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Infrared Spectroscopy

IR radiation was first discovered in 1800 by Sir William Herschel, who used a glass prism with blackened thermometers as detectors to measure the heating effect of sunlight within and beyond the boundaries of the visible spectrum. Coblentz laid the groundwork for IR spectroscopy with a systematic study of organic and inorganic absorption spectra. Experimental difficulties were immense; since each point in the spectrum had to be measured separately, it could take 4 h to record the full spectrum. But from this work came the realization that each compound had its own unique IR absorption pattern and that certain functional groups absorbed at about the same wavelength even in different molecules. The IR absorption spectrum provides a “fingerprint” of a molecule with covalent bonds. This can be used to identify the molecule. Qualitative identification of organic and inorganic compounds is a primary use of IR spectroscopy. In addition, the spectrum provides a quick way to check for the presence of a given functional group such as a carbonyl group in a molecule. IR spectroscopy and spectrometry as used by analytical and organic chemists is primarily *absorption* spectroscopy. IR absorption can also be used to provide quantitative measurements of compounds.

IR spectroscopy became widely used after the development of commercial spectrometers in the 1940s. Double-beam monochromator instruments were developed, better detectors were designed, and better dispersion elements, including gratings, were incorporated. These conventional spectrometer systems have been replaced in the last decade by FTIR instrumentation. This chapter will focus on FTIR instrumentation and applications of IR spectroscopy. In addition, the related techniques of near-IR (NIR) spectroscopy and Raman spectroscopy will be covered.

The wavelengths of IR radiation of interest to chemists trying to identify or study organic molecules fall between 2 and 20 μm . These wavelengths are longer than those in the red end of the visible region, which is generally considered to end at about 0.75 μm . IR radiation therefore is of lower energy than visible radiation, but of higher energy than radiowaves. The entire IR region can be divided into the *near-IR*, from 0.75 to 2.5 μm , the *mid-IR*, from about 2.5 to 20 μm , and the *far-IR*, from 20 to 200 μm . Visible radiation (red light) marks the upper energy end or minimum wavelength end of the IR region; the maximum wavelength end is defined somewhat arbitrarily; some texts consider the far-IR to extend to 1000 μm . The IR wavelength range tells us the IR frequency range from the equation (introduced in Chapter 2)

$$\nu = \frac{c}{\lambda} \quad (4.1)$$

where ν is the frequency, c is the speed of light, and λ is the wavelength. We also know that $\Delta E = h\nu$. When the frequency is high, λ is short and the energy of the radiation is high.

It is common to use *wavenumber*, symbolized by either $\tilde{\nu}$ or $\bar{\nu}$, with units of cm^{-1} , in describing IR spectra. The first symbol is called “nu tilde”; the second symbol is called “nu bar”; both symbols are used in the literature. The unit cm^{-1} is called a *reciprocal centimeter*. The wavenumber is the reciprocal of the wavelength. Wavenumber is the number of waves of radiation per centimeter, $1/\lambda$; frequency is the number of waves per second, c/λ . Wavelength and wavenumber are related by:

$$\text{wavelength } (\mu\text{m}) \times \text{wavenumber } (\text{cm}^{-1}) = 10,000 = 1 \times 10^4 \quad (4.2)$$

Both wavenumbers and wavelengths will be used throughout the chapter, so it is important to be able to convert between these units. The older IR literature used the term *micron* and the symbol μ for wavelength in micrometers (μm).

4.1. ABSORPTION OF IR RADIATION BY MOLECULES

Molecules with covalent bonds may absorb IR radiation. This absorption is quantized, so only certain frequencies of IR radiation are absorbed. When radiation, (i.e., energy) is absorbed, the molecule moves to a higher energy state. The energy associated with IR radiation is sufficient to cause molecules to rotate (if possible) and to vibrate. If the IR wavelengths are longer than $100 \mu\text{m}$, absorption will cause excitation to higher rotational states in the gas phase. If the wavelengths absorbed are between 1 and $100 \mu\text{m}$, the molecule will be excited to higher vibrational states. Because the energy required to cause a change in rotational level is small compared to the energy required to cause a vibrational level change, each vibrational change has multiple rotational changes associated with it. Gas phase IR spectra therefore consist of a series of discrete lines. Free rotation does not occur in condensed phases. Instead of a narrow line spectrum of individual vibrational absorption lines, the IR absorption spectrum for a liquid or solid is composed of broad vibrational absorption **bands**. A typical IR spectrum for a condensed phase (liquid or solid) is shown in Fig. 4.1. This is the spectrum of a thin film of polystyrene; note that the absorption band at about 2950 cm^{-1} is more than 100 cm^{-1} wide at the top. The individual vibration–rotation lines can be seen in gas phase IR spectra. These narrow lines are clearly seen in Fig. 4.2, the gas phase spectrum of hydrogen chloride, HCl.

Molecules absorb radiation when a bond in the molecule vibrates at the same frequency as the incident radiant energy. After absorbing radiation, the molecules have more energy and vibrate at increased amplitude. The frequency absorbed depends on the masses of the atoms in the bond, the geometry of the molecule, the strength of the bond, and several other factors. Not all molecules can absorb IR radiation. The molecule must have a change in **dipole moment** during vibration in order to absorb IR radiation.

4.1.1. Dipole Moments in Molecules

When two atoms with different electronegativities form a bond, the electron density in the bond is not equally distributed. For example, in the molecule hydrogen fluoride, HF, the electron density in the bond shifts away from the H atom toward the more electronegative fluorine atom. This results in a partial negative charge on F and a partial positive charge on H. The bond is said to be **polar** when such charge separation exists. The charge separation can be shown as

