Stark Effect in microwave spectra:-

The splitting of molecular rotational energy levels in the presence of the external electric field E is called Stark Effect. The shift of rotational frequency, $\Delta\nu$, for a linear gaseous molecule in the Stark effect is given by

$$\Delta\nu \propto (\mu E)^2 \quad \text{——— (1)}$$

where $\mu \rightarrow$ electric dipole moment of the molecule

If E and $\Delta\nu$ are known, μ can easily be determined.

The Stark effect is extremely useful for determining the dipole moment of gaseous molecule.

Other Applications of Microwave spectroscopy:-

The two most important applications of microwave spectroscopy are the study of internal rotation and inversion spectrum of NH_3.

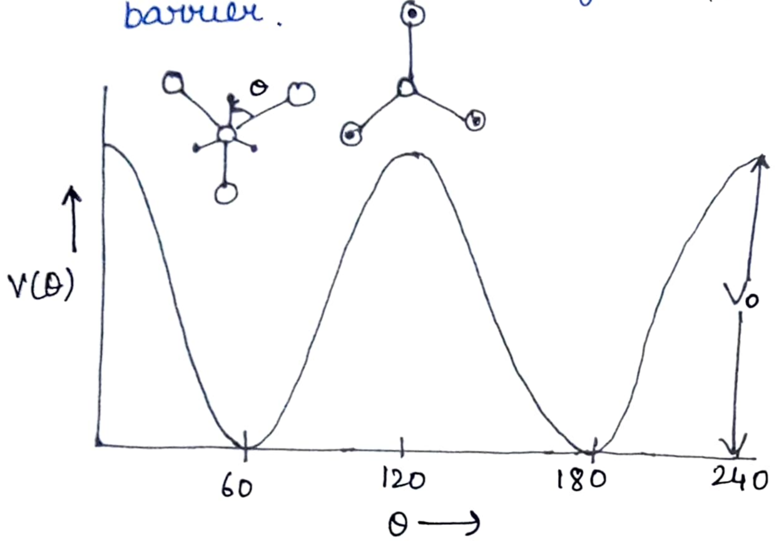
(1) Internal Rotation : If a part of molecule can rotate about a single bond then the internal potential energy of molecule depends upon the orientation of this part with respect to rest of the molecule.

Consider F_3C-CH_3 (1,1,1 - trifluoroethane) molecule. The variation of the potential energy barriers, free rotation takes place.

It rotates about C−C single bond as a function of angle θ is given by

$$V(\theta) = V_0 (1 - \cos 3\theta)$$

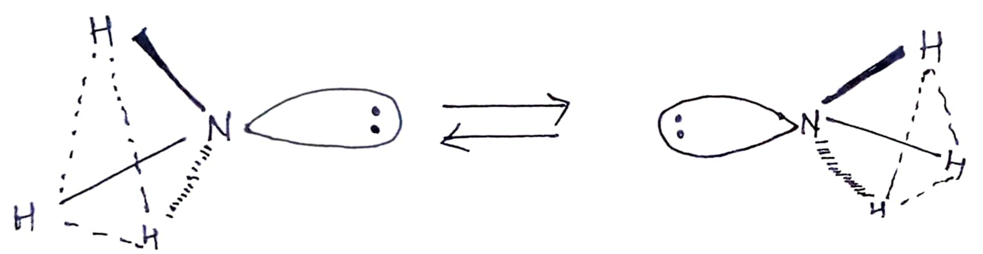
where V_0 is the height of the potential energy barrier.



Potential energy as function of θ in an internal rotation

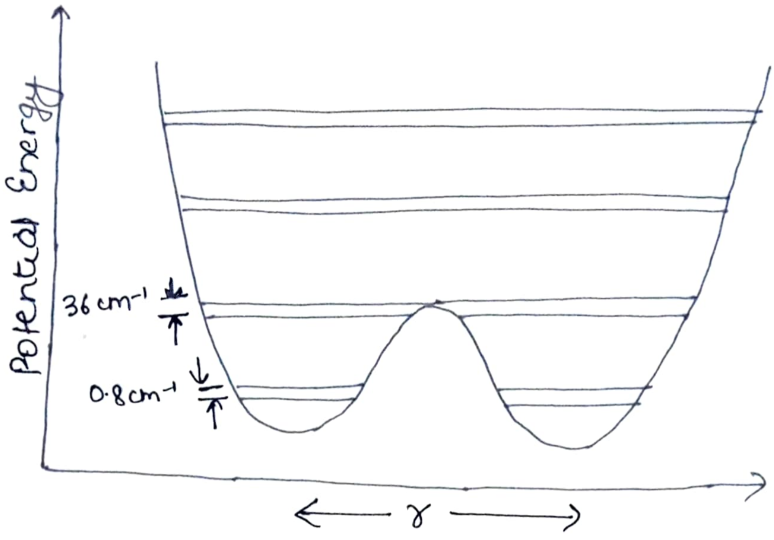
For low potential energy barriers, free rotation takes place. The potential energy barriers of a number of compounds have been determined using microwave spectroscopy. The origin of these barriers still remain obscure.

2. Inversion spectrum of NH_3:-



The inversion of NH_3 molecule.

Consider the inversion of the N atom through the plane of the three H atoms.



- The new configuration is the mirror image of the original configuration; it cannot be obtained by the rotation of the molecule.

- The two configurations have the same energy. A plot of the potential energy curve shows two minima with a hump in between.

- The height of the hump that is potential energy barrier, represents the restrictions to inversion. For NH_3 the value is about 25 kJ mol^{-1}.

- For first two vibrational levels of molecules are impossible to invert. Quantum mechanically it can tunnel through the barrier. The inversion is vibrational motion. Since it is hindered it is observed in microwave region. The splitting of vibrational region is due to resonance interaction. The inversion doubling lead to split the energy levels.

Assignment for the Students

→ Chapter is complete and here are the questions you are requested to solve on paper and mail the scanned sheets on

ankitaojha26@gmail.com.

Q1. Calculate the energy in joules per quantum, joules per mole, and in eV (electron-volts) of photon of wavelength 300 nm.

Q2. Calculate the frequency (in cm^{-1}) and wavelength (in cm) of the rotational transition ($J = 0 \rightarrow 1$) for $D^{35}Cl$.

Q3. Write down selection rules for rotational spectroscopy.

Q4. Point out rotational spectra active ~~of~~ molecule.

H_2, SO_2, CCl_4, $CHCl_3$, Cl_2, HCN, $H_2C=CH_2$.

Deadline of submission:- 14th August, 2020.