2 Advanced Physical Chemistry – Exercizes

2.1 The moment of inertia of the hydrogen molecule is 4.603×10^{-48} kg m^2. Calculate

a) the reduced mass and the bond length of the molecule,
b) the energies of the lowermost three rotation states (The molecule can be treated as a rigid rotator.),
c) the energy differences, the wave numbers, and the wavelengths of the transitions characterized by the quantum numbers $0 \rightarrow 1$, $1 \rightarrow 2$, and $2 \rightarrow 3$.

2.2 Calculate the energies of the lowermost two states of a particle in a 1-dimensional box, the minimal excitation energy (from the ground state), and the wavelength of the corresponding radiation

a) for an electron in a box of the length 2 Å/0.02 pm/0.01 m,
b) for a sphere of 1 g mass in a box of the length 0.1 m.

2.3 Apply the "particle in a box" model to the π electrons of 1,3,5-hexatriene. For simplicity you may assume that the "box" is 1-dimensional, that the zig-zag shape of the molecule is not relevant, that the effective box length is the sum of the C–C and C=C bond lengths (0.154 m and 0.135 nm, respectively) plus 1 C–C bond length, and that the π electrons can move freely along the "box". Estimate

a) the energy of the highest occupied orbital,
b) the energy of the lowest unoccupied orbital,
c) and the wavelength and the wavenumber of the HOMO→LUMO transition!

2.4 The lowermost UV absorption band of molecular oxygen contains the following lines (wavenumbers in cm^{-1}):

49357.6	50045.6	50710.7	51352.2	51969.8
52561.6	53122.8	53656.8	54158.9	54624.4
55053.3	55441.5	55784.6	56085.5	56340.5

a) Use a Birge–Sponer extrapolation to determine the dissociation energy of the first excited state.
b) The dissociation of the ground state of O_2 produces two O atoms in the ground state. The dissociation of the first excited state produces one O atom in the ground state and one in an excited state; its excitation energy is 190 kJ/mol. What is the dissociation energy of the O_2 ground state?

2.5 A modern method for the determination of the energy of emitted electrons—but also other particles—is the time-of-flight spectroscopy (TOF). During a photoionization experiment, frozen nitrogen is irradiated with a short burst of UV light with a photon energy of 21 eV. The highest occupied electronic level of N_2 has an energy of –15.6 eV relative to the vacuum.

a) What is the maximal kinetic energy of the emitted electrons?

b) How long does it take them to arrive at a detector that is 10 cm away?

c) What is the maximal gas pressure that can be tolerated in the apparatus, if at least 90% of the photoelectrons must reach the detector without colliding with a gas molecule? Assume a collision radius of 1 Å for the gas molecules.