5.33 Lecture Notes: A Classical Description of Absorption

Why is there light absorption?

What is your picture? Quantum mechanical?

This quantum mechanical picture may satisfy conservation of energy (when you quantize light and molecular energies), but it has lots of problems and doesn't tell you much.

We can learn a lot from classical models of light absorption

Classically, light interacts with charges:

Molecules are composed of charges particles. Light (an electromagnetic field) exerts a force on these charges. The force exerted on the molecules depends on the strength of the field, the magnitude of the charges, and how far the charges move. (…more on this later).

A classical model of absorption:

We need to describe three things:

(1) Light: An oscillating electric (and magnetic) field
(2) Matter: Treat as a harmonic oscillator
(3) Interactions: Oscillating external force field driving harmonic oscillator

1) *Light*

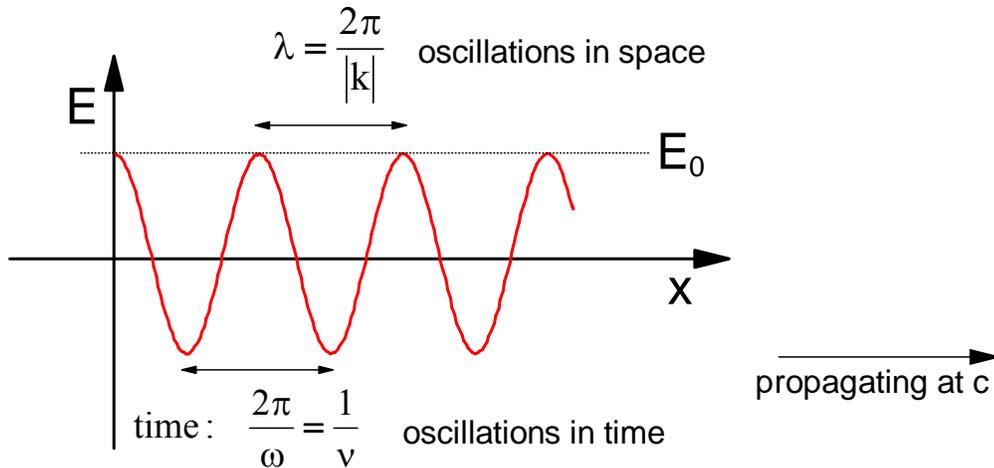An oscillating electromagnetic field, which oscillates in time and space.

$$\overline{E}(\overline{r}, t) = \hat{\varepsilon}(\overline{r}) \; E_o \cos(\omega t - \overline{k} \cdot \overline{r} - \phi)$$

Polarization vector

Amplitude

Frequency (rad/sec)

Wavevector defines direction of propagation

To simplify:

(1) Propagate along $\hat{x}$; (2) $\phi = 0$ (for the time being we will drop the polarization)

$$E(x, t) = E_o \cos(\omega t - kx)$$

$$\lambda = \frac{2\pi}{|k|} \quad \text{oscillations in space}$$

E

E_0

X

propagating at c

$$\text{time}: \quad \frac{2\pi}{\omega} = \frac{1}{\nu} \quad \text{oscillations in time}$$

Now, we will drop wave vector ($|k| \to 0$, since $\lambda \gg x$ and we consider molecules at x=0)

$$E(t) = E_o \cos \omega t \qquad\qquad I = \frac{c}{4\pi} |E_o|^2$$

$$|k| = \frac{2\pi}{\lambda} = \frac{\omega}{c}$$

$$c = 2.998 \times 10^8 \, \text{m/s}$$

(2)   *Molecules*

$\rightarrow$ treat as harmonic oscillator

Why should we be able to call molecules harmonic oscillators? i.e., a mass on a spring?

Molecules feel a restoring force when pushed from equilibrium.

The covalent bond can be thought of as a spring. The equilibrium length is a balance
between attractive and repulsive forces. If we push/pull on this bond, there is a
restoring force that pushes the system back to equilibrium.

This analogy works for other systems also.

$\rightarrow$ Electronic states—think of pushing electron clouds away from equilibrium
distribution. (for instance, benzene pi orbitals)

$\rightarrow$ Magnetic resonance—In a magnetic field, magnetic spin moments—nuclear
spins—align with field.

If we push a spin away from field, it will want to relax back.

Classical Equation of Motion for Harmonic Oscillation

Potential Energy for Harmonic Oscillator
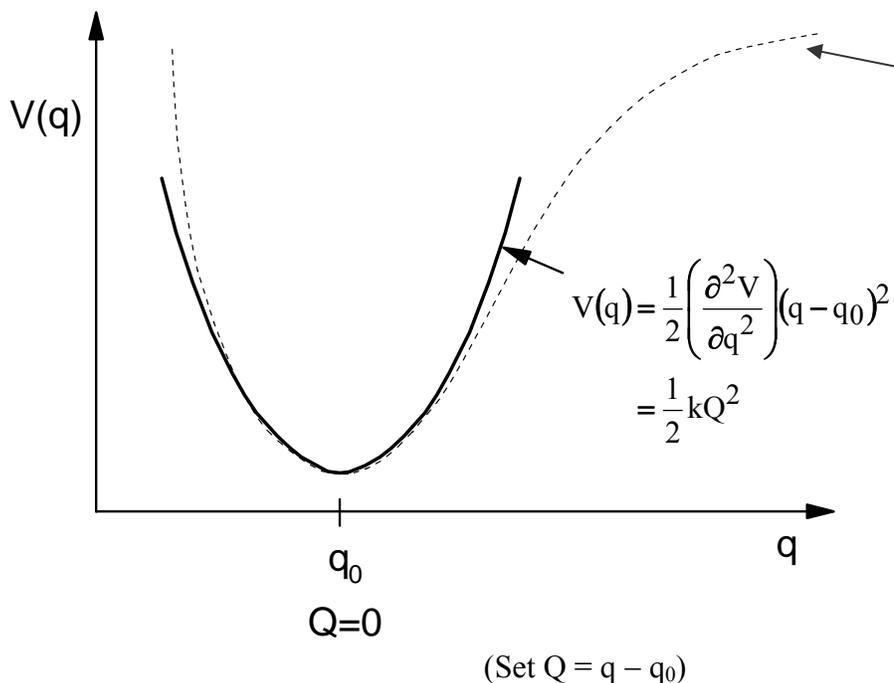
- For molecules, we expect anharmonic curves that reflect attractive and repulsive forces.
- A finite amount of energy pulls the molecule apart.

$$V(q) = \frac{1}{2}\left(\frac{\partial^2 V}{\partial q^2}\right)(q - q_0)^2$$

$$= \frac{1}{2}kQ^2$$

q_0

$Q = 0$

(Set $Q = q - q_0$)

k is force constant

Linear restoring force: $F_{res} = -\dfrac{\partial V}{\partial Q} = -kQ$

Equation of Motion from Newton $\quad F = ma \qquad m\dfrac{\partial^2 Q}{\partial t^2}$

$$m\frac{\partial^2 Q}{\partial t^2} = F_{res} + F_{damp} + F_{ext} \qquad\qquad \text{driving force}$$

$$= -kQ - b\frac{\partial Q}{\partial t} + F_{ext}$$

$$\frac{\partial^2 Q}{\partial t^2} + \frac{b}{m}\frac{\partial Q}{\partial t} + \frac{kQ}{m} = \frac{F_{ext}}{m}$$

with light field
$$F_{ext}(t) = F_o \cos \omega t$$

Solutions:

a) <u>**Harmonic oscillator with no damping/no external force**</u>

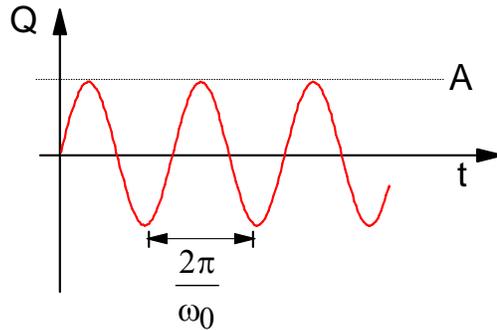$$m\frac{\partial^2 Q}{\partial t^2} + kQ = 0$$

Solution:
$$Q(t) = A \sin(\omega_o t) + B \cos(\omega_o t)$$

drop for now

resonance frequency: $\quad \omega_o = \sqrt{\dfrac{k}{m}}$

Oscillations at ω_0 continue forever.

b) <u>**Now we add damping—H.O. may feel friction that reduces the amplitude of oscillation**</u>

$$m\frac{\partial^2 Q}{\partial t^2} = F_{res} + F_{damp} = -kQ - b\frac{\partial Q}{\partial t}$$

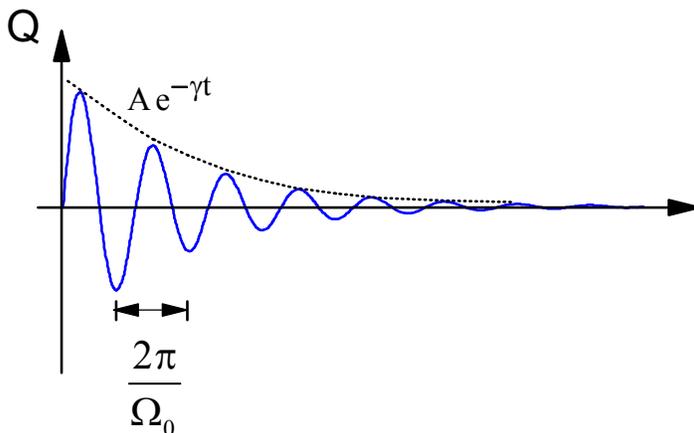$$\frac{\partial^2 Q}{\partial t^2} + \frac{b}{m}\frac{\partial Q}{\partial t} + \frac{kQ}{m} = 0$$

$$Q(t) = A e^{-\gamma t} \sin \Omega_o t \qquad \text{Now oscillation decays away exponentially}$$

$\gamma = b/2m$ $\qquad$ $\Omega_o = \sqrt{\omega_o^2 - \gamma^2} \approx \omega_o$

reduced frequency $\qquad$ for weak damping

Rewrite equation of motion:

$$\frac{\partial^2 Q}{\partial t^2} + 2\gamma \frac{\partial Q}{\partial t} + \omega_0^2 Q = \frac{F_{ext}(t)}{m}$$

$$for \quad F(t) = 0$$
$$Q(t) = e^{-\gamma t} \sin\Omega_{ot}$$

c)   Apply external driving force → interaction of molecule with EM field

You know what to expect:

The effect depends on the frequency of the driving field . . . like pushing someone on a swing.

- The most efficient way to push someone higher is to push at a frequency corresponding to their swinging frequency
- This leads to a big displacement.
- If you push with arbitrary frequency, nothing will happen.

So you know that we should have a "resonance":

- When you drive the system with frequency $\omega \approx \omega_o$ there will be an efficient transfer of power and the displacement of the H.O. will increase

Indeed, that is what an absorption spectrum is! Measure the power absorbed by the system from the field.

Now let's solve the equation:

Set: $F_0 \propto E_0$

$$F_{ext}(t) = F_o \cos\omega t$$

$$Q(t) = A\sin(\omega t + \beta) = \frac{F_o/m}{\left(\left(\omega_o^2 - \omega^2\right)^2 + 4\gamma^2\omega^2\right)^{\frac{1}{2}}} \sin(\omega t + \beta)$$

$$\tan\beta = \frac{\omega_o^2 - \omega^2}{2\gamma\omega}$$

Notice that the coordinate oscillates at the driving frequency ω!

Notice that it oscillates 90° out of phase with field when driven on resonance. →
absorbing power from field.

If $\gamma << \omega_o$ and near resonance $\omega_o \approx \omega$

$$\left(\omega_o^2 - \omega^2\right)^2 = \left(\omega_o - \omega\right)^2 \left(\omega_o + \omega\right)^2 \approx 4\omega_o^2 \left(\omega_o - \omega\right)^2$$

$$Q(t) = \frac{F_o}{2m\omega_o} \frac{1}{\left[\left(\omega_o - \omega\right)^2 + \gamma^2\right]^{1/2}} \sin\left(\omega t + \beta\right)$$
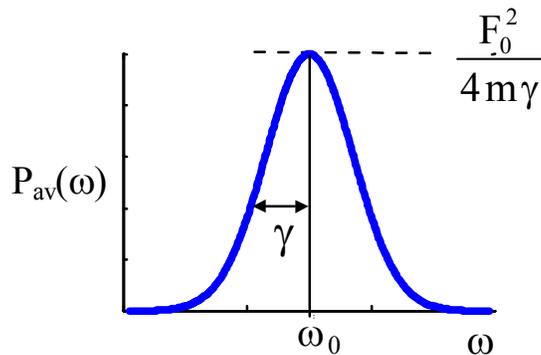
Now we can calculate the absorption spectrum → power absorbed.

Power = force **x** *velocity*

$$P_{avg} = \left\langle F(t) \cdot \frac{\partial Q}{\partial t} \right\rangle_{avg}$$

(avera

Average over several cycles

$$= \frac{\gamma F_0^2}{2m} \frac{1}{\left(\omega - \omega_0\right)^2 + \gamma^2}$$

Let's plot the power absorbed as a function of frequency:

LORENTZIAN LINESHAPE
peak is at $\omega = \omega_o$

$$\frac{F_0^2}{4m\gamma}$$

$P_{av}(\omega)$

γ

ω_0 ω

At what frequency
shift relative to
maximum is the
absorbed power
reduced by ½?
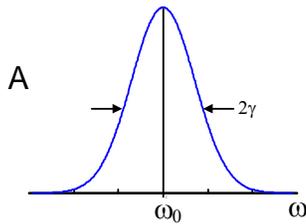
$$\omega - \omega_o = \pm\gamma$$

The full-width at half-maximum intensity (FWHM) is 2γ .

peak → ω_o width → γ Area under lineshape → $\dfrac{\pi F_0^2}{4m}$

So what are we learning about molecules?

Well, you can see from the spectrum that we have been able to determine ω_o and γ.

Take HCl. We take an IR absorption spectrum *in solution*, and we see:

$$\frac{\omega_0}{2\pi c} \cong 3000\,cm^{-1} \quad \gamma \cong 15\,cm^{-1}$$

ω_o : We know the frequency of oscillation of the H-Cl bond:

$$\frac{2\pi}{\omega_0} = \tau = 1 \times 10^{-14}\,s \qquad 10\,fs$$

How do we know that's what we are seeing? We predict an isotope effect!

$$\omega_0 = \sqrt{\frac{k}{m}}$$

Now for the mass *m* we want to use the reduced mass μ or m_R. (This is the effective mass: we need this for 2 masses on a spring with a fixed center of mass.)

$$\mu = m_R = \frac{m_A m_B}{m_A + m_B} \text{ for a diatomic molecule A-B.}$$

$$m_R\left(H^{35}Cl\right) = 0.97$$

$$m_R\left(D^{35}Cl\right) = 1.89$$

$$\frac{\left(\omega_0\right)_A}{\left(\omega_0\right)_B} = \sqrt{\frac{\left(m_R\right)_B}{\left(m_R\right)_A}}$$

Therefore, we predict:
$$\omega_0\left(DCl\right) \rightarrow 2150\,cm^{-1}$$

k: We know the curvature of the HCl potential!

γ: Energy dissipates from HCl bond in roughly $\qquad \tau_{damp} \Rightarrow 2 \times 10^{-12}\,s \rightarrow 2\,ps$

What about F_0 ?

We said the driving force is proportional to $E(t)$.
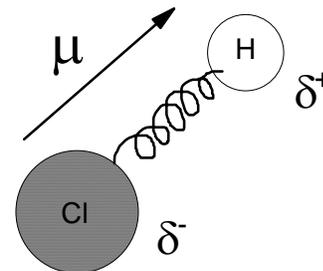
$$F_{ext} = F_0 \cos \omega t = a \, E_0 \cos \omega t$$

What is a?

- An electric field interacts with charges on molecules.
- A neutral body should feel no force, but molecules are made of many charges species and have positive and negative charges.

Dipole moment:

$$\mu = \Sigma \, q \, l$$

charge

distance

In an electric field, this dipole will feel a force.

$$V = -\overline{\mu} \cdot \overline{E}$$

$$F = -\frac{\partial V}{\partial Q} = \left(\frac{\partial \overline{\mu}}{\partial Q} \right) \cdot \overline{E}$$

If there is a large displacement of charge $\rightarrow$ Strong absorption!

Polarity isn't a sufficient criterion: CO_2 is nonpolar but still a strong absorber of infrared radiation. This occurs as a result of radiation inducing distortions of the molecule along the symmetry axis (asymmetric stretch) or perpendicular to the symmetry axis (bend).

Alignment matters!

- The E field oscillates along the polarization direction.
- If the bond is aligned with the electric field, then the oscillating field can act to stretch or compress the bond through attractive and repulsive electrostatic interactions with the charges.
- The ability of the field to act on Q depends on the alignment of the dipole moment with the field. If there is an angle θ between μ and E, then

$$F_0 = \frac{\partial \bar{\mu}}{\partial Q} E_0 \cos\theta \qquad\qquad (\dots\text{for a single molecule})$$

So spectroscopy can tell you about the orientation of molecules!

You can study a crystal where all molecules have the same orientation, and how by rotating the light polarization, you can tell how different vibrations are oriented.

→ We will also look at reorientational motion in liquids and gases!

Summary:

Absorption spectra are characterized by:

- Resonance Frequency $\qquad\qquad \omega_o = \sqrt{\dfrac{k}{m}}$

- Linewidth $\qquad\qquad$ γ: interactions with surroundings

- Integrated Peak Amplitude $\qquad \dfrac{\pi F_0^2}{4m} = I \dfrac{\pi^2}{mc} \left|\dfrac{\partial \bar{\mu}}{\partial Q}\right|^2 \langle \cos^2\theta \rangle$

$$\varepsilon$$