Problem Set 10

Rovibrational Spectroscopy

For each of the diatomic molecules listed below, do the following:

1. For each molecule, determine the energies of rotational transitions.
2. For each molecule, estimate the intensity of each transition using Boltzmann populations and the degeneracy of the transition.
3. For each molecule, make a plot of the rotational spectrum.

Molecule	B_e (cm^{-1})
F_2	0.89019
Cl_2	0.24399
Br_2	0.082107
I_2	0.037372
HF	20.956
HCl	10.593
HBr	8.4649
HI	6.4264

For each of the diatomic hydrides listed below, do the following:

1. For each hydride, determine the energies of the rovibrational transitions.
2. For each hydride, estimate the intensity of each transition using Boltzmann populations and the degeneracy of the transition.
3. For each hydride, make a plot of the rovibrational spectrum.
4. Repeat these calculations to predict the effect of isotopic substitution of deuterium.

Molecule	ω_e (cm^{-1})	B_e (cm^{-1})
LiH	1405.65	7.513
BeH	2060.78	10.314
BH	2366.90	12.021
CH	2858.50	14.457
NH	3282.27	16.699
OH	3737.76	18.911
HF	4138.32	20.956

Some Potentially Useful Equations

Harmonic Oscillator

Vibrational Energy Levels	$E_n = (n + \frac{1}{2})\hbar\sqrt{\frac{k}{\mu}} = (n + \frac{1}{2})h\nu$
Vibrational Energy Levels (in cm^{-1})	$\frac{E_n}{hc} = (n + \frac{1}{2})\omega_e$
Vibrational Frequency	$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$
Reduced Mass	$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

Rigid Rotor

Rotational Energy Levels	$E_{J,M_J} = J(J+1)\frac{\hbar^2}{2\mu R^2} = J(J+1)\frac{\hbar^2}{2I}$
Rotational Energy Levels (in cm^{-1})	$\frac{E_{J,M_J}}{hc} = J(J+1)B_e$
Moment of Inertia	$I = \mu R^2$

Boltzmann Factors

Partition Function	$Q = \sum_i^{\infty} e^{-E_i/k_\text{B}T}$
Probabilities	$p_i = \frac{e^{-E_i/k_\text{B}T}}{\sum_j^{\infty} e^{-E_j/k_\text{B}T}}$
Partition Function (including degeneracy)	$Q = \sum_i^{\infty} g_i e^{-E_i/k_\text{B}T}$
Probabilities (including degeneracy)	$p_i = \frac{g_i e^{-E_i/k_\text{B}T}}{\sum_j^{\infty} g_j e^{-E_j/k_\text{B}T}}$
Vibrational Partion Function (with zero-point energy)	$Q_\text{vib} = \frac{e^{-h\nu/2k_\text{B}T}}{1 - e^{-h\nu/k_\text{B}T}}$
Vibrational Partion Function (without zero-point energy)	$Q_\text{vib} = \frac{1}{1 - e^{-h\nu/k_\text{B}T}}$