RESEARCH ACTIVITIES I
Department of Theoretical Studies

I-A Theoretical Study and Design of New Bonding, Structures, and Reactions

It is an important subject to develop molecules with novel bonding and structures. Thus, new bonds containing heavier atoms are investigated, which are the focus of interest as new building block for molecular design. In addition, cage-like molecules and clusters are investigated to characterize guest-host interactions, which serve as molecular containers and recognition. Efficient computational methods are also investigated to perform calculations of large molecular systems.

I-A-1 Theoretical Investigation of Triple Bonding between Transition Metal and Main Group Elements in (η^5-C_5H_5)$(CO)_2$M≡ER (M = Cr, Mo, W; E = Si, Ge, Sn, Pb; R = Terphenyl Groups)

TAKAGI, Nozomi; YAMAZAKI, Kentaro[1]; NAGASE, Shigeru
([1]Univ. Tokyo)

[*Bull. Korean Chem. Soc. (a special issue)* **24**, 832–836 (2003)]

To extend the knowledge of triple bonding between group 6 transition metal and heavier group 14 elements, the structural and bonding aspects of (η^5-C_5H_5)$(CO)_2$-M≡ER (M = Cr, Mo, W; E = Si, Ge, Sn, Pb) are investigated by hybrid density functional calculations at the B3PW91 level. Substituent effects are also investigated with R = H, Me, SiH_3, Ph, C_6H_3-2,6-Ph_2, C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$, and C_6H_3-2,6-(C_6H_2-2,4,6-*i*Pr_3)$_2$.

I-A-2 Synthesis and Characterization of Cyclic Silicon Compounds of Fullerenes

WAKAHARA, Takatsugu[1]; KAKO, Masahiro[2]; MAEDA, Yutaka[3]; AKASAKA, Takeshi[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Univ. Electron-Communication; [3]Tokyo Gakugei Univ.)

[*Curr. Org. Chem.* **7**, 927–943 (2003)]

Organosilicon compounds are among the most important inter-element compounds, as exemplified by disilanes and polysilanes. Since the availability of C_{60} in preparatively useful quantities, the chemical functionalization has attracted considerable interest, which leads to new cyclic silicon compounds. It is experimentally and theoretically investigated how silylenes, which are derived from a variety of disilanes under thermal and photochemical conditions, react with fullerenes and endohedral metallofullerenes. Mono-, bis-, and even multi-silylation of fullerenes lead to a new class of silicon compounds that are useful in material applications.

I-A-3 Calculation of Packing Structure of Methanol Solid using Ab Initio Latice Energy at the MP2 Level

NAGAYOSHI, Kanade[1]; KITAURA, Kazuo[2]; KOSEKI, Shiro[3]; RE, Suyong; KOBAYASHI, Kaoru; CHOE, Yoong-Kee; NAGASE, Shigeru
([1]IMS and Osaka Prefecture Univ.; [2]AIST; [3]Osaka Prefecture Univ.)

[*Chem. Phys. Lett.* **369**, 597–604 (2003)]

An ab initio MO based lattice energy minimization method is applied to the calculation of packing structures of methanol crystal, α- and β-phases. The second order Møller-Plesset perturbation theory (MP2) is employed to calculate lattice energies. The lattice parameters optimized at the MP2/6-31G++G(*d,p*) level for α- and β-phases are in good and moderate agreement with the experimental values, respectively. The average relative errors of calculated cell lengths are 0.9 and 6.2% for α- and β-phases, respectively.

I-A-4 Computational Procedure of Lattice Energy using the Ab Initio MO Method

NAGAYOSHI, Kanade[1]; IKEDA, Tohru[2]; KITAURA, Kazuo[3]; NAGASE, Shigeru
([1]IMS and Osaka Prefecture Univ.; [2]Osaka Prefecture Univ.; [3]AIST)

[*J. Theor. Comput. Chem.* **2**, 233–244 (2003)]

Recently, we have proposed a computational procedure for calculations of lattice energies of molecular crystals using the *ab initio* MO method. This procedure does not use potential functions and is applicable to a variety of molecular crystals. The procedure has been successfully applied to calculation of packing structure of electron donor-acceptor complex, H_3N-BF_3, and hydrogen bonding crystal, CH_3OH. In this work, we present a full account of the computational procedure. This method is applied to the packing structure calculations of hydrocarbon crystals, C_2H_2, C_2H_4 and C_6H_6. The lattice parameters optimized at the MP2/6-311++G** level are in good agreement with the experimental values. The basis set dependence of the lattice constants is also discussed for several crystals.

I-A-5 $La_2@C_{80}$: Is the Circular Motion of Two La Atoms Controllable by Exohedral Addition?

KOBAYASHI, Kaoru; NAGASE, Shigeru; MAEDA, Yutaka[1]; WAKAHARA, Takatsugu[2]; AKASAKA, Takeshi[2]
([1]Tokyo Gakugei Univ.; [2]Univ. Tsukuba)

[*Chem. Phys. Lett.* **374**, 562–566 (2003)]

Density functional calculations are carried out for the $La_2@C_{80}$ derivatives to investigate whether the motion of metals encapsulated inside fullerenes is controlled by exohedral addition. It is shown that the three-dimensional random motion of two La atoms in $La_2@C_{80}$ can be restricted to the circular motion in a plane by attaching electron-donating molecules on the outer surface of the C_{80} cage. It is expected that the two-dimensional circular motion will help to induce a unique electronic or magnetic field.

I-A-6 A Theoretical Study of Spin Density Distributions and Isotropic Hyperfine Couplings of N and P atoms in $N@C_{60}$, $P@C_{60}$, $N@C_{70}$, $N@C_{60}(CH_2)_6$, and $N@C_{60}(SiH_2)_6$

KOBAYASHI, Kaoru; NAGASE, Shigeru; DINSE, Klaus-Peter[1]
([1]IMS and TU-Darmstadt)

[*Chem. Phys. Lett.* **377**, 93–98 (2003)]

Spin density distributions and isotropic hyperfine coupling constants of $N@C_{60}$, $P@C_{60}$, $N@C_{70}$, $N@C_{60}(CH_2)_6$, and $N@C_{60}(SiH_2)_6$ are theoretically investigated by testing B3LYP and MP2 methods for the free N and P atoms. When N is encapsulated inside C_{60}, the calculated spin density at nucleus N increases. In $P@C_{60}$, the corresponding increase is much larger. $N@C_{60}$ has a slightly larger spin density at N than $N@C_{70}$. These agree well with the observed isotropic hyperfine coupling constants. Upon addition of CH_2 groups on the $N@C_{60}$ cage, the spin density at N is slightly decreased. However, addition of SiH_2 groups increases significantly the spin density at the nitrogen nucleus.

I-A-7 Theoretical Identification of C_{20} Carbon Clusters

LU, Jing[1]; RE, Suyong; CHOE, Yoong-Kee; NAGASE, Shigeru; ZHOU, Yunsong[2]; HAN, Rushan[2]; PENG, Lianmao[2]; ZHANG, Xinwei[2]; ZHAO, Xiangeng[2]
([1]IMS and Peking Univ.; [2]Peking Univ.)

[*Phys. Rev. B* **67**, 125415 (7 pages) (2003)]

Free energies, electron affinities and vibrational modes are theoretically investigated for several C_{20} isomers. The dominant C_{20} species generated by vaporizing graphite is first clarified. It turns out to be the monocyclic ring, followed by a tadpole (a short chain attached to a monocyclic ring), linear chain, and a bicyclic ring. On this basis, the two recently synthesized C_{20} isomers [*Nature* **407**, 60 (2000)] may be exclusively attributed to fullerene and bowl structures. Therefore, the existence of the smallest fullerene and C_{20} bowl isomer appear to be fully confirmed.

I-A-8 Structural and Electronic Properties of Metal-Encapsulated Silicon Clusters in a Large Size Range

LU, Jing[1]; NAGASE, Shigeru
([1]IMS and Peking Univ.)

[*Phys. Rev. Lett.* **90**, 115506 (4 pages) (2003)]

Structural and electronic properties of metal-doped silicon clusters MSi_n (M = W, Zr, Os, Pt, *etc.*) in a large size range $8 \le n \le 20$ are theoretically investigated. In contrast to a recent experiment suggesting that a metal atom is encapsulated inside the Si_n cluster, we reveal that the formation of endohedral structures depends strongly on the size of silicon clusters. Two novel structures of chemically stable endohedral species are manifested. The suitable $M@Si_n$ building blocks of self-assembly materials vary in the range $10 \le n \le 16$. The thermodynamical magic numbers are found to coincide with the chemical magic numbers for five clusters.

I-A-9 Metal-Doped Germanium Clusters MGe_n at the Sizes of $n = 12$ and 10: Divergence of Growth Patterns from the MSi_n Clusters

LU, Jing[1]; NAGASE, Shigeru
([1]IMS and Peking Univ.)

[*Chem. Phys. Lett.* **372**, 394–398 (2003)]

Structural and electronic properties of metal-doped germanium clusters MGe_n (M = Hf, W, Os, Ni, and Zn) in the sizes of $n = 12$ and 10 are investigated using hybrid density functional theory calculations. It is found that the growth patters are different from those of $M@Si_n$ clusters, though the pure Ge_n and Si_n clusters have identical geometries in the two sizes. The MGe_{12} (M = W and Os) and $ZnGe_{12}$ clusters have endohedral distorted hexagonal prismatic and endohedral perfect icosahedral structures, respectively, and show higher chemical stability among these checked MGe_n clusters. This makes them attractive for cluster-assembled materials.

I-A-10 $Ca@C_{72}$ IPR and Non-IPR Structures; Computed Temperature Development of their Relative Concentrations

SLANINA, Zdenek[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]IMS and Academia Sinica)

[*Chem. Phys. Lett.* **372**, 810–814 (2003)]

Relative concentrations of four isomers of $Ca@C_{72}$

(one species with isolated pentagons, two isomers with a pentagon-pentagon junction, one structure with a heptagon) are computed using the Gibbs energy in a broad temperature interval. It is shown that both isomers with pentagon-pentagon junction are relatively close in concentrations at higher temperatures while the structure with isolated pentagons comes as a minor isomer (though it is the highest in potential energy) and the structure with heptagon is always negligible.

I-A-11 Photochemical Bissilylation of C_{70} with Disilane

RAHMAN, G. M. Aminur[1]; MAEDA, Yutaka[2]; WAKAHARA, Takatsugu[2]; KAKO, Masahiro[3]; SATO, Soichi[2]; OKAMURA, Mutsuo[1]; AKASAKA, Takeshi[2]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Niigata Univ; [2]Univ. Tsukuba; [3]Univ. Electro-Communications)

[*ITE Lett. Batt. New Tech. Med.* **4**, 60–66 (2003)]

The photochemical reaction of C_{70} with disilane affords bisadducts and monoadducts as major and minor products, respectively, which are successfully isolated. Theoretical calculations are carried out to disclose the structural features. The reaction patterns are characterized by calculating spin density distributions. It is expected that the silicon derivatives will play an important role in material and catalytic applications.

I-A-12 Redox Properties of Carbosilylated and Hydrosilylated Fullerene Derivatives

WAKAHARA, Takatsugu[1]; RAHMAN, G. M. Aminur[2]; MAEDA, Yutaka[1]; KAKO, Masahiro[3]; SATO, Soichi[2]; OKAMURA, Mutsuo[2]; AKASAKA, Takeshi[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Niigata Univ; [3]Univ. Electro-Communications)

[*ITE Lett. Batt. New Tech. Med.* **4**, 67–73 (2003)]

Experimental results and theoretical calculations suggest that the electrochemical properties of fullerenes, such as reduction and oxidation potentials, are significantly modified by attaching exohedrally silicon atoms on carbon cages. Among these, hydrosilylation and carbosilylation of C_{60} are useful to produce electronegative fullerene derivatives. It is expected that the derivatives with highly low oxidation potentials will open up a new application of C_{60} as a unique electron-donor.

I-A-13 B3LYP/6-31G* Computations of $C_{60}F_{36}$ (*g*) Isomers

SLANINA, Zdenek[1]; BOLTALINA, Olga V.[2]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]IMS and Academia Sinica; [2]Moscow State Univ.)

Three isomers of $C_{60}F_{36}$ have been known from experiment. Previous computations however suggested five low-energy isomers though different methods do not always agree on the separation energetics. The present B3LYP/6-31G* computations support the observation of just three species. However, the computed energetics must still be adjusted in order to reproduce the observed concentration ratios.