Statistical Molecular Thermodynamics

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Video 1.7

Polyatomic Molecular Energy Levels

How is energy stored in a Molecule?

Electronic energy. Changes in the kinetic and potential energy of one or more electrons associated with the *molecule*. Same as many-electron atoms.

Kinetic Energy:

Translational energy. The *molecule* can move (translate) in space. Same particle-in-a-box solutions as for atoms.

Rotational energy. The entire *molecule* can rotate in space. Schrödinger equation: Rigid-rotator.

Vibrational energy. The nuclei can move *relative to one another* in space. Schrödinger equation: Quantum-mechanical harmonic oscillator.

Molecular Degrees of Freedom

To specify completely the position in space of a molecule having n nuclei we require $3n$ coordinates (3 Cartesian coordinates for each nucleus). We say that there are $3n$ *degrees of freedom*.

Degrees of freedom can be divided as translational, rotational, or vibrational:

	degrees of freedom ($3n$ total)
Translation:	
Motion of the center of mass	3
Rotation (orientation about *center of mass*):	
linear molecule	2
nonlinear molecule	3
Vibration (frame-free movement of n nuclei):	
linear molecule	$3n$-5
nonlinear molecule	$3n$-6

diatomic

Polyatomic Rotational Energy Levels

Linear molecules: Same results as for diatomics but with moments of inertia computed generally for more than 2 nuclei:

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0,1,2,\ldots \qquad g_J = 2J+1 \qquad I = \sum_{j=1}^{n} m_j \left(x_j - x_{cm}\right)^2$$

Nonlinear molecules: There is one moment of inertia for *each* of the 3 rotational axes. There are 3 categories,

Spherical top (baseball, CH_4): $I_A = I_B = I_C$

Symmetric top (American football, NH_3):

Any 2 of the 3 moments of inertial are equal. $I_A = I_B \neq I_C$

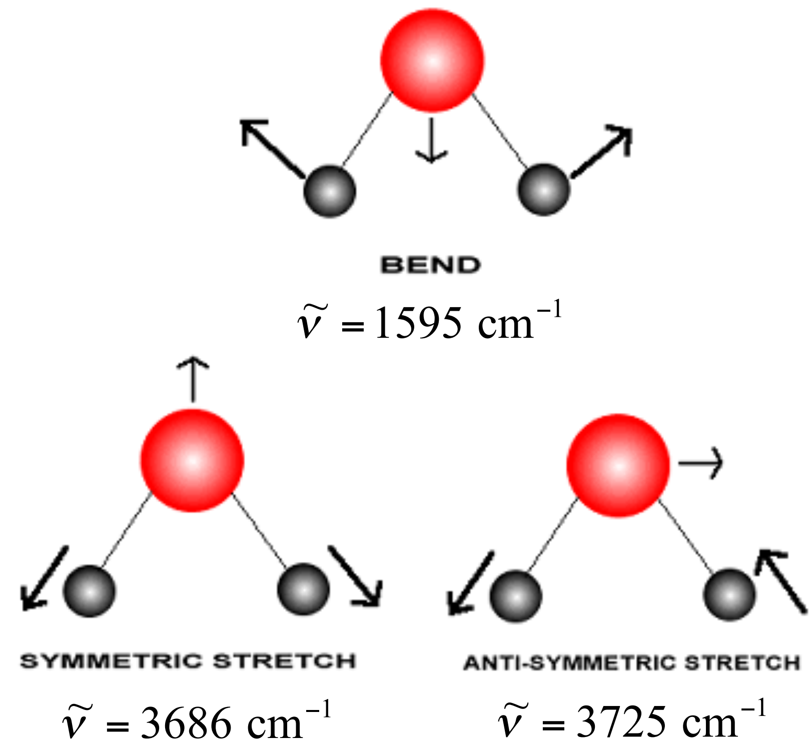
Asymmetric top (Boomerang, H_2O):

All 3 moments of inertial are NOT equal. $I_A \neq I_B \neq I_C$

Polyatomic vibrations: normal modes

For polyatomic molecules we can consider each of the n_{vib} vibrational degrees of freedom as independent harmonic oscillators. We refer to the characteristic independent vibrational motions as *normal modes*.

E.g., water has 3 normal modes:



Since the normal modes are independent of one another, the total energy is simply the sum:

$$\varepsilon_{\text{vib}} = \sum_{j=1}^{n_{\text{vib}}} h\nu_j \left(v_j + \frac{1}{2} \right)$$

Total Energy

The energy of a molecule can be expressed as a sum over all its degrees of freedom.

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}}$$

D_e for diatomics.

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

$$n_x = 1,2,3,\cdots$$

$$n_y = 1,2,3,\cdots$$

$$n_z = 1,2,3,\cdots$$

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1)$$

$$J = 0,1,2,\ldots$$

For linear molecules

$$\varepsilon_v = h\nu\left(v + \frac{1}{2}\right)$$

$$v = 0,1,2,\ldots$$

For each vibrational degree of freedom

Spacing of Energy Levels

There is a general trend in energy spacing

Electronic >> Vibrational > Rotational >> Translational