Since most spectroscopy techniques operate on a sample which is a sizeable fraction of Avogadro's number, 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 (set of quantum numbers) consistent with what is known about the system at a macroscopic level (eg. its temperature)

Example: consider the system composed of 4 independent, identical harmonic oscillators with total energy $E_{\text{tot}} = 7\hbar\omega$ (this is the macroscopic information known to us). What are the possible microstates?

Quantum numbers of individual HOs	# ways of making this assignment
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

The total number of possible arrangments (assignment of quantum numbers) is 56. What is the probability that one of the HO has a quantum number of 0? To answer this we use the fundamental postulate, which says that

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

Doing this for the rest gives

$\mathcal{P}(0) = 21/56$

$\mathcal{P}(1) = 15/56$

$\mathcal{P}(2) = 10/56$

$\mathcal{P}(3) = 6/56$

$\mathcal{P}(4) = 3/56$

$\mathcal{P}(5) = 1/56$

What have we done? We have taken a given macroscopic state ($E_{\text{tot}} = 7\hbar\omega$) and worked out the microscopic energy distribution, namely the probability that a molecule has energy

E. In general, for a large enough collection of molecules it can be shown that this probability, for a system in thermal equilibrium at a temperature T, is

$$e^{-E/k_B T} = e^{-\beta E} \tag{2}$$

where $\beta = 1/k_B T$. Here k_B is the Boltzmann constant.

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

We know that $E_n = (n + 1/2)\hbar\omega$, $n = 0, 1, 2, \ldots$ Thus

$$q = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \qquad \text{(geometric series)} \tag{3}$$

The probability of finding a molecule in level n is thus

$$\mathcal{P}_n = \frac{e^{-\beta\hbar\omega(n+1/2)}}{q} \tag{4}$$

This is the fraction of molecules in level n. It only depends on T, k, and μ. Table 18.3 of Mc-Quarrie/Simon: excited state populations

Gas	$\mathcal{P}_{n>0}$ ($T = 300\,K$)	$\mathcal{P}_{n>0}$ ($T = 1000\,K$)
H_2	1.01×10^{-9}	2.00×10^{-3}
HCl	7.59×10^{-7}	$1.46 \times 10^{-2} = 1.46\%$
N_2	1.30×10^{-5}	$3.43 \times 10^{-2} = 3.43\%$
CO	3.22×10^{-5}	$4.49 \times 10^{-2} = 4.5\%$
Cl_2	$6.82 \times 10^{-2} = 6.8\%$	$4.47 \times 10^{-1} = 44.7\%$
I_2	$3.58 \times 10^{-1} = 35.8\%$	$7.35 \times 10^{-1} = 73.5\%$

Rigid Rotor

$$E_\ell = \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} = \frac{\hbar^2 \ell(\ell + 1)}{2I} \tag{5}$$

The degeneracy of level ℓ is $2\ell + 1$ (from the m_ℓ quantum number). Due to this degeneracty,

$$q = \sum_{\ell=0}^{\infty}(2\ell + 1)e^{-\beta\hbar^2\ell(\ell+1)/2I} \tag{6}$$

Define

$$\theta = \frac{\hbar^2}{2Ik_B} \tag{7}$$

θ has units of temperature.

$$q = \sum_{\ell=0}^{\infty} (2\ell + 1)e^{-\theta\ell(\ell+1)/T} \tag{8}$$

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

$$q \approx \int_0^{\infty} (2\ell + 1)e^{-\theta\ell(\ell+1)/T} \, d\ell \tag{9}$$

Let $x = \ell(\ell + 1)$ so that $dx = (2\ell + 1) \, d\ell$ Then

$$q = \int_0^{\infty} e^{-\theta x/T} \, dx = \frac{T}{\theta} = \frac{8\pi^2 Ik_B T}{h^2} = \frac{2I}{\hbar^2 \beta} \tag{10}$$

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

The fraction of molecules in level ℓ is

$$\mathcal{P}_\ell = \frac{(2\ell + 1)e^{-\theta\ell(\ell+1)/T}}{q} = \frac{\theta}{T}(2\ell + 1)e^{-\theta\ell(\ell+1)/T} \tag{11}$$