VIII-CC Theoretical and Computational Study on Gas Phase Reactions and Chromic Molecules

1. Quantum chemical calculations are used to produce potential energy surface (PES) to do reaction dynamics simulations. We develop the methodology to generate PES efficiently and automatically using quantum chemical calculation results. The method does not need any derivative information in quantum chemical calculations.
2. Another interest of our group is theoretical explanation and prediction of structural and spectral changes of photochromic and electrochromic substances.
3. We also search a reasonable pathway to form H_2 from H atoms *via* PAH related catalysts to solve why H_2 is abundant in interstellar space.

VIII-CC-1 Theoretical Study on Photoinduced Color Change and Charge Transfer of Methylviologen

ISHIDA, Toshimasa; MURAKAMI, Makoto[1]; WATANABE, Go[1]; YOSHIKAWA, Hirofumi[2]; NISHIKIORI, Shin-ichi[2]
([1]Shizuoka Univ.; [2]Univ. Tokyo)

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Methylviologen dication is easily reduced to a monocation radical, and turned to be blue, forming a charge-transfer complex with a donor molecule. Yoshikawa *et al*. recently reported photo-induced reduction and charge transfer complexes in polycyano–polycadmate host clathrates. We study this reduction using quantum chemical calculations. The energy changes with the torsion angle of the two cations and the spectral change, solvent effect and the charge transfer between the dication and other guest molecules in the clathrates are investigated. The Hartree-Fock, DFT, CI singles, time dependent DFT calculations are carried out for the ground state and excited states of the two cations. Solvation effect is treated with the polarizable continuum model, and the charge transfer in the clathrates is modeled based on crystal structures determined experimentally. The optimized geometry of the monocation radical was found to be planar while that of the dication is twisted. These results are consistent with recent calculations for related compounds. The color change upon the photoreduction was reproduced by the calculation. The solvent effect of acetonitrile was found to be small. Charge transfer absorption was reproduced for the mesitylene–methylviologen dication complex in the clathrate host using a small model. The geometry modification and the color change were reproduced satisfactorily. The TDDFTscheme reproduces the observed spectra better than the CIS scheme, but the latter scheme is still valuable to evaluate qualitative feature of spectra.

VIII-CC-2 Crystal Structure and Spectroscopic Properties of the CT Complex of Methyl Viologen Dication and *o*-Dimethoxybenzene Included in a Polycyano-Polycadmate Host, and Theoretical Study on Its Red Shifted CT Absorption

YOSHIKAWA, Hirofumi[1]; NISHIKIORI, Shin-ichi[1]; ISHIDA, Toshimasa
([1]Univ. Tokyo)

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Using the polycyano-polycadmate host that is a negative charged Cd cyanide complex with a framework structure built with Cd^{2+} ions and bridging cyanide ligands, we synthesized a clathrate including methyl viologen dication (MV^{2+}) and *o*-dimethoxybenzene (ODMB) as guests. The color of the clathrate was red and its origin was considered to be charge transfer (CT) interaction of a CT complex formed with MV^{2+} as an acceptor and ODMB as a donor in the host. The wavelength at the CT absorption maximum was largely red shifted compared with that of the CT complex in an acetonitrile solution. The single crystal X-ray diffraction analysis revealed a π-π stacking structure of the CT complex and a 1D arrangement of the CT complexes in a channel-like cavity of the framework host. In the array of the CT complexes, MV^{2+} ions are adjacent to each other and their separation is short. The direction of the transition moment of the CT absorption determined from the structural information and the spectrum measured on a crystalline sample agreed with that derived from *ab initio* calculations at the CIS/6-31+G* level. Our calculations also showed that the red shift of the CT absorption is mainly due to electrostatic effects between the CT complexes, not due to the shortening of the distance between MV^{2+} and ODMB, which is generally believed to be the reason. The negative charged host stabilizes the ground state of the CT complex, but the electrostatic interaction between the CT complexes heightens the ground state and lowers the excited state. In this clathrate, due to the CT complex array with the short separation the effect from the guests overcomes that from the host and the red shift appears.

VIII-CC-3 A Local Interpolation Scheme Using No Derivatives in Potential Sampling: Application to O(^1D) +H_2 System

ISHIDA, Toshimasa; SCHATZ, George C.[1]
([1]Northwestern Univ.)

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We recently proposed a local interpolation scheme, in which interpolant moving least squares (IMLS) and Shepard interpolation are employed to describe potential energy surfaces. This IMLS/Shepard scheme is applicable to do potential interpolation with quantum chemical results for which analytical derivatives are not available. In this study, we apply the scheme to the highly exothermic O(^1D) +H_2 → H + OH reaction and compare it with results based on Shepard interpolation using second order Taylor expansions. An analytical surface is used to define the potential function so that errors in the interpolation function may accurately be determined. We found that the present scheme reproduces the correct reactive cross sections more accurately than the Shepard scheme, and with rms errors for energy and gradients that are significantly smaller than those from Shepard interpolation. This occurs even though the present scheme does not utilize derivative and hessian information whereas the Shepard interpolation does. The Bayesian approach proposed by Bettens and Collins does not improve the IMLS/Shepard results significantly although it does the Shepard-only approach. The accuracy in the IMLS/Shepard scheme is surprising, but can be explained by the more global nature of the interpolation.

VIII-CC-4 Possible Molecular Hydrogen Formation Mediated by the Radical Cations of Anthracene and Pyrene

HIRAMA, Mutsumi[1]; **ISHIDA, Toshimasa;**
AIHARA, Jun-ichi[1]
([1]Shizuoka Univ.)

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Hydrogen molecules cannot be formed readily by the association of gaseous hydrogen atoms. Possible H_2 formation mediated by the radical cations of typical polycyclic aromatic hydrocarbons (PAHs), anthracene and pyrene, was studied at the B3LYP/6-31G** level of theory. We presumed that H_2 is formed by way of two elementary reactions, the addition of an H atom to a PAH molecular cation and the H abstraction from the resulting monohydro-PAH cation (*i.e.*, arenium ion) by a second H atom to yield H_2. The first reaction takes place without any activation energy. The second reaction is also predicted to proceed along almost barrierless pathways although it is far from being a typical ion-molecule reaction. There is a possibility that these reactions might constitute one of the mechanisms for H_2 formation in extremely cold interstellar space. Deuterium enrichment in PAH cations is possibly accompanied by such H_2 formation since deuteration lowers the energies of polyatomic PAH cations appreciably.

VIII-CC-5 Molecular Hydrogen Formation Mediated by a Naphthalene Radical Cation

TOKOSUMI, Takaaki[1]; **HIRAMA, Mutsumi**[1];
TERADA, Yoshihiro[1]; **HAGIWARA, Noriko**[1];
ISHIDA, Toshimasa; AIHARA, Jun-ichi[1]
([1]Shizuoka Univ.)

[*Phys. Chem. Chem. Phys.* submitted]

Hydrogen molecules cannot be formed readily by the association of gaseous hydrogen atoms. Bauschlicher and we independently proposed a possible molecular hydrogen formation mediated by polycyclic aromatic hydrocarbon (PAH) radical cations in space. We studied such a reaction process at the B3LYP/6-31G** level of theory and for the first time succeeded in determining the entire reaction pathway for the H_2 formation mediated by the naphthalene radical cation. We presumed that H_2 is formed by way of two elementary reactions, the addition of an H atom to a naphthalene cation and the H abstraction from the resulting naphthalenium ion by a second H atom to yield H_2. The first reaction takes place without any activation energy. The second reaction is predicted to proceed *via* a van der Waals complex but with little activation energy. These reactions are supposed to enhance the deuteration of the naphthalene cation. Neutral naphthalene also mediates the H_2 formation but needs some activation energy.

VIII-CC-6 Possible Molecular Hydrogen Formation Mediated by the Inner Carbon Atoms of PAH Radical Cations

HIRAMA, Mutsumi[1]; **ISHIDA, Toshimasa;**
AIHARA, Jun-ichi[1]
([1]Shizuoka Univ.)

[in preparation]

Molecular hydrogen in space is believed to form from atomic hydrogen. During the past few years, we have been performing density functional theory (DFT) calculations to explore the possibility of H_2 formation mediated by the radical cations of gaseous polycyclic aromatic hydrocarbons (PAHs). As a continuation of this study, we explored the catalytic ability of inner carbon atoms of some typical PAH cations at the B3LYP/6-31G** level of theory. We presumed as before that H_2 is formed by way of two elementary reactions, the addition of an H atom to a PAH cation and the H abstraction from the resulting arenium ion by another H atom to yield H_2. We found that both reactions proceed without any activation energy. It follows that almost all carbon atoms of a PAH cation give sites for moelcular hydrogen formation. Since there are large compact PAHs abundantly in space, the H_2 formation at the inner carbon atoms of such PAH cations can never be overlooked. Even if inner carbon atoms might be less reactive than peripheral ones, there are many inner carbon atoms in large compact PAH cations.