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

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/or automatically using quantum chemical calculation results. Another interest of our group is theoretical explanation and prediction of structural and spectral changes of photochromic and electrochromic substances.

VIII-R-1 Polycyano–Polycadmate Host Clathrates Including a Methylviologen Dication. Syntheses, Crystal Structures and Photo-Induced Reduction of Methylviologen Dication

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A series of polycyano-polycadmate host clathrates including a methylviologen dication (MV^{2+}), which is a photo-hemically active electron acceptor, and an organic molecule, such as alcohols, haloalkanes, ethers and small aromatics, and two complexes built of a polycyano-polycadmate and MV^{2+} were synthesized. The single crystal X-ray diffraction experiments on ten clathrates and the two complexes revealed their 3-D network polycyano-polycadmate structures built of Cd^{2+} ions and CN. bridges. The network structures are classified into five structure types. Type I, II and III were found in the clathrates, and Type IV and V were turned up in the two complexes. Type I and II have cage-like cavities and each of the cavities includes one guest, MV^{2+} or an organic molecule. Type III has a channel-like cavity where MV^{2+} ions and organic molecules are included. Type IV and V have 3-D space, which is neither a cage-like cavity nor a channel-like cavity, for embracing MV^{2+}. Although all compounds were colorless and the formation of a charge transfer complex between MV^{2+} and a neutral guest in the clathrates was not confirmed from the structural data and diffuse reflectance spectra, some of them showed a color change from colorless to blue on UV irradiation, and which arose from the reduction of MV^{2+} to a methylviologen radical $MV^{+\bullet}$.

VIII-R-2 IR Absorption Spectra of Electrochromic WO_3 Films

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WO_3 films were prepared by thermal evaporation. IR absorption spectra of the films were measured for various amount of injected protons. Three peaks of ν(W–OH), ν(W=O) and ν(O–W–O) vibrations were observed. With increasing of injected protons, the intensity of peak of ν(W–OH) increased and its position shifted hugely from 3200 to 2400 cm^{-1}. We calculated various bond-patterns of OH vibrations. Then OH vibrations accompanied with hydrogen bonds are plausible for observed OH peaks. On the other hand, with increasing of injected protons the intensity of peak of ν(W=O) bond also increased, but its position shifted a little. It is considered that parts of W–O–W–O–W bonds were broken by injected protons and then W=O bonds were brought about.

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

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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 $O(^1D) + H_2 \rightarrow H + OH$ 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-R-4 Theoretical Study on Photoinduced Color Change and Charge Transfer of Methylviologen

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Motivation. Methylviologen dication is easily reduced to be a monocation radical, and turned to be blue, and forms 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 the 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.
Method. The Hartree-Fock and 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.
Results. 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.
Conclusions. The geometrical and the color change was reproduced satisfactorily. The TDDFT scheme reproduces the observed spectra better than the CIS scheme, but the latter scheme is still valuable to evaluate qualitative feature of spectra.

VIII-R-5 Potential Energy Surface Generation Using Ab Initio Calculations and IMLS/Shepard Interpolation for the LiH + H $\rightleftarrows$ Li + H_2 Reactions

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CASSCF following MRCI calculations are employed to generate potential energy surfaces for the reaction of LiH + H $\rightleftarrows$ Li + H_2 and analyze the reactive region for the reaction. Spectroscopic data for LiH and H_2 obtained by our scheme are in good agreement with experiment results. IMLS combined with Shepard interpolation method is used to interpolate the Potential energy surfaces. Trajectory calculations for LiH + H → Li + H_2 on the interpolated potential energy surface illustrate that the initial vibrational content of LiH plays a rather minor role which is explained by the fact there is no energy barrier for the reaction LiH + H → Li + H_2, and the reactive cross section has maximum value, when the initial collision energy is about 0.1 eV. Trajectory calculations for Li + H_2 → LiH + H show that the reaction requires highly excited $H_2(v \geq 4)$ molecules for it to occur at low collision energy and it is more efficient to put the same amount energy into the H_2 vibration energy rather than translational energy.