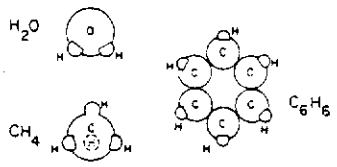
Symmetric Linear molecules include all *homonuclear* diatomic elements and linear polyatomic molecules with a symmetry axis about their center of gravity. These particles have two indistinguishable molecular orientations, $\sigma = 2$.

$$Z_{r,n} = \frac{T}{2\theta_r}$$

Nonlinear Polyatomic molecules can have none or many symmetry axes. Each molecule must be examined as an individual case, $\sigma = ?$ (see Table IIIC-1 and the following exercise).

$$Z_{r,n} = \frac{\pi^{\frac{1}{2}}}{\sigma}\left(\frac{T}{\theta_r}\right)^{3/2}$$

Exercise 9. Identify the indistinguishable molecular orientations possible with the following molecules as sketched: Water, Methane, and Benzene.



The contribution of the rotational-nuclear spin modes to the properties of each type of gaseous molecule is readily completed for each molecule type using its listed combined partition function. The required parameters, σ and θ_r, are listed in Table IIIC-2. The following problems illustrate the procedure. Complete results are given in Table IIIC-1.

Exercise 10. Determine the combined contribution of nuclear spin and molecular rotation to the properties of monatomic gases.

Example 9. Determine the combined rotation-nuclear spin contribution to the internal energy, specific heat, and entropy of a gas composed of nonlinear polyatomic molecules.

Properties are determined by application of eqns. IIIC-3 to 7. The internal energy and specific heat contributions are

$$\bar{u}_{r,n} = \bar{R}T^2 \frac{\partial}{\partial T}\left[\ln \frac{\pi^{\frac{1}{2}}}{\sigma}\left(\frac{T}{\hat{\theta}_r}\right)^{3/2}\right]_{\bar{v}} = \bar{R}T^2\left(\frac{3}{2T}\right) = \frac{3}{2}\bar{R}T \qquad \bar{c}_{v,r,n} = \left(\frac{\partial u_{r,n}}{\partial T}\right)_v = \frac{3}{2}\bar{R}$$

The entropy of an internal mode is given by eqn. IIIC-11c.

$$\bar{s}_{r,n} = \frac{\bar{u}_{r,n}}{T} + \bar{R}\ln Z_{r,n} = \frac{3}{2}\bar{R} + \bar{R}\ln\left[\frac{\pi^{\frac{1}{2}}}{\sigma}\left(\frac{T}{\hat{\theta}_r}\right)^{3/2}\right]$$

Exercise 11. Determine the combined rotation-nuclear spin contribution to the internal energy, specific heat, and entropy of a gas composed of symmetric linear molecules.

C. The Vibrational Mode

The spacing between atoms in a molecule is determined by a balance of forces. Molecules are formed by ionic or covalent bonds between its atoms (see Unit ICS, Sect. I). These attractive bonds are balanced by repulsion (interference between the separate electron clouds of the atoms) if the atoms draw too close. This balance is represented for the atoms of a diatomic molecule in Fig. IIIC-2.

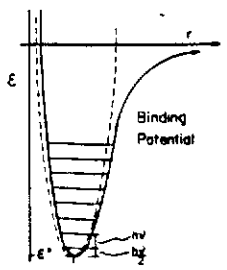


Fig. IIIC-2.
Vibrational Levels