MOLECULES AND RADIATION

What is electromagnetic radiation?

- Radiation consists of photons which have both particle and wave properties.
  - In vacuum, travels in a constant direction with constant speed ($c \cong 3 \times 10^8$ m s^{-1}).
  - Has energy $E = h\nu$.
  - Has wavelength $\lambda = c/\nu$.
  - Has wavenumber $\overline{\nu} = 1/\lambda$ (usually with units cm^{-1}; note that wavenumbers are directly proportional to energy.)

An electomagnetic waves has two components:
- Electric field
- Magnetic field

which are right angles to each other and the direction of propagation (z) of the photon. The amplitude of the electric and magnetic fields fluctuates as the photon propagates.

Since from the perspective of a photon, all a chemical species is is an electrical field, we will be interested only in the electrical component.

If the direction of propagation is the z direction, then the electric field vector has only x and y components.

$$\mathbf{E} = \mathbf{x}E_x + \mathbf{y}E_y$$

.

At any one frequency ν the amplitudes E_x and E_y are:

$$E_x(z,t) \ = \ E_x^{\circ} sin(kz - \omega t + \delta_x)$$

$$E_y(z,t) \ = \ E_y^{\circ} sin(kz - \omega t + \delta_y)$$

where

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

and δ_x and δ_y are arbitrary phase constants.

The above equations hold for electromagnetic radiation in a vacuum. If the medium is not a vacuum, then the relative electric permittivity (ϵ_r) and the relative magnetic permittivity (μ_r) must be considered. For a vacuum $\epsilon_r = 1$ and $\mu_r = 1$.

Polarization of light

If $\delta_x = \delta_y + n\pi$, then light is polarized.

- For light polarized in the x=y plane, $E_x^{\circ} = E_y^{\circ}$.

- x-polarized light, $E_y^{\circ} = 0$.

- y-polarized light, $E_x^{\circ} = 0$.

The most general form of polarization is elliptical:

$$\mathbf{E}\pm = \mathbf{x}E_x^{\circ}cos(kx - \omega t) \pm \mathbf{y}E_y^{\circ}sin(kx - \omega t)$$

where the + sign indicates right elliptical polarized light and the - sign left elliptical polarized light with reference to the rotation of $\mathbf{E}$.

- $E_x^{\circ} = E_y^{\circ}$: circularly polarized light

Measures of Intensity of Radiation

- Considered either in terms of the number of photons at each frequency or in terms of the intensity of the electric field.

- For a monochromatic radiation field (all photons have the same energy), the energy density ρ is:

$$\rho = \frac{1}{2}\epsilon_0(E^\circ)^2$$

  where ϵ_0 is the permittivity of free space.

- Radiation intensity is defined as the flux of radiant energy.

$$I = \text{energy per unit area per unit time} = \rho c$$

- Power of radiation field (relevant for lasers) is product of I and area illuminated.

Blackbody Radiation

- Blackbody curve long observed and characterized, but could not be accounted for by classical physics.

- A blackbody is an idealized absorber and emitter, in which the interior walls of a cavity are in thermal equilibrium with the radiation inside the cavity.
    - The experimental approximation to a blackbody is an aperture of a cavity. All radiation that escapes the aperture was in equilibrium with the walls of the cavity and all radiation that strikes the aperture is absorbed by the cavity.

- Satisfactorily explained for the first time in 1901 by Planck, who postulated the existence of a quantum of light.
    - Classically, energy of a light source depends on its intensity
    - Planck postulated that $E = h\nu$ and that the radiation inside the cavity could be treated as filled with oscillators.

Planck's Treatment of Blackbody Radiation

- Assume set of quantized states of oscillators
    - Frequency of emitted light must correspond to an oscillator frequency, therefore assume allowed frequencies are integer multiples of some ν: $\varepsilon_n = nh\nu$.
    - Assume distribution of oscillators over energies described by the Maxwell-Boltzmann distribution:

$$N(n) = N_0 e^{-\varepsilon_n/kT}$$

- Now consider average energy of an oscillator:

$$\bar{\varepsilon} = \frac{\sum\limits_{n=0}^{\infty} N(n)\varepsilon_n}{\sum\limits_{n=0}^{\infty} N(n)}$$

$$\bar{\varepsilon} = \frac{\sum\limits_{n=0}^{\infty} N_0 e^{-nh\nu/kT} nh\nu}{\sum\limits_{n=0}^{\infty} N_0 e^{-nh\nu/kT}}$$

$$\bar{\varepsilon} = \frac{0 + h\nu e^{-h\nu/kT} + 2h\nu e^{-2h\nu/kT+\dots}}{1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \dots}$$

Let $x = e^{-h\nu/kT}$, then:

$$\bar{\varepsilon} = h\nu x \left(\frac{1 + 2x + 3x^2 + 4x^3 + \ldots}{1 + x + x^2 + x^3 + \ldots} \right)$$

But

$$1 + 2x + 3x^2 + 4x^3 + \ldots = (1-x)^{-2}$$

and

$$1 + x + x^2 + x^3 + \ldots = (1-x)^{-1}$$

Therefore:

$$\bar{\varepsilon} = h\nu x \frac{(1-x)^{-2}}{(1-x)^{-1}} = \frac{h\nu x}{(1-x)}$$

$$\bar{\varepsilon} = \frac{h\nu x}{(1-x)} = \frac{h\nu}{\frac{1}{x} - 1} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

The Jean's number, $n(\lambda) = 8\pi/\lambda^4$ gives the number density of oscillators of wavelength λ. Therefore the energy density per wavelength is:

$$\rho(\lambda; T) = n(\lambda)\bar{\varepsilon} = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

To determine the total energy density of the radiation, this distribution function needs to be integrated over wavelength.

$$\rho(T) = \int_0^\infty \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \, d\lambda$$

(The integrand is denoted $\rho^\lambda(\lambda; T)$.)

This distribution may be written in terms of frequency instead of wavelength. Recalling that $\nu = c/\lambda$; $d\nu = -c \, d\lambda/\lambda^2$:

$$\rho(T) = -\int_\infty^0 \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \, d\nu$$

$$= \int_0^\infty \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \, d\nu$$

(This integrand is denoted $\rho(\nu; T)$.)

Also of interest is the photon density in terms of either wavelength:

$$\rho_\phi^\lambda(\lambda; T) \, d\lambda = \frac{\rho^\lambda(\lambda; T)}{hc/\lambda} \, d\lambda = \frac{8\pi}{\lambda^4} \frac{1}{e^{hc/\lambda kT} - 1} \, d\lambda$$

or of the frequency:

$$\rho_\phi(\nu; T) \, d\nu = \frac{\rho(\nu; T)}{h\nu} d\nu = \frac{8\pi\nu^2}{c^3} \frac{1}{e^{h\nu/kT} - 1} \, d\nu$$

Integration of the blackbody distribution

- Consider the energy distribution function in terms of λ
- Use a substitution of variable, $x = hc/\lambda kT$
  - $dx = -hc/(\lambda^2 kT) d\lambda$
- The integral becomes:

$$\rho(T) = \int_0^\infty \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \, d\lambda$$

$$= -kT \int_0^\infty \frac{8\pi}{\lambda^3} \frac{1}{e^{hc/\lambda kT} - 1} \left(-\frac{hc}{\lambda^2 kT} \right) \, d\lambda$$

$$= -kT \int_{\infty}^{0} \frac{8\pi(kT)^3}{(hc)^3} x^3 \frac{1}{e^x - 1} \, dx$$

$$= \frac{8\pi(kT)^4}{(hc)^3} \int_{0}^{\infty} x^3 \frac{1}{e^x - 1} \, dx$$

- The integral in x is a definite integral found in standard tables of integrals:

$$\int_{0}^{\infty} x^3 \frac{1}{e^x - 1} \, dx = \frac{\pi^4}{15}$$

- Thus:

$$\rho(T) = \frac{8\pi^5 (kT)^4}{15(hc)^3} = \eta T^4 = \frac{4\sigma}{c} T^4$$

where σ is the Stephan-Boltzmann constant.

Fundamental Interactions of Matter and Radiation

- Absorption
  atom + photon → energized atom

- Spontaneous emission
  energized atom → de-energized atom + photon

- Stimulated emission
  energized atom + photon →
    de-energized atom + two identical photons
  - **LASER** is the acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation
  - **MASER** is the acronym for **M**icrowave **A**mplification by **S**timulated **E**mission of **R**adiation
  - The identical photons are said to be coherent.

- What are the probabilities of theses processes?

Probability of interaction of atoms and radiation

- Laid out by Einstein in 1917.
- Assume a sample of atoms (all of one type) at thermal equilbrium.
  - Therefore described by the Boltzmann distribution
- Consider two energy levels, 1 and 2, of an atom with energy $E_2 > E_1$.
  - The ratio of the populations of these energy levels is:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-(E_2 - E_1)/k_B T} = \frac{g_2}{g_1} e^{-h\nu_{12}/k_B T}$$

  where $\nu_{12} = (E_2 - E_1)/h$
- Absorption increases the number of molecules in level 2 and decreases the number of molecules in level 1
- Emission decreases the number of molecules in level 2 and increases the number of molecules in level 1
- If the system is at equilibrium then:

$$\frac{dN_2}{dt} = 0 = \text{absorption rate}$$

$$-\text{spontaneous emission rate}$$

$$-\text{stimulated emission rate}$$

- The rate of absorption may be written as:

$$\text{absorption rate} = N_1 B_{12} \rho(\nu_{12})$$

where $\rho(\nu_{12})$ is the radiation density at ν_{12}.

- Similary the rate of emission may be written as:

$$\text{spontaneous emission rate} = N_2 A_{21}$$

$$\text{stimulated emission rate} = N_2 B_{21} \rho(\nu_{12})$$

where A_{21} is the spontaneous emission coefficient and B_{21} is the stimulated emission coefficient.

Thus:

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\nu_{12})}{B_{21}\rho(\nu_{12}) + A_{21}}$$

Therefore:

$$\rho(\nu_{12}) = \frac{A_{21}\left(\frac{g_2}{g_1}\right) e^{-h\nu_{12}/k_B T}}{B_{12} - B_{21}\left(\frac{g_2}{g_1}\right) e^{-h\nu_{12}/k_B T}}$$

- From quantum mechanics, it can be shown:

$$B_{12} = \frac{g_2}{g_1} B_{21}$$

Therefore

$$A_{21} = \left(\frac{8\pi h\nu^3}{c^3}\right) B_{21}$$

A non-zero value of A_{21} is necessary to maintain equilibrium in a non-zero radiation field.

Beer Lambert Law

- Recall:

$$I(\nu) = I_0(\nu) e^{-abc}$$

where
  - a is the absorbance coefficient (which depends on ν),
  - b is breadth or optical path length
  - c is concentration.

a is related to B_{12}

More about the Beer-Lambert Law

- Often written in logarithmic form:

$$ln\left(\frac{I_0}{I}\right) = abc$$

where $ln\left(I_0/I\right)$ is **absorbance** (base e).

Transmittance is defined as I/I_0.

Many combinations of units are encountered for a, b, and c

- if c is number density in units of m^{-3}, b is length in units of m, then a has units of m^2 and is the **absorption cross section**.
  - The absorption cross section is not to be interpreted as a physical area associated with the molecule.

- if c is concentration in mol L^{-1}, b is in cm, then a has units of $L\ mol^{-1}\ cm^{-1}$ and is known as **molar absorptivity** or **molar absorption coefficient** or **molar extinction coefficient**.

- In using data from literature sources, it is necessary to ascertain whether absorbance is defined with respect to base e or base 10 and what units are appropriate for a.

Atomic Spectroscopy and Selection Rules

- Are transitions among all energy levels of an atom allowed?
  - Why or why not?

- Must first consider electronic configuration of the atom.
  - Each electron is represented by a unique set of quantum numbers $(n,\ l,\ m_l,\ m_s)$
  - These quantum numbers are associated with the corresponding wavefunction.
  - Wavefunctions have symmetry properties.

- The interaction of a photon with an atom is a time dependent perturbation.
  - The effect of the perturbation is described mathematically as an "operator". An operator when applied to a function, performs an operation on the function.

- To determine the probability of a photon being absorbed
  - Take the wavefunction for the initial (unperturbed) state
  - Operate on that wavefunction with the operator corresponding to the photon
  - Multiply by the complex conjugate of the wavefunction for the final state
  - Integrate over all space
- Whether a nonzero number results from this depends on the symmetry of the overall function to be integrated.
- Can set up a matrix of these integrals with one index corresponding to the initial state and the other index corresponding to the final state.
  - Each integral is a matrix element.
  - If the value of the integral is zero, then the transition does not occur.
  - If the value of the integral is non-zero, then the transition does occur. The Einstein absorption coefficient B_{12} is related to the square of the value of the integral.
  - From this it is possible to infer subsets of the quantum states among which transitions are allowed. This is described in terms of the **selection rules**.

More about selection rules

- Consider first some atomic quantum numbers:
  - S - total spin angular momentum
  - L - total orbital angular momentum
  - J - total angular momentum (vector sum of L and S)

- The selection rules for transition due to dipole interaction (i.e. a photon) are:

$$\Delta L\ =\ -1, 0, 1$$

$$\Delta S\ =\ 0$$

Thus:

$$\Delta J\ =\ -1, 0, 1$$

with the exclusion of transitions of the type:

$$L = 0\ \rightarrow\ L = 0 \text{ and } J = 0\ \rightarrow\ J = 0$$

What is the physical significance of this?

Physical significance of selection rules?

- First consider ΔS:
    - If $\Delta S = 0$, then spin multiplicity is maintained. This means that singlet states go to singlet states, triplet state to triplet states, etc.

- Now consider ΔL:
    - The selection rule $\Delta L = -1, 0, 1$ is a consequence of the conservation of momentum. $|\Delta L| = 1$ is due to the angular momentum of the photon.
    - The value of L contains information about the parity of the wavefunction. Therefore if $\Delta L = \pm 1$ (e.g. dipole allowed transitions), then the transition changes the parity of the wavefunction.

- Now consider ΔJ:
    - The $\Delta J = -1, 0, 1$ (exclusive of $J = 0 \rightarrow J = 0$) reflects spin-orbit coupling.

Selection rules allow us to predict spectra.

Spontaneous Emission

- Described by A_{21}.

- Often follows an absorption event.

- If spontaneous emission occurs, then how can an excited state be a stationary state?
    - A stationary state is regarded as having a fixed energy.
    - But the Heisenburg uncertainty principle states $\Delta E \Delta t \geq \hbar/2$
    - Δt may be regarded as the lifetime of the higher energy state.
    - ΔE is the uncertainty in the energy of the excited state. (This is why spectroscopic lines have Lorentzian line shapes.)
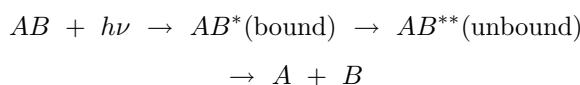
Photodissociation and Photoionization

- Represent irreversible chemical changes:

$$AB + h\nu \rightarrow A + B$$

$$C + h\nu \rightarrow C^+ + e^-$$
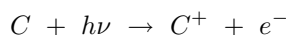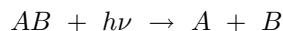
- Consider first photodissociation:
    - Recall (from first year) molecular orbitals.
    - Bonding orbitals are attractive
    - Antibonding orbitals are repulsive

- Consider absorption of photon that excites from a bonding orbital to an antibonding orbital in a transition allowed by the selection rules.
    - The antibonding orbital has no miniumum, so the molecule is now dissociated.

Predissociation

- Another way for photodissociation to occur
    - Energy curves corresponding to molecular orbitals can cross each other.
    - Therefore an excitation from one bonding orbital to another (higher energy) bonding orbital can lead to dissociation if the latter curve crosses another curve which is due to antibonding orbital, dissociation may occur.

$$AB + h\nu \rightarrow AB^*(\text{bound}) \rightarrow AB^{**}(\text{unbound})$$

$$\rightarrow A + B$$

- The first step is absorption of a photon

- Followed by a *nonradiative* transition

- Followed by dissociation

Photoionization

- Consider a transition between atomic orbitals of an oxygen atom.

    - Ground state configuration is $1s^2 2s^2 2p^4$

    - First excitation allowed by selection rules is to $1s^2 2s^2 2p^3 3s^1$ where one of the unpaired $2p$ electrons has been excited to the $3s$ state.

    - Also allowed are transitions to any ns state.

    - Recall that the energy of atomic orbitals (relative to the ionization limit) are proportional to $1/n^2$.

    - Ionization corresponds to $n \to \infty$, leaving O^+ in the ground state ($1s^2 2s^2 2p^3$).

    - Ionization occurs from states other than the atomic ground state to states other than the ionic ground state.