Week 7

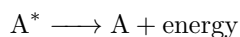# Electronic Relaxation

7.1 Office Hours (Moe)

- Use chemical shift as your x-axis in NMR plots.

- Hexylamine is our substance.

- Interpreting NMR data files: Column E is chemical shift; column C is peak intensity. Column D is hertz (not chemical shift).

  - Chemical shift is in the rightmost column.

- Fitting tutorial: If solver still isn't helping (you get an error message and no convergence), divide the absolute intensities by a million. You can also do this from the get-go.

- M_z should be calculated for each carbon; it is the absolute integral value in the all-integrals spreadsheet.

- Don't let the peaks overlap in the plot of multiple vertically offset T_1 values.

  - Use 3 plots.

- R outputs standard error values automatically.

  - In Excel, it's much more difficult.
  - A residuals plot is a good thing to include, but there won't be points for it. Standard error also isn't worth points. Sarah will have them upload the rubric. Sarah opened the door to email her.
  - We need standard error for all 6 regressions.

- Sarah will send a source for literature values.

7.2 Lecture 12: Electronic Relaxation and Fluorescence Spectroscopy

- Today: What happens after absorption (fluorescence and relaxation).

- Motivating question: What is the fate of electronic excitations?

  - Absorption to an electronic excited state takes a lot of energy.
  - This energy needs to be dissipated to return to equilibrium via

  $$\text{A}^* \longrightarrow \text{A} + \text{energy}$$

  - Many possible routes (radiative [releasing low-energy photons] and non-radiative [various]).

- Review: Electronic absorption leads to vibrational excitation which relaxes vibrationally.
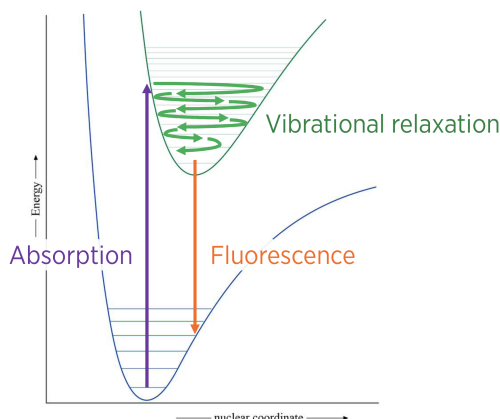

Figure 7.1: The photophysical excitation process.

  - Vibrational energy dissipates non-radiatively via intramolecular vibrational energy redistribution and intermolecular collisions.
    - No change in electronic state is involved.
  - The radiative path (fluorescence) is slower.
    - $k_{\text{rad}} \ll k_{\text{IVR}}$.
    - Most fluorescence occurs from $v' = 0$. Further relaxation requires a change of electronic state.
  - Time scale of relevant processes.
    - The vibrational period of a molecule is 10-100 fs.
    - Vibrational relaxation in solution takes 1-10 ps.
    - Fluorescence emission takes 1-10 ns.
  - Once you get into the ground state, you have further vibrational relaxation.

- k_{rad}: The radiative fluorescence emission rate.

- k_{nr}: The rate of all nonradiative processes leaving the flourescent state. *Given by*

$$k_{\text{nr}} = \sum_i k_{\text{nr},i}$$

- k_{IVR}: The intramolecular vibrational relaxation rate.

- **Reorganization energy**: The amount of energy dissipated on one of the potential energy surfaces. *Denoted by λ.*

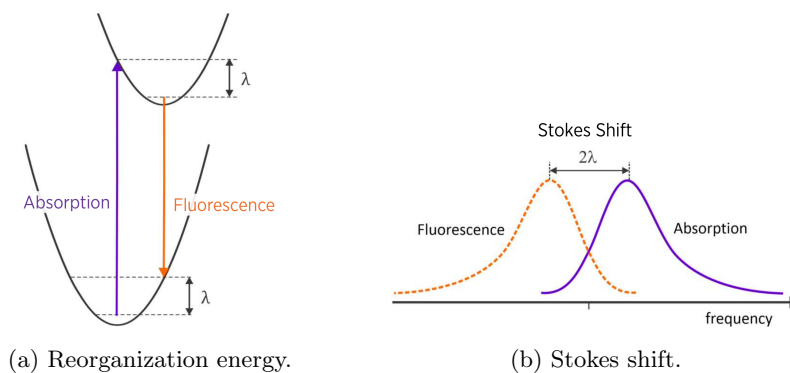(a) Reorganization energy.   (b) Stokes shift.

Figure 7.2: Quantifying photophysical reorganization.

– Per the above, some energy is dissipated in both the ground and excited states. The amount dissipated in both is (roughly??) the same and is denoted by λ.

– The overall energy shift is known as the **Stokes shift** and is the sum of the two reorganizational energies.

- **Stokes shift**: The difference in energy absorbed vs. energy fluoresced. *Denoted by* $\mathbf{2\lambda}$.

- Other non-radiative intramolecular electronic relaxation process.
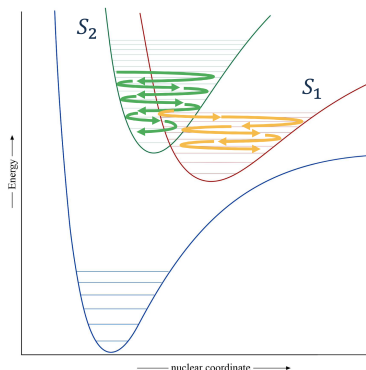
- Internal conversion.

Figure 7.3: Internal conversion.

– Essentially, exchange between higher lying excited singlet states can be very efficient.

– We obey the **energy gap law**.

- **Energy gap law**: The non-radiative relaxation rate scales exponentially in the energy gap between the initial and final states. *Given by*
$$k_{\mathrm{nr}} \propto \exp(-\Delta E)$$

- Intersystem crossing.

– Non-radiative singlet to triplet energy transfer.

– We have to consider what happens when we change the spin angular momentum. Because this takes energy, this is quite improbable unless we have something like spin-orbit coupling present.

– Nominally forbidden in closed shell molecules. Hence, it is slow.

  ■ *ms* in closed shell organics.

  ■ *ps-ns* in metal coordination compounds via SOC, MLCT.

- **Phosphorescence**: Luminescence from triplet states.

– Occurs on a very slow microsecond to millisecond time scale.
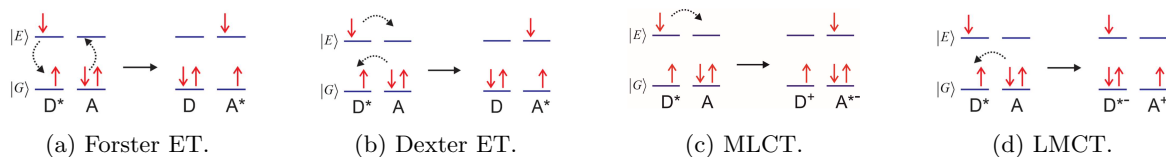
- Intermolecular processes.

(a) Forster ET.   (b) Dexter ET.   (c) MLCT.   (d) LMCT.

Figure 7.4: Intermolecular relaxation mechanisms.

- – Forster energy transfer (through space), aka, electronic resonance energy transfer.
  - ■ Two dipoles couple, and one drives the other.
- – Dexter energy transfer.
  - ■ Wavefunction overlap and electrons move.
- – MLCT (electron transfer).
  - ■ Donor gives a high energy electron to an acceptor.
- – LMCT (hole transfer).
  - ■ Donor gives a hole to the acceptor.
  - ■ Electronic excitation brings electron density to the metal center.
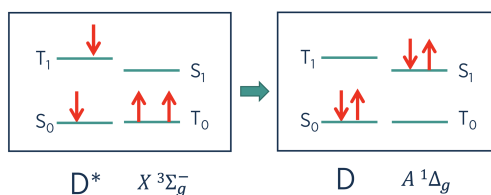
- Triplet quenching by oxygen.

Figure 7.5: Triplet quenching by oxygen.

- – Oxygen is a rare ground-state triplet compound.
- – Thus, it can easily transfer electron density to other excited triplets, quenching them.
- – Rate is partially determined by the proximity of oxygen to whatever it's quenching.

- Photochemistry summary.

  - – Light provides energy to surmount activation barriers (relevant to atmospheric chemistry, photo-synthesis).
  - – Photodissociation (relevant to bond cleavage, ligand release, photoacids, photoionization, and radicals).
  - – Electron transfer and proton-coupled electron transfer.
  - – Photoisomerization (see below).

- Photoisomerization.

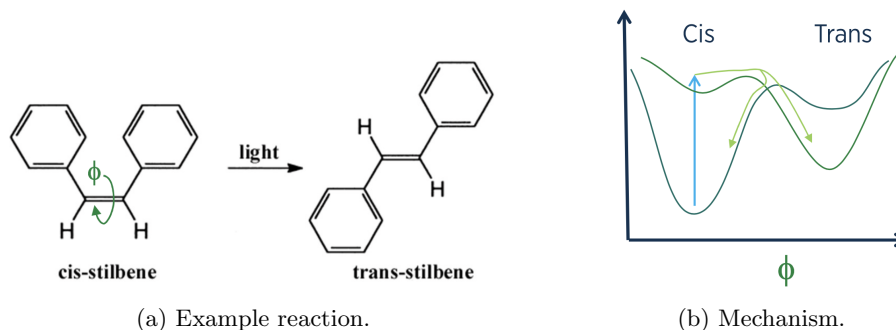

(a) Example reaction.

(b) Mechanism.

Figure 7.6: Photoisomerization.

- – Stilbene possesses *cis/trans* photoisomerization.

- Quantities in fluorescence spectroscopy.

- **Fluorescence quantum yield**: The probability that an absorbed photon led to emission of a photon via fluorescence. *Denoted by* Φ. *Given by*

$$\Phi = \frac{\# \text{ of fluorescence photons emitted}}{\# \text{ of input photons absorbed}} = \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{nr}}}$$

  – Tells you how good of a fluorophore your molecule is, i.e., how good it is at absorbing light and turning it back into fluorescence.

- k_{f}: The rate constant for fluorescence emission. *Given by*

$$k_{\text{f}} = k_{\text{rad}} + k_{\text{nr}}$$

- **Fluorescence lifetime**: The time constant relating to the rate of fluorescence emission. *Denoted by* τ. *Given by*
$$\tau = \frac{1}{k_{\text{f}}}$$

- The underlying theory behind the fluorescence lifetime.

  – The measured fluorescence intensity $I(t)$ is proportional to the number of excited states, i.e.,

$$I(t) \propto A^*(t)$$

  – The rate law for fluorescence decay is

$$\frac{dA^*}{dt} = -k_{\text{f}}A^*$$
$$I(t) = I(0)\exp(-k_{\text{f}}t)$$

- Implication: We can use fluorescence to probe non-radiative processes.

- Example: Quenching experiments.

  – Object of study: Short-range interactions that lead to rapid non-radiative relaxation.
  – Background: The fluorescence lifetime in the absence of quencher is $\tau_0 = k_0^{-1}$. The quencher results in an additional route for non-radiative relaxation.
    ■ Implication: The fluorescence lifetime τ decreases: $\tau < \tau_0$.
    ■ If [Q] denotes the concentration of the quencher and k_q denotes the rate constant associated with quenching by the quencher, then we have

$$-\frac{dA^*}{dt} = k_0 A^* + k_q A^*[Q]$$
$$= (k_0 + k_q[Q])A^*$$

    so that

$$\frac{1}{\tau} = k_0 + k_q[Q] = \frac{1}{\tau_0} + k_q[Q]$$

  – Analysis: Use a **Stern–Volmer plot**.
    ■ Acquire fluorescence lifetime as a function of the quencher concentration using the last equation above.
    ■ This gives us the rate constant k_q as the slope and $1/\tau_0$ as the y-intercept.
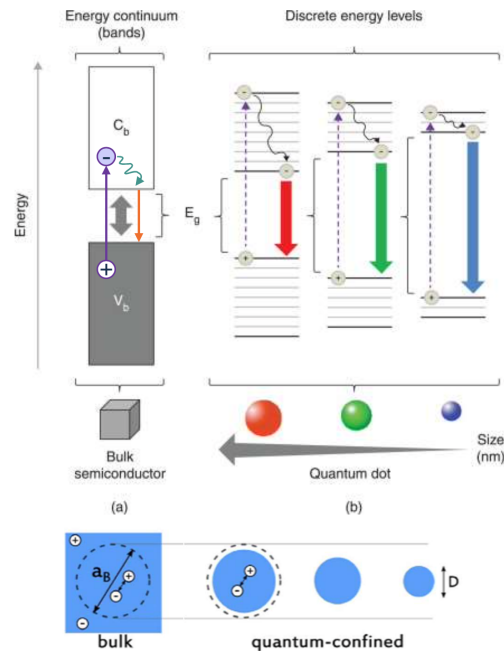
- Quantum dots: Electrons in confinement.

Figure 7.7: Quantum confinement effects in QDots.

  - Nanomaterials: Size-dependent optical properties.
  - The color changes from blue to red as the size of CdSe nanodots grows from $2\,\mathrm{nm}$ to $8\,\mathrm{nm}$.
  - Why?
    - In a bulk semiconductor, excitation creates an **exciton**.
    - Excited electron and hole can diffuse.
    - Dissipation of heat to lattice (via **phonons**).
    - Emission of light at the bandgap E_g.
    - The electron and hole attract coulombically, but there is a length scale in bulk; this is why size affects color.
  - Confinement: We confine the exciton to tiny sphere (like the particle in a box), but then only certain energy levels (corresponding to colors based on size) can be taken on.
  - The Coulomb potential leads to hydrogen-like energies and wavefunctions.

- **Exciton**: An electron-hole pair.