbar \omega = E_b - E_a$ energy of light matches energy difference between states

The amount of net light absorption is dependent on the number of molecules in each state
It can be shown that for radiation centered at frequency $\nu$, the rate at which molecules are transformed from state $a$ to state $b$ is given by

$$\frac{dP_b}{dt} = \frac{d}{dt} \int d\nu |C_b(t)|^2 = \frac{1}{2\hbar^2} |\langle \psi_b | \mathbf{u} | \psi_a \rangle \cdot E_o|^2$$
for polarized light; a specific orientation of the molecule, and single frequency \( \nu \).

More generally, integrating over all orientations, it can be shown that

\[
|\langle \psi_b | \mathbf{u} | \psi_a \rangle \cdot \mathbf{E}_0|^2 = \frac{1}{3} |\langle \psi_b | \mathbf{u} | \psi_a \rangle|^2 |\mathbf{E}_0|^2
\]

then

\[
\frac{dP_b}{dt} = \frac{1}{6\hbar^2} |\langle \psi_b | \mathbf{u} | \psi_a \rangle|^2 |\mathbf{E}_0|^2
\]

From classical E & M:

\[
I(\nu) = \frac{|\mathbf{E}_0|^2}{4\pi} \quad \text{Intensity: energy density incident on the sample at frequency } \nu
\]

We can then define

\[
B_{ab} = \frac{2}{3} \frac{\pi}{\hbar^2} |\langle \psi_b | \mathbf{u} | \psi_a \rangle|^2 \quad \text{transition rate (} a \rightarrow b \text{) per unit energy density}
\]

So that

\[
\frac{dP_b}{dt} = B_{ab} I(\nu) \quad \text{the two components are separable}
\]

Note: \( V = k [C] \) analogy to a first order kinetic “reaction”

This result is for any system initially in state \( a \). It defines the probability of finding that system in state \( b \) at some time \( t \) (as a result of interaction of the system with the electric field component of the light. It contains two components: 1) \( B_{ab} \), the transition rate (analogous to a chemical rate constant) and 2) \( I(\nu) \), the energy density, or intensity, of the light - roughly the density of photons hitting the sample (analogous to “concentration of photons”). Note that at this point we have said nothing about which state is higher in energy.

A similar expression can be written for the transition from state \( b \) to state \( a \). So that light is both emitted and absorbed. The net change then depends on the population of each level, such that the net absorption of light can be written as:

\[
-\frac{dI(\nu)}{dt} = h\nu (N_a B_{ab} - N_b B_{ba}) \quad I(\nu) \text{ The rate at which energy is removed from the light}
\]

where \( h\nu = E_b - E_a \) (the energy of the transition between states)

For simple cases of interest to us, the Einstein coefficients \( B_{ab} = B_{ba} \), so that

\[
-\frac{dI(\nu)}{dt} = h\nu (N_a - N_b) \quad B_{ab} \quad I(\nu) \quad \leftarrow \text{N.B.}
\]
Thus, through the factors $N_a$ and $N_b$, light absorption depends not only on the concentration of the species, but also on the difference in population between the levels. A very important result of this is that no matter how much light you shine on the system, the most you can ever do is equally populate each of the levels. You can not (without getting fancy) “pump” all of the systems from state $a$ to state $b$. We will see this later.

**Light induces dipoles in molecules**

$B_{ab} \propto \langle \psi_b | \mathbf{\mu} | \psi_a \rangle = \text{the dipole moment induced by the light} = \text{transition dipole moment}$

Classically, electromagnetic radiation (light) possesses an electric field component, $E_o$ above. Since light is an oscillating wave, the electric field also oscillates. The oscillating field can then interact with an existing dipole or induce an oscillating dipole in the molecule, $\mathbf{\mu}$ above.

The integral $\langle \psi_b | \mathbf{\mu} | \psi_a \rangle$ (transition dipole moment, it is a vector) describes the ability of light to distort a molecule in state $a$ so as to produce a system which resembles state $b$.

Oscillations have a time component, and so have phase. This will be important when two dipoles are simultaneously excited. Relative phases important.

**Transitions induced in both directions equally.**

Purely a result of quantum mechanics

Net absorption usually observed, due to population of states (see below).

**Dipole-dipole interaction (CS p. 263-265)**

The interaction energy for two point dipoles is given by:

$$E_d = \varepsilon^{-1} \left[ \frac{\mathbf{\mu}_A \cdot \mathbf{\mu}_B}{r^3} - \frac{3 (\mathbf{\mu}_A \cdot \mathbf{r}) (\mathbf{\mu}_A \cdot \mathbf{r})}{r^5} \right]$$

In this point dipole approximation, the charge separation (distance) within each dipole is assumed to be much smaller than the distance separating the two dipoles. This is not necessarily true in chemical systems, but a more rigorous calculation is generally prohibitive. A further approximation is generally made in dropping the second term in the equation. This assumption is generally not too bad.
Note that the dielectric constant, $\varepsilon$, is involved. Pictorially, this means that if the intervening medium has its own dipoles between the two point dipoles, their effect will lessen the interaction between the two dipoles. Note also that there is an angular dependence, such that dipoles oriented 90° with respect to one another have no interaction energy.

Finally, the large distance dependence ($\frac{1}{r^3}$) in this equation shows that only near neighbor atoms in a molecule interact substantially.

**Boltzmann distribution** (VH 2; CS 8.2)

**Boltzmann equation specifies thermal distribution:**

$$n_b = n_a e^{-\frac{(E_b - E_a)}{kT}}$$

$$\frac{n_b}{n_a} = e^{-\frac{\Delta E}{kT}}$$

Thermal energy allows for transitions between states, but this is, of course, limited by the energy separation of the states relative to the thermal energy (i.e. the temperature).

The temperature equivalent of photons are called phonons. Thermal energy (the phonon bath) generally spans a wide range of energies, and so heat can usually bring a system to thermal equilibration.

**Implications:**

For states separated by substantial energy gap, lower energy state will be exclusively populated, i.e. as $\Delta E \to \infty$, $n_b/n_a \to 0$.

For closely spaced states, populations can be almost evenly distributed, i.e. as $\Delta E \to 0$, $n_b/n_a \to 1$.

Temperature dependence: as $T \to 0$(K), high energy states depopulated, $n_b/n_a \to 0.$