## SOME USEFUL CONSTANTS/CONVERSIONS

h = 6.6262(-27) erg-s = 6.626(-34) J-s    c = 2.9979 (10) cm/s = 2.9979(8) m
k = 1.380622(-16) erg/K = 1.380622(-23)J/K    k/hc = 0.695 $cm^{-1}$/K

$\hbar$ = 1.0545(-27) erg-s    1 Å = $10^{-8}$ cm = $10^{-10}$ m    1 eV = 1.602(-12) erg
$\varepsilon_0$ = 8.8542(-12) F $m^{-1}$    1 eV = 1.602(-19) J

$\mu_b/h$ = 1.400 MHz/Gauss    c = $\lambda\nu$  1 $cm^{-1}$ "=" 29.979 GHz

## SOME USEFUL EXPRESSIONS

$R_{u<-l} = 2\pi/3\hbar^2 \; \rho(\nu_{ul}) \, |\mu_{ul}|^2$ (cgs)

$H' = -\mu \bullet \mathbf{E}$ (electric interaction)    $H' = -\mu_\mathbf{m} \bullet B$ (magnetic interaction)
where $\mu_m = -\mu_b \mathbf{L}/h - 2\mu_b \mathbf{S}/h$
$\mu_b$ = Bohr Magneton

$A_{ul}$ (cgs) = $32\pi^3\nu_{ul}^3 \, |\mu_{ul}|^2 / 3\hbar c^3$    $B_{ul}$(cgs) = $2\pi/3\hbar^2 \; |\mu_{ul}|^2$

(Divide by $4\pi\varepsilon_0$ to switch R, A & B to SI system)

$\rho_T(\nu) = \{ 8\pi h\nu^3/c^3 \}\{\exp(h\nu/kT) - 1\}^{-1}$    $I(\nu)d\nu = (c/4\pi)\,\rho_T(\nu)$

(Multiply $\rho$ by $4\pi\varepsilon_0$ for SI units)

$I(\nu) = I_0(\nu)\exp(-\kappa_\nu x)$    $\int \kappa_\nu d\nu = 8\pi^3\nu_{ul} n_l \, |\mu_{ul}|^2 / 3hc$

$\tau_\nu = \kappa_\nu$ x path length l    $\kappa_\nu^{max} = 8\pi^2\nu_{ul} n_l \, |\mu_{ul}|^2 / 3hc\Delta\nu$ (Lorentzian)

$\kappa_\nu = \kappa_\nu^{max} \, \Delta\nu^2/\{(\nu-\nu_{ul})^2 + \Delta\nu^2\}$ (Lorentzian shape; $\Delta\nu$ = HWHM)

$E_n$ (eV) = $-13.60 \, Z^2/n^2$    $E_{n1,n2,..}$ (eV) = $-13.60 \, Z^2\{1/n_1^2 + 1/n_2^2 + ...\}$

1s < 2s < 2p < 3s < 3p <4s < 3d    $\Delta S=0$, $\Delta L = 0,\pm1$, $\Delta l_i = \pm1$, $\Delta J = 0,\pm1$
$^3P < {}^1P < {}^1S$    $\Delta\Lambda = 0,\pm1$, $\Delta S = 0$, g <-> u

$\sigma_g(1s) < \sigma_u^*(1s) < \sigma_g(2s) < \sigma_u^*(2s)[\, < \sigma_g(2p) < \pi_u(2p)] < \pi_g^*(2p) < \sigma_u^*(2p)$ [ ] – reverse for $C_2$

$H' = \Sigma_i \xi_i \ell_i \bullet s_i \approx A\mathbf{L} \bullet \mathbf{S}$ (fine)  $H' = a\mathbf{I} \bullet \mathbf{J}$ (hyperfine)
$E' = A/2 \, \{J(J+1) - L(L+1) - S(S+1)\}$  A>0 $p^2$ ; A<0 $p^4$

**J = L + S**; **F = I + J** (atoms)  $|LSJM_J\rangle$ (Russell - Saunders)
$|l_1 s_1..j_1,j_2...JM_J>$ ( j-j coupling)

Hund's Case (a): $\Lambda\Sigma\Omega$ ; $H' \approx AL_zS_z$    Hund's Case (b): $SM_S$; $H' = \gamma\mathbf{N}\bullet\mathbf{S}$

Rotational Constant (MHz) = $5.05376\ 10^5$ / I(amu-Å$^2$) = $h/8\pi^2I$    $I_a \leq I_b \leq I_c$

ENERGY LEVELS AND WAVE FUNCTIONS

a) **Diatomics**

$E_{vib-rot}/h = \omega_e(v+1/2) - \omega_ex_e(v+1/2)^2 + B_eJ(J+1) - D_eJ^2(J+1)^2 - \alpha_e(v+1/2)J(J+1)$

$E_{rot}/h = B_vJ(J+1) - D_eJ2(J+1)^2$    $\nu_{elec} = T_e'-T_e'' + G_v'-G_v'' + F_v'(J') - F_v''(J'')$

$\nu_{origin}(v',v'') = T_e'-T_e'' + G_v'-G_v''$    $\Delta_{v+1,v} = G_{v+1} - G_v = \omega_e - 2\omega_ex_e\ (v+1)$

$\psi = \psi_e\ \psi_{rot}\ \psi_{ns}$   $\psi = \psi_{a,s}$ for fermions/bosons    $\psi_{rot}$ symmetry goes as $(-1)^J$
No. Symm Nu. Sp States = (2i+1)(i+1)    No. Asymm. Nu. Sp. States = (2i+1)i
Prob(E) = g(E)exp(-E/kT) / q    $q_{rot} = kT/hB$

b) **Symmetric tops**
$E_{rot}/h = BJ(J+1) + (A - B)K_a^2$ (prolate: A>B=C)
$E_{rot}/h = BJ(J+1) + (C - B)K_c^2$ (oblate: A=B>C)
Centrifugal Distortion: $- D_JJ^2(J + 1)^2 - D_{JK}J(J+1)K^2 - D_KK^4$
$q_{rot} = \pi^{1/2}\ (kT/hA)^{1/2}(kT/hB)$

c) **Asymmetric tops**
(A>B>C) levels designated by $J\ K_aK_c$    $\kappa = \{2B - A - C\} / \{A-C\}$   $-1 \leq \kappa \leq 1$

SELECTION RULES

a) **Rotation**
1) linear molecule: $\Delta J = \pm 1$ (Raman: $\Delta J = \pm 2$ (Stokes/AntiStokes) )
2) symmetric top: $\Delta J = 0, \pm 1$    $\Delta K = 0$
3) asymmetric top: $\Delta J = 0, \pm 1$;
a-type: $\Delta K_a=0$, $\Delta K_c=\pm 1$;  b-type: $\Delta K_a=\pm 1$, $\Delta K_c=\pm 1$;  c-type $\Delta K_a=\pm 1$, $\Delta K_c=0$

b) **Vibration**
diatomic molecule $\Delta v = \pm 1$ strongest, but overtones exist. R- branch: J+1 <- J, P-branch J-1 <- J

c) **Electronic**
vibrational bands for diatomic molecules given by Franck-Condon overlap factors $|\langle v'|v''\rangle|2$  In general, R, P, and Q ($\Delta J = 0$) branches occur for each band. Bands can be grouped and assignments confirmed in Deslandres Table by consistency of combination differences $\Delta_{ij}'$ and $\Delta_{ij}''$.

## ASTRONOMY

**Excitation:** $k_{i<-j}\,(cm^3s^{-1})\, n > A_{i->j}$ **Abundance:** $N_l = 3ck\int T_b(\nu)d\nu \,/\, 8\pi^3\nu^2|\mu_{ul}|^2$

## GROUP THEORY

**Theorems**

(1) Number of Irreducible Representations = Number of classes s where classes are defined as collections of group elements that are physically related and are mathematically related by similarity transformations.

(2) $h = \sum_{i=1}^{s} l_i^2$ h = no. elements, $l_i$ = dimensionality of ith representation

(3) $\chi\,(RAR^{-1}) = \chi\,(A)$ where $\chi$ stands for trace or character

(4) orthogonality theorem: $\sum_{i=1}^{s} N_i \chi_j(R_i)\chi_k(R_i) = ()\delta_{jk}$

(5) reduction theorem: $N_j = (1/h)\sum_{i=1}^{s} N_i \chi_{red}(R_i)\chi_j(R_i)$

(6) direct product: $\chi(\text{Basis}_1 \times \text{Basis}_2) = \chi(\text{Basis}_1)\,\chi(\text{Basis}_2)$

## POLYATOMIC VIBRATIONS

Lagrange's Equations: $d/dt(\partial L/\partial \dot{q}_i) - \partial L/\partial q_i = 0;\ L = T - V$

$\lambda = \omega^2 = 4\pi^2\nu^2$

$|b_{ij} - \lambda\delta_{ij}| = 0$