Polyatomic Molecules

- While molecules with more than 2 atoms have increased complexity, we can take similar approach to finding partition function as with diatomics
- Simplest approach
  - assume independent (orthogonal) energy/motion modes
    - $\varepsilon = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el}$
      so $Q = Q_{tr}\, Q_{rot}\, Q_{vib}\, Q_{el}$
- Translational energy mode properties
  - same as atoms/diatomics, if fully-excited

$$Q_{tr} \cong \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

E_{tr} =3/2 RT, $c_{v_{tr}}/R$=3/2

- Electronic energy mode properties
  - same approach as atoms/diatomics: need g_i, ε_i, then truncate sum based on T

$$Q_{el} = \sum_i g_{el,i}\, e^{-\varepsilon_{el,i}/kT}$$

Polyatomic Molecules

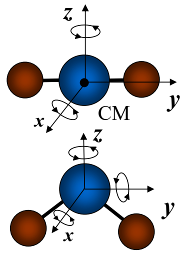
- Rotational energy mode properties
  - use rigid rotor models
- Vibrational energy mode properties
  - use harmonic oscillator models

better models would include: 1) anharmonicity, 2) non-rigid rotors, 3) rot-vib interactions

- Question: how many independent (orthogonal) rotation and vibration motions exist?
  - since each nucleus in a molecule can translate in 3 orthogonal directions, a molecule with N number of nuclei must have a total of
    3N degrees of freedom (DOF)
  - divide these into translation, rotation and vibration

Independent Rotations and Vibrations

- **Translation** of center-of-mass still has 3 DOF
  - so 3N–3 rotation and vibration DOF exist
- **Rotations**: 2 kinds of molecules based on "equilibrium" orientation of nuclei
  - **linear**, e.g., CO_2
    - 2 rotation axes=2 DOF
  - **nonlinear**, e.g., H_2O
    - 3 rotation axes=3 DOF



- **Vibrations**: remaining DOF must be M_{vib} vibrational modes
  - linear: 3N–3–2 DOF = **3N–5 vibration modes**
  - nonlinear: 3N–3–3 DOF = **3N–6 vibration modes**

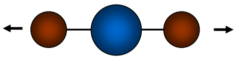
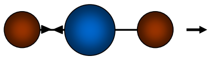
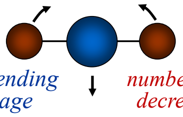
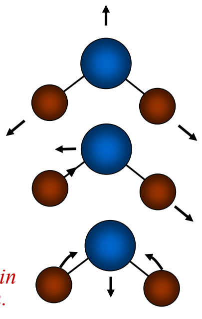
diatomic=6-5=1✓
triatomic, linear
=9-5=4
nonlinear
=9-6=3

Independent Vibration Modes

- Any vibrational motion must be producible from a linear combination/superposition of the independent (normal) vibration modes (and can't move CM or rotate)
- What do these vibrational modes "look like"?
- Triatomic examples

Linear

Nonlinear

	CO_2		H_2O
Symmetric Stretch	1330 cm^{-1}	$\bar{\nu}_1$	3652 cm^{-1}
Asymmetric Stretch	2349 cm^{-1}	$\bar{\nu}_3$	3756 cm^{-1}
Symmetric Bending	667 cm^{-1}	$\bar{\nu}_2$	1595 cm^{-1}

2nd identical bending mode into page

numberings starts with symm. modes in decreasing freq., then same for asym.

- Higher polyatomics: more stretches, complex rotations

for example, see www.chem.purdue.edu/jmol/vibs/

Vibrational Partition Functions

- Assuming
  - each vibrational mode is *independent*
  - harmonic oscillator model for each vibrational mode
- Then the vibrational energy of a molecules is just the sum over each of the M_{vib} different modes

$$\varepsilon_{vib}\left(\mathrm{v}_1,\mathrm{v}_2,\ldots\mathrm{v}_{M_{vib}}\right)=\sum_{\ell=1}^{M_{vib}}\left(\mathrm{v}_\ell+\frac{1}{2}\right)h\nu_\ell$$

- Defining a characteristic vibrational temp. for each mode $\theta_{\mathrm{v}_\ell}\equiv h\nu_\ell/k$

$$\boxed{Q_{vib}=\prod_{\ell=1}^{M_{vib}}\frac{e^{-\theta_{\mathrm{v}_\ell}/2T}}{1-e^{-\theta_{\mathrm{v}_\ell}/T}}}\Rightarrow\boxed{\frac{\hat{e}_{vib}}{\bar{R}}=\sum_{\ell=1}^{M_{vib}}\theta_{\mathrm{v}_\ell}\left(\frac{1}{2}+\frac{1}{e^{\theta_{\mathrm{v}_\ell}/T}-1}\right)}$$

$$\boxed{\frac{\hat{c}_{v,vib}}{\bar{R}}=\sum_{\ell=1}^{M_{vib}}\left(\frac{\theta_{\mathrm{v}\ell}}{T}\right)^2\frac{e^{\theta_{\mathrm{v}_\ell}/T}}{\left(e^{\theta_{\mathrm{v}_\ell}/T}-1\right)^2}}$$

=2/2 for each mode that is fully-excited; e.g., $(c_{v,vib}/R)_{max}$= 8/2 for linear triatomic

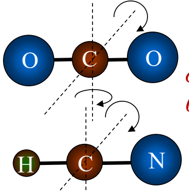
---

Rotational Partition Functions

- Using rigid rotor assumption for each rotation, there are 3 (constant) moments of inertia
  - I_A, I_B, I_C
    - 1 for each of the 3 principal (and orthogonal) axes
- We can define 4 types of polyatomic molecules, based on the relationships between the 3 I's
- **Linear**: only 2 I's, requires $I_A=I_B$ (essentially $I_C=0$)
  - same as diatomics

$$Q_{rot}=\frac{1}{\sigma}\sum_J(2J+1)e^{-\theta_r J(J+1)/T}\cong\frac{T}{\sigma\theta_r}$$

for $T>>\theta_r$



$\sigma = 2$
θ_r=0.561K

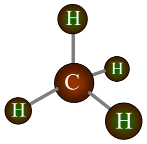
σ=1
θ_r=2.13K

Rotational Partition Functions

- **Spherical Top**: $I_A=I_B=I_C$

$$Q_{rot}=\frac{1}{\sigma}\sum_J (2J+1)^2 e^{-\theta_r J(J+1)/T} \cong \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\theta_r}\right)^{3/2}$$

for $T >> \theta_r$



$\sigma= 12$

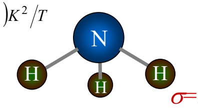
θ_r=7.54K

- **Symmetric Top**: $I_A=I_B\neq I_C$ (and $I_C > 0$)
  - since 2 unique moments of inertia, get 2 quantum numbers

$$Q_{rot}=\frac{1}{\sigma}\sum_J (2J+1) e^{-\theta_{r_A} J(J+1)/T}\sum_{K=-J}^{J} e^{-\left(\theta_{r_C}-\theta_{r_A}\right)K^2/T}$$

for $T >> \theta_{rA}, \theta_{rC}$

$$\cong \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\theta_{r_A}}\right)\left(\frac{T}{\theta_{r_C}}\right)^{1/2}$$



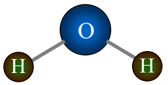
σ=3

θ_{rA}=13.6K

θ_{rC}=8.9K

Rotational Partition Functions

- **Asymmetric Top**: $I_A\neq I_B\neq I_C$
  - most common configuration
  - 3 unique quantum numbers, but no general QM expression, depends on specific molecule, however



σ=2

θ_{rA}=40.1K

θ_{rB}=20.9K

θ_{rC}=13.4K

for $T >> \theta_{rA}, \theta_{rB}, \theta_{rC}$,

$$Q_{rot}\cong \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\theta_{r_A}}\right)^{1/2}\left(\frac{T}{\theta_{r_B}}\right)^{1/2}\left(\frac{T}{\theta_{r_C}}\right)^{1/2}$$

- **So in fully-excited limit** for all non-monatomic molecules

$$\boxed{\frac{\hat{c}_{v,rot}}{R}=\begin{cases}2/2 & linear\\ 3/2 & nonlinear\end{cases}}$$

Mode Interactions

- As with diatomics, using simple rigid rotor and harmonic oscillator models can produce reasonable results at lower temperatures
- More complex models that include interactions between energy modes (so modes not independent) are needed for higher accuracy calculations at higher temperatures
  - can even be more important for polyatomics due to low frequency (bending) vibration modes
  - can include vibration-vibration mode interactions