THE SUMMARY OF Ph. D. DISSERTATION

Major		SURNAME, Firstname
Fundamental Science and Technology		ASANO, Yukako

Title
Theoretical Study on Photodissociation Reactions and Photoisomerization Reactions   - Analyses of Nonadiabatic Transitions and Photochromic Reactions -

Abstract

This dissertation describes the theoretical study on the nonadiabatic transitions in the photodissociation reactions of Cl_2 and Br_2, and the mechanisms of the photoisomerization, in particular, of photochromic reactions of dithienylethenes, on the basis of their electronic structures.

In Chapter 1, the role of "theoretical chemistry" in the current science and technology and the relationship between the reactions caused by a photon and the electronic structures are discussed.   Also, the nonadiabatic transitions in photodissociation reactions and the photochromic reactions of dithienylethenes are explained. The author's motivation to carry out this study and the significance of the study are discussed.

In Chapter 2, the nonadiabatic transitions between the states correlating to the different dissociation limits in the photodissociation reactions of Cl_2 are described.   It was shown that the Rosen-Zener-Demkov (RZD) model can be applied to the noncrossing-type nonadiabatic transitions in the dissociation region of Cl_2.   The radial RZD-type nonadiabatic transition from the 2nd $\Omega = 1_u$ (C $^1\Pi_u$) to 3rd $\Omega = 1_u$ ($^3\Sigma^+_{1u}$) state was the dominant mechanism to produce Cl* with the negative anisotropy parameter β(Cl*).   The RZD model could reproduce the wavelength dependence of the branching ratio Cl*/Cl, β(Cl*), and the quantum-mechanical interference effects in the orientation of the total angular momentum J = 1/2 of the products Cl*.

In Chapter 3, the nonadiabatic transitions between the states correlating to the same dissociation limits in the photodissociation reactions of Cl_2 and Br_2 are discussed.   From the semiclassical calculations with the nonadiabatic couplings between the five $\Omega = 1_u$ states, it was concluded that the essential difference in the nonadiabatic transition from the 2nd $\Omega = 1_u$ to 1st $\Omega = 1_u$ (A $^3\Pi_{1u}$) state can be attributed to the differences in the electronic factors rather than the reduced mass.

In Chapter 4, the quantum yields (QYs) in crystals and solution for the cyclization reactions of 1,2-bis (2-methyl-5-phenyl-3-thienyl) perfluorocyclopentene (1) and 1,2-bis (2-methyl-1-benzothiophen-3-yl) perfluorocyclopentene (2) are described.   In crystals, there is only the reactive conformer of the molecule 1 and the experimental QY is 1.0, while there is only the non-reactive conformer of the molecule 2 and the experimental QY is 0.0.   In solution, the experimental QY of 0.59 for the molecule 1 is interpreted by the population distribution of the other non-reactive conformers, while the QY of 0.35 for the molecule 2 is explained by the structure changes to reactive conformer induced by the thermal vibrations, owing to the shallow potential surface.

In Chapter 5, the role of conical intersections (CIs) in the photochromic cycloreversion reaction of the model molecule for dithienylethenes is studied.   The CI points of dithienylethene were obtained for the first time.   The cycloreversion reaction proceeds via the CI point between the 2A and 1A states (2A/1A CI) in the open-ring side.   It is suggested that the QY of the reaction is determined by the balance of the two factors, (i) the internal conversion rate through 2A/1A CI in the closed-ring side and (ii) the branching ratio into the closed- and open-ring isomers at 2A/1A CI in the open-ring side.