A diatomic molecule is formed by a single molecular bond; it has one mode of intermolecular vibration. A polyatomic molecule has at least two bonds. The number of modes of molecular vibration exhibited by a polyatomic molecule can be determined as follows.

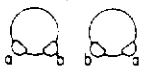
Modes of Molecular Vibration. Consider each atom within a molecule to be a separate mass point. A mass point has three independent directions of motion—*three degrees of freedom.* Thus, the total number of degrees of freedom associated with the n_a atoms composing a molecule is $3n_a$. The translation of the molecule accounts for the three possible directions of motion of the center of gravity of the molecule. This comprises three degrees of freedom. The rotational mode models rigid body rotation of the atoms about the particle's center of gravity. For linear molecules rotation in the two planes of nonzero moment uses two degrees of freedom. For nonlinear molecules the three planes of rotation use three degrees of freedom. All remaining degrees of freedom of the n_a atoms must be accounted for in intermolecular distortions. Thus, the number of modes of molecular vibration in *Linear and Nonlinear Molecules* respectively, are

$$p_\ell = 3n_a - 5 \qquad p_{n\ell} = 3n_a - 6 \qquad \text{(IIIC-16a,b)}$$

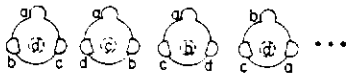
Exercise 14. How many vibrational modes are present in the linear molecule CO_2 and the nonlinear molecules H_2O, NH_3 and C_6H_6?

The natural frequency of each vibrational mode, ν_p, defines its individual characteristic temperature, $\theta_{v,p}$ ($\equiv h\nu_p/k$). (Modes with the same characteristic temperature are common.) At temperatures not more than an order above the lowest value of $\theta_{v,p}$ these

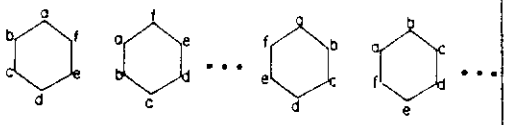
Ans. 9. There are two indistinguishable orientations of a water molecule, as shown. Thus the symmetry number for water is $\sigma = 2$.



Methane can be rotated through three indistinguishable positions with any of the four hydrogen molecules on the axis of rotation. This must be repeated with each of the four hydrogen atoms on the axis of rotation, thus $\sigma = 3 \cdot 4 = 12$.



The hexagonal benzene molecule can be rotated through six indistinguishable positions. Then the molecule can be rotated on a vertical axis to give a new indistinguishable orientation. In this new orientation the previous six horizontal rotations can be repeated. Thus, $\sigma = 6 \cdot 2 = 12$.



Ans. 10. For monatomic gas $Z_{r,n} = 1$. Then $\ln Z_{r,n} = \ln 1 = 0$. Thus, spin-rotation does not contribute to the properties of monatomic gases in the temperature range $T \ll \theta_n$. [A more complete treatment would be $Z_{r,n} = g_n^o$ (= 2 for monatomic gases), see footnote 11. Thus there is a constant contribution to entropy and functions of entropy, but none to other properties.]

Ans. 11.

$$\bar{u}_{r,n} = \bar{R}T^2\left[\left(\frac{\partial}{\partial T}\right)\ln\left(\frac{T}{2\theta_r}\right)\right]_{\bar{v}} = \bar{R}T \quad \text{and} \quad c_{v(r,n)} = \left(\frac{\partial u_{r,n}}{\partial T}\right)_{\bar{v}} = \bar{R}$$

$$\bar{s}_{r,n} = \frac{\bar{u}_{r,n}}{T} + \bar{R}\ln Z_{r,n} = \bar{R} + \bar{R}\ln\left(\frac{T}{2\theta_r}\right)$$