

Energy, Spectroscopy and Solid State Chemistry

§1 SPECTROSCOPY

§1.1 INTRODUCTION

28/10/20 — WEEK 1

§1.1.1 The Born-Oppenheimer Approximation. The assumption that the electronic motion and the nuclear motion in molecules can be separated, due to the difference in mass between the electron and the nuclei.

$$\Psi_{tot} = \psi_{el}\psi_{nuc}$$

Where the resulting total energy is a simple sum.

$$E_{tot} = E_{el} + E_{nuc}$$

It is very convinient, although slightly less rigorous, to factorise Ψ_{nuc} into vibrational and rotational parts. Translational energy is unquantised and so useless for spectroscopy.

$$\Psi_{tot} = \psi_{el}\psi_{vib}\psi_{rot}$$

$$E_{tot} = E_{el} + E_{vib} + E_{rot}$$

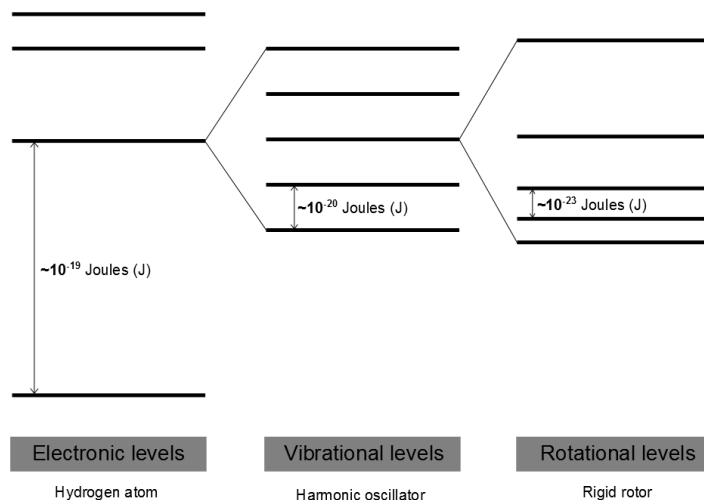


Figure 1: Transitions of different energy levels

$\Delta E \approx$	$10^4 - 10^5 \text{ cm}^{-1}$	$10^2 - 10^3 \text{ cm}^{-1}$	$0.1 - 10 \text{ cm}^{-1}$
Transitions at $\Delta \lambda \approx$	$500 - 100 \text{ nm}$	$100 - 2 \mu\text{m}$	$10 \text{ cm} - 1 \text{ mm}$
Light range	Vis-UV	Infrared	Microwave

Every electronic energy level contains multiple vibrational levels which contains multiple rotational levels. More on this to come.

§1.1.2 **The Boltzmann Law.** At thermal equilibrium the relative population of the i^{th} energy level is given by:

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-\frac{\Delta E_i}{k_B T}}$$

- g_i is the degeneracy of the i th level (the number of states with the same energy)
- ΔE_i is the energy difference between the lowest (ground) and i th levels
- k_B is the Boltzmann constant
- T is the temperature (in Kelvin, obviously)

§§ Degeneracy is when there are multiple energy levels with the same energy. Think back to a Hydrogen atom, only n determines its energy, yet it has different states which are determined by l and m_l , thus it has degenerate states. When $n = 2$ and $l = 0, 1$ there are $(2l + 1)$ states for m_l , each with the same energy. Thus the degeneracy of the $n = 2$ energy level is $(2(0)+1)+(2(1)+1) = 4$.

Example: Find the relative populations of the lowest two energy levels for each in a CO molecule at 298K if

1. The two lowest rotational levels are 3.382 cm^{-1} apart with $g_1 = 3$ and $g_0 = 1$
2. The two lowest vibrational levels are 1743 cm^{-1} apart each with a degeneracy of 1
3. The two lowest electronic levels are 48690 cm^{-1} apart with $g_1 = 6$ and $g_0 = 1$

Since we are given the energy spacings in cm^{-1} we should convert our $k_B T$ to cm^{-1} by using $\frac{E}{hc} = \nu$ so $k_B T = 207 \text{ cm}^{-1}$. From here the calculations are relatively simple.

1. $\frac{3}{1} e^{-\frac{3.382}{207}} = 2.95$
2. $\frac{1}{1} e^{-\frac{1743}{207}} = 2.24 \times 10^{-4}$
3. $\frac{6}{1} e^{-\frac{48690}{207}} = 4.2 \times 10^{-102}$ so small it might as well be 0

What does this tell us? At normal temperatures there is enough energy to promote to higher rotational energy levels. Since $k_B T = 207 \text{ cm}^{-1}$ and rotational levels are separated by only 10 cm^{-1} this should be obvious. It is also clear that there is nowhere near enough energy at normal temperatures for there to be much vibrational transition, and not enough energy for there to be any electronic transitions at all.