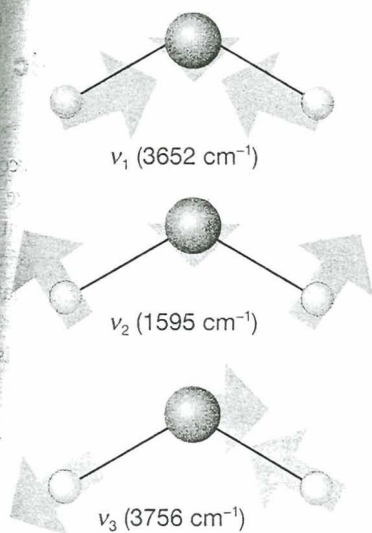


16.48 Alternative descriptions of the vibrations of CO₂. (a) The stretching modes are not independent, and if one C—O group is excited the other begins to vibrate. (b) The symmetric and antisymmetric stretches are independent, and one can be excited without affecting the other: they are normal modes. (c) The two perpendicular bending motions are also normal modes.

mode, q , behaves like an independent harmonic oscillator (if anharmonicities are neglected), so each has a series of terms

$$G_q(v) = (v + \frac{1}{2})\tilde{\nu}_q \quad \tilde{\nu}_q = \frac{1}{2\pi c} \left(\frac{k_q}{m_q} \right)^{1/2} \quad (16.73)$$

where $\tilde{\nu}_q$ is the wavenumber of mode q and depends on the force constant k_q for the mode and on the effective mass m_q of the mode. The effective mass of the mode is a measure of the mass that is swung about by the vibration and in general is a complicated function of the masses of the atoms. For example, in the symmetric stretch of CO₂, the C atom is stationary, and the effective mass depends on the masses of only the O atoms. In the antisymmetric stretch and in the bends, all three atoms move, so all contribute to the effective mass. The three normal modes of H₂O are shown in Fig. 16.49: note that the predominantly bending mode (ν_2) has a lower frequency than the others, which are predominantly stretching modes. It is generally the case that the frequencies of bending motions are lower than those of stretching modes. One point that must be appreciated is that only in special cases (such as the CO₂ molecule) are the normal modes purely stretches or purely bends. In general, a normal mode is a composite motion of simultaneous stretching and bending of bonds. Another point in this connection is that heavy atoms generally move less than light atoms in normal modes.



16.49 The three normal modes of H₂O. The mode ν_2 is predominantly bending, and occurs at lower wavenumber than the other two.

16.15 Infrared absorption spectra of polyatomic molecules

The gross selection rule for infrared activity is that *the motion corresponding to a normal mode should be accompanied by a change of dipole moment*. Deciding whether this is so can sometimes be done by inspection. For example, the symmetric stretch of CO₂ leaves the dipole moment unchanged (at zero, see Fig. 16.48), so this mode is infrared inactive. The antisymmetric stretch, however, changes the dipole moment because the molecule becomes unsymmetrical as it vibrates, so this mode is infrared active. Because the dipole moment change is parallel to the principal axis, the transitions arising from this mode are classified as **parallel bands** in the spectrum. Both bending modes are infrared active: they are accompanied by a changing dipole