

- 1) How the molecular vibrations can be described using quantum mechanics. Start with diatomic molecule. If the molecule is in gas phase how the spectra will look like. How many peaks there are and what kind of transition they corresponds. What property will determine the peak intensities? How the anharmonic effects in vibrations can be taken into account. How you treat many atom molecule. (6 p.)
- 2) Describe in details the bonding in Li_2 , C_2 , N_2 and O_2 molecules. In these what are the atom and molecular orbitals. Describe also the empty molecular orbitals. What is the bond order in these molecules? Can you compare N_2^+ and O_2^+ bond strength and bond length to neutral molecules. In case of N_2 what is the first electronic excited state. (6 p.)
- 3) XPS is a very convenient way to detect atoms in bulk materials and molecules. What kind of spectroscopy it is. Why it have so good resolution. (4 p.)
- 4) Why the general quantum chemical equations are very difficult to solve. What is the simplest approximation (beyond LCAO) and what is the self-consistency problem. How one can improve the description in the theory level, (not computational aspects). Here only general explanation is enough, you do not need to remember the details of the equation are not needed. (4 p.)
- 5) Explain the following: fluorescence, phosphoresce, the Frank-Condon effect. Explain qualitatively the fluorescence adsorption (excitation) and emission spectra below. Explain the quantum states that are involved in the spectra. Why you can assume that the two spectra are roughly mirror images of each other. Explain the position of the highest peaks. (5 p.)

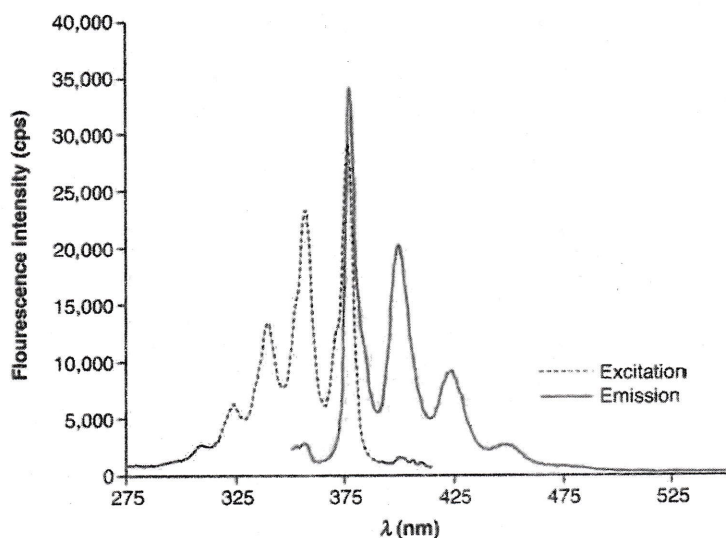


Figure 16.5
Overlay of the emission and excitation spectra of anthracene. Both are taken in toluene.

Constants:

$m_e = 9.10938 \cdot 10^{-31}$ kg, $m_p = 1.67262 \cdot 10^{-27}$ kg, $\text{amu} = 1.66054 \cdot 10^{-27}$ kg, $h = 6.62608 \cdot 10^{-34}$ Js, $\hbar = h/2\pi$,
 $4\pi\epsilon_0 = 1.11265 \cdot 10^{-10}$ C²/Jm, $N_A = 6.02214 \cdot 10^{23}$, $c = 2.9979 \cdot 10^8$ m/s, $e = 1.602176 \cdot 10^{-19}$ C,
 $k = 1.38065 \cdot 10^{-23}$ J/K, $R = 8.31447$ J/Kmol, $a_0 = 5.29177 \cdot 10^{-11}$ m.

Conversions:

$1 \text{ eV} = 1.6022 \cdot 10^{-19}$ J = 96.485 kJ/mol, $1 \text{ kJ/mol} = 1.6605 \cdot 10^{-21}$ J, $1 \text{ cm}^{-1} = 1.9864 \cdot 10^{-23}$ J = 1.43877
K, $1 \text{ \AA} = 10^{-10}$ m.

General Schrödinger equation

$$H = \left[-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{iI} \frac{Z_I e^2}{4\pi\epsilon_0 |r_i - R_I|} + \sum_{j<i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{I>J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |R_I - R_J|} \right]$$

More equation in the appendix.

There are equations related to the course so there is no or very little of explanations. If you use them, you need to explain the terms.

Planck distribution

$$\rho = \frac{8\pi kT}{\lambda^4} \left(\frac{1}{e^{hc/\lambda kT} - 1} \right) \quad (1)$$

de Broglie law:

$$\lambda = h/p \quad (2)$$

Schrödinger equation:

$$\hat{H}\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}) \quad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \quad (3)$$

$$\int_{\Omega} d^3r \psi_n^*(\mathbf{r})\psi_m(\mathbf{r}) = \delta_{nm} = 1 \text{ if } n = m, 0 \text{ if } n \neq m$$

$$\langle A \rangle_n = \int_{\Omega} \psi_n^*(\mathbf{r}) A \psi_n(\mathbf{r}) d^3r, \quad (4)$$

Position expectation value

$$x = \langle x \rangle = \int_{\Omega} \psi^*(\mathbf{r}) x \psi(\mathbf{r}) d^3r \equiv \langle \psi | \hat{x} | \psi \rangle \quad (5)$$

Impuls operator:

$$\hat{p}_x = -i\hbar \frac{d}{dx} \quad (6)$$

impulse expectation value

$$p_x = \langle p_x \rangle = -i\hbar \int_{\Omega} \psi^*(\mathbf{r}) \frac{d\psi(\mathbf{r})}{dx} d^3r \equiv \langle \psi | \hat{p}_x | \psi \rangle \quad (7)$$

Uncertainty principle

$$\Delta x \Delta p \geq \frac{\hbar}{2}, \quad \Delta x = ((x^2) - \langle x \rangle^2)^{1/2} \quad (8)$$

Commutator

$$[A, B] = AB - BA \quad (9)$$

Particle in 1-dimensional box [0,L]. Schrödinger equation inside of the box

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} = E\phi(x) \quad 0 < x < L \quad (10)$$

boundary conditions

$$\phi(0) = \phi(L) = 0 \quad (11)$$

from these we get

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin(k_n x) \quad k_n = \frac{n\pi}{L} \quad E_n = \frac{\hbar^2 k_n^2}{8mL^2} \quad n = 1, 2, \dots \quad (12)$$

2- and 3-dimensional case

$$\psi_{n,m}(x,y) = \phi_n(x)\phi_m(y) \quad \psi_{n,m,k}(x,y,z) = \phi_n(x)\phi_m(y)\phi_k(z) \quad (13)$$

$E_{n,m} = E_n + E_m$ ja $E_{n,m,k} = E_n + E_m + E_k$

Tunneling

$$T = \left(1 + \frac{(e^{L\kappa} - e^{-L\kappa})^2}{16\epsilon(1-\epsilon)} \right)^{-1} \quad \epsilon = E/V, \kappa = \sqrt{(V-E)2m}/\hbar \quad (14)$$

if $\exp(\kappa L) \gg \exp(\kappa L)$ then T is approx.

$$T \approx 16\epsilon(1-\epsilon)e^{-2\kappa L} \quad (15)$$

Harmonic oscillator

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi(x) = E\psi(x) \quad (16)$$

wavefunctions

$$\begin{aligned} \psi_0(x) &= A_0 e^{-\alpha x^2/2} = A_0 e^{-y^2/2} & \alpha &= \sqrt{mk}/\hbar \\ \psi_1(y) &= A_1 2y e^{-y^2/2} & y &= \alpha^{1/2} x \\ \psi_2(y) &= A_2 (4y^2 - 2) e^{-y^2/2} \\ \psi_3(y) &= A_3 y (8y^2 - 12) e^{-y^2/2} \text{ jne...} \\ \psi_n(y) &= A_n H_n(y) e^{-y^2/2} \end{aligned} \quad (17)$$

$H_n(x)$ is Hermite's polynomial, $H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x)$.

$$A_n = \frac{\alpha^{1/2}}{(\pi^{1/2} 2^n n!)^{1/2}} \quad (18)$$

$$E_n = (n + 1/2)\hbar\omega \quad \omega = \sqrt{k/m} \quad (19)$$

$$(20)$$

Selection rules: $\Delta n = \pm 1$
3-dimensional rotation (a linear molecule)

$$-\frac{\hbar^2}{2I} \hat{L}^2 \psi_{l,m}(\theta, \phi) = E_{l,m} \psi_{l,m}(\theta, \phi) \quad I = \mu r^2 \quad (21)$$

$$\psi_{l,m}(\theta, \phi) = Y_{l,m}(\theta, \phi) \quad l = 0, 1, 2, \dots, \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l \quad (22)$$

$$Y_{0,0} = \sqrt{1/4\pi}$$

$$Y_{1,0} = \sqrt{3/4\pi} \cos \theta, \quad Y_{1,\pm 1} = \mp \sqrt{3/8\pi} \sin \theta e^{\pm i\phi}$$

$$Y_{2,0} = \sqrt{5/16\pi} (3 \cos^2 \theta - 1), \quad Y_{2,\pm 1} = \mp \sqrt{15/8\pi} \cos \theta \sin \theta e^{\pm i\phi}$$

$$Y_{2,\pm 2} = \sqrt{15/32\pi} \sin^2 \theta e^{\pm 2i\phi}$$

$$Y_{3,0} = \sqrt{7/16\pi} (5 \cos^3 \theta - 3 \cos \theta), \quad Y_{3,\pm 1} = \mp \sqrt{21/64\pi} (5 \cos^2 \theta - 1) \sin \theta e^{\pm i\phi} \quad (23)$$

$$Y_{3,\pm 2} = \sqrt{105/32\pi} \sin^2 \theta \cos \theta e^{\pm 2i\phi}, \quad Y_{3,\pm 3} = \mp \sqrt{35/64\pi} \sin^3 \theta e^{\pm 3i\phi} \quad (24)$$

$$E_{l,m} = l(l+1) \frac{\hbar^2}{2I} = hcB l(l+1) \quad l = 0, 1, 2, \dots, B = \frac{\hbar}{4\pi c I} \quad (25)$$

Selection rules: $\Delta l = \pm 1, \Delta m_l = 0, \pm 1$
p-orbitals

$$p_z = \frac{z}{r} = \cos(\theta) \sim Y_{1,0}(\theta, \phi)$$

$$p_x = \frac{x}{r} = \sin(\theta) \cos(\phi) \sim (Y_{1,-1}(\theta, \phi) - Y_{1,1}(\theta, \phi))$$

$$p_y = \frac{y}{r} = \sin(\theta) \sin(\phi) \sim i(Y_{1,-1}(\theta, \phi) + Y_{1,1}(\theta, \phi)) \quad (26)$$

Hydrogen atom

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right) \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{M} \quad (27)$$

$$\psi(r, \theta, \phi) = f_{n,l}(\rho) Y_{l,m}(\theta, \phi) \quad f_{n,l}(\rho) = A_{n,l} \rho^l L_{n-l}(\rho) e^{-\rho/2a_0}, \quad \rho = 2Zr/a_0 \quad (28)$$

$L_{n,l}(\rho)$ on Laguerre's polynomial, $a_0 = 0.5292 \text{ \AA}$.

$$f_{n,l} = (Z/a_0)^{3/2} g_{n,l}, \quad g_{1,0} = 2e^{-\rho/2}$$

$$g_{2,0} = (2-\rho/2)e^{-\rho/4}/2\sqrt{2}, \quad g_{2,1} = \rho e^{-\rho/4}/4\sqrt{6}$$

$$g_{3,0} = (6-2\rho+\rho^2/9)e^{-\rho/6}/9\sqrt{3}, \quad g_{3,1} = (4-\rho/3)\rho e^{-\rho/6}/27\sqrt{6},$$

$$g_{3,2} = \rho^2 e^{-\rho/6}/81\sqrt{30}$$

$$E_n = -\frac{Z\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = -\frac{13.6 \text{ eV}}{n^2} \quad (29)$$

$$V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad (30)$$

Quantum numbers: $n = 1, 2, \dots, l = 0, 1, 2, \dots, n-1, m = 0, \pm 1, \pm 2, \dots, \pm l$ and spin $m_s = \pm 1/2$.

Selection rules: $\Delta l = \pm 1, \Delta m_l = 0, \pm 1$

Electron radius expectation value:

$$\langle r \rangle_{n,l} = \int \psi_{n,l}^*(r) r \psi_{n,l}(r) d^3r = \left[1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right] \frac{a_0 n^2}{Z_{\text{eff}}} \quad (31)$$

Atom building principle:

Energy order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, ...
spin = 1/2 two electrons for each state.

Molecules Schrödinger equation

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left[-\sum_{iI} \frac{Z_I}{|r_i - R_I|} + \sum_{i < j} \frac{1}{|r_i - r_j|} + \sum_{I < J} \frac{Z_I Z_J}{|R_I - R_J|} \right] \quad (32)$$

here i is related to electrons and I atoms.

sp³ hybrid orbitals

$$h_1 = (-\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz})/2 \quad h_2 = (-\psi_{2s} - \psi_{2px} - \psi_{2py} + \psi_{2pz})/2$$

$$h_3 = (-\psi_{2s} - \psi_{2px} + \psi_{2py} - \psi_{2pz})/2 \quad h_4 = (-\psi_{2s} + \psi_{2px} - \psi_{2py} - \psi_{2pz})/2 \quad (33)$$

sp² hybrid orbitals

$$h_1 = (-\psi_{2s} + \sqrt{2}\psi_{2px})/\sqrt{3} \quad h_2 = -\psi_{2s}/\sqrt{3} - \psi_{2px}/\sqrt{2} - \psi_{2py}/\sqrt{6}$$

$$h_3 = -\psi_{2s}/\sqrt{3} + \psi_{2px}/\sqrt{2} - \psi_{2py}/\sqrt{6} \quad (34)$$

Variation principle

$$E_{\text{var}} = \frac{\int \psi_{\text{trial}}^* H \psi_{\text{trial}} d^3r}{\int \psi_{\text{trial}}^* \psi_{\text{trial}} d^3r} \quad (35)$$

Selection rules can be computed with the transition dipole.

$\mu_{fi} = -e \langle f | \mathbf{r} | i \rangle$, $|i\rangle = \psi_i(\mathbf{r})$ is systems initial state and $\langle f | = \psi_f^*(\mathbf{r})$ is systems final state.

Morse potential

$$V(R) = hcD_e[1 - e^{-a(R-R_e)}]^2 \quad a^2 = \frac{\mu\omega^2}{2hcD_e} \quad (36)$$

where D_e is the potential well depth (energy unit cm^{-1}) and R_e bond distance.
Energies

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \left(n + \frac{1}{2}\right)^2 \hbar\omega x_e \quad \omega x_e = \frac{a^2\hbar}{2\mu} \quad (37)$$

x_e on anharmonic constant.

$$n_{max} < \frac{4\pi cD_e}{\omega} - \frac{1}{2} \quad (38)$$

Several atom molecule (with harmonic potential)

$$V = 0.5 \sum_{ij} k_{ij} x_i x_j \quad k_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 \quad (39)$$

$$q_i = \sqrt{m_i} x_i \quad T = 0.5 \sum_i \dot{q}_i^2 \quad V = 0.5 \sum_{ij} K_{ij} q_i q_j \quad K_{ij} = \frac{k_{ij}}{\sqrt{m_i m_j}} \quad (40)$$

In normal coordinates Q_i the potential is

$$V = 0.5 \sum_i K_i Q_i^2 \quad (41)$$

Schrödinger equation

$$-\frac{\hbar^2}{2} \frac{\partial^2 \psi(Q_i)}{\partial Q_i^2} + \frac{1}{2} K_i Q_i^2 \psi(Q_i) = E_i \psi(Q_i) \quad (42)$$

LCAO model wavefunction

$$\psi(\mathbf{r}) = \sum_I a_I \phi_I(\mathbf{r} - \mathbf{R}_I) \quad (43)$$

where the $\phi_I(\mathbf{r} - \mathbf{R}_I)$ are atom like functions.