Atmospheric Physics

Lecture 21
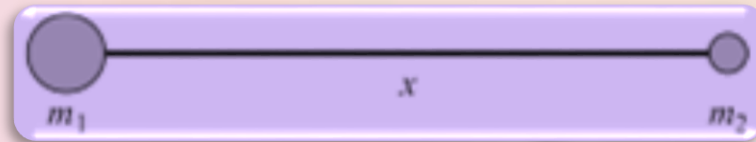
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Basic spectroscopy of molecules

Vibrational and rotational states

As an illustration, we consider the vibrational and rotational states of a diatomic molecule, composed of an atom of mass m_1 and an atom of mass m_2

$$2\pi v_0 = (\frac{K}{m_r})^{1/2} \qquad m_r = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{The reduced mass}$$

The quantum-mechanical theory of the harmonic oscillator requires that we insert the potential function

$$V(x) = \frac{1}{2} K(x - x_0)^2$$

there results an infinite set of energy levels given by:

$$E_v = h v_0 (v + \frac{1}{2}) \quad , \quad v = 0,1,2,...$$

Here v is the vibrational quantum number and takes integer values.

The levels are non-degenerate;
that is, there is only one state corresponding to each energy value E_v

For the strongest vibrational interactions this Hamiltonian takes
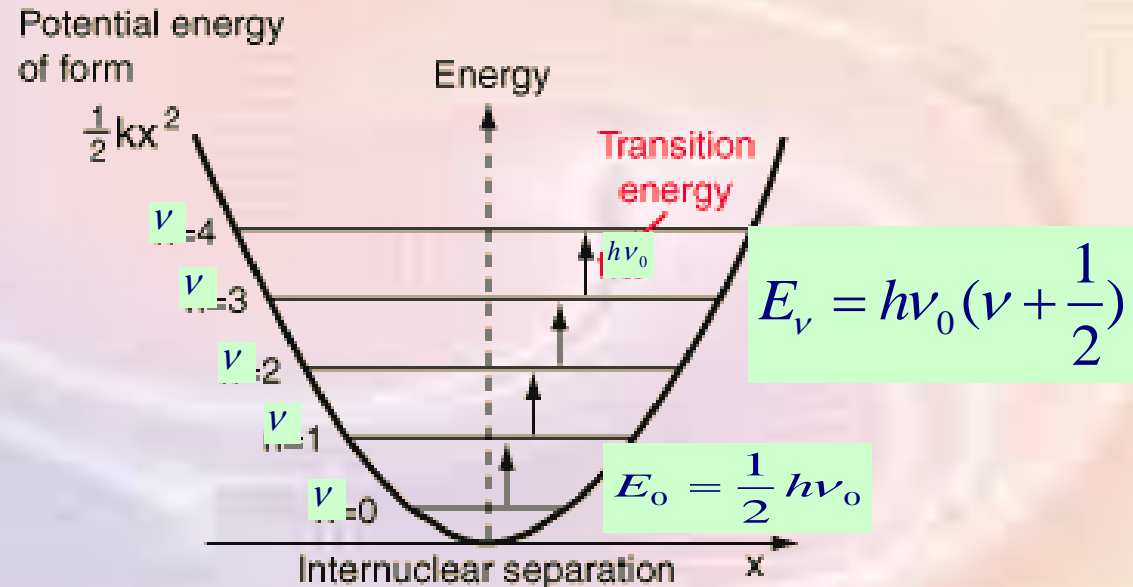
$$-\vec{p}.\vec{E}(t)$$

$\vec{p}$ the electric dipole moment of the molecule

$\vec{E}$ the electric field in the neighbourhood of the molecule.

For such a 'dipole transition' to occur, the dipole moment must change between the initial and final state.

Vibrational Spectra of Diatomic Molecules

The quantum-mechanical selection rule for a diatomic molecule states that in a dipole transition from one vibrational state to another, v can only increase or decrease by unity ($\Delta v = \pm 1$), corresponding to an energy change $\Delta E = h\nu_0$

Potential energy
of form

$\frac{1}{2}kx^2$

Energy

Transition energy

$h\nu_0$

$v = 4$

$v = 3$

$v = 2$

$v = 1$

$v = 0$

$$E_v = h\nu_0(v + \frac{1}{2})$$

$$E_0 = \frac{1}{2}h\nu_0$$

Internuclear separation   x

x=0 represents the equilibrium separation between the nuclei.

We now consider the rotation of the same diatomic molecule, ignoring vibrations so that $x = x_0$

$$I = m_r x_0^2 \qquad\qquad \hbar^2 J(J+1) \qquad\qquad \hbar^2 = h/2\pi$$

J is an integer, the rotational quantum number

$$E_j = \frac{1}{2I} J(J+1)\hbar^2 \quad , \quad J = 0,1,2,...$$

$$E_v = h\nu_0(v + \frac{1}{2}) \quad , \quad v = 0,1,2,...$$

Main underlying physical principles of molecular absorption/emission:

1) The origins of absorption/emission lie in exchanges of energy between gas molecules and electromagnetic field.
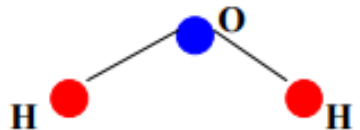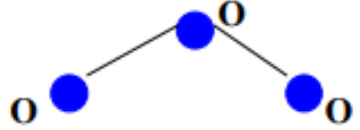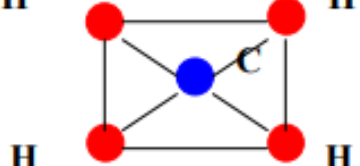
2) In general, total energy of a molecule can be given as:

$$E = E_{rot} + E_{vib} + E_{el} + E_{tr}$$

3) Radiative transitions of purely rotational energy require that a molecule possess a permanent electrical or magnetic dipole moment.

NOTE: A dipole is represented by centers of positive and negative charges q separated by a distance d: the dipole moment = q d

Atmospheric molecule structure and dipole moment status

Molecule	Structure	Permanent dipole moment	May acquire dipole moment
N_2	N ● ——— ● N	No	No
O_2	O ● — ● O	No	No
CO	C ● — ● O	Yes	Yes
CO_2	O ● — ● C ● O	No	Yes (in two vibrational modes)
N_2O	N ● — ● N ● O	Yes	Yes
H_2O	O with H and H	Yes	Yes
O_3	O with O and O	Yes	Yes
CH_4	C with 4 H	Yes*	Yes (in two vibrational modes)

*CH4 is an exemption, it has a spherical top configuration and hence no permanent electric dipole but it possesses a transitional dipole moment. Also, it can acquire the oscillating dipole moment in the vibrational modes.

NOTE: If charges are distributed symmetrically =>

no permanent dipole moment =>

no radiative activity in the far-infrared (i.e., no transitions in rotational energy)

Example: homonuclear diatomic molecules (N_2, O_2);

NOTE: CO, N_2O, H_2O and O_3 exhibit pure rotational spectra.
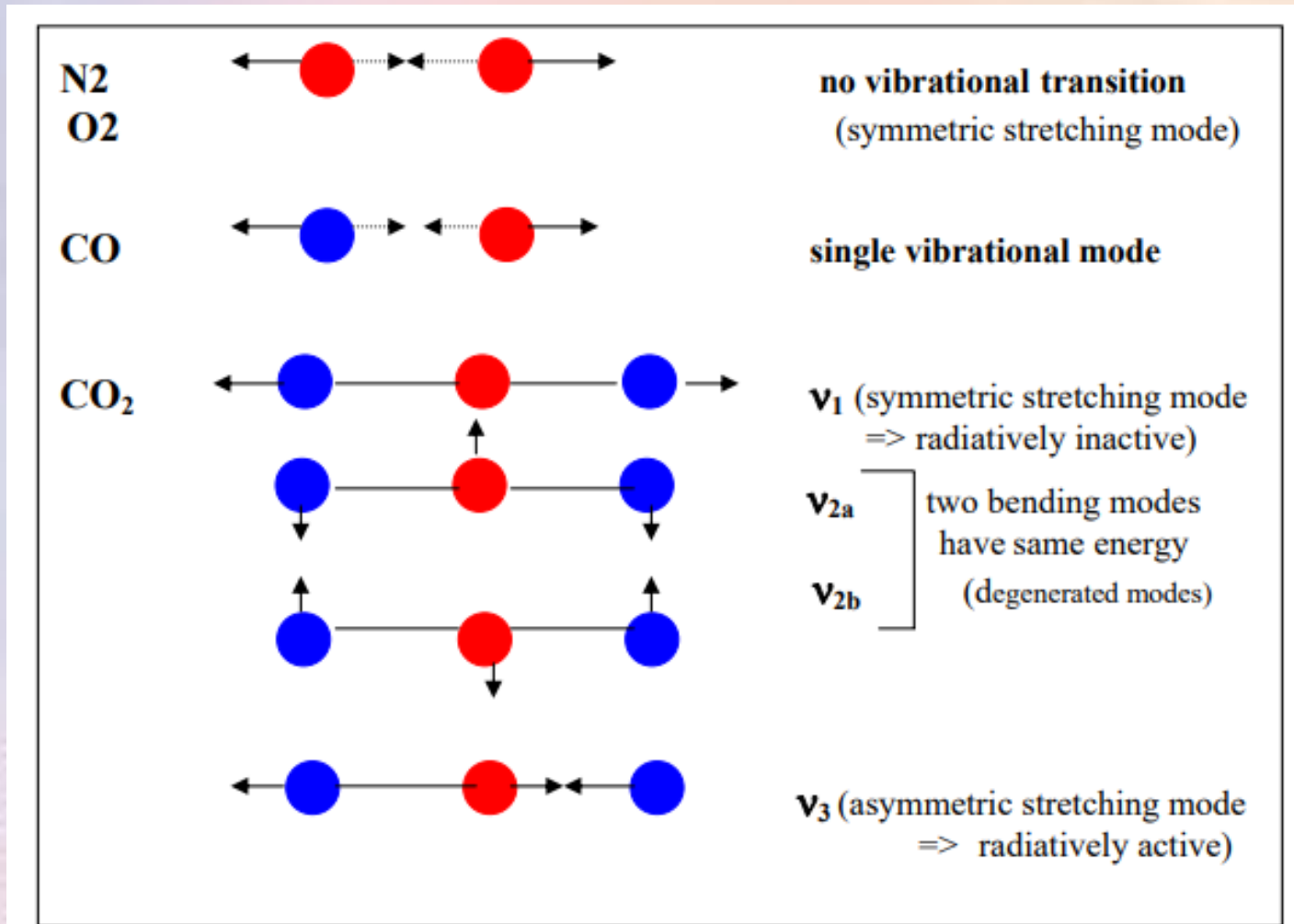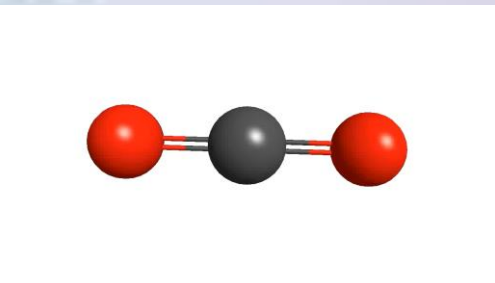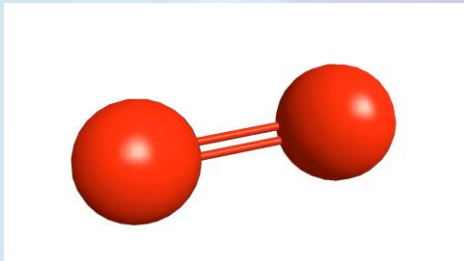

NOTE: CO_2 don't have permanent dipole moment =>

no pure rotational transitions, but can acquire the oscillating dipole moment in the vibrational modes =>
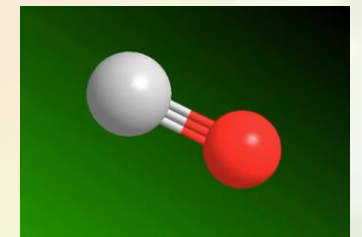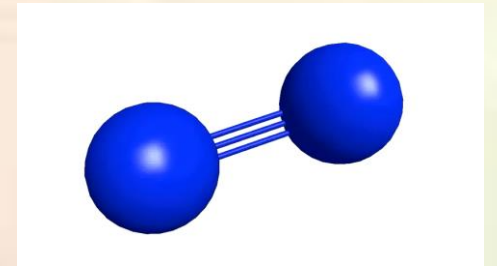
has vibration-rotation bands

4) Radiative transitions of vibrational energy require a change in the dipole moment (i.e., oscillating moment)

Vibrational modes of diatomic and triatomic atmospheric molecules.

Vibration of an oxygen molecule

Vibration of a nitrogen molecule

N2
O2
no vibrational transition
(symmetric stretching mode)

CO
single vibrational mode

CO_2
v_1 (symmetric stretching mode => radiatively inactive)

v_{2a} — two bending modes have same energy
v_{2b} — (degenerated modes)

v_3 (asymmetric stretching mode => radiatively active)

Vibration of a CO molecule

Water vapor (H_2O)

Most important IR absorber

Asymmetric top $\rightarrow$ Nonlinear, triatomic molecule has complex line structure, no simple pattern
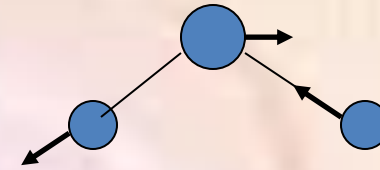3 vibrational fundamental modes
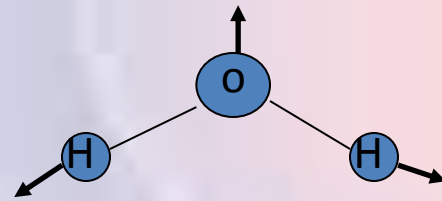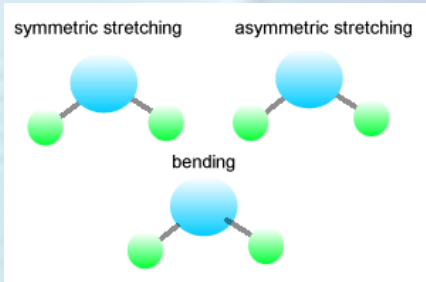
symmetric stretch
v_1 = 2.74 μm
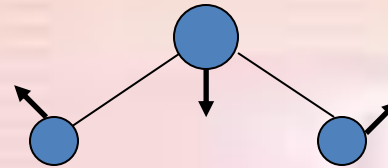
bend
v_2 = 6.25 μm

asymmetric stretch
v_3 = 2.66 μm

Higher order vibrational transitions ($\Delta v > 1$) give weak absorption bands at shorter wavelengths in the shortwave bands
^2H isotope (0.03% in atmosphere) and ^{18}O (0.2%) adds new (weak) lines to vibrational spectrum
3 rotational modes (J_1, J_2, J_3)
Overtones and combinations of rotational and vibrational transitions lead to several more weak absorption bands in the NIR
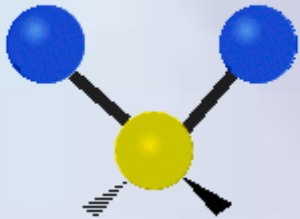
Vibrational modes are not limited to stretching and bending. Below, six types of molecular vibrational modes are shown.
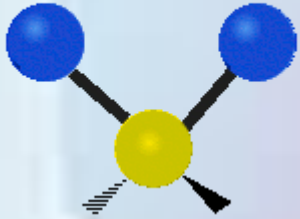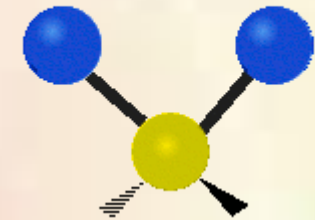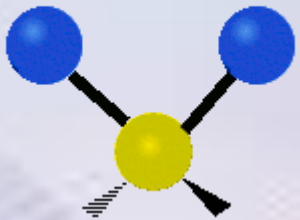

Scissoring or bending
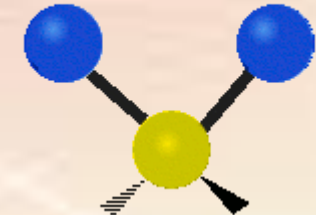
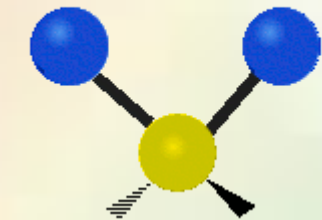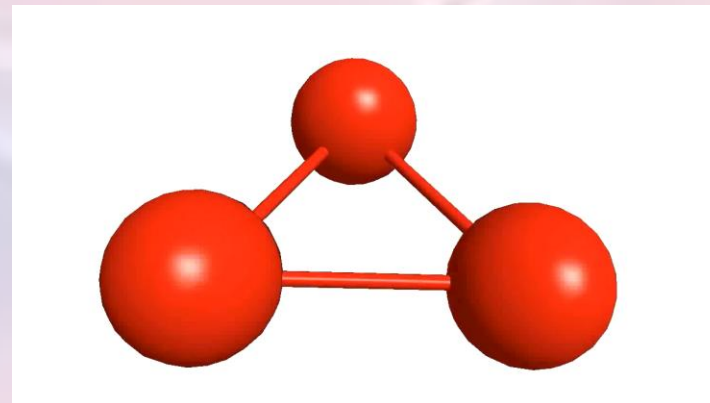Asymmetric Stretch

Symmetric Stretch

Ozone = O_3

Twisting

Wagging

Rocking

NOTE: Homonuclear diatomic molecules N_2 and O_2 don't have neither rotational nor vibrational transitions (because of their symmetrical structures) =>

no radiative activity in the infrared. But these molecules become radiatively active in the UV.

NOTE: The number of independent vibrational modes (called normal modes) of a molecule with N>2 atoms are 3N-6 for non-linear molecules and 3N-5 for a linear molecule.

NOTE: Both H_2O and O_3 have three normal band v_1, v_2 and v_3: all are optically active.

NOTE: CH_4 has nine normal modes but only v_3 and v_4 are active in the IR.
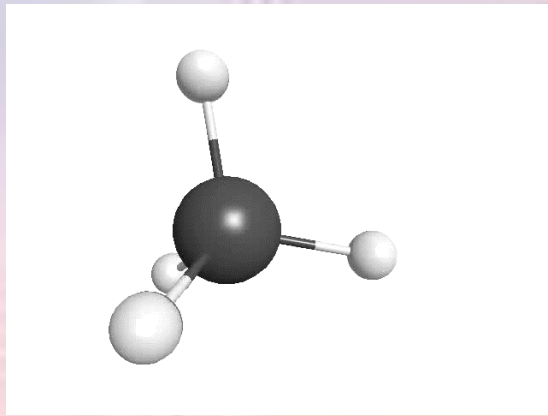
Molecular absorption processes

Electronic transitions

UV and visible wavelengths

$\sim 10^{-18}$ J

Molecular vibrations

Thermal infrared wavelengths

Increasing energy

Molecular rotations

Microwave and far-IR wavelengths
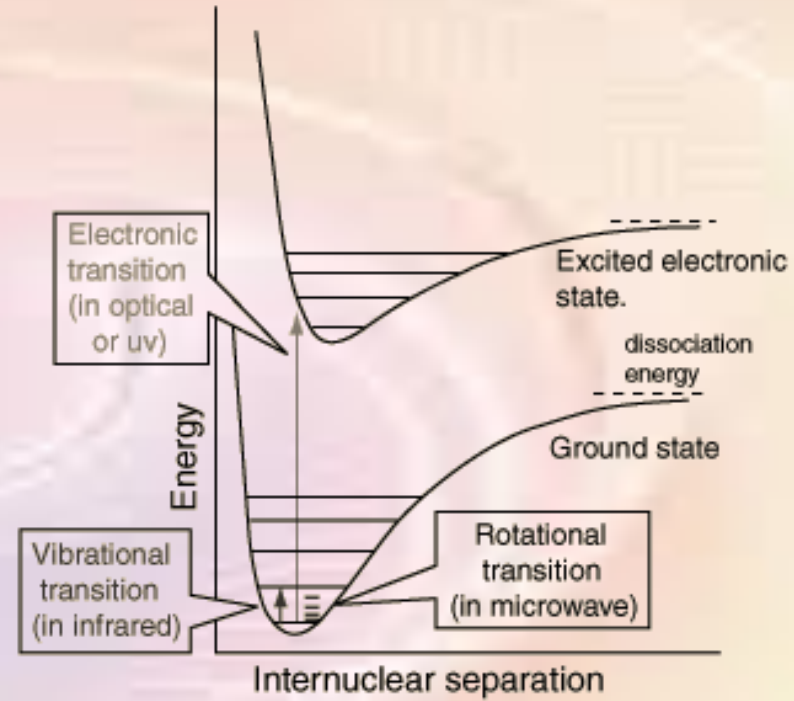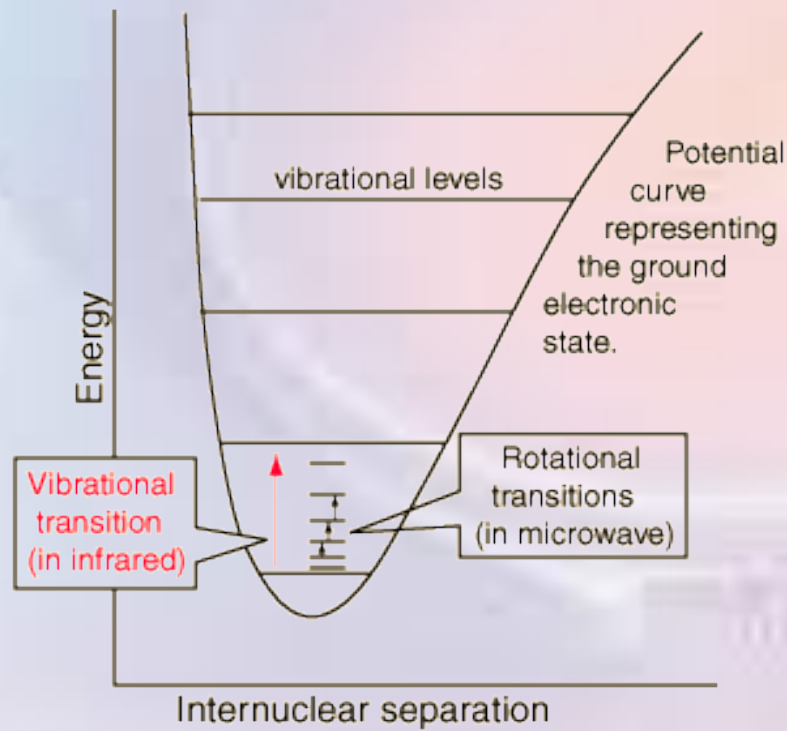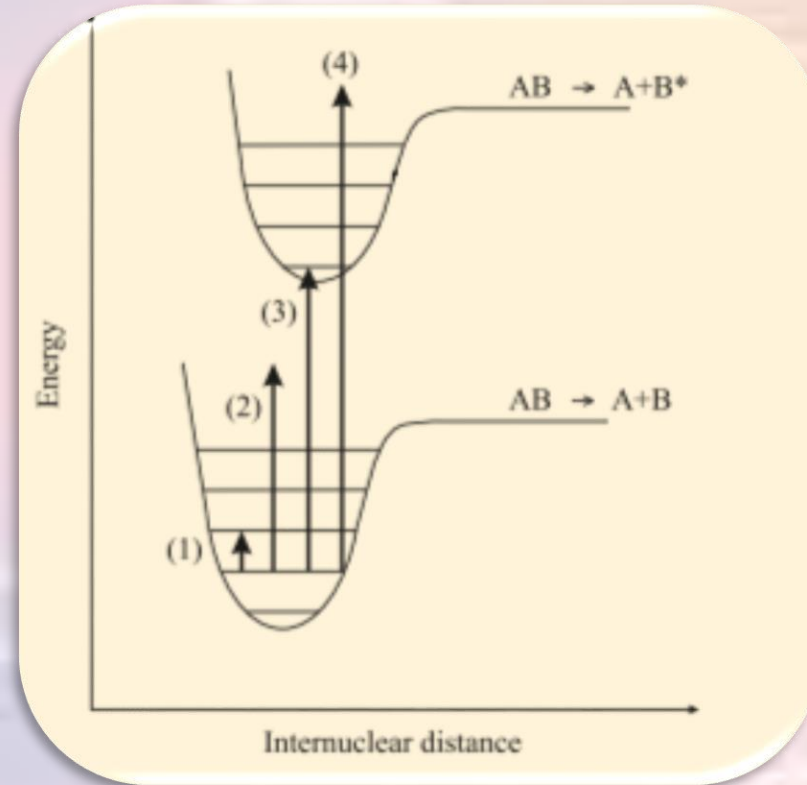
$\sim 10^{-23}$ J

Each of these processes is quantized

Translational kinetic energy of molecules is unquantized

Molecular Spectra

Schematic energy diagram for a diatomic molecule

$$E_\nu = h\nu_0(\nu + \frac{1}{2}) \quad , \quad \nu = 0,1,2,...$$