***Chemistry 24b*** **Lecture 23**
***Spring Quarter 2004***
***Instructor: Richard Roberts***

## Absorption and Dispersion

$\vec{E}$ of light waves has two effects on a molecule or atom.

(1) It induces a dipole moment in the atom or molecule.

$$\vec{\mu}^{in} = \alpha \vec{E}$$

$\alpha \equiv$ molecular polarizability

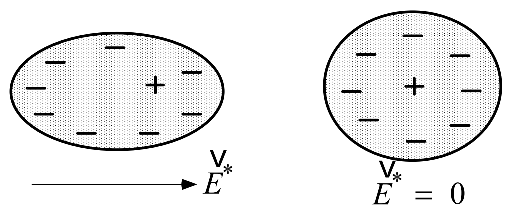



Figure 9-9

(2) If the molecule has a permanent dipole moment, $\vec{\mu}$, it can attempt to align the molecular dipoles (counteracted by thermal motions).

Debye showed that for molecules in a gas or in a dilute solution, $\vec{\mu}$ and $\alpha$ are related to the dielectric constant $\varepsilon$ of the substance.

$$\frac{(\varepsilon-1)}{(\varepsilon+2)}\frac{M}{\rho} = \frac{4\pi N_A}{3}\left(\alpha+\frac{\mu^2}{3k_B T}\right) \qquad \varepsilon = \text{ dielectric constant}$$

At high temperatures, $\vec{E}$ cannot align $\vec{\mu}$ very effectively so $\alpha$ dominates.

Also, when the frequency of light waves becomes very high, permanent dipoles of molecules cannot follow the oscillations of $\vec{E}$ and therefore do not become aligned, even partially, with $\vec{E}$. So,

$$\frac{(\varepsilon_{hf}-1)}{(\varepsilon_{hf}+2)}\frac{M}{\rho} = \frac{4\pi N_A}{3}\alpha$$

and it iturns out $\varepsilon_{hf} = n^2$ or the square of the refractive index of the substance.

## Dielectric Absorption of a Hemoglobin Solution. Dispersion

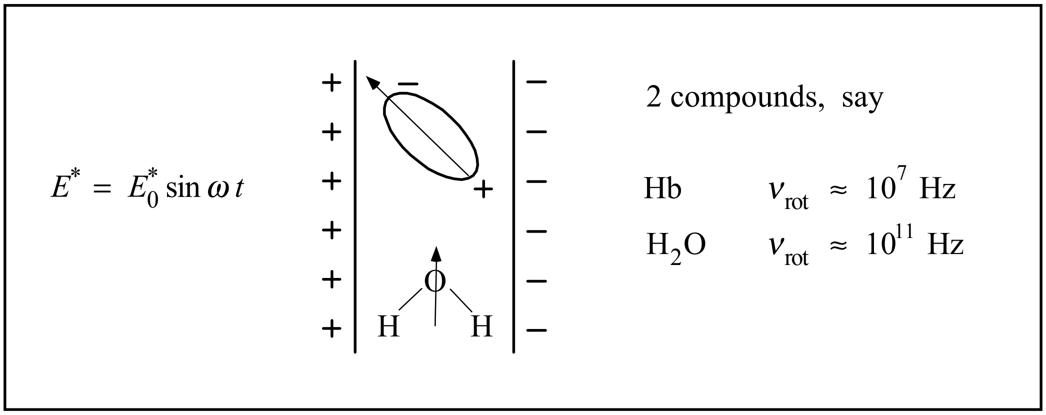



Figure 9-10

At $\omega / 2\pi < 10^7$ Hz, both Hb and $H_2O$ will contribute to $\mu^2$ and to $\varepsilon$ of solution.

As $\omega / 2\pi$ is swept through $10^7$ Hz, the solution will absorb power from *rf* circuit. Absorption is caused by the lagging of Hb dipoles behind the oscillation of the alternating electric field. As $\omega / 2\pi$ passes through this region, the dipoles of the Hb can no longer come to alighment with the a.c. field.

So, at frequencies above $10^7$ Hz, $\mu^2$ of Hb no longer contributes to $\varepsilon$ of solution. This decline in dielectric constant is called a dispersion, and the absorption of energy associated with it is called a dielectric loss.

Similarly, as $\omega / 2\pi$ passes through $10^{11}$ Hz, similar dielectric absorption and dispersion occurs as the water dipoles can no longer come into alignment with $\vec{E}^*$.

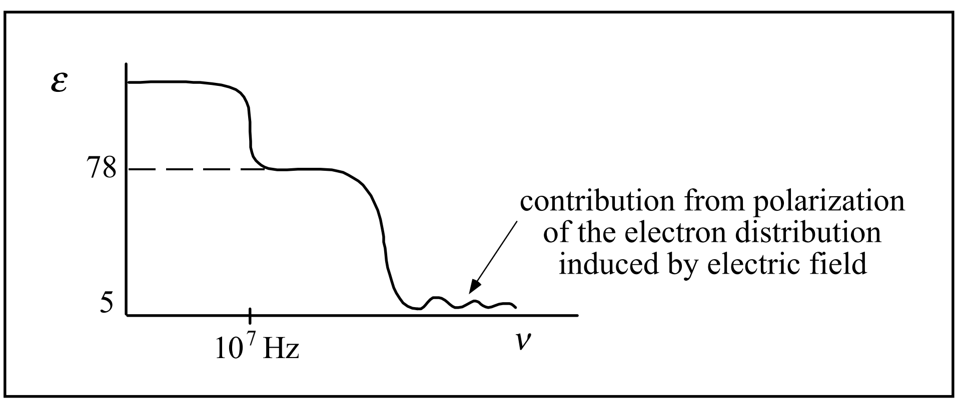
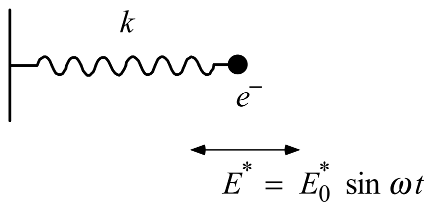



Figure 9-11

**Dipoles Can Absorb Power from *rf* Circuit when Their Oscillations Lag 90° Behind the Polarizing $\vec{E}^*$**

Consider




Driving electric field: $E^* = E_0^* \sin \omega t$

Vibrational frequency of $e^-$: $\omega_0 = \sqrt{k/m}$

At resonance,

$$x = x_0 \sin \omega t + x_{90} \cos \omega t$$

where $x$ = displacement of $e^-$ from equilibrium position

$x_0 \sin \omega t$ is in phase with force $\left(E_0^* \sin \omega t\right)$

$x_{90} \cos \omega t$ is $90^{\circ}$ out of phase with force $\begin{cases} \text{if } x_{90} < 0, & \text{lags} \\ \text{if } x_{90} > 0, & \text{leads} \end{cases}$

The work done on $e^-$ in a complete cycle of the electrostatic field is zero, if the oscillation of the $e^-$ stays in phase with the driving field $\left(x = x_0 \sin \omega t\right)$.

$$\text{Work done by field on charge} = \int_{cycle} F\,dx$$

$$= \int_{cycle} qE^*\,dx = q\int_{cycle} E_0^* \sin \omega t \cdot d\left(x_0 \sin \omega t\right)$$

$$= qE_0^* x_0 \int_0^{2\pi} \sin\theta \; d\,\sin\theta \qquad \theta = \omega t$$

$$= qE_0^* x_0 \left.\frac{\sin^2\theta}{2}\right|_0^{2\pi} = 0$$

Work is done on $e^-$ in a complete cycle of the electrostatic field, if the oscillation of the $e^-$ lags 90° out of phase with the driving field $\left(x = -\left|x_{90}\right| \cos \omega t\right)$.

$$\text{Work done by field on charge} = \int_{cycle} F\,dx$$

$$= q \int E_0^* \sin \omega t \cdot d\left(-|x_{90}| \cos \omega t\right)$$

$$= -q E_0^* |x_{90}| \int_{cycle} \sin \omega t \; d \cos \omega t$$

$$= +q E_0^* |x_{90}| \int_0^{2\pi} \sin^2 \theta \, d\theta$$

$$= \pi q E_0^* |x_{90}| \quad > 0 \qquad \therefore \; e^- \text{ or charge absorbs power from } rf \text{ circuit}$$

Note that when oscillation of $e^-$ (response) leads the driving field by 90°,

$$\text{Work done by field on charge} = -\pi q E^{0*} |x_{90}|$$

So $e^-$ or charge does work on the *rf* circuit.

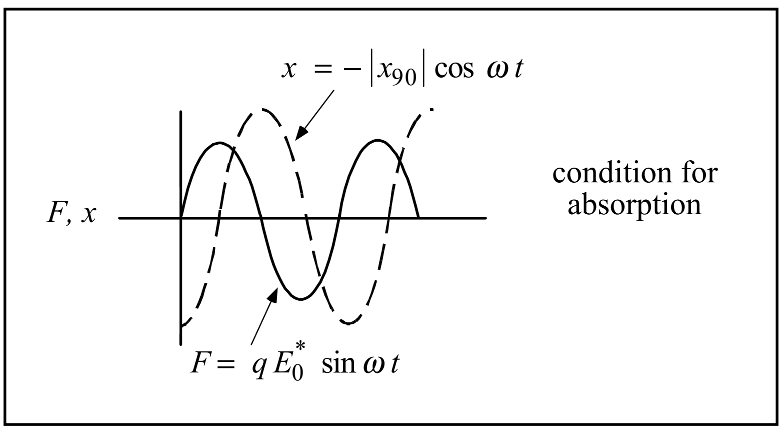
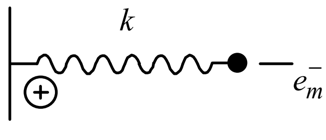



Figure 9-12

## Classical Mechanical Description of Absorption and Dispersion — Detailed Treatment

Problem




$$E^* = E_0^* \sin \omega t$$

(1) Electromagnetic wave: $E_0^* \sin \omega t \qquad \omega = 2\pi\nu$

(2) Natural frequency of oscillator: $\omega_0 = \sqrt{k/m}$

(3) Forces on $e^-$

- (a) Driving force of electromagnetic wave: $-|e|\, E_0^* \sin \omega t$
- (b) Restoring force between negative electron and positive charge: $-kx$
- (c) Damping force, which is proportional to the velocity of the moving electron and arises from frictional and radiative energy losses: $-\eta \dfrac{dx}{dt}$

**Newton's Equation of Motion Applied to e$^-$**

$$\sum \text{Force} = m\frac{d^2x}{dt^2}$$

$$-|e|\, E_0^* \sin \omega t - kx - \eta\frac{dx}{dt} = m\frac{d^2x}{dt^2}$$

General solution to linear second-order differential equation:

$$x = x_0 \sin \omega t + x_{90} \cos \omega t\,; \qquad \text{let } \beta = \frac{x_{90}}{x_0}$$

$$= x_0 \sin \omega t + \beta\, x_0 \cos \omega t$$

Differentiating,

$$\frac{dx}{dt} = \omega x_0 \cos \omega t - \omega\beta x_0 \sin \omega t$$

$$\frac{d^2x}{dt^2} = -\omega^2 x_0 \sin \omega t - \omega^2 \beta x_0 \cos \omega t$$

Substituting into $F = ma$ and collecting terms,

$$\left[-|e|E_0^* - kx_0 + \eta\,\omega\beta x_0 + \omega^2 x_0 m\right]\sin\omega t$$
$$+\left[-k\beta x_0 - \eta\,\omega\,x_0 + m\omega^2\beta x_0\right]\cos\omega t = 0$$

True for all values of time.

Therefore

$$-|e|E_0^* - kx_0 + \eta\,\omega\beta x_0 + m\omega^2 x_0 = 0 \quad \text{and}$$
$$-k\beta x_0 - \eta\,\omega\,x_0 + m\omega^2\beta x_0 = 0$$

Thus $\beta = \dfrac{\eta\,\omega}{m\omega^2 - k}$ and

$$x_0 = \frac{eE_0^*}{m\omega^2 - k + \eta\,\omega\beta}$$

Since $k = m\omega_0^{\,2}$ and

Define $\omega' = \dfrac{\eta}{2m}$

$$\beta = \frac{2m\omega\omega'}{m\omega^2 - m\omega_0^{\,2}} = -\frac{2\omega\omega'}{\omega_0^{\,2} - \omega^2}$$

$$x_0 = \frac{|e|E_0^*}{m\omega^2 - m\omega_0^{\,2} + 2m\omega\omega'\beta}$$

$$= \frac{-|e|E_0^*}{m}\left[\frac{\omega_0^{\,2} - \omega^2}{\left(\omega_0^{\,2} - \omega^2\right)^2 + 4\omega'^2\omega^2}\right]$$

Note that when the periodic driving force is removed, one has a damped oscillator, in which case

$$x = x_0 e^{-\omega' t}\cos\left[\left(\omega_0^{\,2} - \omega'^2\right)^{\frac{1}{2}} t\right]$$

where $\omega' = \dfrac{\eta}{2m}$

**Polarizabilities**

$$\alpha = \frac{\mu^{in}}{E^*} = \frac{-|e|x}{E^*} \qquad \underline{\text{Static field } E^*}$$

For our problem here,

$$\mu^{in} = -|e| x_0 \sin\omega t - |e| \beta x_0 \cos\omega t$$

in phase component — out of phase component ($90^o$)

Define $\alpha_0 = -\dfrac{|e| x_0}{E_0^*}$ in phase polarizability

$\alpha_{90} = \dfrac{|e|\beta x_0}{E_0^*}$ out of phase polarizability (choose sign such that it lags)

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

Substituting

$$\alpha_0 = \frac{e^2}{m} \frac{(\omega_0{}^2 - \omega^2)}{(\omega_0{}^2 - \omega^2)^2 + 4\omega'^2\omega^2}$$

$$\alpha_{90} = \frac{2e^2}{m} \frac{\omega\omega'}{(\omega_0{}^2 - \omega^2)^2 + 4\omega'^2\omega^2}$$

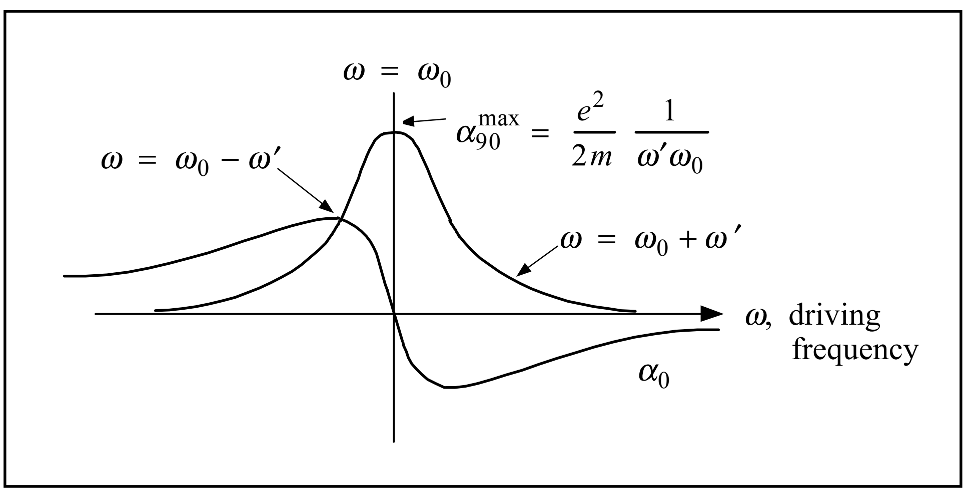



Figure 9-13

It turns out

Extinction coefficient $\varepsilon(\omega) = \dfrac{4\pi N_A}{2303\,c}\,\omega\alpha_{90}$

$$n^2 \cong 1 + \frac{4\pi N_A \rho}{M}\,\alpha_0 \qquad n \equiv \text{refractive index}$$

$$I_s\left(\theta = 90^{\circ}\right) = \frac{I_0\, 16\pi^4\, \alpha_0{}^2\, \nu^4}{r^2 c^4}$$