15.3 Selected Fluorescence Spectra

- 9-methyllanthracene and 2-aminoanthracene are used to show fluorescence which mirrors the absorption spectrum
- naphthalene is used to show how fluorescence from a symmetry forbidden transition destroys the mirror effect
- chrysene and rhodamine B are used to show small and large Stoke’s shifts
- biphenyl and bianthryl are used to show changes in vibronic structure between fluorescence and absorption
The above spectra are plotted as amplitude versus wave number. When plotted versus wavelength the mirror effect is not as pronounced.
The second excited singlet transition in the absorption spectrum appears to have a weak vibronic band appearing as a slight shoulder in the first excited singlet transition (near the arrow). The broad bands are due to the amino group interacting with the solvent.

It's hard to determine if there is a mirror image relationship because the long wavelength absorption is distorted by the stronger second excited singlet transition. The long decay time is also indicative of emission from a forbidden transition.

Chrysene shows almost no difference in solvation between the ground and excited states.
The ~40 nm Stoke's shift is due to the fact that rhodamine B has a charge. The excited state most likely donates electrons to the nitrogen causing a large change in solvation.

The excited state has a node at the single bond between the rings. As a result it's energy is less dependent on twist about the bond. The decrease in energy with twist sharpens the vibronic transitions.

This is an unusual case where the ground state has a node at the single bond, and the excited state does not. As a result the excited state energy is more dependent upon twist about the bond and the spectrum is smeared out.