Chemistry 431

Lecture 21

Excited State Processes
Lasers

NC State University
Excited State Processes

Photophysics
- Fluorescence
- Phosphorescence
- Internal conversion
- Intersystem crossing

Photochemistry
- Electron transfer
- Isomerization
- Photolysis
The fate of electronically excited states

- A radiative decay process involves emission of a photon.
- Non-radiative decay involves the transfer of excess energy into vibration, rotation, and translation of surrounding molecules. The result is to heat the surroundings.
  - Vibrational relaxation
  - Internal conversion processes
Vibrational relaxation

Absorption populates the Franck-Condon active modes of the excited state. This is NOT the equilibrium population. Therefore, relaxation among the vibrational levels occurs.
Internal conversion

A singlet excited state can decay directly back into the ground state by a process known as internal conversion.

Excited State → Ground State
No photon is emitted
Fluorescence

Fluorescence is the spontaneous emission of radiation from an excited singlet state.
1. Absorption leads to population of Franck-Condon active vibrational modes of the excited state.
2. Vibrational relaxation results in a change of the excited state levels.
3. Emission occurs from an equilibrium population of excited state vibrational levels.
Intersystem crossing

The singlet and triplet state potential surfaces may cross and therefore a change of electron spin due to spin-orbit interactions gives rise to the triplet state.
Phosphorescence

Phosphorescence is the emission of radiation from a triplet state.
1. Absorption leads to population of the FC active modes of the singlet.
2. After vibrational relaxation in the singlet intersystem crossing produces the triplet state.
3. Vibrational relaxation continues in the triplet state.
4. Emission occurs from the triplet. Because it is spin-forbidden, the emission rate is very low. Consequently, it is long-lived.
The radiative and non-radiative decay processes can be represented using a diagram. Vertical shifts represent changes in nuclear position.
Photochemistry

Excited state processes that result in changes in bonding are photochemical processes.

• Photodissociation or photolysis is the breaking of a chemical bond. $\text{IR} \rightarrow \text{I}^*\text{R} \rightarrow \text{I} + \text{R}$

• Electron transfer results in a change in bond order due to a process. $\text{DA} \rightarrow \text{D}^*\text{A} \rightarrow \text{D}^+\text{A}^-$

• Isomerization results in a change in molecular structure.
Photolysis

If the excited state is anti-bonding with respect to a particular coordinate the result is dissociation of a chemical bond.
Spontaneous emission is fluorescence.
Stimulated emission is used for lasers.
It is impossible to obtain a population inversion in a two-level system

The intrinsic coefficients for absorption, $B_{12}$, and stimulated emission, $B_{21}$, are equal. Therefore, as the radiation intensity (and therefore energy density, $\rho$) increase the limiting rate for population of the excited state is equal to the limiting rate for stimulated emission.

$w_{12} = N_1 B_{12} \rho$, for absorption
$w_{21} = N_2 B_{21} \rho$, for absorption

Since $w_{12} = w_{21}$, $N_1 = N_2$. The greatest possible Excited state population is 50%.
Lasers in Chemistry

Light Amplification by Stimulated Emission of Radiation

I. Requirements for a laser

II. Two state, three state, and four state systems.

III. Survey of tunable lasers.

IV. Applications
Requirements for a laser

- Gain (population inversion)
- Laser cavity (reflecting mirrors)
- Output coupler (semi-reflective mirror)
- Standing waves can be obtained for $n\lambda = 2L$
- The bandwidth in the laser cavity can be modulated using birefringent filters, etalons, or grating/prism combinations.
Gain can only be achieved with population inversion

- Gain represents the increase in photons emitted from the sample compared to a Boltzmann distribution.
- The Boltzmann distribution will never allow for more population in an excited state than in the ground state.
- Gain represents a non-Boltzmann distribution induced by optical or electrical pumping.
Two Level System in Spectroscopy

- For states 0 and 1 the Einstein $B$ coefficients are equal.
- High fluence limit results in a ratio of populations determined by microscopic reversibility.
- At equilibrium $W_{\text{absorption}} = W_{\text{emission}}$.
- Since $B\rho$ is the same, in the limit of large $\rho$ we have that $n_1 = n_0$, and there is no population inversion ($n_1 > n_0$).
A Three Level System: Laser

- Optical or electrical pumping is used.
- Pump to intermediate state that decays into long-lived emissive state.
- Ground state population must be overcome to make a population inversion in the emissive state.
- Example: the ruby laser, Cr:Al₂O₃ in which Cr d-d transitions give a population inversion in a state that emits at 594 nm.
A three-level system provides a route to a population inversion

- We can simplify the rate equations by assuming that
- If $k_{21}n_2 \gg n_1B\rho$ then a population build-up in $n_1$ can lead to an population inversion $n_1 \gg n_0$.
- Still has disadvantage that population in $n_0$ is dominating at equilibrium.
A four-level system produces superior results for laser design

- A four level system provides ease of creation of an inversion since state 3 is essentially unpopulated at equilibrium.
- In order for this scheme to work the rate from 1 to 2 and from 3 back to 0 must be rapid. The population inversion is set up between 2 and 3.
Comparison of thermal and pumped population

Thermal

Pumped
The laser cavity

The partial reflector is usually called the output coupler.
Laser modes

In the resonant cavity formed by the mirrors we get a standing wave pattern of electric field intensity.

This implies that $n\lambda/2=L$ where $n$ is an integer and $L$ is the optical path length of the cavity. Therefore we get a series of frequencies given by:

$$\nu_n = nc/2L$$

Each $n$ defines an axial mode of the cavity. The separation of the modes is therefore

$$d\nu = c/2L$$

Only those modes which lie within the peak of the gain profile will be amplified and maintained.
The amplified modes

The gain curve

Laser modes

Amplified modes
Scientific Lasers

- Ar and Kr ion lasers
- Nd:YAG and Nd:YLF lasers
- CO$_2$ lasers
- Excimer lasers
- Dye lasers
- Transition metal lasers
- Optical parametric amplification
Ar and Kr ion lasers

- Noble gas ions are created in an electric discharge. The ions have specific electronic transitions.
- Ar ion lines: 514, 501, 488, 476 and 457 nm.
- Kr ion lines: 406, 413 and 752 nm.
- Continuous wave (cw), non-tunable, useful narrow bandwidth source for pumping cw dye lasers.
Argon ion laser

A high discharge current is used to form ions. Powerful Continuous Wave operation can be achieved by discharge (15-50 Amps!) to maximize the pumping power. Several watts CW output or upto 1 kilowatt in microsecond pulses can be generated. Pump to 4P states, 35eV above ground state by multiple collisions. Transitions correspond to 4P-4S, 514.5nm and 488nm. Use Brewster window at ends of gas tube to isolate a single polarization with minimum reflection losses.
Nd:YAG and Nd:YLF lasers

- Flash lamp pumped transitions with strong lasing at 1.064 μm. There are narrow transitions due to the fact that f-orbital transitions are buried below 5s and 5p.
- Cavity is Q-switched for 10 ns every 0.1 seconds. Q-switching is an electronic method to create a short pulse (or burst) of laser light.
- Frequency doubling using KDP to achieve 532 nm, the most frequently used wavelength in biophysical studies of biological molecules.
Frequency doubled Nd:YAG
Nd:YAG

- Nd:YAG is the commonly used laser material today.
- Neodymium-doped yttrium aluminium garnet; Nd:Y$_3$Al$_5$O$_{12}$ is a crystal that is used as a lasing medium for solid-state lasers.
- It is particularly useful in nanosecond pulsed lasers.
- The Nd:YAG fundamental occurs at 1064 nm.
Nd:YLF

- Nd:YLF is used in a diode pumped configuration.
- Neodymium yttrium lithium fluoride; LiY$_{1-x}$Nd$_x$F$_4$.
- It is particularly useful in as a reliable pump source for Ti:sapphire.
- The Nd:YAG fundamental occurs at 1047 nm.
CO$_2$ lasers

- There are four vibrational modes of CO$_2$.
- The point group is $D_{\infty h}$.
- The vibrations are:
  - totally symmetric stretch
  - bend (two dimensions)
  - antisymmetric stretch
- The bend and anti-symmetric stretch form a Fermi resonance.
CO$_2$ lasers are infrared lasers

- N$_2$ can be pumped in an electric discharge into the first excited vibrational state.
- Efficient energy transfer results in excitation of the CO$_2$ symmetric stretch.
- The lasing transition occurs between different rotational states of the anti-symmetric stretch at 2400 cm$^{-1}$ and the other vibrational modes symmetric stretch at 1400 cm$^{-1}$ and bend at 1300 cm$^{-1}$. 
The gain curve of CO$_2$ spans the rotational states energies of the molecule

- It is logical that the tunability of a “vibrational laser” arises from the rovibrational fine structure.
- The population of an independent vibrational level J is $p_J = (2J+1)e^{-hcB/kT[J(J+1)]/q}$ where $q = kT/hcB$ in the high temperature approximation.
- During lasing if a particular level is depleted, there is population flow into that level to maintain a Boltzmann distribution. This implies a build up into a mode where all lasing occurs from a single level.
Excimer laser

- An excimer is an excited state charge transfer complex that is dissociative in the ground state.
- The unstable ground state serves to create a four level system.
- Typical UV lasers
  - XeCl 308 nm
  - ArF 247 nm
Dye lasers

• Tunable lasers pumped both cw by Ar and Kr ion and in pulsed laser applications by Nd:YAG.

• Common dyes
  
  Rhodamine $\lambda_{\text{max}} = 590$ nm
  Stilbene-1 $\lambda_{\text{max}} = 430$ nm
  Coumarin $\lambda_{\text{max}} = 430$ nm
Dye lasers are messy

Pumped liquid contains dye. Dye degrades over time. Result is a frequent exchange of laser dyes.
Solid state alternative: Ar ion laser exciting a Ti:sapphire rod
d-d transitions can give a useful four level system for tunable lasers

- A titanium sapphire laser Ti:Al$_2$O$_3$ is a four level system.
- This is part of a vibronic mechanism which results in a Jahn-Teller distortion of the complex. In this distorted complex e$_u$ is the fourth state.

\[
\begin{array}{c}
\text{Oh Ligand Field} \\
\hline \\
\text{Trigonal Distortion in Al}_2\text{O}_3 \text{ Lattice} \\
\hline \\
\text{Ti is d}^1 \text{ leading to population of a single low energy state in the d-orbitals}
\end{array}
\]
Comparison of three and four state systems

- Cr is $d^3$ and this results in a different behavior than for Ti.
- Because each of the $t_{2g}$ levels is occupied by a single electron there is no Jahn-Teller distortion.
- Ruby has the disadvantage as well that other $t_{2g} \rightarrow e_g$ transitions can occur absorbing the light.

$\text{O}_h$ Ligand Field
Cr(III) ligand field is nearly $O_h$ so help is required from other metals

- Note that the rate equations for triply degenerate $t_{2g}$ ground state of Cr(III) imply that the rate of absorptive transitions is 2 times higher than for the stimulated emission.
- From this viewpoint we see that ruby is definitely not the ideal material. Alexandrite (CrBe:Al$_2$O$_4$) is a four level system and that overcomes these problems.
- Ruby and Alexandrite are transition metal lasers.
Z-shaped laser cavity standard in Ti:sapphire design
Z-shaped laser cavity standard in Ti:sapphire design
Ar ion laser exciting a Ti:sapphire rod
A Ti:sapphire tuning curve
Non-linear optics

• Second harmonic generation (SHG), or frequency doubling, generation of light with a doubled frequency (half the wavelength);
• Sum frequency generation (SFG), generation of light with a frequency that is the sum of two other frequencies (SHG is a special case of this);
• Third harmonic generation (THG), generation of light with a tripled frequency (one-third the wavelength) (usually done in two steps: SHG followed by SFG of original and frequency-doubled waves);
• Difference frequency generation (DFG), generation of light with a frequency that is the difference between two other frequencies;
Second harmonic generation

- A polarization is induced in the material at twice the input frequency.

\[ P(2\omega) = \varepsilon_0 \chi_2 E(\omega)^2 \]

- The SHG susceptibility is \( \chi_2 \).
- SHG only occurs in a non-centrosymmetric crystal.
- It requires a birefringent crystal (i.e. a material that has two different indices of refraction).
Critical phase matching (also called angle phase matching) is a technique for obtaining phase matching of some nonlinear process in a birefringent crystal. The interacting beams are aligned at some angle(s) to the axes of the index ellipsoid. In almost all cases, there are one or two waves polarized along one axis of the index ellipsoid (ordinary beam), while another one or two waves are polarized at some variable angle with the plane spanned by the other two axes (extraordinary beams). Adjustment of the propagation angle affects the refractive index of the extraordinary beam (called extraordinary refractive index), whereas the ordinary index stays constant. For some angular position, phase matching may be achieved.
Beams in a birefringent crystal

Example of phase matching in a birefringent crystal. A birefringent crystal has two different indices of refraction along different directions (polarizations).
Discovery of SHG

Second harmonic generation was first demonstrated by Franken, Hill, Peters, and Weinreich at the University of Michigan, Ann Arbor, in 1961. The demonstration was made possible by the invention of the laser, which created the required high intensity monochromatic light. They focused a ruby laser with a wavelength of 694 nm into a quartz sample. They sent the output light through a spectrometer, recording the spectrum on photographic paper, which indicated the production of light at 347 nm. Famously, when published in the journal *Physical Review Letters*, the copy editor mistook the dim spot (at 347 nm) on the photographic paper as a speck of dirt and removed it from the publication.
Types of SHG

- Second harmonic generation occurs in two types, denoted I and II.
- In **Type I SHG** two photons having ordinary polarization with respect to the crystal will combine to form one photon with double the frequency and extraordinary polarization.
- In **Type II SHG**, two photons having orthogonal polarization will combine to form one photon with double the frequency and extraordinary polarization. For a given crystal orientation, only one of these type of SHG occurs.
Structure of potassium dihydrogen phosphate (KDP)

International Union of Crystallography
Grow your own KDP doubling crystal

This student is removing the first KDP crystal grown at Monte Vista High School.
An 800 pound KDP doubling crystal

National Ignition Facility and Photon Science
Lawrence Livermore National Laboratory
SHG microscopy

In biological and medical science, the effect of second harmonic generation is used for high-resolution optical microscopy. Due to the phase-matching condition only non-centrosymmetric structures are capable of emitting SHG light. One such structure is collagen, which is found in most load-bearing tissues. Using a short-pulse laser such as a femtosecond laser and a set of appropriate filters the excitation light can be easily separated from the emitted, frequency-doubled SHG signal. This allows for very high axial and lateral resolution comparable to that of Confocal microscopy without having to use pinholes.
Image of collagen

Texas A&M Imaging Center