Theoretical Study on Molecular Excited States and Chemical Reactions

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Molecules in the excited states show characteristic photophysical properties and reactivity. We investigate the molecular excited states and chemical reactions which are relevant in chemistry, physics, and chemical biology with developing the highly accurate electronic structure theory. We are also interested in the excited-state dynamics and energy relaxation so that we also develop the methodology of large-scale quantum dynamics. In this report, we report our recent studies on the development of the PCM-SAC-CI method,(1) Molecular double core-hole spectroscopy,(2) and Ultraviolet B blocking molecule.(3)

1. Development of PCM-SAC-CI Method for Solvation Free Energy and Geometry(1)

Electronic excitations of molecules and molecular systems in particular circumstances, such as in solutions, have attracted attention for a long time. Solvatochromism, the shift of transition energies by a solvent, is an important consideration in such research. Photochemical and electrochemical reactions in solution are other considerations. Reliable computational studies are essential for elucidating the mechanism of such complex processes because it is difficult to detect short-lived intermediate states in certain solvents experimentally. There is a strong demand for the development of theoretical and computational methods to understand photochemical and electrochemical phenomena in solution, such as those associated with utilizing photo-energy with functional dyes, organic photovoltaic cells, charge transport in batteries and molecular devices, *etc*.

In this work we present the theory and implementation of the symmetry-adapted cluster (SAC) and symmetry-adapted cluster-configuration interaction (SAC-CI) method, including the solvent effect, using the polarizable continuum model (PCM). The PCM and SAC/SAC-CI were consistently combined in terms of the energy functional formalism. The excitation energies were calculated by means of the state-specific approach, the advantage of which over the linear-response approach has been shown. The single point energy calculation and its analytical energy derivatives are presented and implemented, where the free energy and its derivatives are evaluated because of the presence of solute–solvent interactions. We have applied this method to s-*trans* acrolein and metylenecyclopropene of their electronic excitation in solution. The molecular geometries in the ground and excited states were optimized in vacuum and in solution, and both the vertical and adiabatic excitations were studied. The PCM-SAC/SAC-CI reproduced the known trend of the solvent effect on the vertical excitation energies but the shift values were underestimated. The excited state geometry in planar and nonplanar conformations was investigated. The importance of using state-specific methods was shown for the solvent effect on the optimized geometry in the excited state. The mechanism of the solvent effect is discussed in terms of the Mulliken charges and electronic dipole moment.

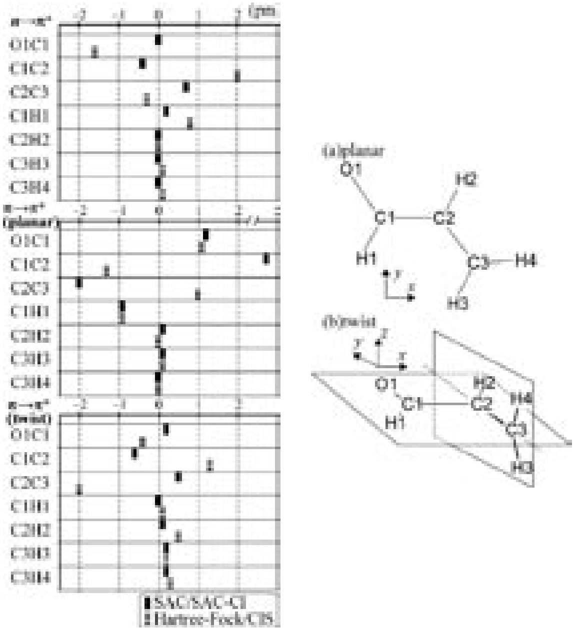

Figure 1. Solvent effect on the changes of bond lengths (in pm) upon electronic excitations for s-*trans* acrolein. The solvent effect denotes the shift in aqueous solution from vacuum.

2. Molecular Double Core-Hole Spectroscopy for Chemical Analysis[2)]

More than two decades ago, Cederbaum *et al*. discovered that the creation of double core vacancies in molecular systems probes the chemical environment more sensitively than the creation of single core vacancies. Two-atomic site double ionization potentials, or briefly two-site DIPs are particularly sensitive to the chemical environment as the examples of the C_2H_2, C_2H_4, C_2H_6 and C_6H_6 molecules demonstrate. The chemical shifts of one-atomic site DIPs, or briefly one-site DIPs, were found to be similar to the chemical shifts of the single core level ionization potentials (IPs), or ionization energies (IEs). This finding has given impetus to a number of theoretical studies aimed at elucidating properties of molecular double core hole states.

In this work, we explore the potential of double core hole electron spectroscopy for chemical analysis in terms of x-ray two-photon photoelectron spectroscopy (XTPPS). The creation of deep single and double core vacancies induces significant reorganization of valence electrons. The corresponding relaxation energies and the interatomic relaxation energies are evaluated by CASSCF calculations. We propose a method how to experimentally extract these quantities by the measurement of single and double core-hole ionization potentials (IPs and DIPs). The influence of the chemical environment on these DIPs is also discussed for states with two holes at the same atomic site and states with two holes at two different atomic sites. Electron density difference between the ground and double core-hole states clearly shows the relaxations accompanying the double core-hole ionization. The effect is also compared with the sensitivity of single core hole ionization potentials (IPs) arising in single core hole electron spectroscopy. We have demonstrated the method for a representative set of small molecules LiF, BeO, BF, CO, N_2, C_2H_2, C_2H_4, C_2H_6, CO_2 and N_2O. The scalar relativistic effect on IPs and on DIPs are briefly addressed.

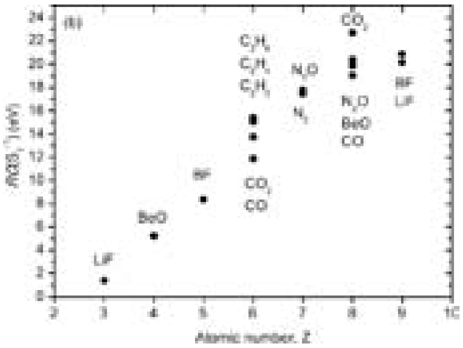

Figure 2. Generalized relaxation energy extracted by the double-core hole IP.

3. Photochemistry of Ultraviolet B Blocking Cinnamates[3)]

We investigated the absorption and emission spectra of UVB blocking cinnamate derivatives with five different substituted positions using the symmetry-adapted cluster configuration interaction (SAC-CI) method. This series included *cis*- and *trans*-isomers of *ortho*-, *meta*-, and *para*-monomethoxy substituted compounds and 2,4,5-(*ortho*-, *meta*-, *para*-) and 2,4,6-(*ortho*-, *para*-) trimethoxy substituted compounds. The ground state and excited state geometries were obtained at the B3LYP and CIS levels of theory. All the compounds were stable as *cis*- and *trans*-isomers in the planar structure in both the S_0 and S_1 states, except the 2,4,6-trimethoxy substituted compound. The SAC-CI calculations reproduced the recently observed absorption and emission spectra satisfactorily. Three low-lying excited states were found to be relevant for the absorption in the UV blocking energy region. The calculated oscillator strengths of the *trans*-isomers were larger than the respective *cis*-isomers, which is in good agreement with the experimental data. In the *ortho*- and *meta*-monomethoxy compounds, the most intense peak was assigned as the transition from next HOMO to LUMO, whereas in the *para*-monomethoxy compound, it was assigned to the HOMO to LUMO transition. This feature was interpreted as being from the variation of the MOs due to the different substituted positions, and was used to explain the behavior of the excited states of the trimethoxy compounds. The emission from the local minimum in the planar structure was calculated for the *cis*- and *trans*-isomers of the five compounds. The relaxation paths which lead to the non-radiative decay were also investigated briefly. Figure 3 compares the UV and SAC-CI spectra of *para*-methoxy-methyl- cinnamate.

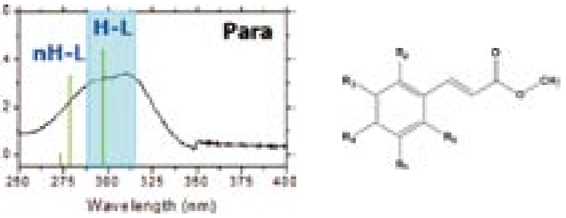

Figure 3. Absorption spectrum of *para*-methoxy-methyl- cinnamate.

References

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Award

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