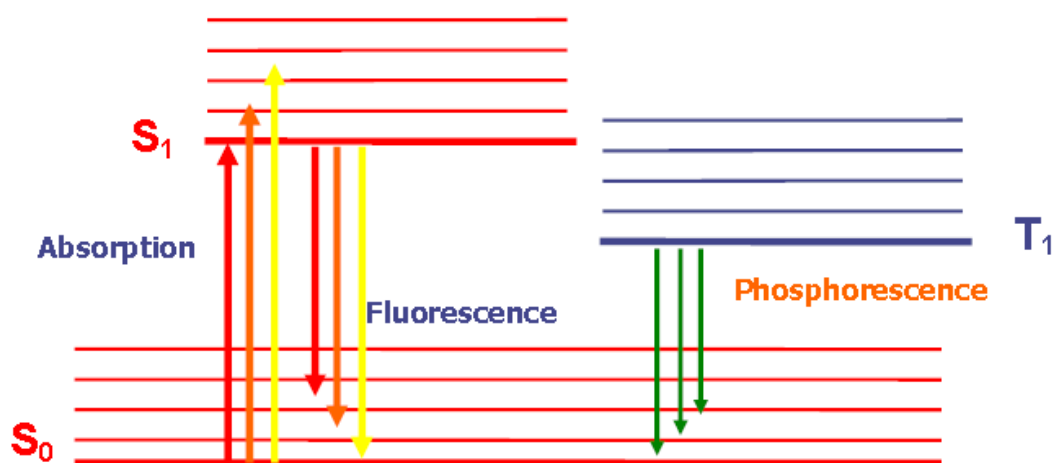
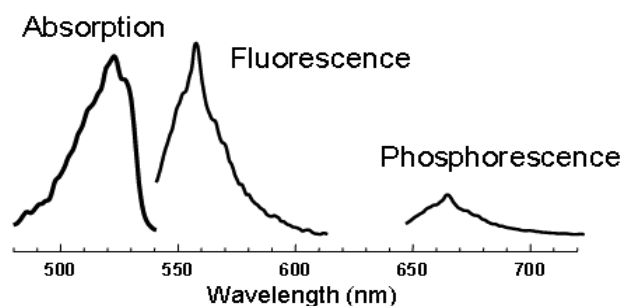
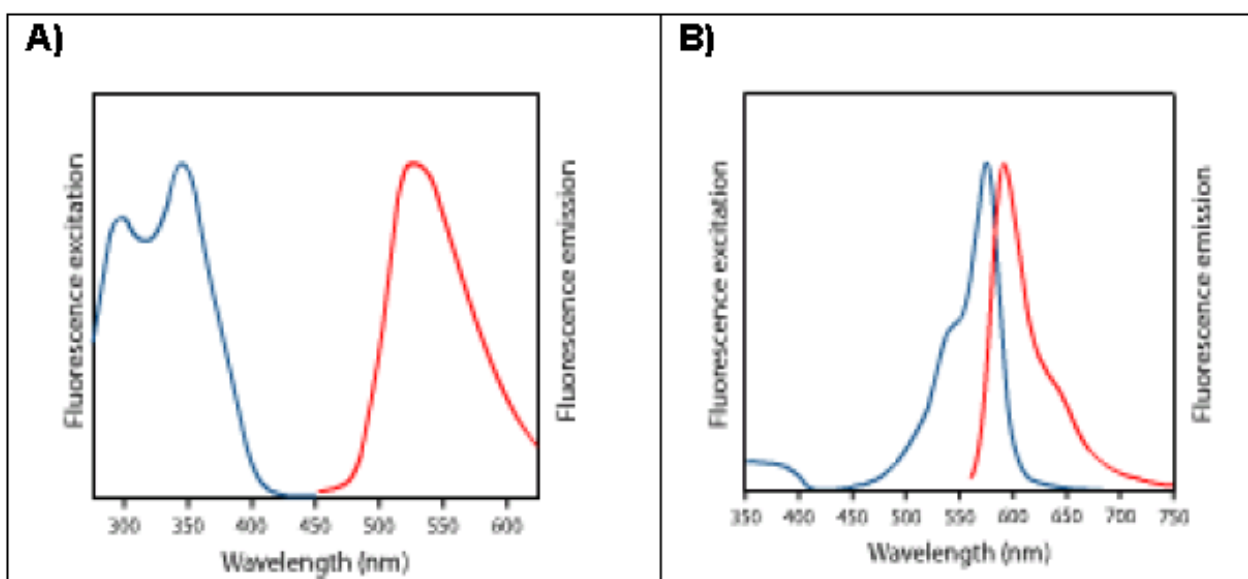


- The figure below shows the absorption and fluorescence spectra of a common organic dye. Why is the phosphorescence spectrum significantly red shifted compared to the fluorescence spectrum?



As shown on the Jablonski diagram above, the lowest triplet state, T_1 , is nearly always below S_1 therefore the phosphorescence emission is significantly red-shifted (lower energy) than fluorescence.

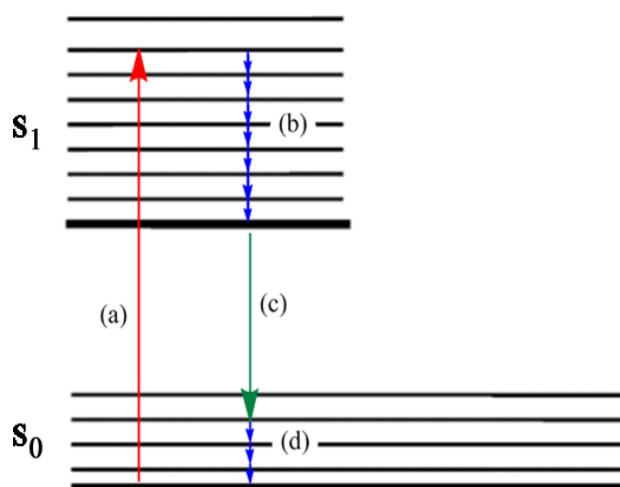
- The spectra below show the fluorescence excitation (blue) and fluorescence emission spectrum (red) of two large molecules. Explain, the following features of the spectra, using a Jablonski diagram to illustrate your answer.



- (a) **The Stokes shift is quite different for molecules A and B. Explain how this difference arises, and give an example of what molecular property might give rise to a large Stokes shift.**

The Jablonksi diagram opposite shows:

- (a) absorption from the ground state, S_0 , to a high lying vibrational level of the excited state, S_1
 (b) non-radiative decay where S_1 transfers vibrational energy to solvent,
 (c) fluorescence from the lowest vibrational level of S_1 to a high lying vibrational level of S_0 and
 (d) non-radiative decay where S_0 transfers its vibrational energy to solvent.



The Stokes shift depends on the difference in the length of (a) and (d): the amount of non-radiative decay that occurs.

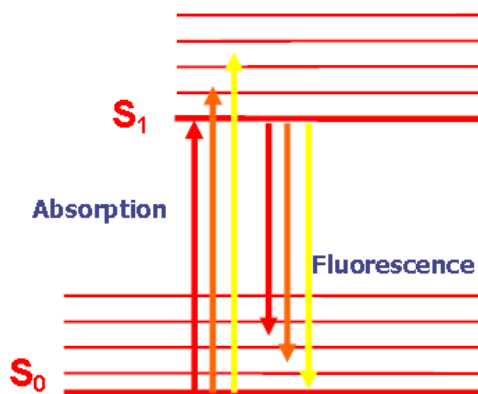
If the molecular geometry, such as the bond lengths, of S_0 and S_1 are very different, the potential energy curves for S_1 and S_0 will be displaced from each other and the vertical transition from the ground state will hit the curve for S_1 at a high vibrational level. Considerable non-radiative decay then occurs leading to a large Stokes shift.

- (b) **Molecule B in particular is a nice example of “mirror symmetry” between excitation and emission spectra. How does this mirror symmetry arise?**

The lines in the absorption spectrum correspond to transitions from the $v'' = 0$ level of S_0 (the ground state) to various values of v' in the excited state S_1 . For a large molecule, like a dye, the separate lines are not resolved and a broad band results.

In the fluorescence spectrum, the lines correspond to transitions from the $v' = 0$ level of S_1 to various value of v'' in the ground state.

As can be seen in the Jablonski diagram, the absorption lines are then at shorter wavelength (higher frequency) than the fluorescence lines.

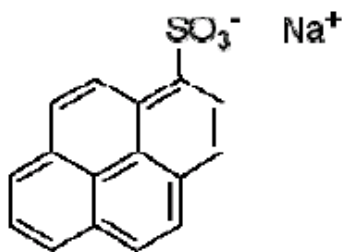


The shortest wavelengths in the absorption spectrum correspond to the transitions to the highest vibrational levels in the excited state. The longest wavelengths in the fluorescence spectrum correspond to the emission to the highest vibrational levels in the ground state.

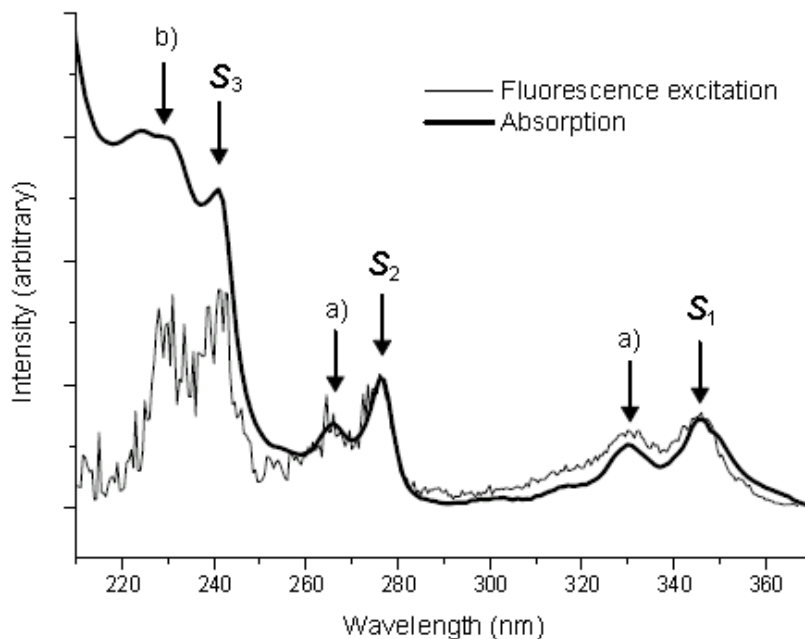
The longest wavelengths in the absorption spectrum correspond to the transitions to the lowest vibrational levels in the excited state. The shortest wavelengths in the fluorescence spectrum correspond to the emission to the lowest vibrational levels in the ground state.

The absorption and fluorescence spectra are thus “mirror images” of each other.

3. The two spectra below show the fluorescence excitation and absorption spectra of pyrenesulfonic acid.

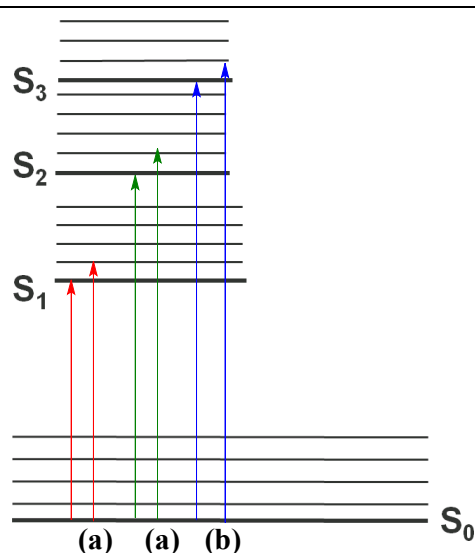


Pyrenesulfonic acid (sodium salt)



(a) In addition to the identified electronic origin transitions, there are other peaks in the absorption spectrum, as indicated by “a)” in the figure. Using a Jablonski diagram, explain how these other peaks arise.

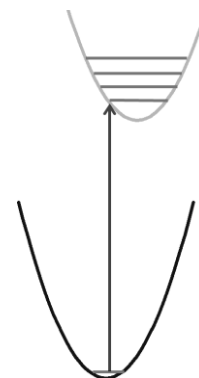
The other peaks in absorption spectrum correspond to excitations to higher vibrational levels within the excited states S_1 and S_2 .



(b) In the absorption spectrum, for the S_1 and S_2 transitions, the origin band is stronger than the two satellite bands marked by “a)”. In the S_3 transition, the origin band is weaker than the satellite, marked by “b)”. Explain, using the Franck-Condon principle, how this arises.

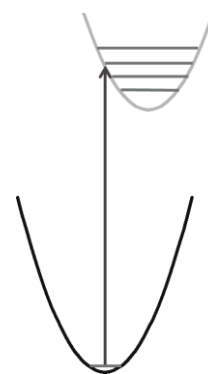
The geometries of the excited states S_1 and S_2 must be close to that of the ground state. The vertical transition from the equilibrium geometry of S_0 then hits a fairly low vibrational level of the excited state.

The origin band is then more intense than transitions to higher vibrational levels of S_1 and S_2 .

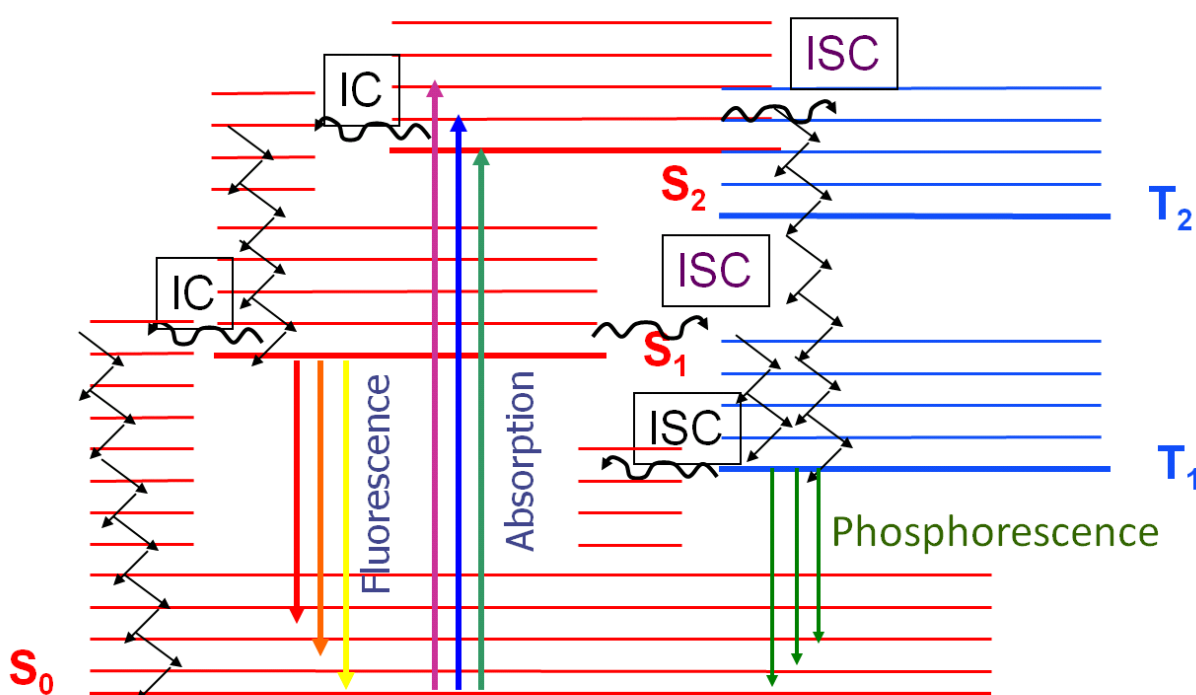


The geometry of the excited state S_3 must be less close to that of the ground state. The vertical transition from the equilibrium geometry of S_0 then hits a fairly high vibrational level of the excited state.

The intensity of the transitions to higher vibrational levels of S_3 are then more intense than that for the transition to the lowest vibrational level.



- (c) Using a Jablonski diagram, describe one such process that can give rise to the observed difference in the relative intensities of the fluorescence excitation and absorption spectra at $\lambda < 245$ nm



At $\lambda < 245$ nm, the molecule absorbs strongly but very little fluorescence results. This indicates the molecule is returning to the ground state via other routes.

These include:

- (i) Internal conversion (IC) where the electron relaxes to the ground state with no radiation. The molecule transfers to a high vibrational level of the ground state and then loses the vibrational energy through non-radiative decay via collisions with solvent.
- (ii) Intersystem crossing (ISC) where the molecules transfer to a triplet state by flipping an electron spin. The triplet state then undergoes non-radiative decay and ultimately phosphoresces.