THE DEGREES OF FREEDOM OF A GAS MOLECULE

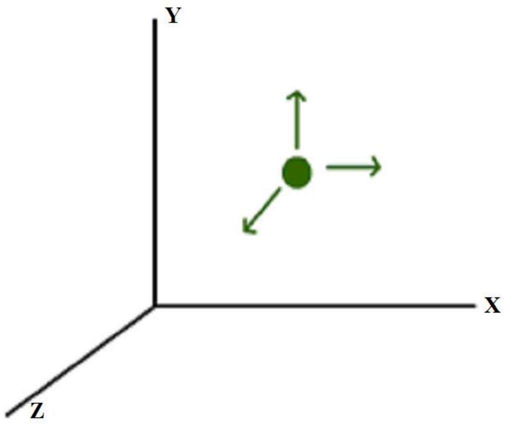
- Molecular degrees of freedom refer to the number of ways a molecule in the gas phase may move, rotate, or vibrate in space.
- It is defined as the number of coordinates required to specify the position of all the atoms in a molecule.
- Three coordinates x, y and z are required to specify the position of one atom in space.
- A monoatomic gas molecule thus will have 3 degrees of freedom.
- The molecule containing '*n*' atoms will have ***3n*** degrees of freedom which are distributed among the different kinds of motion.

The translational motion

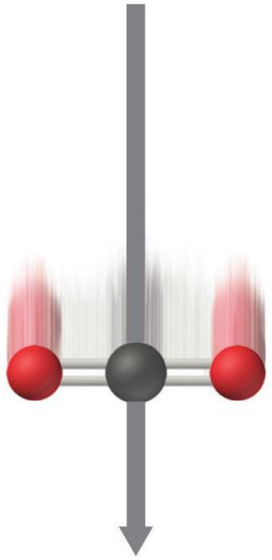
The rotational motion

The vibrational motion

The translational motion

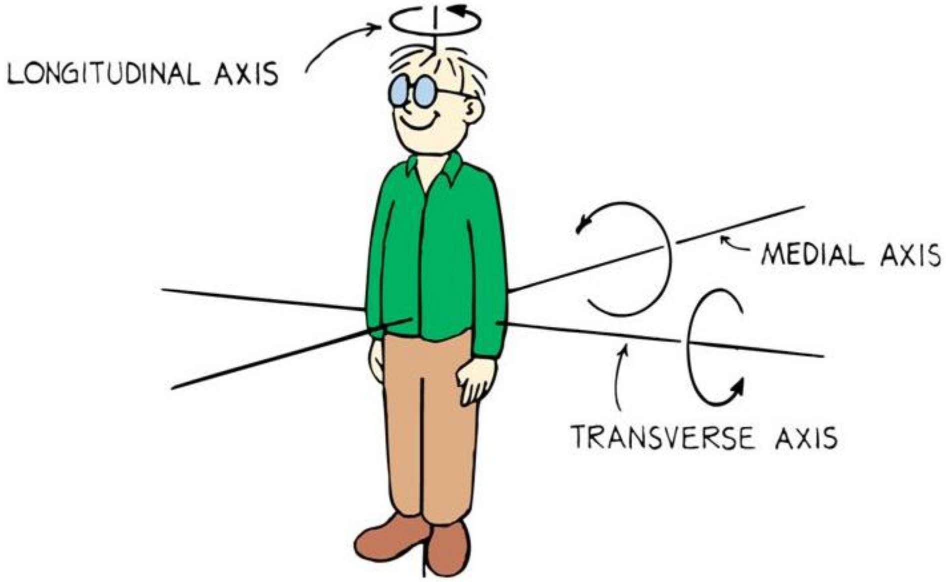


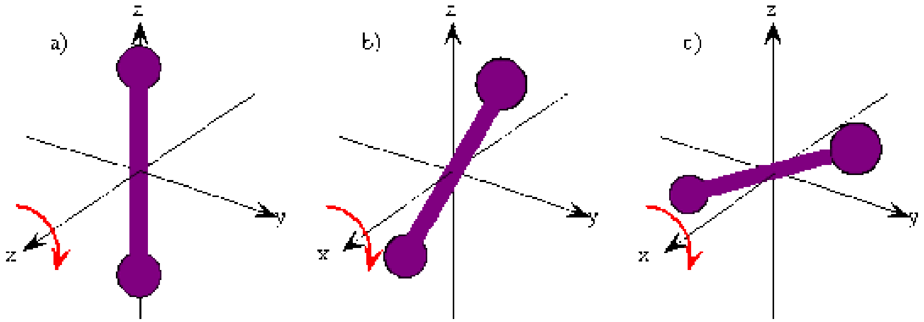
- The motion by which a molecule shifts from one point in space to another.
- During this motion the centre of mass of the molecule changes from one point to other.
- 3 coordinates are required to specify the centre of mass of the molecule hence there are ***3 translational degrees of freedom*** for it.

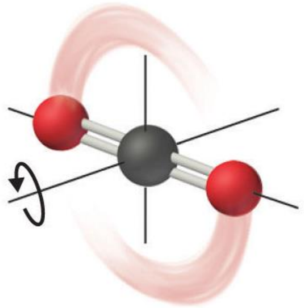


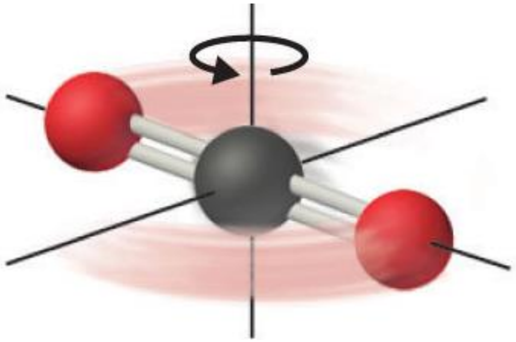
The rotational motion

- the movement of a molecule around an axis.
- For any diatomic molecule or any linear polyatomic molecule there are ***only 2 rotational degrees of freedom***. The rotation about the molecular axis is not counted.
- For a non-linear molecule, there are ***3 rotational degrees of freedom*** corresponding to rotation about all the three Cartesian axes.



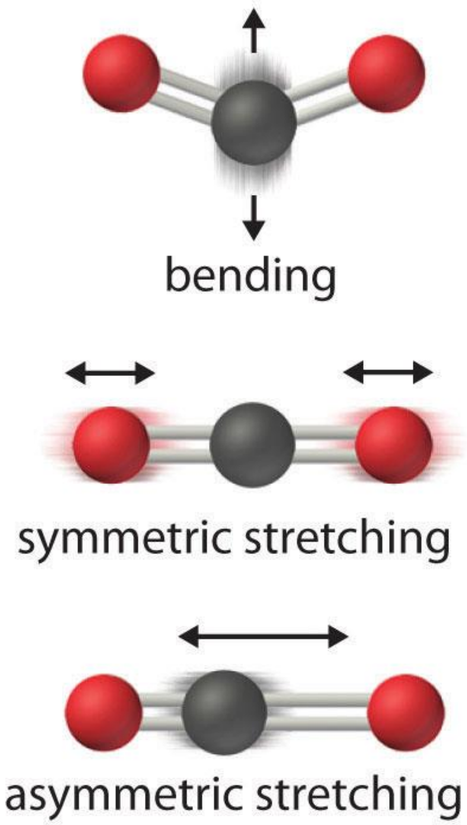






The vibrational motion

- mechanical phenomenon whereby oscillations occur about an equilibrium point.
- Remaining (3n-5) coordinates for a linear molecule and (3n-6) coordinates for a non-linear molecule, describe the bond length and bond angles within the molecule.
- Motion with respect to these coordinates correspond to the vibrations (stretching and bending) of the molecule.
- Linear molecule does have 3n-5 and 3n-6 vibrational degrees of freedom.



	Linear Molecule	Non-linear Molecule
Translational Degrees of Freedom	3	3
Rotational Degrees of Freedom	2	3
Vibrational Degrees of Freedom	3n-5	3n-6
Total	3n	3n

CO_2

	Linear Molecule
Translational Degrees of Freedom	3
Rotational Degrees of Freedom	2
Vibrational Degrees of Freedom	3n-5 = 9 – 5 = 4
Total	9

H_2O

	Non-Linear Molecule
Translational Degrees of Freedom	3
Rotational Degrees of Freedom	3
Vibrational Degrees of Freedom	3n-6 = 9 – 6 = 3
Total	9

LAW OF EQUIPARTITION OF ENERGY:

- The law of equipartition of energy states that the *total energy of a molecule is equally distributed amongst the various degrees of freedom of a molecule*, the amount of energy associated with each being equal to ½kT per molecule.
- The term degree of freedom can also be referred to as the number of independent square terms required to express the energy of a molecule. Hence the law of equipartition can also be stated as follows.
- ***"If the energy of a molecule can be written in the form of a sum of terms, each of which is proportional to the square of a velocity component or position component, the contribution of each of these terms to the total energy is equal to ½kT per molecule or ½RT per mole***.

Translational Energy:

The translational kinetic energy is given by:

$$E_{trans} = \frac{1}{2}mv_x{}^2 + \frac{1}{2}mv_y{}^2 + \frac{1}{2}mv_z{}^2$$

Where, v_x, v_y *and* v_z are the component velocities in *x*, *y* and *z* directions.

Applying law of equipartition energy, the translational energy of a molecule is given by;

$$E_{trans} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$$

Each degree of freedom contributes, ½kT per molecule to the total energy.

Rotational Energy:

Rotational energy is given by the equation:

$$E_{rot} = \frac{1}{2} I_x \omega_x^{\,2} + \frac{1}{2} I_y \omega_y^{\,2} \qquad \text{(Linear molecule)}$$

$$E_{rot} = \frac{1}{2} I_x \omega_x^{\,2} + \frac{1}{2} I_y \omega_y^{\,2} + \frac{1}{2} I_z \omega_z^{\,2} \qquad \text{(Non-linear molecule)}$$

Applying law of equipartition energy, the rotational energy of a molecule is given by;

$$E_{rot} = \frac{1}{2} kT + \frac{1}{2} kT = kT \qquad \text{(Linear molecule)}$$

$$E_{rot} = \frac{1}{2} kT + \frac{1}{2} kT + \frac{1}{2} kT = \frac{3}{2} kT \qquad \text{(Non-linear molecule)}$$

Vibrational Energy:

Vibrational energy constitutes vibrational potential energy and vibrational kinetic energy terms. It is given by:

$$E_{vib} = \frac{1}{2}\mu\left[\frac{dr}{dt}\right]^2 + \frac{1}{2}k\left(r - r_0\right)^2$$

Where, 'μ' is the reduced mass, 'k' is the force constant, 'r_0' is the equilibrium value of the coordinate, 'r' is the bond length and (dr/dt) is the velocity.

Vibrational energy of each vibrational mode is given by;

$$E_{vib} = \frac{1}{2}kT + \frac{1}{2}kT = kT$$

Total Energy of Linear Molecule:

$$E = E_{trans} + E_{rot} + E_{vib}$$

$$E = 3\left(\frac{1}{2}kT\right) + 2\left(\frac{1}{2}kT\right) + (3n-5)\cdot kT$$

$$E = \left(3n - \frac{5}{2}\right)\cdot kT$$

Total energy of linear molecule per mole is given by:

$$E = \left(3n - \frac{5}{2}\right)\cdot RT$$

Total Energy of Non-Linear Molecule

$$E = E_{trans} + E_{rot} + E_{vib}$$

$$E = 3\left(\frac{1}{2}kT\right) + 3\left(\frac{1}{2}kT\right) + (3n-6)\cdot kT$$

$$E = (3n-3)\cdot kT$$

Total energy of linear molecule per mole is given by:

$$E = (3n-3)\cdot RT$$

Heat Capacity from the Equipartition Principle

Monoatomic gas molecules:

Monoatomic gas molecules (n=1), possess only translational kinetic energy and Hence

$$C_V = \frac{3}{2}R$$

Linear molecules:

Total energy of linear molecule per mole is given by:

$$E = \left(3n - \frac{5}{2}\right) \cdot RT$$

Now heat capacity at constant volume is given by:

$$C_V = \frac{q_V}{\Delta T}$$

$$C_V = \frac{\left(3n - \frac{5}{2}\right) \cdot R(T+1) - \left(3n - \frac{5}{2}\right) \cdot RT}{1}$$

Or, we get

$$C_V = \left(3n - \frac{5}{2}\right) \cdot R$$

Non-Linear Molecule

Total energy of non-linear molecule per mole is given by:

$$E = (3n - 3) \cdot RT$$

Now heat capacity at constant volume is given by:

$$C_V = \frac{q_V}{\Delta T}$$

$$C_V = \frac{(3n-3) \cdot R(T+1) - (3n-3) \cdot RT}{1}$$

Or, we get

$$C_V = (3n - 3) \cdot R$$