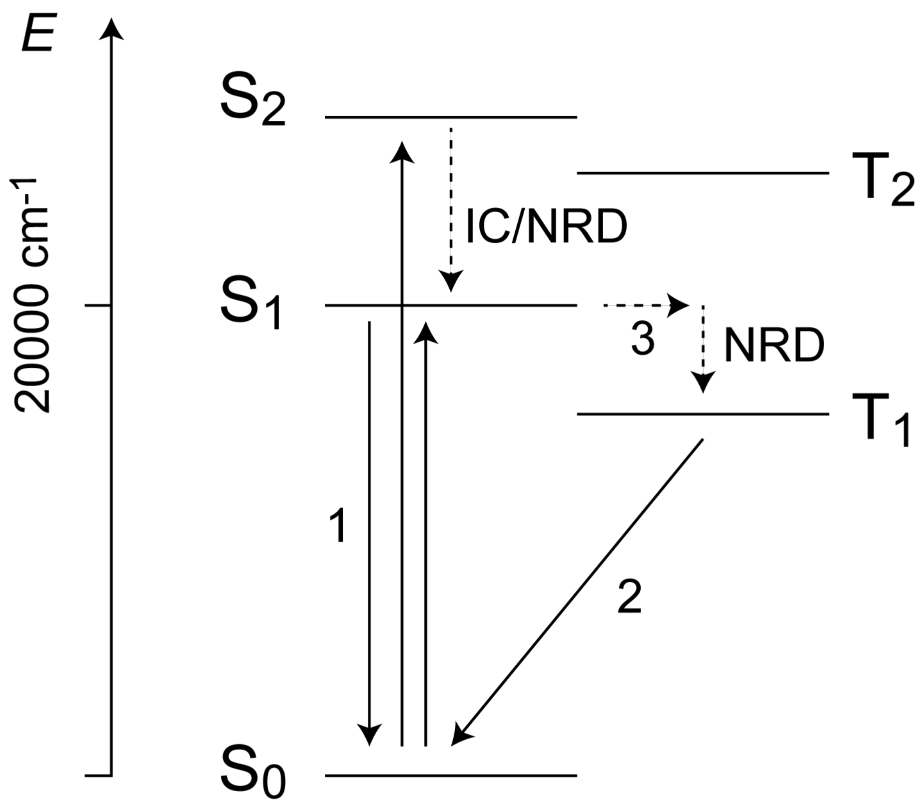


(a) A generic Jablonski diagram is shown above for an organic dye molecule. If the process labeled as **1** is fluorescence, name processes **2** and **3**. [2 marks P]

Process 2 is *phosphorescence*. Process 3 is *intersystem crossing* (ISC).

(b) What do the abbreviations IC and NRD stand for?

[2 marks P]

IC is *internal conversion*. NRD is *non-radiative decay*.

(c) What is the essential difference between processes marked with solid lines and dashed lines in the above diagram?

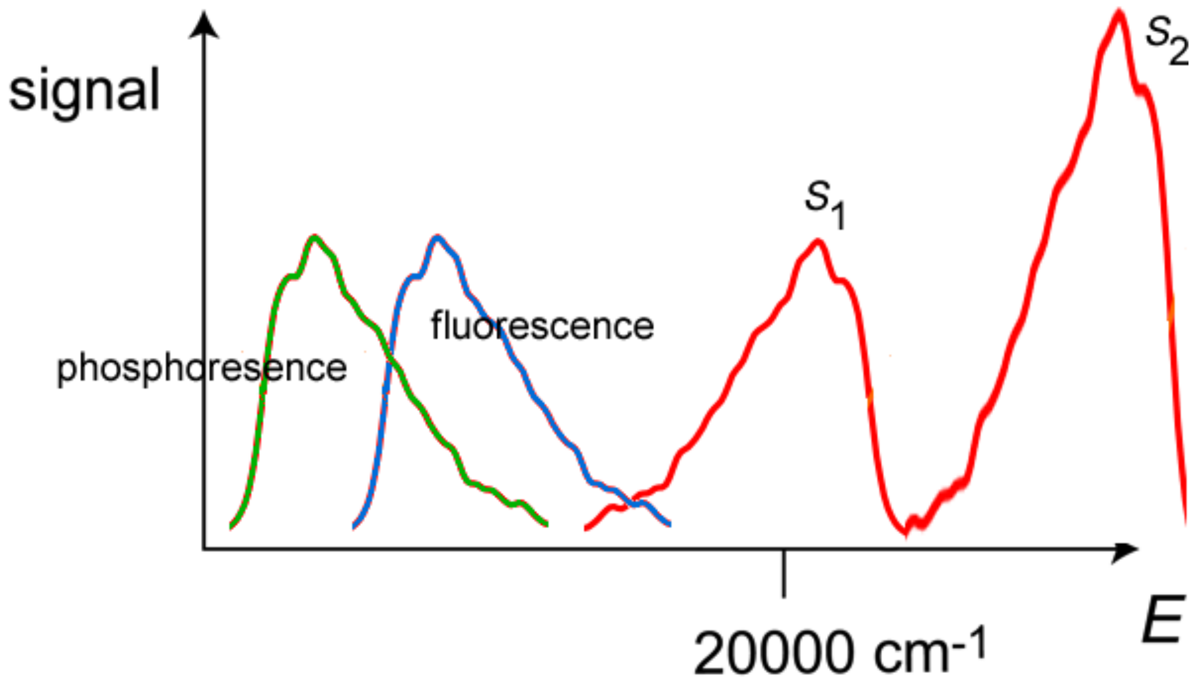
[1 mark CR]

The solid lines represent processes in which radiation is absorbed or emitted. The dashed lines represent processes in which no radiation is absorbed or emitted.

(d) On the diagram below, draw an absorption spectrum for the molecule, given that the $S_0 \rightarrow S_2$ transition occurs with twice the intensity as $S_0 \rightarrow S_1$. Both bands possess some vibrational structure.

[4 marks P/CR]

See *sketch* below. The band labelled S_2 is twice as intense as the band labelled S_1. There is some evidence of vibrational structure on the band.



(e) Draw and clearly label the fluorescence spectrum on the same diagram

[2 marks P/CR]

A *sketch* of the fluorescence spectrum is labelled on the spectrum above. Note that:

- **It occurs at lower energy than the absorption, with the shift due to non-radiative decay (loss of vibrational energy in S_1)**
- **It is the mirror image of the absorption spectrum of $S_0 \rightarrow S_1$**
- **Fluorescence only occurs from S_1 and *not* S_2. This is Kasha's Law.**

(f) Process **3** competes with process **1** to depopulate the S_1 state. If both rates are the same, and process **2** is 100% efficient, draw the spectrum of emitted light due to process **2** on the same diagram. Clearly label the spectrum either with a '**2**' or with its name.

[3 marks 1P 2CR]

Process 3 is phosphorescence and a *sketch* is labelled above. Note that:

- **It occurs at lower energy than fluorescence as the triplet state T_1 lies at lower energy than S_1.**

(g) What wavelength corresponds to 20000 cm^{-1}?

[1 mark P]

Wavenumber is the reciprocal of wavelength. Hence, the wavelength, λ, is:

$$\lambda = 1/20000 \text{ cm} = 5 \times 10^{-5} \text{ cm} = 5 \times 10^{-7} \text{ m} = 500 \times 10^{-9} \text{ m} = 500 \text{ nm}$$

(h) The S_1 state may be described principally as the result of the excitation of an electron from the HOMO to the LUMO. What do HOMO and LUMO stand for?

[2 marks P]

HOMO = highest occupied molecular orbital.
LUMO = lowest unoccupied molecular orbital.

(i) In the T_1 state, are the HOMO and LUMO electrons of the same or different spin? (Let $S_z=\pm1$)

[1 mark P]

A *T* state is a triplet: the electrons have the same spin.

(j) What colour is this substance in transmitted light?

[1 mark D]

20000 cm^{-1} corresponds to 500 nm. Green light is absorbed. As the molecule absorbs green, its colour is the complementary colour of green. The molecule is red.

Note that absorption to S_2 is at *higher* energy.

(k) An experiment is performed which shows that blue light is emitted for about 500 femtoseconds following excitation of the molecule with 300 nm light. Explain this phenomenon.

[2 marks HD]

Blue light is *higher* in energy than green light. As S_1 absorbs green light, its fluorescence will be at *lower* energy than its absorption (see (l)). The blue emission must be from S_2 rather than S_1.

(l) Subsequently, green light is emitted with a 20 nanosecond lifetime, followed by dull red luminescence with a 10 microsecond lifetime. Explain these phenomena.

[3 marks D/HD]

In 20 nanoseconds, there is time for internal conversion from the S_2 state to excited vibrational levels of S_1. After non-radiative decay involving energy transfer to the solvent, fluorescence then occurs from the lowest vibrational level of S_1 to the ground state.

Intersystem crossing (ISC) from the S_1 to T_1 state also occurs. This requires changing the spin of an electron to give the more stable parallel spin arrangement in the triplet state. After non-radiative decay, the molecule will be at the lowest vibrational level of T_1. Emission from T_1 to S_1 involves changing the spin. This emission – called phosphorescence – is a low probability process and takes microseconds to occur.

The T_1 state is lower in energy than the S_1 state, as there is less repulsion between electrons with parallel spin. The phosphorescence from T_1 therefore occurs at lower frequency than the fluorescence from S_1.