21.6: The Visible and Ultraviolet Spectra of Molecules- Molecular Orbitals

When molecules absorb or emit radiation in the ultraviolet and visible regions of the spectrum, this almost always corresponds to the transition of an electron from a low-energy to a high-energy orbital, or vice versa. One might expect the spectra of molecules to be like the atomic line spectra shown in Figure $21.6.1$, but in fact molecular spectra are very different. Consider, for example, the absorption spectrum of the rather beautiful purple-violet gas I_2. This molecule strongly absorbs photons whose wavelengths are between 440 and 600 nm, and much of the orange, yellow, and green components of white light are removed. The light which passes through a sample of I_2 is mainly blue and red. When analyzed with an average quality spectroscope, this light gives the spectrum shown in Figure $21.6.2a$. Instead of the few discrete lines typical of atoms, we now have a broad, apparently continuous, absorption band. This is typical of molecules.

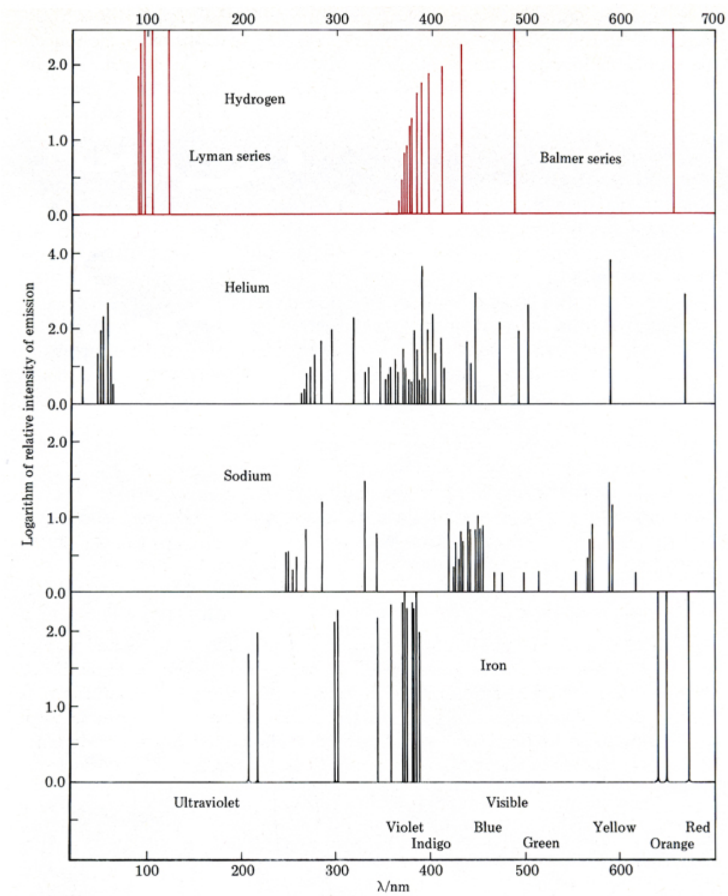

Figure 21.6.1: The ultraviolet and visible emission spectra of gaseous hydrogen, helium, sodium and iron. For comparison the colors of visible light are given the bottom of the figure. All spectral lines indicated in color can be derived from energy levels.

Why is there this difference between atomic and molecular spectra? An answer begins to appear if we use a somewhat more expensive spectroscope. Figure $21.6.2b$shows a tracing of the I_2 spectrum made with such an instrument. What originally appeared to he a continuous band is now shown to consist of a very large number of very narrow, closely spaced lines. Thus the broad absorption band of I_2 is actually made up of discrete lines. The reason molecules give rise to such an enormous number of lines is that molecules can vibrate and rotate in a very large number of ways while atoms cannot. Furthermore both rotational levels and vibrational motion are quantized. When a molecule absorbs a photon of light and an electron is excited to a higher orbital, the molecule will not be stationary either before or after the absorption of the photon.

Because of the large number of energy possibilities both before and after the transition, a very large number of lines of slightly different wavelengths is obtained. A careful analysis of these lines yields much valuable information about the way in which the molecule rotates and vibrates. In particular, very accurate values of bond enthalpies and bond lengths can be obtained from a study of the fine structure of an absorption band like that shown in Figure $21.6.2b$

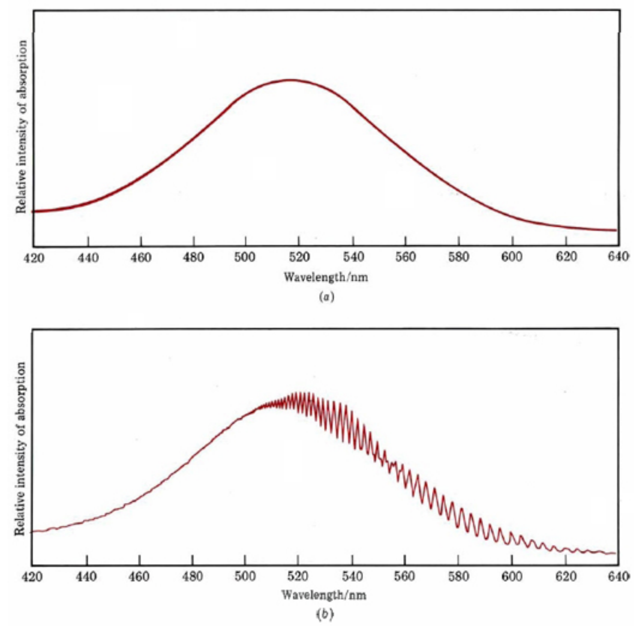

Figure 21.6.2: Absorption band of $I_2(g)$ in the visible region. (a) Result obtained with low-resolution spectroscope; (b) result obtained with high-resolution spectroscope.