IX-Y Theoretical and Computational Study on Gas Phase Reactions

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. We search a reasonable pathway to form H_2 and the other interstellar molecules *via* PAH related catalysts.
3. We also calculate (electronic) CD spectra to determine the absolute configuration of several chiral molecules in collaboration with experimentalists.

IX-Y-1 Aromatic Character of Annelated Dimethyldihydropyrenes

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Aromaticity is one of the fascinating concepts in modern organic chemistry. It has been defined in structural, magnetic and energetic terms. Historically, many chemists have discussed aromaticity most conveniently in terms of ^1H chemical shifts. Mitchell and coworkers noted that ^1H chemical shifts of the internal methyl groups in dimethyldihydropyrene (DDP) and its annelated derivatives serve to assess the relative local aromaticities of the DDP nuclei. They recently estimated the order of aromaticity for DDP nuclei in annelated derivatives using nucleus-independent chemical shifts (NICS). We found that two graphtheoretically defined energetic quantities, percentage topological resonance energy (% TRE) and bond resonance energy (BRE), can be used to predict readily the relative aromaticities of these hydrocarbons and their DDP nuclei, respectively. Since these quantities are not dependent on the areas of individual rings, they are better suited for estimating the degree of aromaticity.

IX-Y-2 Possible Molecular Hydrogen Formation Mediated by the Inner and Outer Carbon Atoms of Typical PAH Cations

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We have been exploring the possibility of H_2 formation mediated by the radical cations of gaseous polycyclic aromatic hydrocarbons (PAHs). In this study, we estimated the catalytic ability of the inner carbon atoms of some typical PAH cations at the B3LYP/6-31G** level of theory and compared it with that of the outer carbon atoms. 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 molecular 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.

IX-Y-3 One-Pot Synthesis of Helical Aromatics: Stereoselectivity, Stability against Racemization, and Assignment of Absolute Configuration Assisted by Experimental and Theoretical Circular Dichroism

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Helical aromatics (**1**) were synthesized *via* one step in good quantity by solvent-free condensation of *N,N'*-*p*-phenylenediamine (**2**) and various carboxylic acids in the presence of Lewis acid. Microwave irradiation greatly facilitated the condensation reaction to furnish **1** with a 100% diastereo- and a 50% enantioselectivity, when a chiral carboxylic acid was utilized. **1f**, derived from 2-methylglutaric acid, was quite stable, no racemization taking place even at 200 °C. The assignment of the absolute configurations to the helical aromatics has been attempted by CD exciton chirality method and comparison of experimental and theoretical CD spectra calculated by time-dependent density functional theory.

IX-Y-4 A Local Interpolation Scheme Using No Derivatives in Potential Sampling: Application to OH + H_2 System

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[in preparation]

We recently proposed a local interpolation scheme, in which interpolant moving least squares (IMLS) and the modified Shepard interpolation proposed by Collins 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. We applied the scheme to a four atomic system $OH + H_2 \rightarrow H_2O + H$

reaction. As for the former system, we compared the results with those based on the modified 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 energy and gradient errors in the present scheme is comparable to those in the modified Shepard scheme. Note that the present scheme does not utilize derivative and hessian information whereas the Shepard interpolation does. The accuracy in the IMLS/Shepard scheme is surprising, but can be explained by the more global nature of the interpolation.

IX-Y-5 Possible Interstellar Molecule Formations Mediated by Naphthalene Cation

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[in preparation]

We have studied the possibilities of interstellar molecule formation mediated by the radical cations in the gas phase. In this letter, we explored the catalytic role of a typical PAH cation, a naphthalene cation, at the both B3LYP/6-31G** and MP2/6-31G** levels of theory. We presumed that interstellar molecule 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 one interstellar molecular species to form another interstellar molecular species. It was found that the first reactions proceed with no activation energies. Refinement of the activation energies with both spin-projected and unrestricted MP2 procedures confirmed no or very small activation energies for the second reactions.

We employ the simplest PAH, a naphthalene, as molecular catalyst and consider that the naphthalenium ion is one of the key intermediates not only in the formation of molecular hydrogen but also in the formation of interstellar molecular species. We studied some formations of their species, *i.e.*, HCCH, CH_4, HCN, HNC, H_2O, NH_3, NH_2, CH_3, and CH_2. All of these species and these precursors have observed in space.

IX-Y-6 Molecular Rattles Using Excited States and Non-Adiabatic Transition

ISHIDA, Toshimasa; NANBU, Shinkoh; NAKAMURA, Hiroki

[in preparation]

Non-adiabatic phenomena play crucial roles in the molecular science, in particular, in the molecular material field. Nakamura and Nanbu proposed the idea for the molecular switching with aggressive use of the phenomena although the virtual system composed of an ideal one-dimensional finite periodic potential system was used. The key-phenomena in the idea are the complete reflection and complete transmission. Once we find the appropriate condition for those phenomena in the corresponding system, the molecular motion can be completely controlled without any exception.

We newly propose the application of our idea to the transmission of hydrogen atom through cyclic molecule. This may be regarded as a model of encapsulation by carbon nanotubes.

We explored lots of systems with theoretical calculations, and finally it is found that several model systems seem to be suitable. Two of them are (1) cyclopentadienyl radical (C_5H_5) + H reaction model and (2) C_9H_9 + alkaline atom system.

In these systems, we found complete transmission and reflection, which is based on two non-adiabatic transition of non-adiabatic tunneling type. We will discuss possible application to real systems.

IX-Y-7 Quantum Chemical Study of H_2 Formation Reaction *via* the Benzene Cation Catalyst

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[in preparation]

We have been exploring a possibility that polycyclic aromatic hydrocarbon (PAH) cations may catalyze the H_2 formation because PAHs are ubiquitous in interstellar space and are probably partly ionized by stellar UV radiation. Benzene is not a PAH, but is an aromatic hydrocarbon, so that it is expected to give similar energy profile to PAHs. Thus, we undertake to use benzene cations to investigate the effect of more sophisticated method for electron correlation on the energy profile of the H_2 formation reaction.

$C_6H_6^+ + H \rightarrow C_6H_7^+$
$C_6H_7^+ + H \rightarrow C_6H_6^+ + H_2$

We employed coupled cluster singles and doubles (CCSD) and its modification with the third order perturbation energy (CCSD(T)) as well as QCISD(T) at the MP2-optimized geometries to make comparison of the results with the B3LYP and MP2 ones to estimate higher correlation effects. In addition, use of both the B3LYP and MP2 results proposed by Turecek was valuated. CCSD, CCSD(T), and QCISD(T) calculations gave us activation energies between B3LYP and MP2 values. From these results, hybrid use of B3LYP and MP2 would be justified to estimate activation energies for larger PAH cation catalyst systems.