

# Theoretical Study on Photochemistry and Catalysis

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We investigate the photochemistry or photophysical properties of molecules based on the accurate coupled cluster methodologies, that are of interest in view of fundamental chemistry or material chemistry. We also focus on the mechanism and theoretical design of the various types of catalytic reactions on nanoparticles or bulk surface by developing the theoretical approaches of hetero junction. In this report, we present our recent studies on the mechanism for solvatochromic shifts of free-base porphine,<sup>1)</sup> electronic excitations of C<sub>60</sub> fullerene,<sup>2)</sup> theoretical design of dye-sensitized solar cells,<sup>3)</sup> and interatomic relaxation effects of double core hole states.

## 1. Mechanism for Solvatochromic Shifts of Free-Base Porphine

It has been known that  $\pi$ - $\pi^*$  excitation energies of non-polar conjugated molecules generally exhibit a bathochromic shift (redshift) in solution. The origin of this bathochromic shift is considered to be the dispersive interaction between solute and solvent molecules. Several studies have been conducted on the mechanisms of the solvatochromic shift for nonpolar molecules, and many models have been proposed. However, different approximations lead different conclusions. The dispersive interaction in excited electronic states has not yet been well understood.

The solvatochromic shifts of free-base porphine in the Q- and B-bands were studied using the polarizable continuum model (PCM) and explicit solvent molecules employing TDDFT and the SAC-CI method. The state-specific and linear-response methods were examined in the PCM calculations. These

methods involve different types of solute-solvent interactions. The SAC-CI calculation with explicit solvent molecules includes all types of microscopic solute-solvent interactions including dispersive interaction. Based on our calculations the experimental trends in the solvatochromic shifts of free-base porphine can be explained as follows.

1. The observed bathochromic shift of the B-band in solution is attributed to the interaction of transition dipole with the solvent reaction field.
2. The dispersive interaction caused by the polarizability difference between the ground and excited states is an origin of the observed decrease in the Q-band splitting in nonpolar solvents.
3. The observed refractive index-dependence of the solvent shift in n-alkane can be explained by the dispersive interaction, which relate to the optical dielectric constants of bulk solvent
4. The remarkable decrease in the Q-band splitting in dipolar and quadrupolar solvents cannot be explained by the dispersive interaction alone. Specific solute-solvent interactions are important. Anisotropic interactions are more important than the geometry relaxation for the decrease in the Q-band splitting in solution.

## 2. Electronic Excitations of C<sub>60</sub> Fullerene

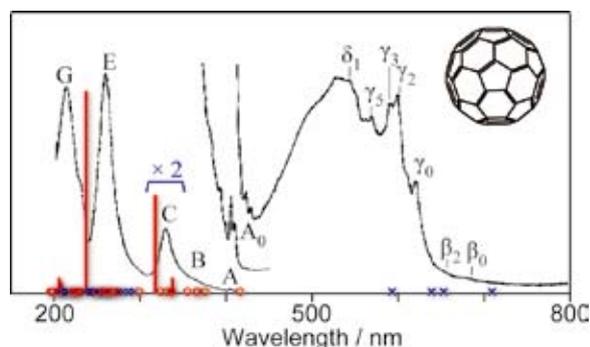
Because of its unique photo-electronic properties, C<sub>60</sub> fullerene well known as buckyball, is receiving an extensive interest in terms of scientific and practical purposes. Derivatives of C<sub>60</sub> are expected to be practical materials for organic thin-film solar cells. Their electronic structure is, however,

quite complicated; it is highly-degenerated and delocalized. Therefore, it has been difficult to perform quantum chemical calculations for excited states of  $C_{60}$  fullerene using highly accurate theories. We successfully applied the direct SAC-CI method to  $C_{60}$  fullerene. The excited states of  $C_{60}$  were accurately calculated by the direct SAC-CI method in the visible to near UV region (below 6.2 eV, 200 nm).

Figure 1 shows the comparison between the SAC-CI results and experimental spectrum of  $C_{60}$ , where circles and x-marks denote optically-forbidden states by the selection rule. The absorption in 500–600 nm corresponds to optically-forbidden states, and therefore, very weak absorption peaks are observed induced by vibronic couplings.

The assignments of photoabsorption spectrum based on the direct SAC-CI results are partially different from the previous assignments based on the semi-empirical molecular orbital calculations. In the previous study, the band A observed around 400 nm has been assigned to the optically-allowed  $1^1T_{1u}$  state; based on the direct SAC-CI calculations, however, this peak should be assigned to the optically-forbidden  $1^1T_{2u}$  state. The present assignment based on the direct SAC-CI results can explain the experimental findings more consistently than the previous study.

To understand the electronic excited states of fullerenes and to predict their energetics are essentially important for the development of molecular electronics such as organic thin-film solar cells. For such purpose, semi-empirical molecular orbital method and density functional theory are insufficient. It is necessary to use highly accurate wavefunction theories that are applicable to large systems such as the direct SAC-CI method.

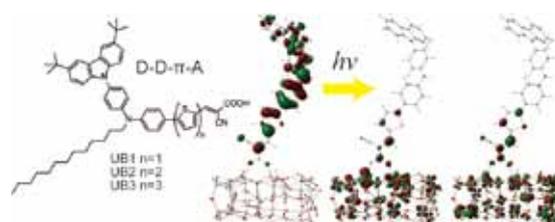


**Figure 1.** The SAC-CI results and experimental absorption spectrum of  $C_{60}$  fullerene.

### 3. Theoretical Study on Dye-Sensitized Solar Cells (DSSCs)

Dye-sensitized solar cell (DSSC) is a solar battery using cheap metal oxides like titanium oxide ( $TiO_2$ ). It is expected as a low-cost solar battery without using the silicon semiconductor. Because  $TiO_2$  does not have photoabsorption in the visible region, the organic dyes adsorbed on the titanium oxide is used as a sensitizer and the electromotive force and electric

current are achieved by the electron transfer from the electronically excited dyes to  $TiO_2$ . Because many factors concern to the efficiency and durability of the cells, the design based on the quantum chemical calculations is necessary. The D-D- $\pi$ -type organic dyes with two electron donors (D),  $\pi$ -spacer ( $\pi$ ), and acceptor (A) suggested by experiment show relatively high energy conversion efficiency. We obtained detailed assignments of the excited states, stability, and assembly of these dyes by theoretical calculations. In addition, the electronic injection process to  $TiO_2$  conduction band was calculated using a cluster model. “Direct” mechanism where the electron injection from dyes to  $TiO_2$  occurs directly was suggested by calculations and the high efficiency of electron injection was supported theoretically.



**Figure 2.** Structure of the D-D- $\pi$ -type DSSC and direct mechanism. Electronic transition occurs from the dye MO to  $TiO_2$  conduction band.

### 4. Polarization and Site Dependence of Interatomic Relaxation Effects in Double Dore Hole States

The interatomic relaxation (IR) effects of two-site double core hole (tsDCH) states in selected molecules with a polarizable unit have been systematically investigated using *ab initio* calculations. The IR effects are analyzed by varying size of this polarizable unit and its position relative to the DCHs. The systems with the DCHs located at the opposite sides of the polarizable unit show large negative IR energies, while those at the same side of the polarizable unit have smaller negative IR effects. Here, the IR energies can even be positive if the polarizable unit is large enough. The generalized Wagner plots of tsDCH states are used to visualize the trend of the IR effects in the molecules studied.

#### References

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