Chemistry 24b
Spring Quarter 2004 ***EXTRAS***
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From last lecture,

$$\alpha_0 = \frac{e^2}{m}\left[\frac{(\omega_0{}^2-\omega^2)}{(\omega_0{}^2-\omega^2)^2+4\omega'^2\omega^2}\right] \qquad \text{contribution to dispersion}$$

$$\alpha_{90} = \frac{2e^2}{m}\left[\frac{\omega\omega'}{(\omega_0{}^2-\omega^2)^2+4\omega'^2\omega^2}\right] \qquad \text{contribution to absorption}$$

where $\mu^{in} = \alpha_0 E_0^* \sin\omega t - \alpha_{90} E_0^* \cos\omega t$

For w ~ w$_0$ (Resonance)

$$\alpha_0 \cong 0$$

$$\alpha_{90} > 0 \qquad \alpha_{90}^{\max} = \frac{e^2}{m}\frac{1}{\omega'\omega_0}$$

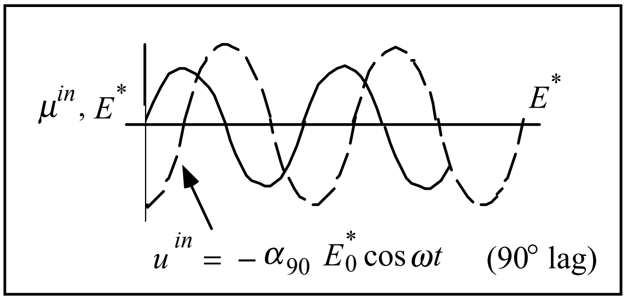


Figure 10-1

For w >> w$_0$ or w << w$_0$

$$(\omega_0{}^2-\omega^2)^2 >> 4\omega'^2\omega^2$$

$$\alpha_0 = \frac{e^2}{m}\frac{1}{(\omega_0{}^2-\omega^2)}$$

$$\alpha_{90} = \text{small}$$

$\therefore \quad \mu^{in} = \alpha_{90} E_0^* \sin\omega t$ (in phase only) depending on sign of α_0
or 180°out - of - phase

At low frequencies,

$$\omega_0 \gg \omega, \quad \alpha_0 > 0$$

$$\mu^{in} \quad \text{in phase}$$

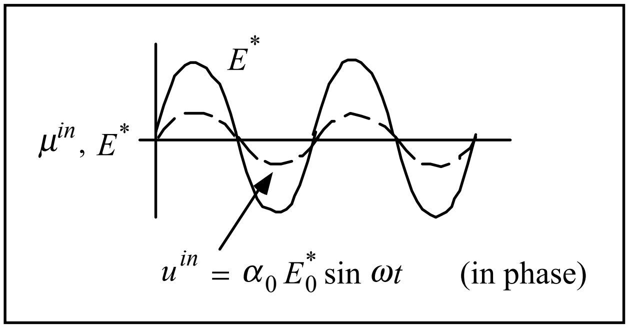


Figure 10-2

At high frequencies,

$$\omega_0 \ll \omega, \quad \alpha_0 < 0$$

$$\mu^{in} \quad \text{out - of - phase by } 180^{\circ}$$

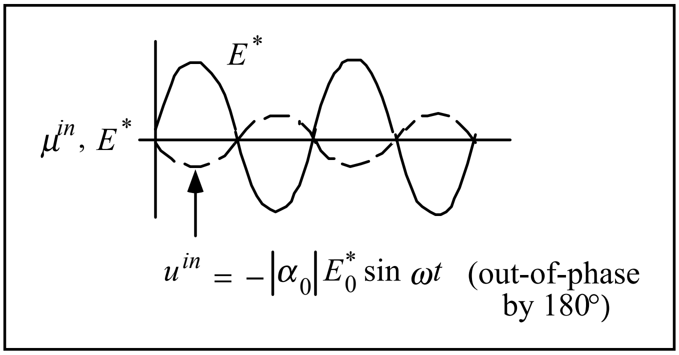


Figure 10-3

Interaction of Light with Molecules — Quantum Mechanical Treatment

Must solve time-dependent Schroedinger equation.

$$H = H^{0}_{\text{isolated molecule}} + v(t)$$

where $v(t)$ describes the interaction of electrons with light waves.

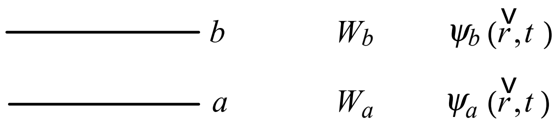
Assume one electron.

If electric interaction, $\quad v(t) = -\vec{\mu}_{el} \cdot \vec{E}^*$

If magnetic interaction, $\quad v(t) = -\vec{\mu}_{m} \cdot \vec{E}^*$

Discuss electric interaction, where $\vec{\mu}_{el} = -|e|\,\vec{r}$.

Treat, for simplicity, a two-level system.



$$\left.\begin{aligned} \psi_a(\vec{r},t) &= \phi_a(\vec{r})\, e^{\frac{-iW_a t}{\hbar}} \\ \psi_b(\vec{r},t) &= \phi_b(\vec{r})\, e^{\frac{-iW_b t}{\hbar}} \end{aligned}\right\} \begin{array}{l}\text{solution to time-dependent}\\ \text{Schroedinger equation for } v(t)=0\end{array}$$

In the presence of $v(t)$,

$\psi(\vec{r},t)$ must be a linear combination of these two states, but the coefficients c_a and c_b are time-dependent, i.e.,

$$\psi(\vec{r},t) = c_a(t)\,\phi_a(\vec{r})\,e^{\frac{-iW_a t}{\hbar}} + c_b(t)\,\phi_b(\vec{r})\,e^{\frac{-iW_b t}{\hbar}}$$

Substituting this solution into the time-dependent Schroedinger equation, we get

$$i\hbar\left(\phi_a(\vec{r})\,e^{\frac{-iW_a t}{\hbar}}\frac{dc_a}{dt} + \phi_b(\vec{r})\,e^{\frac{-iW_b t}{\hbar}}\frac{dc_b}{dt}\right)$$

$$= v(t)\left[\phi_a(\vec{r})\,e^{\frac{-iW_a t}{\hbar}}c_a(t) + \phi_b(\vec{r})\,e^{\frac{-iW_b t}{\hbar}}c_b(t)\right]$$

Multiplying and integrating above from the left by $\phi_a^*(\vec{r})\,e^{\frac{iW_a t}{\hbar}}$ or $\phi_b^*(\vec{r})\,e^{\frac{iW_b t}{\hbar}}$, we obtain

$$i\hbar\frac{dc_a}{dt} = v_{aa}c_a(t) + v_{ab}c_b(t)\,e^{\frac{-i(W_b-W_a)t}{\hbar}}$$

$$i\hbar\frac{dc_b}{dt} = v_{ba}c_a(t)\,e^{\frac{-i(W_a-W_b)t}{\hbar}} + v_{bb}c_b(t)$$

$$
\begin{aligned}
\text{where} \quad v_{aa} &= \left(\int \phi_a^*(\vec{r})\, v(t)\, \phi_a(\vec{r})\, d\vec{r} \right) \\
v_{ab} &= \left(\int \phi_a^*(\vec{r})\, v(t)\, \phi_b(\vec{r})\, d\vec{r} \right) = v_{ba} \\
v_{bb} &= \left(\int \phi_b^*(\vec{r})\, v(t)\, \phi_b(\vec{r})\, d\vec{r} \right)
\end{aligned}
$$

a set of coupled first-order differential equations.

If we take

$$
\begin{aligned}
v(t) &= -\vec{\mu} \cdot E_0^* e^{i\omega t} \\
\text{where} \quad \vec{\mu} &= -|e|\,\vec{r} \\
\text{then} \quad v_{aa} &= 0\,, \quad v_{bb} = 0 \qquad \text{and}
\end{aligned}
$$

$$
\begin{aligned}
-i\hbar \frac{dc_a}{dt} &= c_b(t)\vec{\mu}_{ab} \cdot \vec{E}_0^* e^{-i\left(\frac{W_b - W_a}{\hbar} - \omega\right)t} \\
-i\hbar \frac{dc_b}{dt} &= c_a(t)\vec{\mu}_{ba} \cdot \vec{E}_0^* e^{-i\left(\frac{W_a - W_b}{\hbar} - \omega\right)t}
\end{aligned}
$$

Solving simultaneously, with boundary condition $|c_b(0)|^2 = 0$ at $t = 0$, i.e., electron is in quantum state <u>*a*</u> at $t = 0$, and for small E_0^*

$$
|c_b(t)|^2 = \left|\vec{\mu}_{ba} \cdot E_0^*\right|^2 t^2 \, \frac{\sin^2\left[\left(\frac{W_b - W_a}{\hbar} - \omega\right)\frac{t}{2}\right]}{2\left[\left(\frac{W_b - W_a}{\hbar} - \omega\right)\frac{t}{2}\right]^2}
$$

$$
\text{where} \quad \vec{\mu}_{ba} = \int \phi_b^* \vec{\mu}\, \phi_a\, d\vec{r} = \vec{\mu}_{ab} = \int \phi_a^* \vec{\mu}\, \phi_b\, d\vec{r}
$$

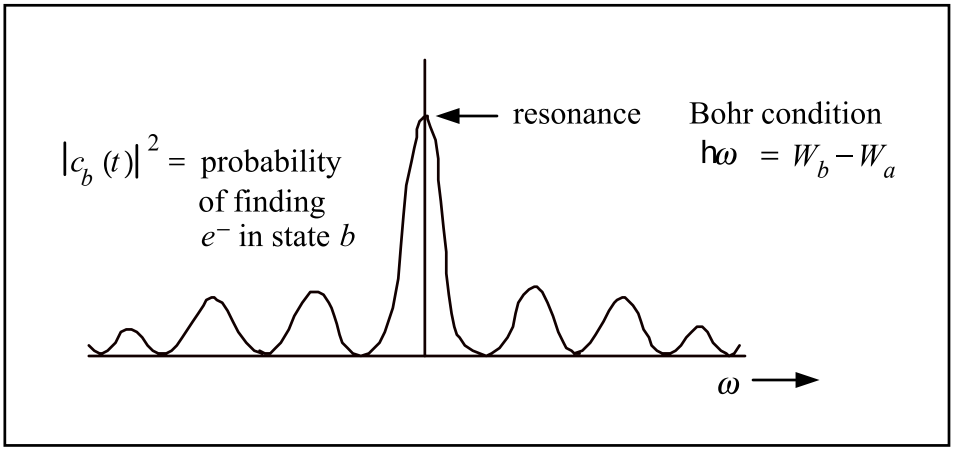


Figure 10-4

Now, the rate at which molecules in state a are transformed to state b by the presence of light is

$$\begin{aligned}\frac{dP_b}{dt} &= \frac{d}{dt}\int |c_b(t)|^2 \, d\nu \\ &= \frac{1}{2\hbar^2}\left|\vec{\mu}_{ba}\cdot E_0^*\right|^2\end{aligned}$$

It is customary to write

$$\frac{dP_b}{dt} = B_{ab}\, I(\nu)$$

where B_{ab} = transition rate per unit energy density of radiation
a = initial state
b = final state
$I(\nu)$ = energy density incident on the sample at frequency ν

From E and M,

$$I(\nu) = \frac{\left|E_0^*\right|^2}{4\pi}$$

so $$B_{ab} = \left(\frac{2\pi}{\hbar^2}\right)|\vec{\mu}_{ab}|^2 \cos^2\theta$$

where θ = angle between $\vec{\mu}$ and $\vec{E}_0^*$

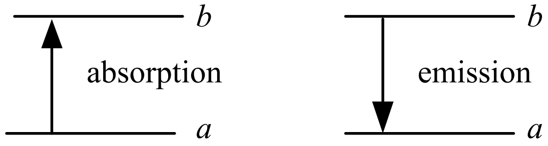
The above result is for <u>oriented</u> molecules illuminated by <u>polarized</u> light.

In solution, molecules reorient with respect to E^*, so you must average $\cos^2\theta$.

Since $\overline{\cos^2\theta} = \dfrac{1}{3}$

$$B_{a\to b}\ (\text{solution}) = \left(\frac{2\pi}{3\hbar^2}\right)|\vec{\mu}_{ab}|^2$$

The above derivation is for <u>stimulated</u> absorption $(a \to b)$.



Stimulated B coefficient can be obtained for stimulated emission $(b \to a)$, i.e.,

$$\left.\begin{aligned} B_{a\to b} &= B_{b\to a} \\ \text{or}\quad B_{ab} &= B_{ba} \end{aligned}\right\}\ \begin{array}{l}\text{Einstein coefficient for stimulated} \\ \text{absorption and emission}\end{array}$$

Now the rate at which energy is renewed from light will depend on the number of $a \to b$ absorption transitions stimulated by the light, on the number of $b \to a$ emission transitions (also stimulated by the light), and on the energy of the photon $(W_b - W_a = h\nu)$ where $W_b - W_a = \hbar\omega$.

$$-\frac{d\,I(\nu)}{dt} = h\nu\left(N_a B_{ab} - N_b B_{ba}\right) I(\nu)$$

where N_a, N_b $\equiv$ number of molecules per cm^3 in state a and b respectively

$I(\nu) \equiv$ ν

Beer-Lambert's Law

For optical transitions, N_b is negligible.

$$-\frac{d\,I(\nu)}{dt} \cong h\nu\, N_a B_{ab}\, I(\nu)$$

$$= h\nu \frac{C N_A}{1000} B_{ab}\, I(\nu) \qquad C \equiv \text{concentration of absorbers (all in state } a\text{)}$$

Now
$$\underset{\substack{\Uparrow \\ \text{path length}}}{\frac{dI(\nu)}{dl}} = \frac{dI(\nu)}{dt}\left(\frac{dt}{dl}\right) = \frac{1}{c_{light}}\frac{dI(\nu)}{dt} = \frac{h\nu}{c_{light}}\frac{CN_A}{1000}B_{ab}I(\nu)$$

or
$$dI(\nu) = \left(\frac{h\nu CN_A}{1000\,c_{light}}B_{ab}\right)I(\nu)\,dl$$

or
$$\varepsilon(\nu) = \frac{h\nu N_A}{1000\,c_{light}}B_{ab} \qquad \varepsilon \equiv \text{extinction coefficient}$$

or
$$B_{ab} = \frac{1000\,c_{light}}{h\nu N_A}\,\varepsilon(\nu)$$

or integrating over absorption band

$$B_{ab} = \frac{1000\,c_{light}}{h N_A}\int_{\substack{absorption \\ band}}\frac{\varepsilon(\nu)}{\nu}\,d\nu$$