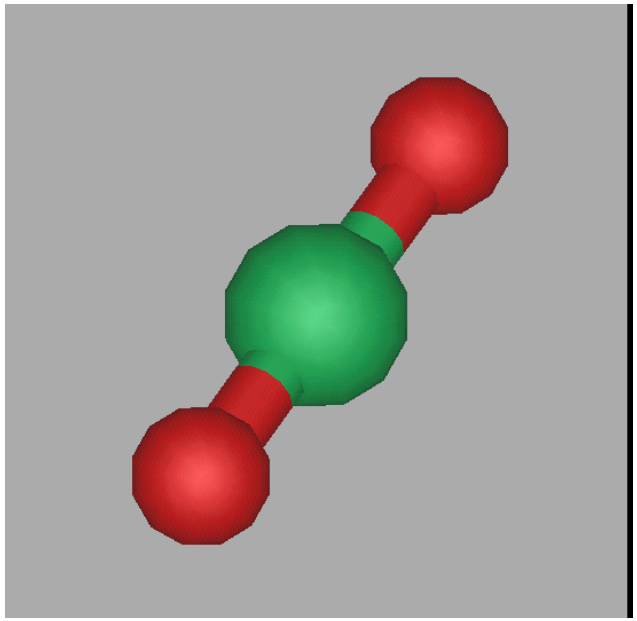
Polyatomic Gases

John W Daily

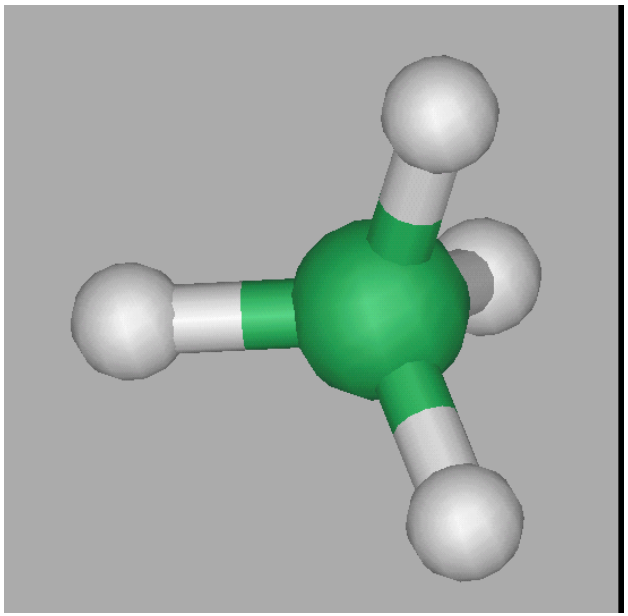
Polyatomic Molecules

- For a body made up of n atoms, there are $3n$ degrees of freedom.
- Translation take up 3 degrees of freedom
- Rotation takes up 2 for a linear molecule, and 3 for a non-linear molecule
- Vibration then takes $3n$-5 or $3n$-6.

Rotational Modes



CO_2 is linear
Rotates about two axis

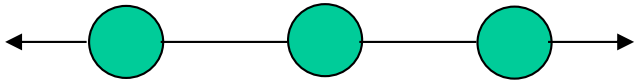


CH_4 is non-linear
Rotates about three axis

Vibrational Modes

Linear Triatomic (CO_2) - Four Modes

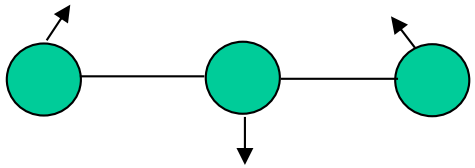
Symmetric stretch



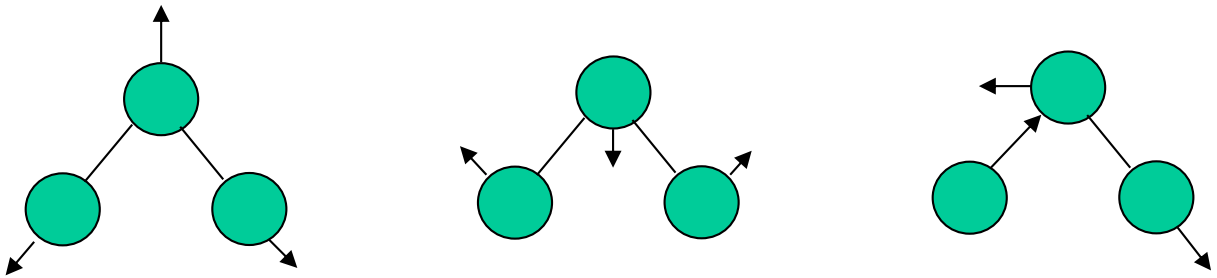
Asymmetric stretch



Bending in two planes



Non-linear Triatomic (H_2O) - Three Modes



If we assume that each vibrational and rotational mode is independent, then we can separate the partition function for each mode. Furthermore, if we assume that the harmonic oscillator and rigid rotator models apply, then we can write for the general case

$$q_v = e^{\frac{D_e}{kT}} \prod_i^{3n-6} \left\{ \frac{e^{-\Theta_{v_i}/2T}}{1 - e^{-\Theta_{v_i}/T}} \right\}$$

$$q_r = \frac{1}{\sigma} \left\{ \frac{\pi T^3}{\Theta_{r_1} \Theta_{r_2} \Theta_{r_3}} \right\}$$

Start 10/2/18

Equi-partition of Energy

- Each mode of energy contributes 1/2 kT to the total energy and thus $k/2$ to c_v.
- Translation - 3
- Rotation - 1 for each axis of rotation (up to 3)
- Vibration - 1 each for kinetic and potential energy (up to 3n-3 minus number of rotational modes)
- Modes must be “fully excited” for full $k/2$ to kick in.

Fully Excited

$$c_v = k\left[\frac{3}{2} + \frac{2}{2} or \frac{3}{2} + \sum_{\text{vib modes}} \left\{\frac{\Theta_{v_i} / 2T}{Sinh(\Theta_{v_i} / 2T)}\right\}^2\right]$$

