

24.8: The Vibrational Partition Function of A Diatomic Ideal Gas

We base the electronic potential energy for a diatomic molecule on a model in which the nuclei are stationary at the bottom of the electronic potential energy well. We now want to expand this model to include vibrational motion of the atoms along the line connecting their nuclei. It is simple, logical, and effective to model this motion using the quantum mechanical treatment of the classical (Hooke's law) harmonic oscillator.

A Hooke's law oscillator has a location, r_0 , at which the restoring force, $F(r_0)$, and the potential energy, $\epsilon(r_0)$, are zero. As it is displaced from r_0 , the oscillator experiences a restoring force that is proportional to the magnitude of the displacement, $dF = -\lambda dr$. Then, we have

$$\int_{r_0}^r dF = -\lambda \int_{r_0}^r dr$$

so that $F(r) - F(r_0) = -\lambda(r - r_0)$. Since $F(r_0) = 0$, we have $F(r) = -\lambda(r - r_0)$. The change in the oscillator's potential energy is proportional to the square of the displacement,

$$\epsilon(r) - \epsilon(r_0) = \int_{r_0}^r -F dr = \lambda \int_{r_0}^r (r - r_0) dr = \frac{\lambda}{2} (r - r_0)^2$$

Since we take $\epsilon(r_0) = 0$, we have $\epsilon(r) = \lambda(r - r_0)^2/2$. Taking the second derivative, we find

$$\frac{d^2\epsilon}{dr^2} = \lambda$$

Therefore, if we determine the electronic potential energy function accurately near r_0 , we can find λ from its curvature at r_0 .

In [Chapter 18](#), we note that the Schrödinger equation for such an oscillator can be solved and that the resulting energy levels are given by $\epsilon_n = h\nu(n + 1/2)$ where ν is the vibrational frequency. The relationship between frequency and force constant is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\lambda}{m}}$$

where the oscillator consists of a single moving mass, m . In the case where masses m_1 and m_2 oscillate along the line joining their centers, it turns out that the same equations describe the relative motion, if the mass, m , is replaced by the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Therefore, in principle, we can find the characteristic frequency, ν , of a diatomic molecule by accurately calculating the dependence of the electronic potential energy on r in the vicinity of r_0 . When we know ν , we know the vibrational energy levels available to the molecule. Alternatively, as discussed in [Section 24.7](#), we can obtain information about the molecule's vibrational energy levels from its infrared absorption spectrum and use these data to find ν . Either way, once we know ν , we can evaluate the vibrational partition function. We have

$$z_v = \sum_{n=0}^{\infty} \exp \left[-\frac{h\nu}{kT} \left(n + \frac{1}{2} \right) \right] = \frac{\exp(-h\nu/2kT)}{1 - \exp(-h\nu/kT)}$$

where we take advantage of the fact that the vibrational partition function is the sum of a geometric series, as we show in [Section 22.6](#).

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