Vibrational spectroscopy

Diatomic molecules:

The vibrational energy levels E_v of a diatomic molecule, treated by the harmonic oscillator approximation, are given by

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

$v \rightarrow$ vibrational quantum number 0, 1, 2 .....

The classical vibrational frequency ν is related to the reduced mass ~~$\mu = [m_1/m_2$~~

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

and force constant can be regarded as measure of strength of the spring in the ball-and-spring model for molecular vibration

Force constant k

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \quad — ②$$

k increases with the bond order

$$\frac{E_v}{hc} = G(v) = \omega\left(v + \frac{1}{2}\right) \quad — ③$$

$\omega \rightarrow$ vibration wavenumber

Infra Red Spectra :

The transition moment for a transition between lower and upper states with vibrational wave functions ψ_v'' and ψ_v' respectively is given by

$$R_v = \int \psi_v' \, \mu \, \psi_v'' \, dx \quad — ①$$

$x \rightarrow (r - r_e)$ displacement of the internuclear distance from the equilibrium.

$\mu \rightarrow$ dipole moment

(μ is zero for homonuclear diatomic molecule)

$R_v = 0$ for " " "

This equation can be expressed as Taylor series expansion

$$\mu = \mu_e + \left(\frac{d\mu}{dx}\right)_e x + \frac{1}{2!}\left(\frac{\partial^2 \mu}{dx^2}\right)_e x^2 + \cdots\cdots$$

② e → refers to equilibrium configuration

$$R_v = \mu_e \int \psi_v'^* \, \psi_v'' \, dx + \left(\frac{d\mu}{dx}\right)_e \int \psi_v'^* x \, \psi_v'' \, dx + \cdots \quad — ③$$

ψ_v' and ψ_v'' are eigenfunctions of the same Hamiltonian, they are orthogonal which means that, when $v' \neq v''$

$$\int \psi_v^* \, \psi_v'' \, dx = 0 \quad — ④$$

$$R_v = \left(\frac{d\mu}{dx}\right)_e \int \psi_v'^* \, x \, \psi_v'' \, dx + \cdots\cdots \quad — ⑤$$

The first term in this series is non-zero only if

$$\Delta v = \pm 1 \quad — ⑥$$

This equation gives the vibrational selection rule. Since Δv refers to v(upper) − v(lower) the selection rule is effectively

$$\Delta v = \cancel{\pm 1} \;\; +1$$

In the harmonic oscillator where all level spacings are equal, all transitions obeying this selection rule are coincident at a wave number ω.

The population N_v of vth vibrational level is related to N_0 by the Boltzmann factor

$$\frac{N_v}{N_0} = \exp\left(-\frac{E_v}{kT}\right) \quad \text{—} ⑦$$

The vibrational transition observed in gas phase refers to band of the spectrum.

All bands with $v'' \neq 0$ are called hot bands because the population of lower levels of such transitions and their intensities increase with temperature.