Physical Chemistry I

【2 pages】

Answer the following questions on Hückel molecular orbital method.

Ⅰ－a   Fill appropriate formulae, matrices, or numbers in the blanks ①－③ in the following text.

When the π electrons system of an ethylene molecule is treated with the Hückel molecular orbital method, the following secular equation (simultaneous equation) holds, for the coefficients c_1 and c_2 to the atomic orbitals (AO) of carbon atoms 1 and 2, χ_1 and χ_2, respectively.

$$\left[\boxed{①} \right] \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \qquad (1)$$

where α and β represent the Coulomb integral and resonance integral, respectively, and have negative values, and E denotes the energy of the molecular orbital. By solving this equation, we obtain the energies of the respective orbitals as follows,

$$E_1 = \boxed{②}$$
$$\qquad (2)$$
$$E_2 = \boxed{③}$$

where E_1 is lower than E_2.

Ⅰ－b   Let us find the molecular orbital energies of a cyclopentadienyl molecule C_5H_5 (a radical molecule, right figure) based on the Hückel molecular orbital method. The molecular structure is assumed to be a regular pentagon and all the carbon atoms are equivalent.
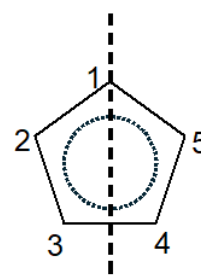
（1） Write down the secular equation for the molecular orbitals of this molecule.

（2） Let us consider the symmetry with respect to the mirror plane crossing one of the carbon atoms (see the figure). Write down the equations that hold among c_1 to c_5.

（3） By using the relation obtained in Question （2）, the simultaneous equation obtained in Question （1） can be simplified. Write down the simultaneous equations simplified by the symmetric property of the molecule. The answer should be separated into the symmetric and anti-symmetric cases.

（4） Find all the molecular orbital energies by requiring that the simultaneous equations have physically meaningful solutions.

（5） Describe the spin multiplicities and the stabilities for the monovalent anion and cation of the molecule.

（6） When one of the CH groups is separated far from the rest of the molecule (C_4H_4), the interaction between the separated CH group and other part (i.e., exchange of the π electrons) can be considered negligible. Write down the secular equation for the molecular orbitals of this system.

（7） Compare the stabilities of the neutral cyclopentadienyl molecules, for the regular pentagonal case and the distant CH-group case. If necessary, you can use the orbital eigen energies of the butadiene π electrons under the Hückel method to be $E = \alpha - \frac{1 \pm \sqrt{5}}{2}\beta, \alpha - \frac{-1 \pm \sqrt{5}}{2}\beta$.

Physical Chemistry II

【2 pages】

II − a Answer the following questions on 1,2-dichloroethane ($C_2H_4Cl_2$).

（1） Illustrate the three rotational isomers using the Newman projection diagram.

（2） For each of the three rotational isomers, identify the symmetry operations that can be applied and determine to which point group they belong.

（3） Answer the number of normal modes. Also, for each rotational isomer, illustrate all C-Cl stretching vibrations.

（4） Answer the infrared and Raman activity of the C-Cl stretching vibrations of each isomer, and provide the reasons for it.

（5） The IR absorption and Raman spectra of this molecule in the solid state showed one peak attributed to the C-Cl stretching vibration in each spectrum, but at different wavenumbers. Based on these results, discuss the rotational isomerism of 1,2-dichloroethane in the solid state.

II − b Consider a three-level system consisting of a ground state (S_0), an excited singlet state (S_1), and an excited triplet state (T_1), as shown on the right: the deactivation process of the S_1 state include the transition to the S_0 state by radiative and non-radiative processes and intersystem crossing to the T_1 state, with rate constants k_S and k_{ISC} respectively. The deactivation process of the T_1 state is the transition to the S_0 state by radiative and non-radiative processes, with a rate constant k_T.
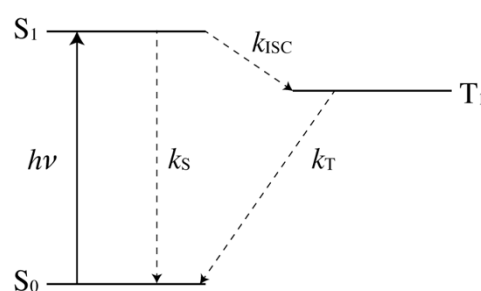
（1） Considering the case where two electrons are in HOMO and LUMO, explain the difference in the electron spin configuration in the singlet states (S_1 and S_0) and the triplet state (T_1) based on Pauli's exclusion principle.

Consider exciting the S_0 state and generating the S_1 state instantaneously using a pulsed laser. The initial concentration of the S_1 state immediately after the excitation is $[S_1]_0$.

（2） Express the quantum yield Φ_T of the T_1 state using the given rate constants.

（3） Write rate equations for the concentrations $[S_1]$ and $[T_1]$ of the S_1 and T_1 states, respectively.

（4） Solve rate equations obtained in question （3） and express $[S_1]$ and $[T_1]$ as a function of time t, assuming that k_s is negligibly small. Also, illustrate the plot of the obtained temporal variations.