Chemistry 2

Lecture 11

Electronic spectroscopy of polyatomic molecules
Learning outcomes from lecture 10

• Be able to draw the potential energy curves for excited electronic states in diatomics that are bound and unbound
• Be able to explain the vibrational fine structure on the bands in electronic spectroscopy for bound excited states in terms of the classical Franck-Condon model
• Be able to explain the appearance of the band in electronic spectroscopy for unbound excited states

Assumed knowledge

For bound excited states, transitions to the individual vibrational levels of the excited state are observed with intensities that depend on the Franck-Condon factors. The ‘vertical’ transition is the strongest. For unbound excited states, the electronic spectrum is broad and diffuse
Franck-Condon Principle (reprise)
Electronic spectra of larger molecules...

- A molecule has $3N-6$ different vibrational modes
- As there are no selection rules any more on vibrational transitions, the spectrum quickly becomes so complicated that the vibrational states cannot be readily resolved
Electronic spectra of larger molecules...

An atom

A diatomic (or other small) molecule

A large molecule

$1s$

$2s$

$2p$

$3s$

Energy $E$

Distance $R$

Absorption

$S_0$

$S_1$
Jablonski Diagrams...

Electronic states
(thick lines)

Vibrational levels
(thin lines)

\[ E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} \]

Again, this is the Born-Oppenheimer approximation.
Correlation between diatomic potential energy surface (PES) and Jablonski diagram
One of the most important pieces of information about the electronic state is the total electron spin, $S$

- **If the total electron spin is zero:** $S = 0$, then there is only one way to arrange the spins, and we have a singlet state, denoted, $S$

- **If there is one unpaired electron:** the total spin is $S = \frac{1}{2}$ and there are 2 ways the spin can be aligned (up and down), and we have a doublet state, denoted, $D$

- **If there are two unpaired spins:** the total spin is $S = \frac{1}{2} + \frac{1}{2} = 1$ and there are 3 ways the spins can be aligned. This is a triplet state, denoted, $T$

<table>
<thead>
<tr>
<th>Total Spin</th>
<th>Name</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>singlet</td>
<td>S</td>
</tr>
<tr>
<td>$\frac{1}{2}$</td>
<td>doublet</td>
<td>D</td>
</tr>
<tr>
<td>1</td>
<td>triplet</td>
<td>T</td>
</tr>
</tbody>
</table>
The ground state gets the symbol “0”
Other states are labelled in order, 1, 2, ... according to their multiplicity
The x-axis doesn’t mean anything in a Jablonski diagram. Position the states to best illustrate the case at hand.
Chromophores

- Any electron in the molecule can be excited to an unoccupied level. We can separate electrons in to various types, that have characteristic spectral properties.
- A chromophore is simply that part of the molecule that is responsible for the absorption.

- Core electrons: These electrons lie so low in energy that it requires, typically, an X-ray photon to excite them. These energies are characteristic of the atom from which they come.
- Valence electrons: These electrons are shared in one or more bonds, and are the highest lying occupied states (HOMO, etc). Transitions to low lying unoccupied levels (LUMO, etc) occur in the UV and visible and are characteristic of the bonds from which they come.
Types of valence electrons

• **σ-electrons** are localised between two atoms and tightly bound. Transitions from s-orbitals are therefore quite high in energy (typically vacuum-UV, 100-200 nm)

• **π-electrons** are more delocalised (even in ethylene) than their σ counterparts. They are bound less tightly and transitions from π orbitals occur at lower energy (typically far UV, 150-250nm, for a single, unconjugated π-orbital).

• **n-electrons** are not involved in chemical bonding. The energy of a non-bonding orbital lies typically between that for bonding and antibonding orbitals. Transitions are therefore lower energy. *n*-orbitals are commonly O, N lone pairs, or non-bonding π-orbitals
Transitions involving valence electrons

- Vacuum (or far) uv
  - \(\pi \rightarrow \pi^*\)
  - \(\sigma \rightarrow \sigma^*\)
  - \(n \rightarrow \sigma^*\)

- Near uv
  - \(\pi \rightarrow \pi^*\)

- Visible
  - \(n \rightarrow \pi^*\)

- Near IR

Wavelength (nm)

energy, frequency, wavenumber
Chromophores in the near UV and visible

There are two main ways that electronic spectra are shifted into the near-UV and visible regions of the spectrum:

1. Having electrons in high lying levels. These are commonly non-bonding such as $d$ and $f$-electrons in transition metal complexes.

\[ \text{Ni(OH}_2\text{)}_6^{2+} \]
\[ \text{Ni(H}_2\text{NCH}_2\text{CH}_2\text{CH}_3\text{)}_3^{2+} \]
\[ \text{Mn(OH}_2\text{)}_6^{2+} \]
2. Delocalised $\pi$-electrons. Recall from the “particle-in-a-box” and “particle on a ring” models that linear and cyclic polyenes have a large number of extended, delocalised $\pi$ orbitals, with low energy separation. The separation decreases with the length of the chain so transitions involving larger chromophores occur at lower energy (in the visible)

\[
\begin{align*}
\text{β-carotene (all trans)}
\end{align*}
\]
Effect of chromophore size

Wavelength (nm)

Chromophore

Effect of chromophore size

Chromophore
Chromophores in the near UV and visible

- Aromatic chromophores:
Chromophores at work

trans-retinal
(light absorber in eye)

Dibenzooxazolyl-ethylenes
(whiteners for clothes)
After absorption, then what?

- After molecules absorb light they must eventually lose the energy in some process. We can separate these energy loss processes into two classes:
  - radiative transitions (fluorescence and phosphorescence)
  - non-radiative transitions (internal conversion, intersystem crossing, non-radiative decay)
Fluorophore in Ground State

High energy

Ground state
Low energy

Fluorophore

Energy levels

Slide taken from “Invitrogen” tutorial
(http://probes.invitrogen.com/resources/education/, or Level 2&3 computer labs)
Absorption of Light Energy

Fluorophore

Energy levels

Absorbed light

Ground state

High energy

Low energy
Excited Fluorophore

Fluorophore

Energy levels

Excitation

High energy

Excited state

Low energy

Slide taken from “Invitrogen” tutorial
(http://probes.invitrogen.com/resources/education/, or Level 2&3 computer labs)
Energy Loss

Fluorophore

Excited states

Energy levels

Slide taken from “Invitrogen” tutorial
(http://probes.invitrogen.com/resources/education/, or Level 2&3 computer labs)
Energy Loss

Fluorophore

Excited lifetime

$10^{-15}$ to $10^{-9}$ seconds

Excited states

Energy levels

Slide taken from “Invitrogen” tutorial
(http://probes.invitrogen.com/resources/education/, or Level 2&3 computer labs)
Fluorescence Emission

Absorbed Light

Fluorophore

Emitting Light

High energy

Energy levels

Low energy

Slide taken from “Invitrogen” tutorial (http://probes.invitrogen.com/resources/education/, or Level 2&3 computer labs)
Summary

Fluorescence is ALWAYS red-shifted (lower energy) compared to absorption.

1 = Absorption
2 = Non-radiative decay
3 = Fluorescence
**Franck-Condon Principle (absorption)**

![Diagram showing Franck-Condon Principle](image)
If vibrational structure in the ground and exited state are similar, then the spectra look the same, but reversed -> the so-called “mirror symmetry”
The shift between $l_{\text{max}}$ (absorption) and $l_{\text{max}}$ (fluorescence) is called the STOKES SHIFT. A bigger Stokes shift will produce more dissipation of heat.
The Origin of the Stokes shift and mirror symmetry

Stokes shift = \((v' 0 - 4) + (v'' 0 - 4)\)

Note:
- mirror symmetry: if 0 \(\rightarrow\) 4 is the most intense in absorption, 0 \(\rightarrow\) 4 is also most intense in emission
- Stokes shift here is \(G'(4) + G''(4)\)
Different Stokes shifts

A.

B.

C.

D.

E.

F.

Note mirror symmetry in most, but not all dyes.
Fluorescence spectrum

Excitation

Emission

Non radiative decay

Loss of Energy

Absorbed light

Emitted light

Wavelength of light (nm)
Real data...

- Fluorescence is always to longer wavelength
- Stokes shift = (absorption max.) – (fluorescence max.)
  
  [= 50 nm here]
- Mirror symmetry
Learning outcomes

• Be able to use $S$, $D$ and $T$ to label the spin multiplicity of an electronic state
• Be able to describe how energy is lost after absorption by radiative transitions and non-radiative transitions
• Be able to explain the “mirror symmetry” and Stokes shift of absorption and fluorescence spectra explained using a Jablonski diagram
Next lecture

• Non-radiative processes and phosphorescence

Week 13 homework

• Electronic spectroscopy worksheet in tutorials
• Practice problems at the end of lecture notes
Practice Questions

1. The figure opposite shows the absorption and fluorescence spectra of a common organic dye.

(a) Explain using a Jablonski diagram why the absorption and fluorescence spectra appear like “mirror images” of each other.

(b) Estimate the value of the Stokes shift and explain its origin.

2. The figure opposite shows a Jablonski diagram.

(a) Draw an arrow to represent absorption to a high lying vibrational state in $S_1$.

(b) Draw arrows to represent non-radiative decay to the zero-point level of $S_1$.

(c) Draw an arrow to represent fluorescence to a high lying vibrational state of $S_0$.

(d) Draw arrows to represent non-radiative decay to the zero-point level of $S_0$.

(e) Using your diagram, explain why (i) fluorescence emission is longer wavelength than the corresponding absorption and (ii) why radiationless decay results in the heating of a sample.