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

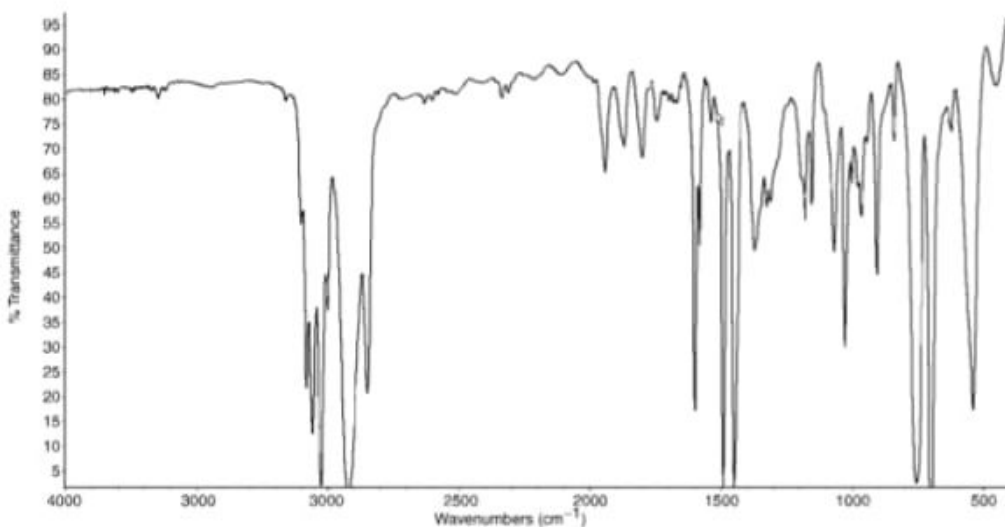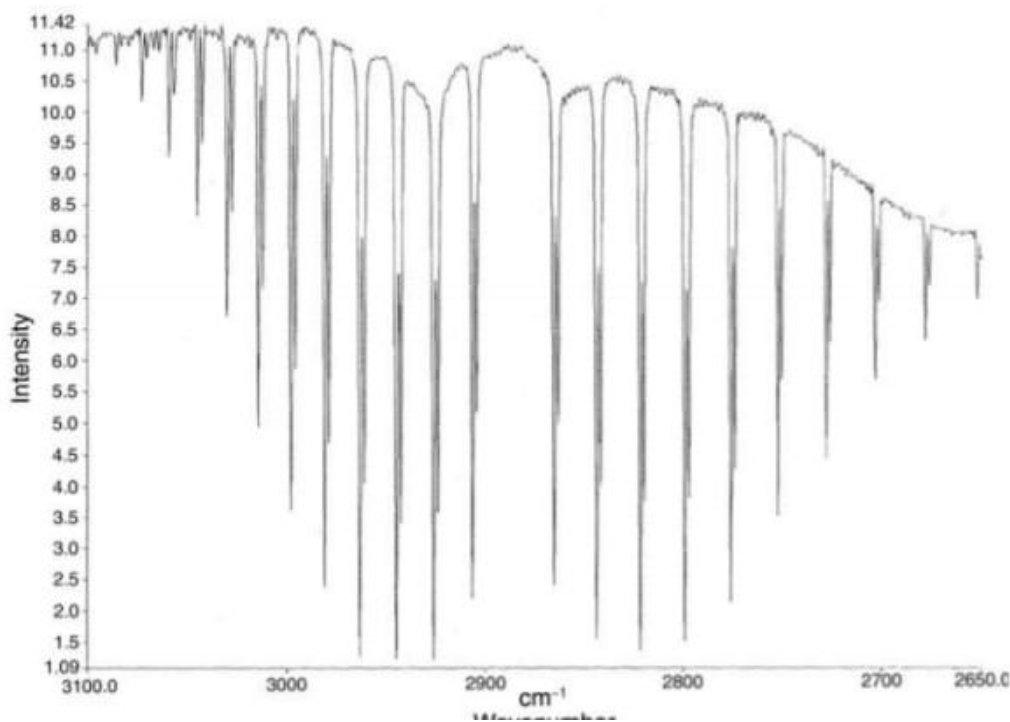$$\overset{\delta^+}{H}\!\!-\!\!\overset{\delta^-}{F}$$

Figure 4.1 Fourier transform IR spectrum of a thin film of polystyrene. The y axis unit is %T, the x axis is in wavenumbers (cm^{-1}). Collected on a ThermoNicolet 6700 FTIR spectrometer with a DTGS detector. Courtesy of Thermo Electron Corp. (www.thermo.com).

where δ indicates a partial charge. The dipole in the bond is indicated by a crossed arrow placed with the point on the more negative end of the bond as shown:

$$\longmapsto$$
H—F

The HF molecule is a linear diatomic molecule with one polar bond; therefore, the molecule is polar and has a dipole moment. The dipole moment μ is the product of the charge Q and the distance between the charges, r:

$$\mu = Q \times r \qquad (4.3)$$

The partial positive and negative charges in HF must be equal in magnitude but opposite in sign to maintain electrical neutrality. We can imagine that the HF molecule vibrates by having the bond stretch and compress over and over, just as a spring can be stretched and compressed by first pulling and then squeezing the spring. On vibration of the HF bond, the dipole moment changes because the distance between the charges changes. Because the dipole moment changes in a repetitive manner as the molecule vibrates, it is possible for HF to absorb IR radiation. It follows that diatomic molecules containing atoms of the same element such as H_2, N_2, O_2, and Cl_2 have no charge separation because the electronegativity of each atom in the bond is the same. Therefore they do not have dipole moments. Since a change in dipole moment with time is necessary for a molecule to absorb IR radiation, symmetrical diatomic molecules do not absorb IR radiation. Diatomic molecules made up of different atoms such as HCl and CO do have dipole moments. They would be expected to absorb IR radiation or to be "IR-active".

Molecules with more than two atoms may or may not have permanent dipole moments. It depends on the geometry of the molecule. Carbon dioxide has two equal C=O bond dipoles but because the molecule is linear the bond dipoles cancel and the molecule has no net dipole moment:

$$\longleftarrow\!\!\!+ \quad +\!\!\!\longrightarrow$$
O=C=O
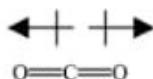
Water, H_2O, has two equal H—O bond dipoles. Water has a bent geometry and the vector sum of the bond dipoles does not cancel. The water molecule has a permanent net dipole moment.

Bond Dipoles in Water   Net Dipole in Water
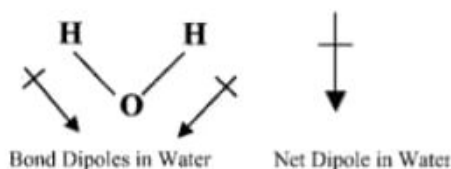
Predicting the IR absorption behavior of molecules with more than two atoms is not as simple as looking at diatomic molecules. It is not the net dipole moment of the molecule that is important, but any change in the dipole moment on vibration. We need to understand how molecules vibrate. This is relatively simple for diatomic and triatomic molecules. Large molecules cannot be evaluated simply, because of their large number of vibrations and interactions between vibrating atoms. It can be said that most molecules do absorb IR radiation, which is the reason this technique is so useful.

4.1.2. Types of Vibrations in Molecules

The common molecular vibrations that are excited by IR radiation are **stretching** vibrations and **bending** vibrations. These are called **modes** of vibration. Stretching involves a change in bond lengths resulting in a change in interatomic distance. Bending involves a change in bond angle or a change in the position of a group of atoms with respect to the rest of the molecule. For a group of three or more atoms, at least two of which are the same type of atom, there are two stretching modes: symmetrical stretching and asymmetrical stretching. These two modes of stretching are shown, respectively, in Fig. 4.3 for a CH_2 group. In Fig. 4.3(a) the two H atoms both move away from the C atom—a symmetrical stretch. In Fig. 4.3(b) one H atom moves away from the C atom and one moves toward the C atom—an asymmetrical stretch. Bending modes are shown in Fig. 4.3(c)–(f). Scissoring and rocking are in-plane bending modes—the H atoms remain in the same plane as the C atom (i.e., in the plane of the page). Wagging and twisting are out-of-plane (oop) bending modes—the H atoms are moving out of the plane containing the C atom. The + sign in the circle indicates movement above the plane of the page toward the reader, while the − sign in the circle indicates movement below the plane of the page away from the reader. Bends are also called deformations and the term antisymmetric is used in place of asymmetric in various texts.

For the CO_2 molecule, we can draw a symmetric stretch, an asymmetric stretch, and a bending vibration, as shown:

$$\overset{\leftarrow}{O}=C=\vec{O} \qquad \vec{O}=\underset{\leftarrow}{C}=\vec{O} \qquad \overset{\uparrow}{O}=\underset{\downarrow}{C}=\overset{\uparrow}{O}$$
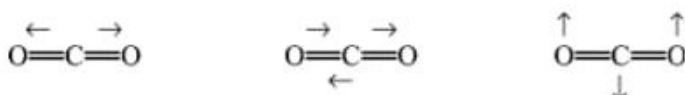
The CO_2 molecule on the left is undergoing a symmetric stretch, the one in the middle an asymmetric stretch and the one on the right an in-plane bend. The symmetric
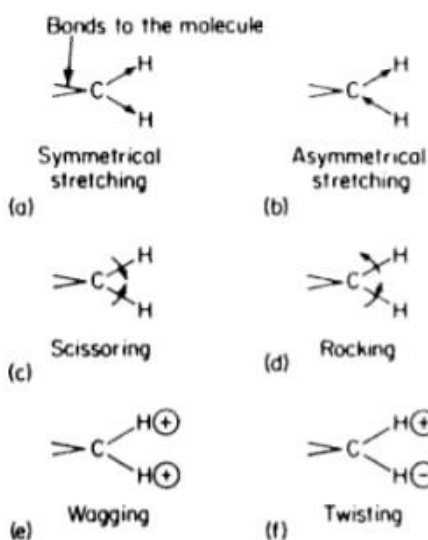

Figure 4.3 Principal modes of vibration between carbon and hydrogen in an alkane: (a) symmetrical stretching, (b) asymmetrical stretching and the bending vibrations, (c) scissoring, (d) rocking, (e) wagging, and (f) twisting.

stretching vibration does *not* change the dipole moment of the molecule. This vibrational mode does not absorb IR radiation—it is said to be *IR-inactive*. However, the other two modes of vibration do change the dipole moment—they are *IR-active*. The asymmetric stretching frequency occurs at 2350 cm^{-1} and the bending vibration occurs at 666 cm^{-1}.

For diatomic and triatomic molecules, it is possible to work out the number and kind of vibrations that occur. To locate a point in three-dimensional space requires three coordinates. To locate a molecule containing N atoms in three dimensions, $3N$ coordinates are required. The molecule is said to have $3N$ degrees of freedom. To describe the motion of such a molecule, translational, rotational, and vibrational motions must be considered. Three coordinates or degrees of freedom are required to describe translational motion and three degrees of freedom are required to describe rotational motion about the molecule's center of gravity. This leaves $3N - 6$ degrees of freedom to describe vibrational motion. There are $3N - 6$ possible normal modes of vibration in a molecule of N atoms. For example, the water molecule contains 3 atoms, so it has $3 \times 3 = 9$ degrees of freedom and $(3 \times 3) - 6 = 3$ normal modes of vibration. For the water molecule, these normal modes of vibration are a symmetric stretch, an asymmetric stretch, and a scissoring (bending) mode. Linear molecules cannot rotate about the bond axis. As a result, only two degrees of freedom are needed to describe rotation, so linear molecules have $3N - 5$ normal modes of vibration. If we look at CO_2 above, three modes of vibration are shown, but $3N - 5 = 4$ normal modes of vibration, so one is missing. The fourth is a bending mode equivalent to that shown, but oop:

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+    -    +
O══C══O
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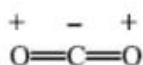
where $+$ indicates movement toward the reader and $-$ indicates movement away from the reader. The oop bending mode and the in-plane bending mode already shown both occur at 666 cm^{-1}. They are said to be *degenerate*. Both are IR-active, but only one absorption band is seen since they both occur at the same frequency.

For simple molecules, this approach predicts the number of fundamental vibrations that exist. Use of the dipole moment rule indicates which vibrations are IR-active, but the IR spectrum of a molecule rarely shows the number of absorption bands calculated. Fewer peaks than expected are seen due to IR-inactive vibrations, degenerate vibrations, and very weak vibrations. More often, additional peaks are seen in the spectrum due to overtones and other bands.

The excitation from the ground state V_0 to the first excited state V_1 is called the *fundamental transition*. It is the most likely transition to occur. Fundamental absorption bands are strong compared with other bands that may appear in the spectrum due to overtone, combination, and difference bands. *Overtone* bands result from excitation from the ground state to higher energy states V_2, V_3, and so on. These absorptions occur at approximately integral multiples of the frequency of the fundamental absorption. If the fundamental absorption occurs at frequency v, the overtones will appear at about $2v$, $3v$, and so on. Overtones are weak bands and may not be observed under real experimental conditions. Vibrating atoms may interact with each other. The interaction between vibrational modes is called *coupling*. Two vibrational frequencies may couple to produce a new frequency $v_3 = v_1 + v_2$. The band at v_3 is called a *combination* band. If two frequencies couple such that $v_3 = v_1 - v_2$, the band is called a *difference* band. Not all possible combinations and differences occur; the rules for predicting coupling are beyond the scope of this text.