CHAPTER OVERVIEW

6: Vibrational States

In this chapter we use the harmonic oscillator model and a combination of classical and quantum mechanics to learn about the vibrational states of molecules. The first section of the chapter introduces the concepts of normal modes and normal coordinates in order to deal with the complexity of vibrational motion found in polyatomic molecules. The second section of the chapter reviews the classical treatment of the harmonic oscillator model, which is very general. Anything with a potential energy that depends quadratically on position, or equivalently experiences a linear restoring force, is a harmonic oscillator. In addition to vibrating molecules, the harmonic oscillator model therefore describes physical systems such as a pendulum, a weight hanging from a spring, or weights connected by springs.

The remainder of the chapter treats the vibrational states of molecules using quantum mechanics, starting with the solutions to the Schrödinger equation. Quantum mechanics provides the probability density function for positions of the atomic nuclei and the vibrational energy level structure, and is used to calculate spectroscopic selection rules, explain intensities in spectra, and calculate the vibrational force constants. Our analysis will identify the molecular properties that determine the frequency of radiation that is absorbed, determine which vibrations appear in the infrared spectrum (and which do not), and determine why some vibrations absorb radiation strongly (and others do not).

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")