Spectroscopy

Formulas one should definitely know

This is a list of formulas one should know after completing the course. It does not imply that one should not know any of the other formulas used in the course. One should be able to explain the terms in these formulas. One should also be able, using the formulas given here to explain results we found in the course: solutions harmonic Oscillator, Hydrogen atom, etc. If you need any other expression than given here to solve a problem for the written part of the exam it will be given to you.

Important: Knowing these formulas does not imply that you know the course content. Think about what these expressions mean, where do they come from and what do they imply, that's what science is about.

Basics of Quantum Mechanics:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \qquad \hat{H}\psi_n(x) = E_n\psi_n(x) \qquad \int_{-\infty}^{\infty} \Psi_n^*(x,t)\Psi_m(x,t)dx = \delta_{nm}$$

$$\langle \mathrm{A} \rangle = \int_{-\infty}^{\infty} \psi^*(x)\hat{\mathrm{A}}\psi(x)dx \qquad E = h\nu$$

Separability of the Hamiltonian:

If $\hat{H}(q_1, q_2, q_3, q_4, \ldots) = \hat{H}(q_1) + \hat{H}(q_2) + \hat{H}(q_3) + \hat{H}(q_4) + \ldots$

where the q_i's are any set of orthogonal coordinates,

then $\psi(q_1, q_2, q_3, q_4, \ldots) = \psi(q_1)\psi(q_2)\psi(q_3)\psi(q_4)\ldots$

and $E = E_1 + E_2 + E_3 + E_4 + \ldots$

Angular Momentum:

$$\hat{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l(l+1) Y_l^m(\theta,\varphi) \qquad l = 0,1,2,3,\ldots$$

$$\hat{L}_z Y_l^m(\theta,\varphi) = \hbar m Y_l^m(\theta,\varphi) \qquad m = 0, \pm 1, \pm 2, \ldots, \pm l$$

Spin is an angular momentum:

Eigenvalues: $\hat{S}^2 \Rightarrow \hbar^2 S(S+1)$ $\qquad \hat{S}_z \Rightarrow \hbar M_S$

Harmonic Oscillator:

$$V(x) = \frac{1}{2} k x^2$$

$$E_v = h\nu\left(n + \tfrac{1}{2}\right) \qquad n = 0,1,2,\ldots \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Rigid Rotor:

$$V(r) = 0$$

$$E_{lm} = \frac{\hbar^2 l(l+1)}{2\mu r_e^2} \qquad l = 0,1,2,3,\ldots \qquad m = 0, \pm 1, \pm 2, \ldots, \pm l$$

$$\psi_{lm}(\theta,\varphi) = Y_l^m(\theta,\varphi)$$

Hydrogen Atom:

$$E_{nlm} \propto -\frac{1}{n^2}$$

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r) Y_l^m(\theta,\varphi) \qquad n = 1,2,3,\ldots \qquad l = 0,1,2,\ldots,n-1 \qquad m = 0, \pm 1, \pm 2, \ldots, \pm l$$

Symmetry/Group Theory:

$$\Gamma^{red} = \oplus \sum_i a_i \Gamma_i \qquad a_i = \frac{1}{h} \sum_c N_c \chi^i(c)^* \chi^{red}(c)$$

$$\int \psi_2^* \mu \psi_1 \neq 0 \qquad \text{if} \qquad \Gamma(\psi_2) \otimes \Gamma(\mu) \otimes \Gamma(\psi_1) \subset \text{ Totally symmetric representation}$$

Born-Oppenheimer Approximation:

$$\hat{H} = -\frac{1}{2}\sum_a \frac{1}{m_a} \nabla_\alpha^2 - \frac{1}{2}\sum_i \nabla_i^2 + \sum_a \sum_{\beta > a} \frac{Z_a Z_b}{r_{\alpha\beta}} - \sum_\alpha \sum_i \frac{Z_a}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \qquad \text{(in atomic units)}$$

Rovibrational levels of a diatomic molecule:

$$E_{vJ} = \omega_e\left(v + \tfrac{1}{2}\right) - \omega_e x_e \left(v + \tfrac{1}{2}\right)^2 + B_e J(J+1) - \alpha\left(v + \tfrac{1}{2}\right) J(J+1) - D J^2 (J+1)^2 \qquad \text{(in units of cm}^{-1}\text{)}$$

Spectroscopic Intensities and spectral broadening:

$$g_1 B_{12} = g_2 B_{21} \qquad A_{21} \propto \nu^3 B_{21} \qquad \tau = \frac{1}{A_{21}}$$

$$I \propto B_{12} \propto [(\mu_x)_{21}^2 + (\mu_y)_{21}^2 + (\mu_z)_{21}^2]$$

$$(\mu_i)_{21} = \int \psi_{2tot}^{\ *}\, \mu_i\, \psi_{1tot}\, d\tau$$

$$f_i = \frac{N_i}{N} = \frac{g_i\, e^{-E_i/kT}}{\sum_i g_i\, e^{-E_i/kT}} = \frac{g_i\, e^{-E_i/kT}}{Q}$$

Rotational Spectroscopy:

Linear molecule:

$$F(J) = B_v J(J+1) - DJ^2(J+1)^2 \qquad \text{with} \qquad B_v = B_e - \alpha\left(v + \frac{1}{2}\right)$$

Selection rules: $\Delta J = \pm 1$ $\Delta m = 0, \pm 1$

$$\mu_e = \int \psi_{1el}(q_i; r)^* \psi_{1vib}(r)^* \mu(q_i, r) \psi_{1el}(q_i; r) \psi_{1vib}(r)\ d\tau_{q_i} d\tau_r \neq 0$$

Symmetric top:

$$F(J,K) = BJ(J+1) + (A-B)K^2 \qquad \text{Prolate symmetric top}$$

$$F(J,K) = BJ(J+1) + (C-B)K^2 \qquad \text{Oblate symmetric top}$$

$$A \propto \frac{1}{I_A} \ > \ B \propto \frac{1}{I_B} \ > \ C \propto \frac{1}{I_C}$$

Selection rules: $\Delta J = \pm 1 \quad \Delta K = 0$ $\Delta m = 0, \pm 1$ $\mu_e \neq 0$?

Vibrational Spectroscopy:

$$I \propto \left[\int \psi_{2vib}(r)^*\ \ \mu_{vib}(r)\ \ \psi_{1vib}(r)\ d\tau_r\right]^2$$

$$\mu_{vib}(r) = \int \psi_{1el}(q_i)^*\, \mu(q_i, r) \psi_{1el}(q_i)\ d\tau_{q_i}$$

Linear Molecule:

$$G(\mathrm{v}) = \omega_e\left(\mathrm{v}+\frac{1}{2}\right) - \omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2$$

Selection Rules: $\Delta \mathrm{v} = \pm 1$ $\Delta J = \pm 1$ $\frac{d\mu_{vib}}{dr} \neq 0$

Polyatomics:

$$\hat{H} = \sum_i \hat{H}_i = \sum_i -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_i^2} + \kappa_i Q_i^2$$

$$E = \sum_i E_i \qquad E_i = h\nu_i\left(\mathrm{v}_i+\frac{1}{2}\right)$$

$$\psi(Q_1, Q_2, Q_3, \ldots) = \psi_1(Q_1)\psi_2(Q_2)\psi_3(Q_3)\ldots\ldots$$

Selection rules: $\Delta \mathrm{v}_i = \pm 1$ $\frac{d\mu_{vib}}{dQ_i} \neq 0$

Symmetric tops:

$\Delta J = 0, \pm 1$	$\Delta K = 0$	Parallel transitions
$\Delta J = 0, \pm 1$	$\Delta K = \pm 1$	Perpendicular transitions

Electronic Spectroscopy:

$$I \propto \mu_{el}(R_e)^2\left[\int \psi_{2vib}(r)^* \psi_{1vib}(r)\, d\tau_r\right]^2$$

$$\mu_{el}(r) = \int \psi_{2el}(q_i; r)^* \mu(q_i, r)\psi_{1el}(q_i; r)\ d\tau_{q_i}$$

$$E_{vJ} = T_e + \omega_e(\mathrm{v}+\tfrac{1}{2}) - \omega_e x_e(\mathrm{v}+\tfrac{1}{2})^2 + B_\mathrm{v} J(J+1) - DJ^2(J+1)^2$$

Selection rules: $\Delta J = 0, \pm 1$ $\Delta S = 0$

$\mu_{el}(R_e) \neq 0$ Franck-Condon Factor $\neq 0$