

CHAPTER 8

IDEAL POLYATOMIC GAS

Can we directly extend the previous methods and approximations to polyatomic molecules?

- The introduction of the **normal coordinates** will allow us to treat the **vibrational** problem of polyatomic molecules as a simple extension of the vibration of diatomic molecules.
- The quantum mechanical **rotational** energy levels cannot be written in a closed form, and shall be treated by the method of **classical statistical mechanics**, which is applicable anyway for most polyatomic molecules, and temperatures.
- One new feature that arises with polyatomic molecules is **hindered** internal rotation.

8-1 THE VIBRATIONAL PARTITION FUNCTION

Problem: the Born-Oppenheimer potential depends on a number of inter-nuclear distances.

Each of the n atoms requires 3 coordinates to locate it. $\rightarrow 3n$ coordinates.

Among $3n$ coordinates, 3 are needed to specify the center of mass of the molecule. $\rightarrow -3$

Need 2 more coordinates (θ, ϕ) to specify its orientation if linear $\rightarrow -2$ (or -3 if nonlinear)

Conclusion: the potential in which the nuclei vibrate is a function of $3n-5$ or $3n-6$ relative coordinates, and thus is a complicated energy surface.

Example: Let the Cartesian coordinates of each nucleus in the molecule be $x_1, y_1, z_1, \dots, x_n, y_n, z_n$.

For small vibrations about the equilibrium configuration, we have the potential energy

$u(x_1, x_2, \dots, z_n) \sim u_0 + \frac{1}{2}k(x_2 - x_1)^2 + \frac{1}{2}k(x_3 - x_1)^2 + \dots$: a quadratic function of $3n-5$ or $3n-6$ relative coordinates such as $x_2 - x_1, x_3 - x_1, y_2 - y_1$, and so on. The presence of cross terms such as x_1x_2, x_1x_3, y_1y_2 , and so on makes the potential energy a complicated mixture of x_1, x_2, \dots .

Solution = Normal Coordinates

By the introduction of certain linear combinations of the Cartesian coordinates, x_1, x_2, \dots , it is possible to eliminate the cross terms in the potential and to write it as a sum of squares of these new coordinates, say Q_1, Q_2, \dots . In other words, it is possible to transform a Hamiltonian which contains cross terms in terms of $x_1, x_2, \dots, y_1, y_2, \dots$, to a Hamiltonian, which when written in terms of Q_1, Q_2, \dots , becomes

$$H = -\sum_{j=1}^{\alpha} \frac{\hbar^2}{2\mu_j} \frac{\partial^2}{\partial Q_j^2} + \sum_{j=1}^{\alpha} \frac{k_j}{2} Q_j^2 \quad (8-4)$$

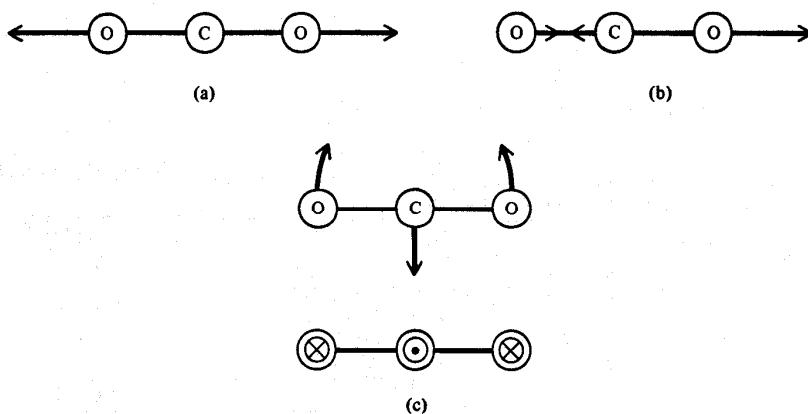
α the number of vibrational degrees of freedom, $3n-5$ ($3n-6$) for a linear (nonlinear) molecule,
 μ_j effective reduced masses,
 k_j force constants.

(8-4) is the Hamiltonian of a sum of independent harmonic oscillators, and so the total energy is

$$\varepsilon = \sum_{j=1}^{\alpha} \left(n_j + \frac{1}{2} \right) h\nu_j \quad \text{where} \quad \nu_j = \frac{1}{2\pi} \left(\frac{k_j}{\mu_j} \right)^{1/2} \quad n_j = 0, 1, 2, \dots \quad (8-5)$$

The Q_j 's are called **normal coordinates**, and their determination for any particular molecule is called a **normal coordinate analysis**. The α fundamental frequencies ν_j are obtained automatically in a normal coordinate analysis, but in practice they are usually determined from spectroscopy.

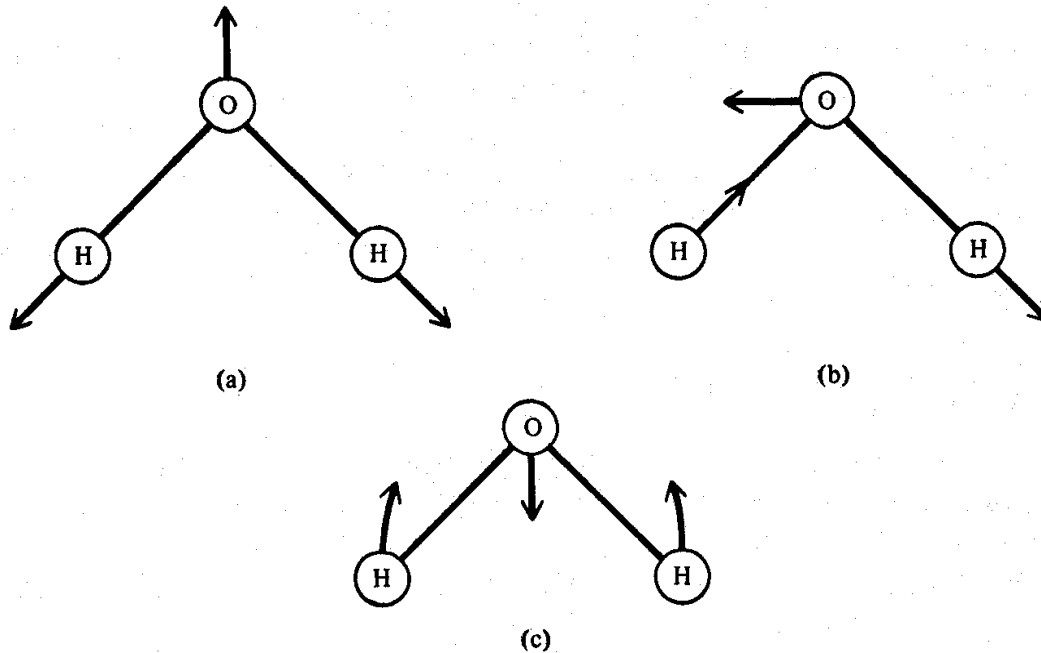
Ex. 1 The normal coordinates for a linear molecule



The mode labeled (a) is a symmetric stretch; the one labeled (b) is an asymmetric stretch; and the one labeled (c) is a bending mode. This mode is doubly degenerate, with one of the modes being in the plane of the page and the other being perpendicular to the page.

Ex. 2 Nonlinear molecule

A nonlinear triatomic molecule such as water has the following three modes.



Vibrational contribution to thermodynamics

Because of (8-4), each normal mode of vibration makes an independent contribution to thermodynamic functions such as E , C_V , S and so on. If the normal frequencies $\nu_1, \nu_2, \nu_3, \dots, \nu_\alpha$ where $\alpha = 3n - 5$ or $3n - 6$ are known, we have equations such as

$$q_{\text{vib}} = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{vj}/2T}}{(1 - e^{-\Theta_{vj}/T})}$$

$$E_{\text{vib}} = Nk \sum_{j=1}^{\alpha} \left(\frac{\Theta_{vj}}{2} + \frac{\Theta_{vj} e^{-\Theta_{vj}/T}}{1 - e^{-\Theta_{vj}/T}} \right)$$

$$C_{V,\text{vib}} = Nk \sum_{j=1}^{\alpha} \left[\left(\frac{\Theta_{vj}}{T} \right)^2 \frac{e^{-\Theta_{vj}/T}}{(1 - e^{-\Theta_{vj}/T})^2} \right]$$

where

$$\Theta_{vj} = \frac{h\nu_j}{k}$$

See Table 8-1 for values of Θ_{vj} for a number of molecules.

8-2 THE ROTATIONAL PARTITION FUNCTION

The rotational properties of a polyatomic molecule depend upon the general shape of the molecule.

The case of linear polyatomic molecule

If the molecule is linear, such as CO_2 and C_2H_2 , the problem is exactly the same as for a diatomic molecule. The energy levels are given by

$$\varepsilon_J = \frac{J(J+1)h^2}{8\pi^2 I} \quad J = 0, 1, 2, \dots \quad (8-9)$$
$$\omega_J = 2J + 1$$

where, in this case, the moment of inertia I is

$$I = \sum_{j=1}^n m_j d_j^2 \quad (8-10)$$

where d_j is the distance of the j -th nucleus from the center of mass of the molecule. Recall that the coordinates of the center of mass of a molecule are given by

$$x_{cm} = \frac{1}{M} \sum_{j=1}^n m_j x_j, \quad y_{cm} = \frac{1}{M} \sum_{j=1}^n m_j y_j, \quad z_{cm} = \frac{1}{M} \sum_{j=1}^n m_j z_j, \quad M = m_1 + m_2 + \dots + m_n \quad (8-11)$$

The rotational partition function of a **linear** polyatomic molecule is

$$q_{\text{rot}} = \frac{8\pi^2 I kT}{\sigma h^2} = \frac{T}{\sigma \Theta_r} \quad (8-12)$$

$\sigma = 1$ for unsymmetrical molecules such as N_2O and COS

$\sigma = 2$ for symmetrical molecules such as CO_2 and C_2H_2 .

The symmetry number is the number of different ways the molecule can be rotated into a configuration indistinguishable from the original. Classically, it is a factor introduced to avoid over counting indistinguishable configurations in phase space.

The energy calculated from (8-12) is kT , in accord with energy equipartition, since there are two degrees of rotational freedom of a linear molecule, i.e., $kT/2 + kT/2 = kT$

The principle axes

The rotational properties of a rigid body are characterized by the principal moments of the body. The moments of inertia about these three axes are

$$I_{xx} = \sum_{j=1}^n m_j \left[(y_j - y_{cm})^2 + (z_j - z_{cm})^2 \right], \quad I_{yy} = \dots, \quad I_{zz} = \dots$$

In addition to these, there are also products of inertia, such as

$$I_{xy} = \sum_{j=1}^n m_j (x_j - x_{cm})(y_j - y_{cm}) \dots$$

There always exists a particular set of Cartesian coordinates X, Y, Z , called the **principal axes**, passing through the center of mass of the body such that all the products of inertia vanish. The moments of inertia about these axes I_{xx}, I_{yy}, I_{zz} are called the principal moments of inertia. The principal moments of inertia are customarily denoted by I_A, I_B , and I_C .

Table 1

Table 8-1. Values of the characteristic rotational temperatures, the characteristic vibrational temperatures, and D_0 for polyatomic molecules*

molecule	$\Theta_{\text{rot}}(^{\circ}\text{K})$			$\Theta_{\text{vib}}(^{\circ}\text{K})$	$D_0(\text{kcal/mole})$
CO_2		0.561		3360, 954(2), 1890	381.5
H_2O	40.1	20.9	13.4	5360, 5160, 2290	219.3
NH_3	13.6	13.6	8.92	4800, 1360, 4880(2), 2330(2)	276.8
ClO_2	2.50	0.478	0.400	1360, 640, 1600	90.4
SO_2	2.92	0.495	0.422	1660, 750, 1960	254.0
N_2O		0.603		3200, 850(2), 1840	263.8
NO_2	11.5	0.624	0.590	1900, 1980, 2330	221.8
CH_4	7.54	7.54	7.54	4170, 2180(2), 4320(3), 1870(3)	392.1
CH_3Cl	7.32	0.637	0.637	4270, 1950, 1050, 4380(2), 2140(2), 1460(2)	370.7
CCl_4	0.0823	0.0823	0.0823	660, 310(2), 1120(3), 450(3)	308.8

* These parameters were obtained from a variety of sources and do not necessarily represent the most accurate values since they are obtained under the rigid rotor-harmonic oscillator approximation.

$$** \quad D_0 = D_e - \sum_j \frac{1}{2} h\nu_j$$

If $\Theta_A = \Theta_B = \Theta_C$, the body is called a spherical top: $\text{CH}_4, \text{CCl}_4$

If $\Theta_A = \Theta_B \neq \Theta_C$, the body is called a symmetric top: $\text{CH}_3\text{Cl}, \text{NH}_3$

If $\Theta_A \neq \Theta_B \neq \Theta_C$, the body is called an asymmetric top: $\text{H}_2\text{O}, \text{NO}_2$

Spherical top

The quantum mechanical problem of a spherical top is readily solvable, having energy levels and degeneracy given by

$$\varepsilon_J = \frac{J(J+1)\hbar^2}{8\pi^2 I} \quad J = 0, 1, 2, \dots \quad (8-14)$$
$$\omega_J = (2J+1)^2$$

The high-temperature limit of the partition function is

$$q_{\text{rot}} = \frac{1}{\sigma} \int_0^\infty (2J+1)^2 e^{-J(J+1)\hbar^2/2IkT} dJ \approx \frac{1}{\sigma} \int_0^\infty 4J^2 e^{-J^2\hbar^2/2IkT} dJ = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 IkT}{h^2} \right)^{3/2} \quad (8-15,16)$$

Here we may neglect 1 compared to J since high temperature means that high values of J are important.

Again we have introduced a symmetry number σ . The symmetry number σ for a polyatomic molecule is simply the number of ways that the molecule can be rotated "into itself."

$\sigma = 2$ for H_2O

$\sigma = 3$ for NH_3

$\sigma = 12$ for methane (3 fold symmetry about each of the 4 C-H bonds)

$\sigma = 4$ for ethylene

$\sigma = 12$ for benzene

Classically, σ is to avoid over-counting indistinguishable configurations in phase space. In some group theory, σ is the # of pure rotational elements in the point group of a nonlinear molecule.

Symmetric top

The quantum mechanical problem of a symmetric top ($I_A = I_B \neq I_C$) is also solvable in closed form. In this case the energy levels depend upon two quantum numbers:

J : a measure of the total rotational angular momentum of the molecule, and

K : a measure of the component of the rotational angular momentum along the unique axis of the symmetric top, customarily I_C .

It might be pointed out here that any molecule with an n -fold axis of symmetry, with $n \geq 3$, is at least a symmetric top. The expression for the energy levels is

$$\varepsilon_{JK} = \frac{\hbar^2}{2} \left\{ \frac{J(J+1)}{I_A} + K^2 \left(\frac{1}{I_C} - \frac{1}{I_A} \right) \right\}$$

where $J = 0, 1, 2, \dots$; $K = J, J-1, \dots, -J+1, -J$; and the degeneracy is

$$\omega_{JK} = 2J + 1$$

The partition function is, then,

$$q_{\text{rot}} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\alpha_A J(J+1)} \sum_{K=-J}^{+J} e^{-(\alpha_C - \alpha_A) K^2}$$

where

$$\alpha_j = \frac{\hbar^2}{2I_j kT} \quad j = A \text{ or } C$$

Problem 8-3 converts this to a double integral over J and K , which results in

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 I_A kT}{h^2} \right)^{2/2} \left(\frac{8\pi^2 I_C kT}{h^2} \right)^{1/2} \quad (8-17)$$

Notice that this reduces to the rotational partition of a spherical top [(8-16)] when $I_A = I_C$.

Asymmetric top

$I_A \neq I_B \neq I_C$. This is the most commonly occurring type of molecule. The quantum mechanical problem of the rotational levels of an asymmetric top is a fairly involved problem and must be solved numerically. Consequently a quantum-statistical treatment is awkward, and it is desirable to use classical mechanics. Even the classical Hamiltonian of a rigid asymmetrical rotor is quite complicated. We confine ourselves, therefore, to the statement that insertion of the classical Hamiltonian into the classical phase integral leads, after a rather long but straightforward integration, to (see Problem 8-16)

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 I_A kT}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_B kT}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_C kT}{h^2} \right)^{1/2} \quad (8-18)$$

If we introduce the characteristic rotational temperatures into (8-18), we have

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \quad \text{or} \quad q_{\text{trans}} = \left[\frac{T}{\Theta_T} \right]^{3/2} \quad (8-19)$$

See Table 8-1 for $\Theta_A, \Theta_B, \Theta_C$. The rotational contributions to some thermodynamic functions are

$$E_{\text{rot}} = \frac{3}{2} NkT \quad (8-20)$$

$$S_{\text{rot}} = Nk \ln \left[\frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right] \quad (8-21)$$

$$C_{V,\text{rot}} = \frac{3}{2} Nk \quad (8-22)$$

Note that since there are three degrees of rotational freedom, the rotational kinetic energy here is $3NkT/2$, in accord with equipartition of energy.

8-3 THERMODYNAMIC FUNCTIONS

Diatomic molecules

$$q(V, T) = \left[\left(\frac{2\pi(m_1 + m_2)kT}{h^2} \right)^{3/2} V \right] \left[\frac{8\pi^2 IkT}{\sigma h^2} \right] \left[\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right] \left[\omega_{e1} e^{D_e/kT} \right] \quad (6-51)$$

$$-\frac{A}{NkT} = \ln \left[\left(\frac{2\pi M kT}{h^2} \right)^{3/2} \frac{Ve}{N} \right] + \ln \frac{T}{\sigma \Theta_r} - \left[\frac{h\nu}{2kT} + \ln(1 - e^{-h\nu/kT}) \right] + \frac{D_e}{kT} + \ln \omega_{e1}$$

$$\frac{E}{NkT} = \frac{5}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \frac{D_e}{kT} \quad (6-52)$$

$$\frac{C_V}{Nk} = \frac{5}{2} + \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad (6-53)$$

$$\frac{S}{Nk} = \ln \left[\frac{2\pi(m_1 + m_2)kT}{h^2} \right]^{3/2} \frac{Ve^{5/2}}{N} + \ln \frac{8\pi^2 IkTe}{\sigma h^2} + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln(1 - e^{-h\nu/kT}) + \ln \omega_{e1} \quad (6-54)$$

$$pV = NkT \quad (6-55)$$

Linear polyatomic molecules

$$q(V, T) = \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} V \right] \left[\frac{T}{\sigma \Theta_r} \right] \left[\prod_{j=1}^{3n-5} \frac{e^{-\Theta_{vj}/2T}}{1 - e^{-\Theta_{vj}/T}} \right] \left[\omega_{e1} e^{D_e/kT} \right] \quad (8-23)$$

$$-\frac{A}{NkT} = \ln \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} \frac{Ve}{N} \right] + \ln \frac{T}{\sigma \Theta_r} - \sum_{j=1}^{3n-5} \left[\frac{h\nu_j}{2kT} + \ln \left(1 - e^{-h\nu_j/kT} \right) \right] + \frac{D_e}{kT} + \ln \omega_{e1} \quad (8-24)$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5} \left(\frac{h\nu_j}{2kT} + \frac{h\nu_j/kT}{e^{h\nu_j/kT} - 1} \right) - \frac{D_e}{kT} \quad (8-25)$$

$$\frac{C_V}{Nk} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5} \left(\frac{h\nu_j}{kT} \right)^2 \frac{e^{h\nu_j/kT}}{\left(e^{h\nu_j/kT} - 1 \right)^2} \quad (8-26)$$

$$\frac{S}{Nk} = \ln \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} \frac{Ve^{5/2}}{N} \right] + \ln \frac{Te}{\sigma \Theta_r} + \sum_{j=1}^{3n-5} \left[\frac{h\nu_j/kT}{e^{h\nu_j/kT} - 1} - \ln \left(1 - e^{-h\nu_j/kT} \right) \right] + \ln \omega_{e1} \quad (8-27)$$

$$pV = NkT \quad (8-28)$$

Nonlinear polyatomic molecules

$$q(V, T) = \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} V \right] \left[\frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right] \left[\prod_{j=1}^{3n-6} \frac{e^{-\Theta_{vj}/2T}}{1 - e^{-\Theta_{vj}/T}} \right] \left[\omega_{e1} e^{D_e/kT} \right] \quad (8-29)$$

$$-\frac{A}{NkT} = \ln \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} \frac{Ve}{N} \right] + \ln \frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} - \sum_{j=1}^{3n-6} \left[\frac{h\nu_j}{2kT} + \ln \left(1 - e^{-h\nu_j/kT} \right) \right] + \frac{D_e}{kT} + \ln \omega_{e1} \quad (8-30)$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left(\frac{h\nu_j}{2kT} + \frac{h\nu_j/kT}{e^{h\nu_j/kT} - 1} \right) - \frac{D_e}{kT} \quad (8-31)$$

$$\frac{C_V}{Nk} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left(\frac{h\nu_j}{kT} \right)^2 \frac{e^{h\nu_j/kT}}{\left(e^{h\nu_j/kT} - 1 \right)^2} \quad (8-32)$$

$$\frac{S}{Nk} = \ln \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} \frac{Ve^{5/2}}{N} \right] + \ln \frac{\sqrt{\pi} e^3}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} + \sum_{j=1}^{3n-6} \left[\frac{h\nu_j/kT}{e^{h\nu_j/kT} - 1} - \ln \left(1 - e^{-h\nu_j/kT} \right) \right] + \ln \omega_{e1} \quad (8-33)$$

$$pV = NkT \quad (8-34)$$

8-4 Some other Issues

Vibrational Energy

Table 8-2 shows $C_V \neq Nk$ at the temperatures listed, meaning that energy not in equipartition.

Residual Entropy

In Table 8-3, calculated values of the entropy agree well to those measured calorimetrically. There is, however, a class of molecules for which the agreement is not found. E.g., for carbon monoxide, $S_{\text{calc}} = 47.3$ e.u. and $S_{\text{exp}} = 46.2$, for a discrepancy of 1.1 e.u. In all cases of such discrepancies it is found that $S_{\text{calc}} > S_{\text{exp}}$. This difference is often referred to as *residual entropy*.

Carbon monoxide has a very small dipole moment, and so when carbon monoxide is crystallized, the molecules do not have a strong tendency to line up. The resultant crystal, then, is a random mixture of the two possible orientations CO and OC. As the crystal is cooled down toward 0° K, each molecule gets locked into its orientation and cannot realize the state of lowest energy with $\Omega = 1$, that is, all the molecules oriented in the same direction. Instead, $\Omega = 2^N$ since each of the N molecules exists equally likely in two states. Thus the entropy of the crystal at 0° K is $S = k \ln \Omega = Nk \ln 2 \approx 1.4$ [entropy units] instead of zero. If this extra entropy is added to the experimental entropy, the agreement in the case of carbon monoxide becomes satisfactory.

A similar situation occurs with nitrous oxide.

For H_3CD , the residual entropy is 2.8 esu. Each molecule of monodeuterated methane can assume four different orientations in the low-temperature crystal, and so $S_{\text{resi}} = Nk \ln 4 = 2.7$ esu.

Hindered Rotation

In molecules such as ethane ($\text{CH}_3\text{-CH}_3$), one of the most important internal degrees of freedom is a rotation about the single C-C bond. Because of the interactions between the H atoms on each carbon, this rotation is not free, but is said to be restricted or hindered. As the two methyl groups rotate about the C-C bond, the hydrogen atoms become alternately eclipsed (directly opposite each other) and staggered. The potential energy associated with this rotation has the maxima when the H atoms are eclipsed, and the minima when they are staggered. At $kT \gg V_0$, the internal rotation is essentially free and can be treated by methods similar to the rigid rotor. At $kT \ll V_0$, the molecule is trapped at the bottom of the wells, and the motion is that of a simple torsional vibration, which can be treated by a method similar to that used for the simple harmonic oscillator (Fig. 8-1).