Problem Set 9

Rotational and Vibrational Spectroscopy

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

1. For each hydride, calculate the force constant (in cm^{-1}) from the harmonic vibrational frequency.
2. For each hydride, calculate the bond length (in Å) from the rotational constant.
3. Assuming the force constant does not change upon isotopic substitution, calculate the harmonic vibrational frequency, ω_e, (in cm^{-1})of the deuteride.
4. Assuming the bond length does not change upon isotopic substitution, calculate the rotational constant, B_e, (in cm^{-1}) of the deuteride.

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

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

1. Determine the population of the ground vibrational state at room temperature (300K).
2. Determine the temperature at which the population if the first excited vibrational state is 0.1.
3. Determine the population of the lowest 10 rotational energy levels at room temperature.
4. What is the most populous rotational energy level at room temperature?

Molecule	ω_e (cm^{-1})	B_e (cm^{-1})
F_2	916.64	0.89019
Cl_2	559.72	0.24399
Br_2	325.32	0.082107
I_2	214.50	0.037372
HF	4138.32	20.956
HCl	2990.95	10.593
HBr	2648.98	8.4649
HI	2309.01	6.4264

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