The rotational energy levels of a diatomic molecule are given by

\[E_{rot}(J) = \tilde{B} J (J + 1)\] \label{Eq0}

where

\[\tilde{B} = \frac{h}{8 \pi^2 I c}\]

Here, \(\tilde{B}\) is the rotational constant expressed in cm\(^{-1}\). The rotational energy levels are given by

\[E_j = \frac{J(J+1) h^2}{8 \pi I}\]

where \(I\) is the moment of inertia of the molecule given by \((\mu r^2)\) for a diatomic and \((\mu)\) is the reduced mass and \((r)\) the bond length (assuming rigid rotor approximation). The energies can be also expressed in terms of the rotational temperature, \(\Theta_{rot}\), which is defined as

\[\Theta_{rot} = \frac{r^2}{8 \pi^2 I k}\] \label{3.12}

In the summation for the expression for rotational partition function \(q_{rot}\), Equation \(\ref{3.13}\), we can do an explicit summation

\[q_{rot} = \sum_{j=0} (2J+1) e^{-E_J/ k_B T}\] \label{3.13}

if only a finite number of terms contribute. The factor \((2J+1)\) for each term in the expansion accounts for the degeneracy of a rotational state \(J\). For each allowed energy \(E_J\) from Equation \(\ref{Eq0}\), then there are \((2 J + 1)\) states eigenstates it, then, the Boltzmann factor \(e^{-E_J / k_B T}\) has to be multiplied by \((2J+1)\) to properly account for all these states.

If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for \(q_{trans}\) previously to get

\[q_{rot} = \int _0 ^{\infty} (2J+1) e^{\frac{-E_J}{k_B T}} dJ\]

This the integration can be easily be done by substituting \(x = J ( J+1)\) and \(dx = (2J + 1) dJ\)

\[q_{rot} = \frac{k_B T}{\tilde{B}}\] \label{3.15}

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is indistinguishable from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by \(\sigma\), which is called the symmetry number, which is equal to the distinct number of ways by which a molecule can be brought into identical configurations by rotations. The rotational partition function becomes,

\[q_{rot} = \frac{k_B T}{\tilde{B} \sigma}\] \label{3.16}

or commonly expressed in terms of \(\Theta_{rot}\)
Example \ref{PageIndex(1)}

What is the rotational partition function of \(H_2\) at 300 K?

Solution

The value of \(\tilde{B}\) for \(H_2\) is 60.864 cm\(^{-1}\). The value of \(k_B T\) in cm\(^{-1}\) can be obtained by dividing it by \(hc\), i.e., which is \(k_B T/hc = 209.7\; cm^{-1}\) at 300 K. \(\sigma = 2\) for a homonuclear molecule. Therefore from Equation \ref{3.16},

\[
q_{\text{rot}} = \frac{k_BT}{\tilde{B} \sigma} = \frac{209.7\; cm^{-1}}{(2) (60.864\; cm^{-1})} = 1.723
\]

Since the rotational frequency of \(H_2\) is quite large, only the first few rotational states are accessible at 300 K.

Contributors

- [http://www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf](http://www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf)