3.5: Quantum Yield of Fluorescence

The **quantum yield** (φ_F) is a ratio that expresses the number of species that fluoresce relative to the total number of species that were excited. Earlier we said that anything that reduces the number of excited state species that undergo fluorescence is said to quench the fluorescence. The expression for the quantum yield will depend on the rate constants for the different processes that can occur for excited state species. Referring back to our original drawing of the different processes that can occur, we can write the following expression for the quantum yield, where k_F is the rate constant for fluorescence, k_{IC} is the rate constant for internal conversion, k_{EC} is the rate constant for external conversion, k_{ISC} is the rate constant for intersystem crossing and k_C is the rate constant for any other competing processes and includes photodecomposition of the sample. Excited state species sometimes have sufficient energy to decompose through processes of dissociation or predissociation. In dissociation, the electron is excited to a high enough vibrational level that the bond ruptures. In predissociation, the molecule undergoes internal conversion from a higher electronic state to an upper vibrational level of a lower electronic state prior to bond rupture. When putting a sample into a fluorescence spectrophotometer, it is usually desirable to block the excitation beam until just before making the measurement to minimize photodecomposition.

$$\varphi_F = \frac{k_F}{k_F + k_{IC} + k_{EC} + k_{ISC} + k_C}$$

Since this is a ratio, the limits of φ_F are from 0 to 1. Species with quantum yields of 0.01 or higher (1 out of 100 excited species actually undergo fluorescence) are useful for analysis purposes.

Which method is more sensitive, absorption or fluorescence spectroscopy?

On first consideration it might seem reasonable to think that absorption spectroscopy is more sensitive than fluorescence spectroscopy. As stated above, for some compounds that we measure by fluorescence, only one of the 100 species that is excited undergoes fluorescence emission. In this case, 100 photons are absorbed but only one is emitted. The answer though requires a different consideration.

The measurement of absorption involves a comparison of P to P_o. At low concentrations, these two values are large and similar in magnitude. Therefore, at low concentrations, absorption involves the measurement of a small difference between two large signals. Fluorescence, on the other hand, is measured at 90o to the source. In the absence of fluorescence, as in a blank solution, there ought to be no signal reaching the detector (however, there is still some scattered and stray light that may reach the detector as noise). At low concentrations, fluorescence involves the measurement of a small signal over no background. For comparison, suppose you tried to use your eyes to distinguish the difference between a 100 and 99 Watt light bulb and the difference between complete darkness and a 1 Watt light bulb. Your eyes would have a much better ability to determine the small 1 Watt signal over darkness than the difference between two large 100 and 99 Watt signals. The same occurs for the electronic measurements in a spectrophotometer. Therefore, because emission involves the measurement of a small signal over no background, any type of emission spectroscopy has an inherent sensitivity advantage of one to three orders of magnitude over measurements of absorption. Fluorescence spectroscopy is an especially sensitive analysis method for those compounds that have suitable quantum yields.