Information Sheet for Chem322 Midterm Exam

Planck constant, $h = 6.626 \times 10^{-34}$ J s
Speed of light, $c = 3 \times 10^{8}$ m s^{-1}
Boltzmann constant, $k = 1.38 \times 10^{-23}$ J K^{-1}
1 Å = 10^{-10} m
Hydrogen atom energy: $E = -R/n^2$ where R is Reydberg constant.
Rotational constant in cm^{-1}, $B = h/(8\pi^2 cI)$
Moment of inertia: $I = \mu r^2$

Rotational energy (in cm^{-1}): $E_{rot}/hc = BJ(J+1) - DJ^2(J+1)^2$

Vibrational energy (in cm^{-1}): $E_{vib}/hc = (v+½)\omega_e - (v+½)^2\omega_e\chi_e$

A general expression for rotational constant and centrifugal distortion constant:

$$B_v = B_e - \alpha(v + 1/2),\ D_v = D_e - \beta(v + 1/2)$$

Boltzmann population distribution: $P_i/P_j = \exp[-(E_i - E_j)/kT]$

Spin-orbit coupling energy,

$$E_{SO}/hc = \frac{\alpha^2 RZ^4}{n^3 l(l+½)(l+1)}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

Second-order Stark energy,

$$E_{Stark}^{(2)} = \frac{\mu_Z^2 E_0^2}{2BhcJ(J+1)}\left[\frac{J(J+1) - 3M_J^2}{(2J-1)(2J+3)}\right]$$

Spectral intensity distribution across rotational levels: $J_{max} = \frac{1}{2}\sqrt{\frac{2kT}{hcB} + \frac{1}{4}} - \frac{3}{4}$

<u>Selection rules in atomic spectroscopy</u>:

Δn = anything, $\Delta L = \pm 1$, $\Delta S = 0$, $\Delta J = 0, \pm 1$ (except $J = 0 \rightarrow J = 0$), $\Delta F = 0, \pm 1$ (except $F = 0 \rightarrow F = 0$);
Additional rules in the presence of an external electric/magnetic field: $\Delta M_J = 0, \pm 1$ and $\Delta M_F = 0, \pm 1$

<u>Selection rules in molecular spectroscopy</u>:

Pure rotational spectroscopy: (1) Molecules must have a permanent dipole moment; (2) $\Delta J = \pm 1$.
Vibrational spectroscopy: Δv = anything, $\Delta J = 0$ (forbidden for homonuclear diatomics), ± 1.
Raman spectroscopy: Δv = anything, $\Delta J = 0, \pm 2$.