ME 687 Handout: Diatomic Gases: Population Distributions over Internal Energy Modes

1. Heteronuclear Molecules: Rotational, Vibrational and Electronic Distributions

- Boltzmann distribution law is applied separately to each mode: for the translational mode this led to the Maxwell velocity distribution.
- Rotational: Assume that \( T \gg \theta_{rot} \), heteronuclear molecule, ground vibrational level of ground electronic level. Then

\[
\frac{N_{i,j^n}}{N_{i^v}} = \frac{g_j \exp(-\epsilon_j / k_B T)}{g_{i,\text{elec}} Z_{\text{rot}}} = \frac{(2J^n + 1) \exp[-J^n(J^n+1) \theta_{rot}/T]}{g_{i,\text{elec}} (T/\theta_{rot})}
\]

Note: level population proportional to \( 2J^n + 1 \), \( J^n \) can be half-integral or integral

- Determination of the rotational level with the maximum population. Assume that \( J \) varies continuously,

\[
\frac{dN_j}{dJ} = 0 \quad \text{for} \quad J_{\text{max}} = \sqrt{\frac{T}{2\theta_{rot}}} - \frac{1}{2}
\]

- Vibrational Distribution

\[
\frac{N_{i,v}}{N_{i^v}} = \frac{g_{i,vib} \exp(-\epsilon_{vib} / k_B T)}{Z_{\text{vib}}} = \exp\left[-(v + \frac{1}{2})\theta_{vib}/T\right] \frac{1 - \exp(-\theta_{vib}/T)}{\exp(-\theta_{vib}/2T)}
\]

Note: zero-point energy divides out

\[
\frac{N_{i,v}}{N_{i^v}} = \exp[-v(\theta_{vib}/T)] \left[1 - \exp(-\theta_{vib}/T)\right]
\]

- Electronic Distribution

\[
\frac{N_{i,\text{elec}}}{N} = \frac{g_i \exp(-\epsilon_{i,\text{elec}} / k_B T)}{Z_{\text{elec}}}
\]
2. Rotational Level Populations for Homonuclear Molecules

For nuclei of odd mass number (fermions) the total wavefunction $\psi_{\text{tot}} = \psi_{\text{rot}} \psi_{\text{vib}} \psi_{\text{elec}} \psi_{\text{nuc}}$ must be antisymmetric with respect to exchange of nuclei.

$$\psi_{\text{tot}}(x, y, z) = - \psi_{\text{tot}}(-x, -y, -z)$$

$$\psi_{\text{rot}}(x, y, z) = - \psi_{\text{rot}}(-x, -y, -z) \quad (J \text{ odd})$$

$$\psi_{\text{rot}}(x, y, z) = + \psi_{\text{rot}}(-x, -y, -z) \quad (J \text{ even})$$

$$\psi_{\text{vib}}(x, y, z) = + \psi_{\text{vib}}(-x, -y, -z) \quad (\text{all } v)$$

Diatomic Hydrogen

Diatomic hydrogen has a symmetric $^1\Sigma_g^+$ ground electronic level.

<table>
<thead>
<tr>
<th>$^1\text{H}_2$</th>
<th>$\psi_{\text{rot}}$</th>
<th>$\psi_{\text{vib}}$</th>
<th>$\psi_{\text{elec}}$</th>
<th>$\psi_{\text{nuc}}$</th>
<th>$\psi_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{\text{odd}}$</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$</td>
<td>$+$</td>
<td>$-$</td>
</tr>
<tr>
<td>$J_{\text{even}}$</td>
<td>$+$</td>
<td>$+$</td>
<td>$+$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

- For $\text{H}_2$ molecules with a symmetric nuclear spin wavefunction, only rotational states with odd $J$ are possible. For $\text{H}_2$ molecules with an antisymmetric nuclear spin wavefunction, only rotational states with even $J$ are possible.

- There are a total of $(2I + 1)^2 = (g_o)^2$ nuclear spin states, and $\left(\frac{g_o (g_o + 1)}{2}\right)$ of the nuclear spin states are symmetric, and $\left(\frac{g_o (g_o - 1)}{2}\right)$ are antisymmetric.

The population of the rotational levels is given by

$$\frac{N_J}{N_V} = \frac{g_o (g_o + 1)}{2} \frac{(2J + 1)}{Z_{\text{rot,nuc}}} \exp \left[-J(J+1) \theta_{\text{rot}} / T \right] \quad (J \text{ odd})$$
\[
\frac{N_J}{N_v} = \frac{g_o(g_o - 1)}{2} \frac{(2J + 1)}{Z_{(rot,nuc)}} \exp \left[ -J(J + 1) \frac{\theta_{rot}}{T} \right] \quad (J \text{ even})
\]

where \( g_o = (2I + 1) \), and \( Z_{(rot,nuc)} = \frac{1}{2} g_o^2 \frac{T}{T_{rot}} = \frac{1}{2} (2I + 1)^2 \frac{T}{T_{rot}} \). For \( \text{H}_2 \), \( I = 1/2 \), \( g_o = 2 \):

\[
\frac{N_J}{N_v} = 3 \frac{(2J + 1)}{Z_{(rot,nuc)}} \exp \left[ -J(J + 1) \frac{\theta_{rot}}{T} \right] \quad (J = 1, 3, 5, \ldots) \text{ \( \text{ortho H}_2 \)}
\]

\[
\frac{N_J}{N_v} = 1 \frac{(2J + 1)}{Z_{(rot,nuc)}} \exp \left[ -J(J + 1) \frac{\theta_{rot}}{T} \right] \quad (J = 0, 2, 4, \ldots) \text{ \( \text{para H}_2 \)}
\]

**Diatomc Nitrogen**

Diatomc nitrogen also has a symmetric \(^1\Sigma_g^+\) ground electronic level. However, the nuclear spin of the \(^{14}\text{N} \) nucleus is \( I = 1 \), and therefore diatomic nitrogen obeys boson statistics. Nuclei of even mass number are bosons because the nuclear spin will be integral and the total wavefunction \( \psi_{tot} = \psi_{rot} \psi_{vib} \psi_{elec} \psi_{nuc} \) must be symmetric with respect to exchange of nuclei.

<table>
<thead>
<tr>
<th>(^{14}\text{N}_2)</th>
<th>(\psi_{rot})</th>
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<td>(J_{\text{odd}})</td>
<td>-</td>
<td>+</td>
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- For \( \text{N}_2 \) molecules with a symmetric nuclear spin wavefunction, only rotational states with even \( J \) are possible. For \( \text{N}_2 \) molecules with an antisymmetric nuclear spin wavefunction, only rotational states with odd \( J \) are possible.

For \( \text{N}_2 \), \( I = 1 \), \( g_o = 3 \). For even \( J \), \( J = 0, 2, 4, \ldots \):

\[
\frac{N_J}{N_v} = \left( \frac{g_o (g_o + 1)}{2} \right) \frac{(2J + 1)}{Z_{(rot,nuc)}} \exp \left[ -J(J + 1) \frac{\theta_{rot}}{T} \right] = 6 \frac{(2J + 1)}{Z_{(rot,nuc)}} \exp \left[ -J(J + 1) \frac{\theta_{rot}}{T} \right]
\]
For odd J, \((J = 1, 3, 5, \ldots)\)

\[
\frac{N_J}{N_v} = \left( \frac{g_o (g_o - 1)}{2} \right) \frac{(2J + 1)}{Z_{(\text{rot,nuc})}} \exp\left[ -\frac{J(J+1) \theta_{\text{rot}}}{T} \right] = 3 \frac{(2J + 1)}{Z_{(\text{rot,nuc})}} \exp\left[ -\frac{J(J+1) \theta_{\text{rot}}}{T} \right]
\]

**Diatominc Oxygen**

For diatomic oxygen the nuclei are bosons and the total wavefunction must be symmetric with respect to exchange of nuclei. For oxygen, which has an antisymmetric \(^3\Sigma_g^-\) ground electronic level, we develop the following table,

<table>
<thead>
<tr>
<th>(^{16}\text{O}_2)</th>
<th>(\Psi_{\text{rot}})</th>
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- The population of the rotational levels is given by

\[
\frac{N_J}{N_v} = \frac{g_o (g_o + 1)}{2} \frac{(2J + 1)}{Z_{(\text{rot,nuc})}} \exp\left[ -\frac{J(J+1) \theta_{\text{rot}}}{T} \right] \quad (J \text{ odd})
\]

\[
\frac{N_J}{N_v} = \frac{g_o (g_o - 1)}{2} \frac{(2J + 1)}{Z_{(\text{rot,nuc})}} \exp\left[ -\frac{J(J+1) \theta_{\text{rot}}}{T} \right] \quad (J \text{ even})
\]

- For \(^{16}\text{O}\), \(I = 0, g_o = 1\).

\[
\frac{N_J}{N_v} = 1 \frac{(2J + 1)}{Z_{(\text{rot,nuc})}} \exp\left[ -\frac{J(J+1) \theta_{\text{rot}}}{T} \right] \quad (J = 1, 3, 5, \ldots)
\]

\[
\frac{N_J}{N} = 0 \frac{(2J + 1)}{Z_{(\text{rot,nuc})}} \exp\left[ -\frac{J(J+1) \theta_{\text{rot}}}{T} \right] = 0 \quad (J = 0, 2, 4, \ldots)
\]

The even rotational levels are missing for the oxygen molecules, at least for the most common isotopic species \(^{16}\text{O}_2\). The isotope \(^{16}\text{O}^{18}\text{O}\) has both even and odd rotational levels, however.