Types of molecular energies and Born-Oppenheimer approximation

Molecules possess four different kinds of energies.

1) Translational energy (E_t) is due to translational motion of the molecule (change of centre of gravity as a result of motion)
2) Rotational energy (E_r) is due to rotation of the molecule about an axis perpendicular to the internuclear axis.
3) Vibrational energy (E_v) is due to the to and fro motion of the nuclei of the molecule without any change in the position of centre of gravity of the molecule.
4) Electronic energy (E_e) is due to absorption of energy by the electrons resulting in the transition from ground state to excited state.

According to Born-Oppenheimer approximation, the total energy of a molecule is the sum of translational rotational and, vibrational and electronic energies. i.e.

$$E = E_t + E_r + E_v + E_e.$$

It has been found that E_t is negligible as compared to E_r, E_v and E_e. Hence Born Oppenheimer approximation can be written as

$$E = E_r + E_v + E_e.$$

Remarks

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Degree of freedom or Molecular motions.

The motion of atoms or molecules is described in terms of degree of freedom. When a gas molecule is heated, it brings about three types of motions.

1) Translational motion
2) Rotational motion
3) Vibrational motion.

For a molecule containing 'n' atomic nuclei, there will be '3n' degree of freedom for all the nuclear masses in the molecule, because each mass point required three co-ordinates to specify the position in space.

Translational degree of freedom.

It refers to translational motion of the molecule in space as a whole. Mono and polyatomic molecules possess three translational degree of freedom in x, y and z axes.

Atoms possess only translational degree of freedom without any rotational and vibrational degree of freedom.

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Rotational degree of freedom-

It refers to rotational motion of the molecule about its axis.

Linear molecules such as H_2, N_2, O_2 CO, HBr, CO_2, C_2H_2 etc possess only two independent rotational degree of freedom about the two mutually perpendicular axes which are perpendicular to the ~~mutual axi~~ molecular axis.

Non-linear molecules such as H_2O CH_4, C_6H_6 etc possess three independent rotational degree of freedom.

* ~~Solid possess only vibrational degree~~

Vibrational degree of freedom.

It is to and fro motion of the nuclei of various constituent atoms with respect to one another. During vibrational motion the bond behaves like spring and the molecule exhibits a simple harmonic motion (S.H.M). Modes of vibration may be symmetric or asymmetric while bending may be in plane or out of plane.

For diatomic molecules (H_2, O_2, CO, HCl) and linear poly-atomic molecules (CO_2, C_2H_2)

no. of vibrational degree of freedom = $3n-5$

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Q-

For nonlinear polyatomic molecules (H_2O, CH_4, C_6H_6 etc), no. of vibrational degree of freedom = $3n-6$.

Q- ~~Find the~~

* Solids possess only vibrational degree of freedom. The translational and rotational ~~mo~~ motions in solid are converted into vibrational motion, where the atoms in lattice vibrates about their equilibrium positions.