

# Summary for C2 Spectroscopy

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## 1.2 Rotational Quantisation

The rotational energy of a molecule is quantised by the **rotational quantum number**  $J$ :

$$E_{\text{rot}} = E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad (2)$$

$$\varepsilon_J = \frac{E_J}{hc} = BJ(J+1) \quad (3)$$

$$B = \frac{h}{8\pi^2 c I} \quad (4)$$

where  $B$  is the rotational constant and is unique for different molecules of different inertia.

Rotational transition obeys the selection rule of:

$$\Delta J = \pm 1$$

## 1 Rotational Spectroscopy

Rotational spectroscopy provides information down to the molecular level, including bond length and isotopic distribution, as well as different conformers of a molecule, granted they have unique moments of inertia. Note that rotational spectra can be obtained only for molecules which have a dipole.

### 1.1 Diatomic Molecules

The moment of inertial at the centre of mass between two atoms of mass  $m_1$  and  $m_2$ , which has a bond length of  $r_0$  is given by:

$$I = \mu r_0^2 \quad (1)$$
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The intensity of each peaks relates to how many molecules are in the corresponding rotational mode, the ration between two levels are governed by the Boltzmann distribution:

$$\frac{N_J}{N_0} = (2J+1) \exp\left(-\frac{2hcB(J+1)}{k_B T}\right) \quad (5)$$

where  $N_J$  is the number of molecules in the rotational energy level  $J$ , and  $k_B$  is the Boltzmann factor.

Through setting the derivative of the above equation to zero,  $J_{\text{max}}$  can be found:

$$J_{\text{max}} = \sqrt{\frac{k_B T}{2hcB}} - \frac{1}{2} \quad (6)$$

note the  $T$  dependence of  $J_{\text{max}}$ , which arises from the fact that temperature may provide enough kinetic energy for some molecules to occupy the higher state.

## 2 Vibrational Spectroscopy

### 2.1 Harmonic Oscillator

A reasonable approximation of molecular vibrations of diatomic molecules is to envisage them as simple harmonic oscillators which are comprised of two bodies of mass  $m_1$  and  $m_2$  with a spring of force constant  $k$  coupling them. The potential energy, from Hooke's Law, for the system may be given:

$$E = \frac{1}{2}k(r - r_{\text{eq}})^2 \quad (7)$$

By solving the SHM ODE, the oscillation frequency for a diatomic molecule with reduced mass  $\mu$  is given:

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (8)$$

$$\bar{\omega} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (9)$$

The energy is quantised by the vibrational quantum number  $v$  in increments of  $h\omega$ :

$$E = (v + \frac{1}{2})h\omega \quad (10)$$

$$\varepsilon = (v + \frac{1}{2})\bar{\omega} \quad (11)$$

The zero point energy associated with this system can be found by setting  $v = 0$ :

$$\varepsilon_0 = \frac{1}{2}\bar{\omega} \quad (12)$$

Similarly to rotational spectroscopy, vibrational transitions follow the selection rule of:

$$\Delta v = \pm 1$$

### 2.2 Population of Vibrational Energy Levels

Once again, the ratio of the population between two vibrational levels can be found using the Boltzmann distribution:

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{g_{\text{upper}}}{g_{\text{lower}}} \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (13)$$

the  $g$  value indicate the number of modes that are degenerate for a particular vibrational quantum number, and for vibrational spectroscopy,  $g_{\text{lower}} = g_{\text{upper}} = 1$

Transition	Name	$\Delta\varepsilon$
$v = 0 \rightarrow 1$ (High)	Fundamental	$\bar{\omega}_e(1 - 2x_e)$
$v = 0 \rightarrow 2$ (Low)	First Overtone	$2\bar{\omega}_e(1 - 3x_e)$
$v = 0 \rightarrow 3$ (Negligible)	Second Overtone	$3\bar{\omega}_e(1 - 4x_e)$
$v = 1 \rightarrow 2$	Hot Band	$\bar{\omega}_e(1 - 4x_e)$

### 2.3 Energies of Vibration Transitions

The energy between levels  $v$  and  $v + 1$  is:

$$\varepsilon_{v+1} - \varepsilon_v = \bar{\omega} \quad (14)$$

**n.b.** The vibrational transition in a harmonic oscillator is equal to the oscillation frequency.

### 2.4 Polyatomic Molecules

The number of degenerate modes increase based on the degrees of freedom:

$$\text{Linear: } 3N - 5$$

$$\text{Non-Linear: } 3N - 6$$

It is important to note that symmetric stretching, which doesn't result in the change in dipole moment will not absorb infrared and thus not visible on the spectrum.

The frequency and the energy level can be calculated for each mode. using the above equations for  $\omega$  and  $\varepsilon$ .

### 2.5 Anharmonic Oscillator

Correcting the anharmonicity of the oscillators (applying the pair potential). The energy of a vibrational level  $v$  is given as follows:

$$\varepsilon = (v + \frac{1}{2})\bar{\omega}_e - (v + \frac{1}{2})\bar{\omega}_e x_e \quad (15)$$

The zero point energy is also adjusted as follows:

$$\varepsilon_0 = \frac{1}{2}\bar{\omega}_e(1 - \frac{1}{2}x_e) \quad (16)$$

The three transitions of importance and their transition energy is outlined below:

## 3 Electronic Spectroscopy

The total energy of a transition is the sum of the individual electronic, vibrational, and rotational energy:

$$E = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} \quad (17)$$

These energies are completely independent of each other.

The energies can be quantified generally by means of the Rydberg equation for hydrogen atom:

$$\bar{\nu} = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad (18)$$

The energy for an electron in the hydrogen atom with principal quantum number  $n$  is:

$$E_n = -\frac{hcR}{n^2} \quad (19)$$

$$R = \frac{m_e e^4}{8h^3 \epsilon_0^2} \quad (20)$$