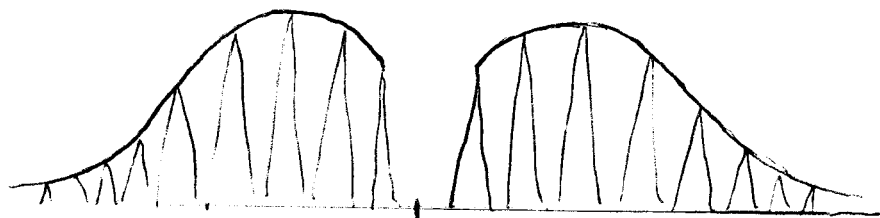


Statistical Mechanics

For the rotationally resolved $n=0 \rightarrow 1$ vibrational excitation in HCl that we looked at previously, what explains the intensity (height) of the peaks?



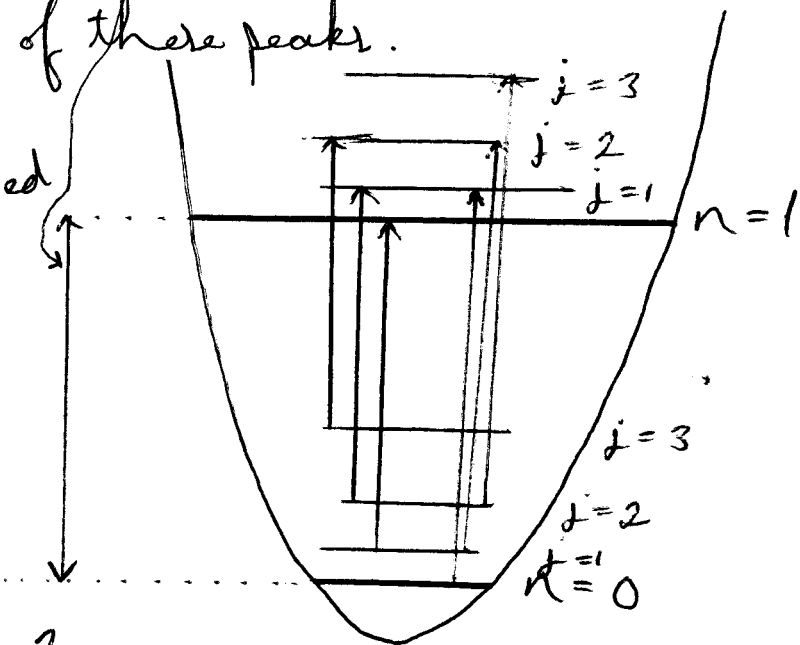
Look again at the origin of these peaks.

One factor that determines the peak intensity is to ask:

"What fraction of molecules are in the $n=0, j=1$ state

compared to the $n=0, j=2$ state before excitation (ie before any photons are absorbed or emitted)?

not observed



If the population of the $n=0, j=2$ state was zero for some reason, how would this affect the spectrum?

- photons must have correct frequency
- transition must be allowed
- population

(71)

The observed spectrum comes from how many HCl molecules?
1, 10, 100, 1000? How about $\sim N_A$.

With this many molecules involved, we can invoke some statistical methods to understand and predict the peak intensities.

Fundamental Postulate of Statistical Mechanics

Given an isolated system at equilibrium, it is found with equal probability in each of its accessible microstates, (consistent with what is known about the system eg its total energy)

↳ set of quantum numbers

Example: 4 independent, identical harmonic oscillators.

For simplicity, redefine the energy of one harmonic oscillator as $E_n = \frac{(n+1/2)h\nu}{h\nu} - 1/2$

then we have

n	E_n
0	0
1	1
2	2
3	3
4	4
⋮	⋮

Total energy is $E_{tot} = 5$.

(72)

What are the possible microstates? Use the fundamental postulate of stat. mech.

<u>Energies of individual H.O.</u>	<u># ways</u>
5, 0, 0, 0	4
4, 1, 0, 0	12
3, 2, 0, 0	12
3, 1, 1, 0	12
2, 2, 1, 0	12
2, 1, 1, 1	4

Total # of arrangements = 56

What is the probability that one of the H.O. has an energy of 0?

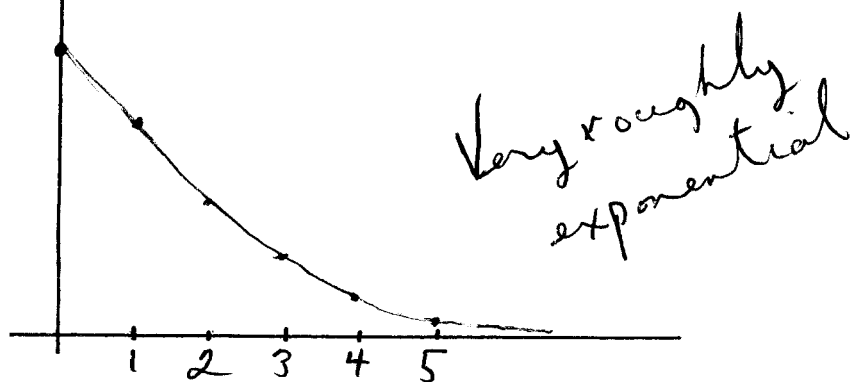
$$P(0) = \frac{3}{4} \cdot \frac{4}{56} + \frac{1}{2} \cdot \frac{12}{56} + \frac{1}{2} \cdot \frac{12}{56} + \frac{1}{4} \cdot \frac{12}{56} + \frac{1}{4} \cdot \frac{12}{56} = \frac{21}{56}$$

Doing this for the rest gives

$$\begin{aligned} P(0) &= \frac{21}{56} = 0.375 \\ P(1) &= \frac{15}{56} = 0.268 \\ P(2) &= \frac{10}{56} = 0.179 \\ P(3) &= \frac{6}{56} = 0.107 \\ P(4) &= \frac{3}{56} = 0.054 \\ P(5) &= \frac{1}{56} = 0.018 \end{aligned}$$

Plot this.

(73)



What have we done? We have taken a given macroscopic state ($E_{tot} = 5$) and worked out the microscopic energy distribution: the prob. that a molecule has energy E .

The full answer, for a system in thermal equilibrium at a temperature T , is $e^{-E/k_B T}$

It is traditional to define $\beta = 1/k_B T$, giving $e^{-\beta E}$

But, just like in quantum mechanics, it only makes sense to talk about probabilities if the probability distribution is normalized.

The normalization constant, which we will work out for a few cases, is given a special name in statistical mechanics: the partition function and it is given a symbol: q .

Let us work things out for the rigid rotor and the harmonic oscillator models.

Harmonic Oscillator

En = (n + 1/2) h w, n = 0, 1, 2, ...

q = sum from n=0 to infinity of e^-beta(n + 1/2) h w

Geometric series Sum = first term / (1 - ratio)

q = e^-beta h w / 2 / (1 - e^-beta h w)

The probability of finding a molecule in level n is thus Pn = e^-beta h w (n + 1/2) / q

this is the fraction of molecules in level n.

Only depends on T, k, mu

Table 18.3 McQuarrie/Simon : excited state populations

Table with 3 columns: Gas, Pn>0 (T=300K), Pn>0 (T=1000K). Rows include H2, HCl, N2, CO, Cl2, I2 with numerical values and percentages.

Fig. from Atkins:

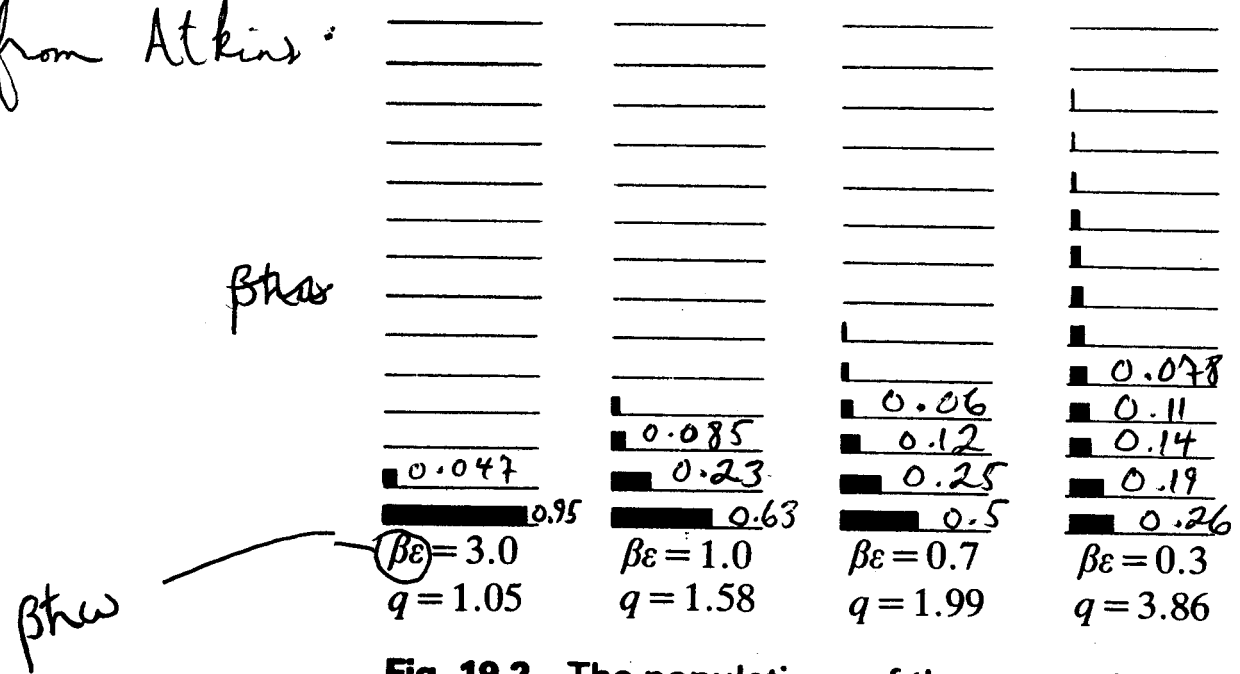


Fig. 19.2 The populations of the energy levels of the system shown in Fig. 19.1 at different temperatures, and the corresponding values of the partition function calculated using eqn 9. Note that $\beta = 1/kT$.

Rigid Rotor

$$E_l = \frac{\hbar^2 l(l+1)}{2I} = \frac{\hbar^2 l(l+1)}{2I}$$

The degeneracy of level l is $2l+1$
 (from the m_l quantum number)

Due to this degeneracy, $q = \sum_{l=0}^{\infty} (2l+1) e^{-\beta \hbar^2 l(l+1) / 2I}$

define $\theta = \frac{\hbar^2}{2Ik_B}$. θ has units of temperature.

$$q = \sum_{l=0}^{\infty} (2l+1) e^{-\theta(l)(l+1) / T} \quad \text{where we used } \beta = \frac{1}{k_B T}$$

We cannot perform the sum, but we can use an integral approximation.

$$q \approx \int_0^{\infty} (2l+1)e^{-\theta l(l+1)/T} dl$$

Let $x = l(l+1)$, $dx = (2l+1) dl$

$$q = \int_0^{\infty} e^{-\theta x/T} dx = \frac{T}{\theta} = \frac{8\pi^2 I k_B T}{h^2} = \frac{2I}{h^2 \beta}$$

Note: the integral approx. is only good if $\theta \ll T$.

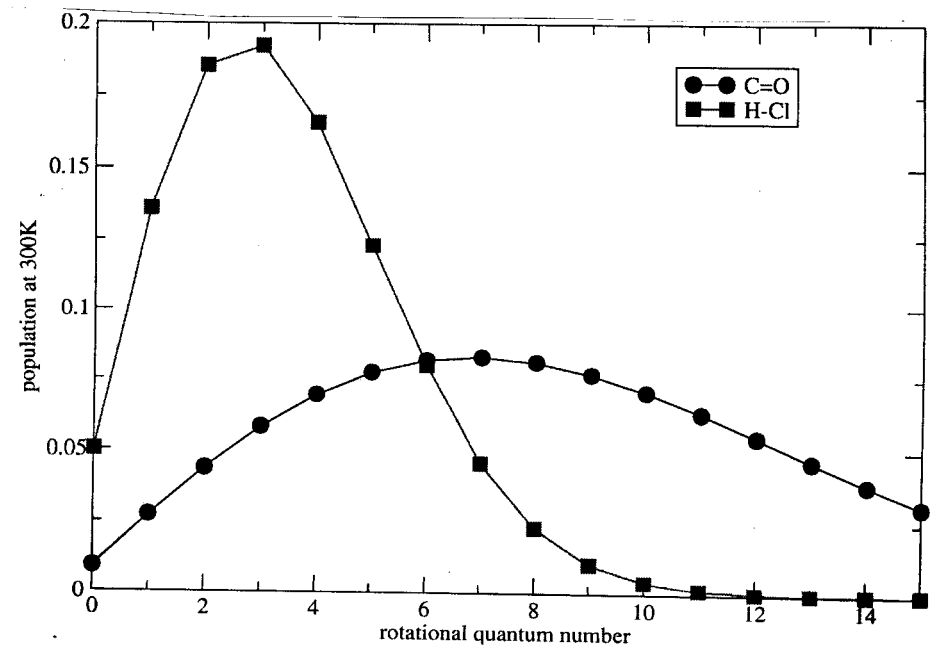
The fraction of molecules in level l is

$$P_l = \frac{(2l+1)e^{-\theta l(l+1)/T}}{q} = \frac{\theta}{T} (2l+1)e^{-\theta l(l+1)/T}$$

For CO, $\theta = 2.77 \text{ K}$, so at $T = 300 \text{ K}$ we have

$$\theta/T = 0.00923 \text{ so } P_l = (0.009)(2l+1)e^{-0.009 l(l+1)}$$

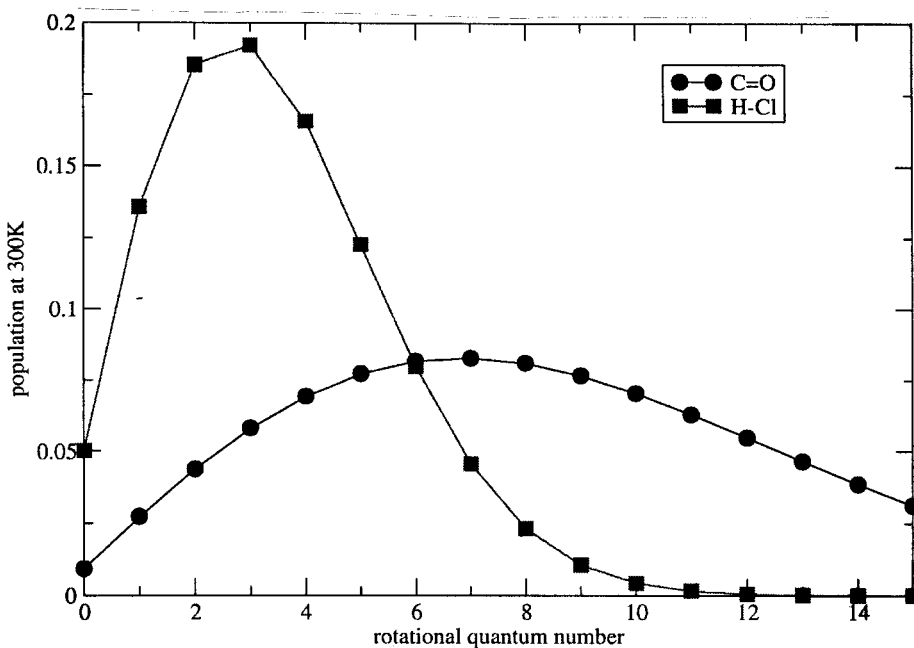
l	P_l
0	0.009
1	0.027
2	0.044
3	0.058
5	0.077
7	0.083
9	0.076
11	0.063



For HCl, $\theta = 15.02$ so at $T = 300\text{K}$,

$$\theta/T = 0.05 \quad \text{so} \quad P_l = 0.05 (2l+1) e^{-0.05 l(l+1)}$$

j	P_j
0	0.05
1	0.14
2	0.19
3	0.19
4	0.17
5	0.12
7	0.045
9	0.01



Now come back to the rotational/vibrational spectrum of HCl that we started with, and notice two things.

First, we only looked at the $n=0 \rightarrow 1$ vibrational transition. Why?

Second, the rotational intensities are similar to the populations of rotational levels we just looked at.

This is because the intensity of the rotational lines is proportional to the number of molecules in the rotational level from which the transition occurs.