10.4: Laser Spectroscopy

Typical **spectroscopy** experiments require four elements: 1) a light source, 2) a sample, 3, a monochrometer and 4) a detector. In laser methods, a laser can serve as both a light source and a monochrometer. It can also serve as just one of those two, or be used in a totally different way such that it serves as neither!

Total Fluorescence

In a **total fluorescence** experiment, the laser is used as both the light source as well as the monochrometer. The data obtained is similar to that obtained in a regular absorption spectroscopy experiment.

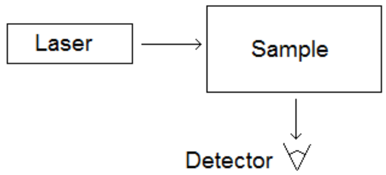

Figure 10.4.1

The laser used in this kind of experiment would typically be a tunable dye laser that will be scanned through a range of wavelengths in order to map the absorption spectrum of the sample. The detector must be placed at an angle to the incident laser beam in order to minimize direct exposure to the laser light, which will swamp the signal (and probably ruin the detector!) What is detected is actually photons produced in the fluorescence of the sample, which is increased whenever the laser frequency coincides with a resonance frequency.

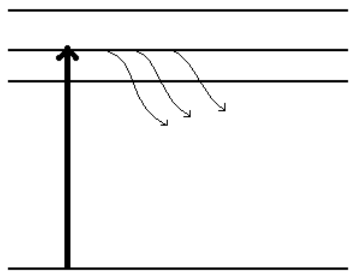

Figure 10.4.2

Monitoring fluorescence intensity as a function of excitation laser wavelength produces an absorption spectrum of the molecule. By and large, the total fluorescence method yields information about the upper state of a transition since scanning the tunable laser maps the energy levels in the upper state.

Dispersed Fluorescence

In a **dispersed fluorescence** spectrum, The wavelength of the excitation laser is fixed and the fluorescence is collected by a monochrometer and separated into its wavelength components.

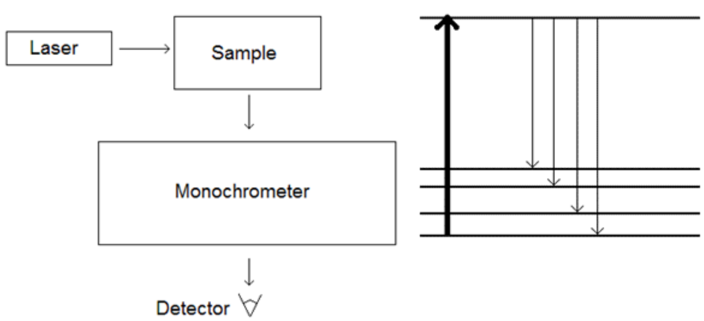

Figure 10.4.3

By separating the fluorescence into its wavelength components, the lower level energy levels are mapped. As such, this experiment is similar to an emission spectrum, but has the advantage of having only a single upper level quantum state. This type of experiment yields information about the lower level of the transition.

Molecular Beam Spectroscopy (A Sub-Doppler Method)

Laser excitation (total fluorescence) spectroscopy and dispersed fluorescence spectroscopy have resolution that is limited by the instrumentation and the natural **Doppler width** of the lines in the spectrum (caused by the motion of molecules in the gas phase, which can be parallel, antiparallel or at some angle to the direction of the laser beam propagation.) A number of techniques exist that allow for sub-Doppler resolution (resolution that is better than the **Doppler limit** would otherwise allow.