Chapter 5 – MOLECULAR SPECTROSCOPY

The Schrödinger equation for H_2^+

$$\left(T_{nuc} + H_{el} + \frac{e^2}{R}\right)\Psi(\vec{R},\vec{r}) = E\Psi(\vec{R},\vec{r})$$

When the Born-Oppenheimer approximation is applied, the electronic motion can be separated from the nuclear motion;

$$\left[H_{el} + \frac{e^2}{R}\right]\psi_{el}(R,\vec{r}) = E(R)\psi_{el}(R,\vec{r})$$

where

$$H_{el} = -\frac{\hbar^2}{2m}\nabla_e^2(\vec{r}) - e^2\left(\frac{1}{r_{Ae}} + \frac{1}{r_{Be}}\right)$$

Once ψ_{el} and E(R) have been determined as a function of R, the nuclear motion may be treated;

$$\left[T_{nuc} + E(R)\right]\psi_{nuc}(\vec{R}) = E\psi_{nuc}(\vec{R})$$

Transitions in molecules

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

$$1 \text{ wavenumber} = 1 \text{ cm}^{-1}$$

Electronic:	$\Delta E \sim 5$ eV $\lambda \sim 250$ nm $\bar{\nu} \sim 40{,}000$ cm^{-1}	UV-visible
Vibrational:	$\Delta E \sim 0.2$ eV $\lambda \sim 6.2$ μm $\bar{\nu} \sim 1600$ cm^{-1}	Infra-red
Rotational:	$\Delta E \sim 4\times10^{-4}$ eV $\lambda \sim 3$ mm $\bar{\nu} \sim 3$ cm^{-1}	Microwave