1. The figure below 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.

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.

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

The Stokes shift is approximately 50 nm. It is the difference between the wavelengths of the most likely absorption and the most likely emission.

The most likely absorption corresponds to the transition from \( v'' = 0 \) in the ground state to the vibrational level in the excited state with the largest Franck-Condon overlap.

After absorption, the excited state undergoes non-radiative decay, losing energy to the solvent, to reach the \( v' = 0 \) level. Emission then occurs to vibrational levels of the ground state with the most likely emission being to the vibrational level with the largest Franck-Condon overlap. The difference between the maxima corresponds to the total amount of non-radiative decay.
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 $S_0$.

See diagram below.

(e) Using your diagram, explain why

(i) fluorescence emission is longer wavelength than the corresponding absorption

The absorption arrow, (a), on the left is much longer than the fluorescence arrow, (c), indicating that the energy of the photon absorbed is much higher than the energy of the photon re-emitted. Therefore, the fluorescence photon is longer wavelength than the absorbed photon.

(ii) why radiationless decay results in the heating of a sample.

The non-radiative decay (NRD), represented by a series of arrows cascading down to the zero-point level in both $S_0$ and $S_1$, is caused by molecules colliding with the solvent, or matrix molecules losing vibrational energy in a series of collisions. This vibrational energy of the molecule is being converted into heat in the surroundings. So NRD causes heating of the sample.