Optical Spectroscopy

Lecture 1

Basic Concepts

I. Classical Electron Theory of Optics. .

1. Reference: Quantum Chemistry by Walter Kauzmann, Academic Press, (1957), Chapter 15.

2. Introduction

Optical spectroscopy is the study of the interaction of light with matter. We will be concerned mainly with the absorption, emission, and rotation of light by biological molecules. Measurements of these properties provide important structural information and probes that allow the investigation of molecular and cellular mechanisms.

A classical, i.e., non quantum mechanical, theory was developed toward the end of the last century. Although this theory is deficient in important respects, it is easier to understand and less mathematically demanding than the more correct quantum mechanical theory. Many of the deficiencies of the classical theory can be repaired by a simple reinterpretation in quantum mechanical terms. Therefore we will begin with a brief introduction to the classical theory, then discuss some aspects of the quantum interpretation, and, finally, consider specific spectroscopies and applications to biological problems.

2. Interaction of Electrons with Electromagnetic Radiation: Basic Assumptions

A. Model: At the end of the 19'th century, i.e., prior to the Rutherford Scattering Experiment, the atom was viewed as consisting of a massive diffuse cloud of positive charge in which the negatively charged electrons were embedded. The electrons were supposed to execute simple harmonic motion relative to the positive charged cloud, thereby, generating oscillating dipole moments. These oscillating dipole moments are crucial to the interaction of light with matter.

B. Basic Assumptions (valid for both classical and quantum interpretations)

(1) A charge, e, in an electric field, E, experiences a force $F = eE$.

(2) Light consists of oscillating electric and magnetic fields:

$$E = E_0 \cos \omega(t - z/c)$$

$$H = H_0 \cos \omega(t - z/c)$$

$$\omega = 2\pi\nu$$

H, E, and the direction of propagation of the light are mutually perpendicular.

(3) An electric field in a vacuum has an energy density, $W = E^2/4\pi$.

(4) An electric charge, e, subjected to an acceleration, a, emits electromagnetic radiation. The magnitude of the electric field associated with this radiation is
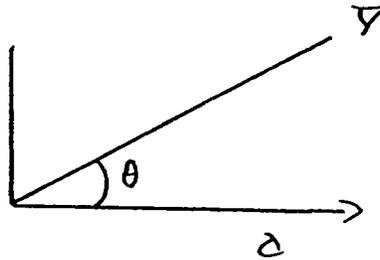
$$E = ea \sin\theta / rc^2$$

where

c = velocity of light;
r = the magnitude of the vector drawn from the charge to the observer;
θ = the angle between the direction of acceleration and r.

3. Radiation from a charge undergoing simple harmonic motion, $x = x_0 \cos\omega t$.

$$a = d^2x/dt^2 = -x_0\omega^2 \cos\omega t$$

$$E = -ex_0\omega^2 \cos\omega t \sin\theta/rc^2$$

To compute the rate at which energy is radiated by a charge undergoing acceleration a, begin with the energy density $W = E^2/4\pi$. The energy radiated per second is the energy in a sphere of radius c with the oscillating charge at its center and therefore can be computed by integrating the energy density over that spherical volume.

$$R = \int_0^c dr \int_0^\pi d\theta \int_0^{2\pi} d\phi [(ea \sin\theta / rc^2)^2 / 4\pi] r^2 \sin\theta = 2(ea)^2 / 3c^3$$

To obtain the mean rate of emission we must integrate the radiated energy over an oscillation period:

$$<a^2> = \int_0^{2\pi/\omega} a^2 dt / \int_0^{2\pi/\omega} dt = \omega^4 x_0^2 \int_0^{2\pi/\omega} \cos^2 \omega t dt / 2\pi / \omega = \omega^4 x_0^2 / 2$$

Hence, $<R> = (ex_0\omega^2)^2/3c^3$, where $<Q>$ indicates the average value of Q.

The wavelength of the radiation is related to its frequency as $\lambda = c/v$, and so

$$R = [(2\pi)^2 ex_0]^2 c/3\lambda^4$$

Note the wavelength dependence. Light is scattered by induction of oscillating dipole moment in the scattering particles. This equation demonstrates that the energy of ~~blue~~ blue scattered light decreases as λ^4. Hence, if both colors are of equal intensity, more ~~red~~ light is scattered than ~~blue~~ red light.

      Up to now the discussion is general, valid both for classical and quantum mechanical analyses. Now we move to an explicitly classical interpretation of atomic structure and electron dynamics.

4. Classical model of forces acting on an electron.
We will describe the dynamics of the electron in terms of Newton's laws. To do this we must list the forces that can act on the electron.

(1) Inertial forces, $f_1 = -ma$, where m is the mass of the electron, and a is its acceleration.

(2) Harmonic restoring force, $f_2 = -kx$, where x is the displacement of the electron from its equilibrium position, and k is a constant.

(3) Electric fields, $f_3 = eE$, where e is the charge of the electron and E is the electric field vector.

(4) Magnetic fields, $f_4 = (e/c)v \times H$, where c is the speed of light, v is the velocity of the electron, and H is the magnetic field vector. Since $E = H$ in a light wave and $v \ll c$ for all of our purposes, we can neglect f_4.

(5) Radiation damping, $f_5 = -\mu v$, where μ is a constant. This force results from the emission of radiation by the moving electron. This radiation depletes the kinetic energy of the electron, and therefore acts effectively as a force which slows down the motion of the electron.

(6) "viscous" dissipation, i.e., conversion of kinetic energy into heat, $f_6 = -\eta v$. This is a rather ill-defined force that accounts for dissipation of energy of motion apart from radiation damping, e.g., as might occur in an atomic collision.

(7) Interaction with other electrons, $f_7 = e^2 \Sigma r_i /r_i^3$.

      The radiation damping constant, μ, can be calculated from the rate of dissipation of energy of an oscillating electron. The rate of energy dissipated from an electron acting against a force, f_5, with a velocity, v, is

$$R = v\int_0^{1/v} f_5 v dt = \mu v \int_0^{1/v} v^2 dt = \mu v (x_0 \omega)^2 \int_0^{1/v} \sin^2 \omega t dt = \mu x_0^2 \omega^2 / 2$$

But we have already shown that $R = e^2 x_0{}^2 \omega^4 / 3c^2$. Hence, $\mu = 2\,(e\omega)^2 / 3c^3$. Therefore, as seems reasonable, the rate of energy dissipation and therefore the radiation damping constant is greater the higher the frequency of the motion of the electron.

5. An example: Emission by a single bound electron in the absence of electric fields.

The equation of motion for this example, $f_1 + f_2 + f_5 + f_6 = 0$, which is equivalent to

$$m\,d^2x/dt^2 + (\eta + \mu)dx/dt + kx = 0.$$

This equation is readily solved, for example, by using Laplace transforms to yield,

$$x = x_0 \exp(-\omega't)\,\cos(\omega_1 t),$$

where $\omega' = (\eta+\mu)/(2m)$, $\omega_1{}^2 = \omega_0{}^2 - \omega'^2$, and $\omega_0{}^2 = k/m$. This solution can be verified by substitution. The electron behaves as a damped oscillator.
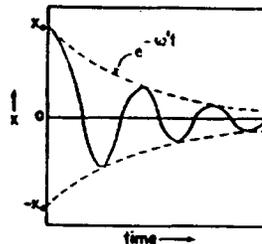

Fig. 15-4. Damped oscillations of an elastically bound electron. In the classical atom the damping would be much less rapid than is shown here.

Hence, ω' is an inverse "relaxation time" for the decay of the excitation energy due to dissipative forces, ω_0 is the "natural frequency" of the spring, and ω_1 is the effective oscillation frequency in the presence of the dissipative forces. Generally ω' is much smaller than ω_0 and so the oscillation frequency is nearly equal to ω_0. The radiated field is $E = E_0 \exp(-\omega't)\cos\omega_1 t$, where the amplitude is $E_0 = (e\omega_1 x_0)^2 \sin\theta/rc^2$. The duration of the wavetrain of radiation emitted by the electronic motion is $\tau_R = 1/\omega'$.

This is an interesting result from the point of view of the classical theory of fluorescence. Suppose that an electron is set into oscillatory motion by absorption of energy from electromagnetic radiation, i.e., light. We shall suppose that there are no other pathways for the release of this energy; $\eta = 0$. Hence all of the excitation energy will be dissipated as radiation, fluorescence emission. The energy, and therefore the fluorescence intensity, will decay with an exponential "radiative" lifetime $\tau_R = 1/\omega' = 2m/\mu$, proportional to the inverse of the radiation damping constant. This is the longest lifetime possible for the excited state. In most situations, other forces, such as intermolecular collisions, will provide additional pathways for deexcitation, and so will shorten the excited state lifetime.

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6. Response of a Bound Electron to Light.

Now we include in the equation of motion the force due to the electric field component of the light wave,

$f_1 + f_2 + f_3 + f_5 + f_6 = 0$, which translates to the differential equation,

$md^2x/dt^2 + (\eta + \mu) dx/dt + kx = eE_0 \sin\omega t$. Here ω is the circular frequency of the incident light and x is the diplacement in the direction of the incident electric field vector E_0.

At steady state this equation will have the solution,

$x = x_0' \sin\omega(t + \delta) = x_0 (\sin\omega t + \beta \cos\omega t)$, where x_0 is the amplitude of the component in phase with the incident light wave and βx_0 is the amplitude of the component $90°$ out of phase. Here,

$\beta = 2\omega\omega'/(\omega^2 - \omega_0^2)$ where ω_0 and ω' are defined above, and

$x_0 = e/m[\omega_0^2 - \omega^2]/[(\omega_0^2 - \omega^2)^2 + 4(\omega\omega')^2]E_0$, while,

$\beta x_0 = -e/m [2\omega\omega']/[(\omega_0^2 - \omega^2)^2 + 4(\omega\omega')^2]E_0$.

The oscillatory motion of the electron relative to the positively charged environment in which it is embedded generates an induced oscillating dipole moment: $m = ex$. There are two components with amplitudes:

in phase, $m_0 = ex_0$ and out of phase, $m'_0 = -\beta ex_0$.

Now we are in a position to introduce the polarizability, α, a property which has plays an important role in the optical properties of atoms and molecules. The polarizability is defined by the following equation $m = \alpha E$, i.e. α is the ratio of the induced dipole moment to the incident electric field strength (which is inducing the moment). Hence, there is an in phase component of the polarizability, , $\alpha = m_0/E_0$, and an out of phase component, , $\alpha' = m_0'/E_0$.
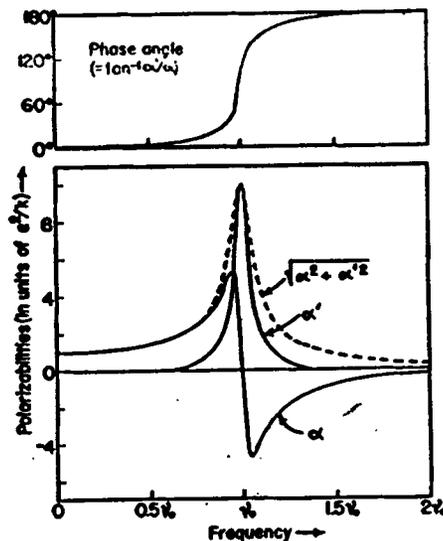
Near the natural frequency ω_0 the incident light drives a motion of the electron which approaches a resonance condition. Then there is a substantial dissipative component and so the out of phase amplitude is significant. Far from the natural frequency and therefore far from the resonance frequency of the electron, the out of phase amplitude becomes quite small and only the in phase component is significant in the induced oscillatory motion of the electron.

7. The absorption of light by a bound electron.

The force responsible for dissipating the incident light into heat or scattered radiation is determined by the term, $(\eta+\mu)dx/dt$. This term is therefore responsible for light absorption, i.e., the subtraction of energy from the incident radiation by the absorbing molecule or atom. The rate of energy dissipation, R, is the product of this force times the velocity of the electron, $R = (f_5 + f_6)\cdot dx/dt = (\eta+\mu)(dx/dt)^2$. The energy dissipated per second is

$$R = v\int_0^{1/\nu} (\eta + \mu)(dx/dt)^2 dt = x_0^2 \omega^3 / 2\pi \int_0^{2\pi/\omega} (\cos\omega t - \beta \sin\omega t)^2 dt = 1/2\omega\alpha' E_0^2.$$

$$= 2\pi^2 (\eta + \mu) \nu^2 x_0^2 (1 + \beta^2) = \tfrac{1}{2}\omega\alpha'|E_0|^2$$

We can relate this to the Beer-Lambert law for the absorption of light. This law states that the light intensity, dI, which is absorbed when light of incident intensity I passes through an absorbing medium of thickness dx, containing an absorbing substance of molar concentration C with absorption coefficient, ε, is $dI = 2.303\, C\, I\, \varepsilon\, dx$, or, in integrated form, $I = I_0\, 10^{-\varepsilon C x}$. But it is also true that $dI = - n\, R\, dx$, where n is the number of absorbing molecules per cubic centimeter. Hence, $\varepsilon = nR/2.303CI$. The incident light intensity, I, is the amount of light energy passing through an area of one square centimeter in one second. That is, the velocity of light times the light energy density in one cubic centimeter. After integrating the energy density over a 1 cm distance, this turns out to be $1 = CE_0^2/8\pi$. Taking into account that $n = CN/1000$, where N is Avogadro's number, we have $\varepsilon = (4\pi N/2303c)\omega\alpha'$. The important point about this result is its demonstration that the out of phase polarizability, α', is directly proportional to the molar extinction coefficient. Hence, the classical theory provides an evaluation of the molar extinction coefficient as a function of frequency in terms of "structural" parameters such as μ, η, k, and m. This theory predicts that the shape of the absorption band should be given by the dependence of α' on ν. In fact, this predicts much sharper dependence of absorption on frequency, i.e., narrower absorption bands, than are actually observed. The observed broadening is mainly due to environmental effects which influence electronic interactions and potential functions. Furthermore, the classical theory does not provide an explanation either of the specific frequencies of absorbance and their dependence on molecular structure or of the wide range of absorbance intensities that are observed in atoms and molecules of various kinds. To explain these important properties requires a quantum mechanical interpretation.

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8. Light Scattering.

When the frequency of the incident light is far from the resonant absorbance condition, little energy is absorbed from the incident radiation field. Then the motion of the electron and its induced dipole moment are in phase with the incident light and so optical effects are governed by α, the in phase component of the polarizability. Light is radiated, i.e., scattered, by the induced electronic dipole at the same frequency as the incident light and in directions that depend on the orientation of the dipole.

II. Review of Quantum Mechanics

1. Background

Quantum mechanics provides a way of characterizing molecular and atomic structure and the interactions of atoms and molecules with light which is more accurate and comprehensive than the classical mechanical approach. According to quantum mechanics the electrons in atoms and molecules are in states with discrete characteristic energies. This is in contrast to the classical mechanical model in which an electron, attached by a spring to the "nucleus" can have a continuous range of energies. These states are characterized by mathematical functions known as wavefunctions, $\psi(r)$. The square of the wavefunction of a set of particles provides the probability density for the locations of the particles which it characterizes. (More accurately probability density is provided by the square **magnitude** of the wavefunction, which can be a complex function. We will deal only with real wavefunctions.) For example, consider an electron constrained to the x-axis between x = a and x = b. Then the probability that the electron is within a small interval dx at x=c (a < c < b) is $\psi^2(c)dx$. Moreover, since the electron is required to be in the interval (a,b),

$$\int_a^b \psi^2(x)dx = 1.$$

Wavefunctions and energies are calculated using the Schroedinger equation. In one dimension we can represent this equation as

$$(-h^2 / 8\pi^2 m)d^2\psi(x)/dx^2 + V(x)\psi(x) = E\psi(x)$$

In this equation h is Planck's constant, V(x) is the potential energy of the electron as a function of position, and E is the total energy of the electron. Hence, the potential function determines the mechanics of the system. For example, there are characteristic solutions for the "particle in a box" (V(x) = 0 for 0<x<a and V(x) = infinity for x<0 and for x > a); for the harmonic oscillator (V(x) = $kx^2/2$); and for a Coulomb potential (V(r) = $-e_1 e_2/r$). [Here we are considering only the time independent form of the Schroedinger equation and are therefore restricting ourselves to defined energy states of the system. More generally, a time dependent form of the Schroedinger equation is necessary to characterize the transitions among states. Hence, the basic quantum theory for optical

spectroscopy, which must account for the ability of radiation to promote electrons from one state to another, must originate from the time dependent analysis.]

Solution of the Schroedinger equation for a specified system provides the discrete energy values, E_i, which characterize the allowed states of the system. Light which is absorbed or emitted by an atom or molecule is associated with transitions from one state to another, e.g., from state i to state j. The light absorbed or emitted then has a frequency, v_{ij}, given by

$v_{ij} = E_j - E_i /h$.

2. Interaction of light with molecules (See Cantor and Schimmel, p. 356-368.)

The oscillating electric field of the incident light wave can cause the molecule to pass from one defined energy state to another. The probability that a molecule will go from state a to state b will depend on the intensity of the incident light which has a frequency that satisfies the condition, $v_{ab} = E_b - E_a /h$. The transition rate, expressed as the rate of change of the probability that the molecule is in state b, can be expressed as $dP_b /dt = B_{ab} I(v)$, where B_{ab} is the transition rate from state a to state b and $I(v)$ is the energy density incident at frequency v. By an analysis using the time dependent Schroedinger equation, one finds that B_{ab} is proportional to the square magnitude of the transition dipole moment ($|<b|\mu|a>|^2$), the "dipole strength", $D_{ab} = |<b|\mu|a>|^2 = |\int \psi_a \mu \psi_b d^3r|^2$. Hence, as we have seen above, the interaction of a molecule with light is governed by the dipole moment induced in the molecule by the oscillating electric field of the incident light. By relating this transition probability to Beer-Lambert law, it is possible to derive a relationship between the transition dipole moment and the molar extinction coefficient:

$D_{ab} = 9.180x10^{-3} \int (\varepsilon(v)/v)dv$ (debye)^2.

One of the problems that confounded the classical electron theory of optical spectroscopy was its inability to determine whether a molecule should have an intense or a weak absorbance. Quantum mechanics provides a more useful answer in the equations above. Whether or not light is absorbed is determined by $<b|\mu|a>$ and this in turn is determined by the structure of the orbitals described by ψ_a and ψ_b and therefore by the structure of the molecule. For example, if $<b|\mu|a> = 0$, the molecule would absorb little, if any, of the incident light even if it were at a frequency that matched a difference in levels of the molecule. This would be a "forbidden transition". A good example of allowed and forbidden transitions in formaldehyde is given in Cantor and Schimmel, pp. 370-374.

3. Example. The Particle in a Box.