homonuclear ≙ covalent bonding
heteronuclear ≙ ionic bonding
molecular spectra: change of (spin | configuration | orientation | e^- distribution) measurement of mol. sizes: transp. properties in gas phase, X-ray diff. in single crystal (e^--density), light scattering (intensity over angle)
mol. imaging: TEM (e^- through specimen or projection surface)
$\lambda_D = h/mv$; resol. $d_{min} = C_s \lambda_D^{3/4}$
particle in a box: $E_n = \frac{n^2 h^2}{8mL^2}$; $n = 1, \ldots$

Fine structure: $a = \mu_0 Z e^2 \hbar^2 / (8\pi m_e^2 r^3)$
$\Delta E = \gamma_s B_p = g_s \mu_B \frac{\mu_0 Z e}{4\pi r^3 m_e} (\vec{s}\cdot\vec{l})$
$= \frac{a}{2}[j(j+1) - l(l+1) - s(s+1)]$ only $l \neq 0$ only spin-orbit
$E_{nj} = E_n\left[1 + \frac{Z^2\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]$ mass corr + spin orbit

Lamb shift: 0-point fluctuations E-field
many e^-: $\psi(\vec{r}_1, \vec{r}_2) \approx \psi(\vec{r}_1)\psi(\vec{r}_2)$
Hartree-Fock: self-consistent approx
1s 2s 2p 3s 4s 3d 4p 5s 4d 5p 6s
ionic: e^- transfer, covalent: e^- sharing
adiabatic approx. no dependency on nuclear velocity – n fixed, e^- free
Born-Opp. approx. additionally coupling between nuclei and e^- density. Breakdown: level crossing in E(R) diagram. LCAO:
overlap $S = \int \psi_a \psi_b \, dV$ coulomb $C = \int \psi_a(r_a)\left(-\frac{e^2}{4\pi\varepsilon_0 r_b}\right)\psi_a(r_a)\, dV$ $D = \int \psi_a(r_a)\left(- \,\text{"}\, -\right)\psi_b(r_b)\, dV$ bond. energy
$E_B = (C \pm D)/(1 \pm S) + \frac{e^2}{4\pi\varepsilon_0 R_{ab}}$; $E = E_0 + E_B$
$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g < 1\pi_g < \pi_u < 3\sigma_u$
bond order $b = \frac{\text{bonding } e^- - \text{antibond } e^-}{2}$
particle in a box (circle) $E = \frac{2\pi^2\hbar^2 n^2}{mL^2}$, $n = 0, \pm 1, \pm 2$
HF: sel rules $\Delta l = \pm 1$, $\Delta m_l = 0, \pm 1$
$B_{12} = B_{21}$; $A_{21} = 8\pi h \tilde{\nu}^3 B_{12}$
Lambert-Beer $\alpha = \sigma C$ (C density)
absorbance: integration over spectral width
lifetime broad.: Lorentzian, Doppler: Gauss
uncerty: $\Delta E \Delta t > \hbar/2 \Rightarrow \Delta\nu \geq A_{nm}/2\pi$
Lorentzian: $A(\tilde{\nu}) = A_0 \gamma_L^2 / (\gamma_L^2 + (\tilde{\nu} - \tilde{\nu}_0)^2)$
FWHM: $\gamma_D = 2(\nu/c)\sqrt{2 \ln 2 \, kT/m}$

$A(\tilde{\nu}) = A_0 \exp(-4\ln(2)(\tilde{\nu} - \tilde{\nu}_0)^2/\gamma_D^2)$
permanent el. dipole moment required for rotational spectr.
rigid rotor: $E_{rot} = \frac{1}{2} I\omega^2$, $|\vec{J}| = I\omega$
$E_{rot} = \hbar^2 J(J+1)/2I$, $|J| = [J(J+1)]^{1/2}\hbar$
$J_z = m_J \hbar$, $J = 0, 1, \ldots$ $B = h/(8\pi^2 c I)$
$F(J) = E_{rot}/(hc) = BJ(J+1)$ $\mu \neq 0$
$\Delta J = \pm 1$, $\Delta m_J = 0, \pm 1$ $\tilde{\nu}_{J+1 \leftarrow J} = 2B(J+1)$
Stark eff. E: $2J+1$ components
$\Delta E_{J,m_J} = \frac{\mu^2 E^2}{2hcB} \frac{J(J+1) - 3m_J^2}{J(J+1)(2J-1)(2J+3)}$
Diatomic non-rigid rotor:
$E_{rot} = \frac{\hbar^2}{2m_{eff}R_e^2} J(J+1) - \frac{\hbar^4 J^2 (J+1)^2}{2k m_{eff}^2 R_e^6}$ $\Delta J = \pm 1$
$F(J) = \frac{E_{rot}}{hc} = BJ(J+1) - DJ^2(J+1)^2$ $D = \frac{\hbar^3}{4\pi k I^2 R_e^2}$
$\tilde{\nu}_{J+1 \leftarrow J} = F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3$

Rot. Raman: $\Delta J = \pm 2, \pm 1$ rigid
$|\Delta\tilde{\nu}| = F(J+2) - F(J) = B(4J+6)$
$|\Delta\tilde{\nu}| = (4B_0 - 6D_0)(J + \frac{3}{2}) - 8D_0(J + \frac{3}{2})^3$ non-rigid
Diatomic harm. osz.
$E_v = (v + \frac{1}{2})h\nu$, $G(v) = (v + \frac{1}{2})\tilde{\nu}$ $v = 0, 1, 2, \ldots$
$\nu = \sqrt{k/\mu}/(2\pi)$ $d\mu/dx \neq 0$, $\Delta v = \pm 1$
Diatomic anharm. osz. $\tilde{G}(v) = (v + \frac{1}{2})\tilde{\nu} - (v + \frac{1}{2})^2 x_e \tilde{\nu}$; $x_e = \frac{a^2\hbar}{4\pi m_{eff}\nu} = \frac{\tilde{\nu}}{4\tilde{D}_e}$ $a = \sqrt{\frac{m_{eff}\nu^2}{hc\tilde{D}_e}}$
$E_0 = \frac{\hbar\omega}{2}(1 - \frac{1}{2}x_e)$ $\Delta v = \pm 1, \pm 2, \ldots$
morse: $V = hc\tilde{D}_e\{1 - \exp[-a(R - R_e)]\}^2$ $\Delta v = \pm 1$
Vibrator: $E(v,J) = (v + \frac{1}{2})\hbar\omega - (v + \frac{1}{2})^2\hbar\omega x_e + hcB_v J(J+1) - hcD_v J^2(J+1)^2$ $\Delta J = \pm 1$
Blackbody rad. $\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right)$
centrosymmetric: either Raman or IR
Vibrational Raman
$I = K I_0 (\tilde{\nu}_0 - \tilde{\nu}_i)^4 (\partial\alpha/\partial Q)^2$ $\Delta v = \pm 1, \pm 2$
$I_{Stokes}/I_{anti\text{-}Stokes} = \exp(hc\tilde{\nu}_{vib}/kT)$
cross section 10^{-x}: UV(18), IR(21), RR(24)
Rayleigh (26), Raman (29) Fluorescence (19)
time-resolved RR: $\Delta t_r = 2r_r/v$

$\Lambda = 0, 1, 2, 3\ (\Sigma, \Pi, \Delta, \Phi, \Gamma)$ $\Lambda = (\Sigma\lambda_i)$
$\lambda = \sigma, \pi, \delta, \varphi$ ${}^{2S+1}\Lambda^{+/-}_{g/u}$ sym. par.
Hund coupling
cases $\Delta\Lambda = 0, \pm 1$, $\Delta S = 0$, $\Delta\Sigma = 0$
$\Delta\Omega = 0, \pm 1$ $g \to u$, $g \not\to g$ only vibronic
Hund decoupl.
$\Delta E^{(2)} = (2(hcB)^2 L(L+1)J(J+1))/(E(\Pi) - E(\Sigma_g^+))$
FC-Factor $|S(v', v)|^2 = |\int \psi^*_{v'}\psi_v \, d\vec{r}|^2$

Dissociation only with vibr. excitation
transition lifetime $\tau_{eff} = \frac{1}{k_{rad} + k_{nonrad}}$ quantum yield $\phi = \frac{k_{rad}}{k_{rad} + k_{nonrad}}$
10^{-x} absorption (15), vib (12–10), fluor. (10–13)
intersys cross (10–8) int. conv. (11–9) phosphor. (6–0)
fluorescence q.y. $\phi_f = \frac{k_f}{k_f + k_{isc} + k_{ic} + k_Q}$
Stern-Volmer $\phi_f/\phi = I_0/I = 1 + k_Q\tau_0$
$\tau_f = (k_f + k_{isc} + k_{ic})^{-1}$ FRET: $\frac{1}{\tau_0} = \phi_0/\tau_D$
$R_0^6 = \frac{\phi_0\kappa^2 J}{n^4}$; $k_T = \left(\frac{R_0}{R}\right)^6 \frac{1}{\tau_0}$
eff $E = \frac{k_T}{k_T + (\tau_D)^{-1}} = \frac{R_0^6}{R_0^6 + R^6}$

Laser threshold $\Delta N = N_2 - N_1 > \frac{8\pi n^3\nu^2}{c^2 A_{21}}\frac{\gamma}{L}$
coherence $l_c = \lambda^2/(2\Delta\lambda)$
q-factor $Q = \nu/\Delta\nu = 2\pi\nu E_c t/E_c^{loss}$ cavity
Jahn-Teller effect: coupling vibration/e^-
mode locking: $I \propto E_0^2 \frac{\sin^2(N\pi ct/2L)}{\sin^2(\pi ct/2L)}$
Nd:YAG: ${}^4F_{3/2} - {}^4I_{11/2}$
polarizability molec.: $\alpha' = \frac{\alpha}{4\pi\varepsilon_0} \approx \frac{2e^2R^2}{\Delta E}$
$B = |\mu_{fi}|^2/(6\varepsilon_0\hbar^2)$; $A = \frac{\pi\nu_{fi}N_A|\mu_{fi}|^2}{3\varepsilon_0\hbar c}$
oscillator strength
$f = (4\pi m_e\nu_{fi}/3e^2\hbar)|\mu_{fi}|^2 = \frac{4m_e c\varepsilon_0}{N_A e^2}A$
permittivity $\varepsilon_r = \frac{1 + 2\alpha(N/V)/3\varepsilon_0}{1 - \alpha(N/V)/3\varepsilon_0}$
suscept. $\chi_e = \varepsilon_r - 1$ polar mol. Debye-Langevin
Born energy $P = \left(\alpha + \frac{\mu_0^2}{3kT}\right)\frac{N}{V}E^*$
$\Delta\mu^i = -z^2e^2/(8\pi\varepsilon_0 a)\left[\frac{1}{\varepsilon_1} - \frac{1}{\varepsilon_2}\right]$
$\approx e^2/(4\pi\varepsilon_0\varepsilon(a_+ + a_-))$
One ion: $\mu^i = q^2/(8\pi\varepsilon_0 a\varepsilon)$

A, B, C: $AB \approx r - \frac{1}{2}l\cos\theta$
$AC \approx r + \frac{1}{2}l\cos\theta$ $w(r) = -\frac{Qq}{4\pi\varepsilon_0\varepsilon}\left[\frac{1}{AB} - \frac{1}{AC}\right]$
$AB = \sqrt{(r - \frac{1}{2}l\cos\theta)^2 + (\frac{1}{2}l\sin\theta)^2}$
energy of +c-d+ $w'(r) \approx -\frac{Qql\cos\theta}{4\pi\varepsilon_0\varepsilon r^2}$
of a perm. dipole in field: $w(r) = -qlE(r)\cos\theta$

hydration number ≙ # H_2O; rotating dipoles:
$w(r) \approx \langle w(r,\Omega) - \frac{w(r,\Omega)^2}{kT} + \ldots\rangle$ Keesom ind.
$w(r) = -u_1^2u_2^2/(3(4\pi\varepsilon_0\varepsilon)^2 kT r^6)$ for $kT > \frac{u_1u_2}{4\pi\varepsilon_0\varepsilon r^3}$
solvent: $z = 4\pi\varepsilon_0\varepsilon$ $u_{ind} = z\frac{(\varepsilon_i - \varepsilon)}{(\varepsilon_i + 2\varepsilon)}a_i^3 E$
$\alpha_i = z\left(\frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon}\right)a_i^3$
$w(r) = -\left[\frac{Q_1^2}{8\pi\varepsilon_0\varepsilon r^4} + \frac{3kT}{r^6}\left(\frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon}\right)a_1^3\right]\left(\frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + 2\varepsilon}\right)a_2^3$

London disp. force $w(r) = -\frac{3}{4}h\nu(\alpha_0^2/k^2r^6)$, $\alpha \approx Q^2/k$
two diff. molecules:
$w(r) = -\frac{3}{2}\frac{(\alpha_{01}\alpha_{02})}{(4\pi\varepsilon_0)^2 r^6}\frac{I_1 I_2}{(I_1 + I_2)}$ two diff polar mol.
$w(r) = -\left[(u_1^2\alpha_{02} + u_2^2\alpha_{01}) + \frac{u_1^2u_2^2}{3kT} + \frac{3h\nu_1\nu_2\alpha_{01}\alpha_{02}}{2(\nu_1 + \nu_2)}\right]/((4\pi\varepsilon_0)^2 r^6)$ Mie-pot. $V = \frac{C_n}{r^n} - \frac{C_m}{r^m}$
LJ: $V = 4\varepsilon\{(\frac{r_0}{r})^{12} - (\frac{r_0}{r})^6\}$
vdW: excited higher bond energy

ESR: only paramagnetic; $\nu_L = \gamma_e B_0/(2\pi)$
Hückel $E_{k,cyc} = C + 2D\cos\left(\frac{2k\pi}{N}\right)$ $k = 0, \pm 1, \pm \frac{N}{2}$
$E_{k,lin} = C + 2D\cos\left(\frac{k\pi}{N+1}\right)$ $k = 0, 1, \ldots, N$
deloc. E: $E_{DE} = E_\pi - E_{DB}$; $E_{DB} = 2(C + D)$
Li-N_2: $1\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4\, 3\sigma_g^2\, 2\pi_g^4\, 4\sigma_u^2$
O-F: $1\sigma_g^2\, 2\sigma_u^2\, 3\sigma_g^2\, 1\pi_u^4\, 2\pi_g^4\, 4\sigma_u^2$
CO_2 box: [illegible] π (N d): ligand theory
Renner-Teller: BO breakdown in linear
*Λ-doubling: $\Lambda \geq 1$: splitting for lin. mol.
Jahn-Teller: non lin, deg. ⇒ red. symmetry ⇒ no deg.
EPR: param. dipole
$g = 1 + (j(j+1) + s(s+1) - l(l+1))/(2j(j+1))$
change in dipole moment ⇒ IR active
– " – polarizability ⇒ Raman active
O=C=O R→ O=C=O IR MO: $(\phi_a + \phi_b)(\phi_a' + \phi_b')$
$\nu_D = \nu_S(c \pm v_R)/(c \mp v_S)$ ionic / VR: $\phi_a\phi_a' + \phi_b'\phi_a$
$\alpha = e^2/(4\pi\varepsilon_0\hbar c)$ [illegible] cov.

$$\int_{-\infty}^{\infty} e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

$$\int_0^{\infty}(x^n e^{-ax})\,dx = \frac{n!}{a^{n+1}}$$