4.S: Electronic Spectroscopy of Cyanine Dyes (Summary)

In this chapter we used a very simple model called the particle-in-a-box model or the infinite-potential-well model to obtain very crude approximate wavefunctions for pi electrons in cyanine dye molecules. With the particle in the box model, we can estimate the wavelengths at which the peaks occur in the absorption spectra from estimated bond lengths, or we can use the wavelength information to determine average bond lengths in a series of dye molecules. By evaluating the transition moment integral, we can explain the relative intensities of these peaks and obtain selection rules for the spectroscopic transitions. The selection rules also can be deduced from qualitative symmetry considerations.

This model assumes the electrons are independent of each other and uses a particularly simple form for the potential energy of the electrons. The model also assumes that the atomic nuclei are fixed in space, i.e. the molecule is not vibrating or rotating. This latter assumption, which is known as the Crude Born-Oppenheimer Approximation, will be discussed in a later chapter. The physical basis for this approximation is the fact that the mass of the electron is much smaller than the mass of an atomic nucleus. The electrons therefore respond to forces or are accelerated by forces much faster than the nuclei (remember $a = f/m$) so the electron motion in a molecule can be examined by assuming that the nuclei are stationary.

We did not discuss the widths and shapes of the peaks. Contributions to the line widths and shapes come from motion of the nuclei; which we will consider later. Nuclei in a molecule vibrate, i.e. move relative to each other, and rotate around the center of mass of the molecule. The rotational and vibrational motion, as well as interaction with the solvent, which also is neglected, produce the spectral band widths and shapes and even affect the position of the absorption maximum. When light is absorbed the vibrational and rotational energy of the molecule can change along with the change in the electronic energy. Line widths and shapes therefore depend upon the absorption of different amounts of vibrational and rotational energy. Actually, in a condensed phase, molecular rotation is hindered. This hindered rotation is called libration.

An outcome of our examination of the cyanine dye wavefunctions was a glimpse at three fundamental properties of quantum mechanical systems: orthogonality of wavefunctions, the Heisenberg Uncertainty Principle, and the zero-point energy of bound systems. We also observed that quantum numbers result from the boundary conditions used to describe the physical system. Another observation was that the energy levels for the particle in the box get further apart as the quantum number n increases, but closer together as the size of the box increases. Lastly, the spectra we observe occur because of the interaction of molecules with electromagnetic radiation and the resulting transition of the molecule from one energy level to a higher energy level.

Questions for Thought

1. What is the difference between the spectroscopic wavelength and the wavefunction wavelength?
2. What is the total probability of finding any pi electron on one half-side of a cyanine dye molecule?
3. What is a molecular orbital and how is it related to visible-ultraviolet spectroscopy?
4. Why does a series of conjugated dye molecules, such as the cyanines, have colors ranging from red to blue?
5. Write a few paragraphs describing the origins of the absorption spectra for conjugated dye molecules using the particle-in-a-box model and the terms HOMO and LUMO.
6. Write a paragraph discussing the feasibility of determining the ionization potential for a dye molecule using the particle-in-a-box model.

Contributors and Attributions

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