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, multiple bonds between heavier atoms are investigated which are the focus of interest as new building block for molecular design. In addition, large cage-like molecules and clusters are investigated to characterize guest-host interactions, which serve as molecular containers and recognition. To develop new reactions, the catalytic reactions of enzymes are investigated. A theoretical method to predict molecular crystal structures is in progress.

I-A-1 A Silicon-Silicon Triple Bond Surrounded by Bulky Terphenyl Groups

TAKAGI, Nozomi; NAGASE, Shigeru

[*Chem. Lett.* 966 (2001)]

Since the first synthesis in 1981, a number of stable silicon-silicon doubly bonded compounds have been synthesized and isolated. However, stable silicon-silicon triply bonded compounds, disilynes ($R\mathrm{Si{\equiv}Si}R$), are still unknown, which are the focus of interest in silicon chemistry. In search of an isolable disilyne, effects of bulky terphenyl groups on silicon-silicon triple bonding are investigated. It is predicted that $\mathrm{Ar^{*}Si{\equiv}SiAr^{*}}$ (Ar* = 2,6-bis(2,4,6-triisopropylphenyl)phenyl) is an interesting synthetic target.

I-A-2 The Quest of Stable Silanones: Substituent Effects

KIMURA, Masahiro; NAGASE, Shigeru

[*Chem. Lett.* 1098 (2001)]

Recent remarkable progress in the heavier analogues of ketones is marked by the isolation of silanethione ($R_2\mathrm{Si{=}S}$) and silaneselone ($R_2\mathrm{Si{=}Se}$). As the member of this family, however, isolable silanones ($R_2\mathrm{Si{=}O}$) are still missing except for the transient intermediates and spectroscopic detection, because of the high reactivities due to the polarized $\mathrm{Si^{\delta+}{=}O^{\delta-}}$ bond. DFT and ONIOM calculations are systematically carried out to suppress the high reactivities. Several isolable silanones are predicted, which are worthy of experimental testing.

I-A-3 Substituent Effects on Germanium-Germanium and Tin-Tin Triple Bonds

TAKAGI, Nozomi; NAGASE, Shigeru

[*Organometallics* **20**, 5498 (2001)]

Triple bonds between heavier main group elements are of widespread interest. We have suggested that disilynes ($R\mathrm{Si{\equiv}Si}R$) are a viable synthetic target when they bear proper bulky substituents [*Organometallics* **20**, 234 (2001)]. It is an important question whether the still heavier analogues are also synthetically accessible and isolable as stable molecules. Effects of bulky aryl groups such as $\mathrm{C_6H_2\text{-}2,4,6\text{-}\{CH(SiMe_3)_2\}_3}$ and $\mathrm{C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}}i\mathrm{\text{-}Pr_3)_2}$ on germanium-germanium and tin-tin triple bonds are theoretically investigated in search of isolable digermynes ($R\mathrm{Ge{\equiv}Ge}R$) and distannynes ($R\mathrm{Sn{\equiv}Sn}R$).

I-A-4 Theoretical Study of an Isolable Compound with a Short Silicon-Silicon Triple Bond; $(t\mathrm{Bu_3Si})_2\mathrm{MeSiSi{\equiv}SiSiMe(Si}t\mathrm{Bu_3)_2}$

TAKAGI, Nozomi; NAGASE, Shigeru

[*Eur. J. Inorg. Chem.* 2775 (2002)]

According to our theoretical investigations [*J. Organomet. Chem.* **611**, 264 (2000)], electropositive silyl groups are electronically more effective than aryl groups in realizing a less trans-bent disilyne with a short silicon-silicon triple bond. However, it has been found that silyl groups such as $\mathrm{Si}t\mathrm{Bu_3}$ and $\mathrm{SiDep_3}$ (Dep = 2,6-diethylphenyl) are not sufficiently bulky to make disilynes isolable under normal conditions. Therefore, the effects of a very bulky silyl group, $R^{**} = \mathrm{SiMe(Si}t\mathrm{Bu_3)_2}$, on silicon-silicon triple bonding are investigated using density functional theory. It is found that $R^{**}\mathrm{Si{\equiv}Si}R^{**}$ is stable enough to be isolable and has a silicon-silicon triple bond that is as short as 2.072 Å.

I-A-5 Intersting Compounds Featuring Double Bonding between Heavier Group 15 Elements

SASAMORI, Takahiro[1]; TAKEDA, Nobuhiro[1]; TOKITOH, Norihiro[1]; OKAZAKI, Renji[3]; KIMURA, Masahiro; NAGASE, Shigeru
([1]Kyoto Univ.; [2]Japan Women's Univ.)

[*Angew. Chem. Int. Ed.* **41**, 139 (2002)]
[*Bull. Chem. Soc. Jpn.* **75**, 661 (2002)]

Distibene ($R\mathrm{Sb{=}Sb}R$), dibismuthene ($R\mathrm{Bi{=}Bi}R$), and phosphabismutene ($R\mathrm{P{=}Bi}R$) have been synthesized by taking advantage of steric protection using an efficient steric protection group, $\mathrm{C_6H_2\text{-}2,4,6\text{-}\{CH(SiMe_3)_2\}_3}$, as the first examples of double bonds to fifth-row and sixrow elements in group 15. The structural features are investigated using density functional theory by changing the substituent groups.

I-A-6 The First Halogen-Substituted Cyclotrigermenes: A Unique Halogen Walk over the Three-Membered Skeleton and Facial Stereoselectivity in the Diels-Alder Reaction

SEKIGUCHI, Akira[1]; ISHIDA, Yutaka[1]; FUKAYA, Norihisa[1]; ICHINOHE, Masaki[1]: TAKAGI, Nozomi; NAGASE, Shigeru
([1]Univ. Tsukuba)

[*J. Am. Chem. Soc.* **124**, 1158 (2002)]

Unsaturated three-membered ring compounds consisting of heavier group 14 elements, cyclotrimetallenes, have attracted considerable attention because of their unique structures; the chemistry has developed very rapidly. However, the heteroatom-substituted cyclotrimetallenes are unknown because of the synthetic difficulty and instability. By introducing electronegative halogen atoms, the first hetero-substituted cyclotrigermenes are synthesized and the structural features are theoretically investigated. The interaction between the low-lying exo σ* (Ge–halogen) and high-lying endocyclic π (Ge=Ge) orbitals play an important role.

I-A-7 Effects of the σ* Orbital of C-Apical O-Equatorial Spirophosphoranes on the Structure, Stereomutation, and Reactivity

AKIBA, Kin-ya[1]; MATSUKAWA, Shiro[2]; ADACHI, Takahiro[2]; YAMAMOTO, Yohsuke[2]; RE, Suyong; NAGASE, Shigeru
([1]Waseda Univ.; [2]Hiroshima Univ.)

[*Phosphorus, Sulfur Silicon Relat. Elem.* **177**, 1671 (2002)]
[*J. Am. Chem. Soc.* **124**, 13154 (2002)]

Interesting effects of the σ* orbital of C-apical O-equatorial (O-*cis*) spirophosphoranes are investigated from theoretical and experimental points of view. It is experimentally found that O-*cis* phosphoranes are much more electrophilic on the phosphorus atom than the O-*trans* isomers. It is calculated that the $\sigma^*_{\text{P–O}}$ orbital level of O-*cis* phosphoranes is 19 kcal/mol lower than the $\sigma^*_{\text{P–C}}$ orbital level of O-*trans* phosphoranes. The low-lying σ* orbital plays an important role in enhancing the electrophilicity of spirophosphoranes.

I-A-8 Theoretical Calculations of Vibrational Modes in Endohedral Metallofullerenes: La@C_{82} and Sc_2@C_{84}

KOBAYASHI, Kaoru; NAGASE, Shigeru

[*Mol. Phys.* in press]

The electronic properties and reactivities of endohedral metallofullerenes have been extensively investigated both theoretically and experimentally. The metal motion and cage structure are currently of considerable interest in the far-infrared and Raman spectroscopic study. Thus, theoretical calculations are performed for the representative metallofullerenes, La@C_{82} and Sc_2@C_{84}, to provide insight into the metal-cage vibrational modes as well as cage structures. The La-based vibrational modes and wave numbers calculated for La@C_{82} are in good agreement with those assigned experimentally. An interesting finding is that the vibrational frequencies are little changed upon reduction or oxidation. The Sc-based vibrations calculated for Sc_2@C_{84} are also compared with the available experimental data. In addition, the structures of the Sc_2@C_{84} isomers are discussed.

I-A-9 A Stable Unconventional Structure of Sc_2@C_{66} Found by Density Functional Calculations

KOBAYASHI, Kaoru; NAGASE, Shigeru

[*Chem. Phys. Lett.* **362**, 373 (2002)]

In 1997 we predicted that the isolated pentagon rule (IPR) established in fullerene chemistry could be violated by metal-mediated interactions [*J. Am. Chem. Soc.* **119**, 12693 (1997)]. In this context, the recent isolation of Sc_2@C_{66} and Sc_3N@C_{68} is noteworthy because there is no IPR-satisfying isomer between C_{60} and C_{70}. The cage structure and metal position of Sc_2@C_{66} are theoretically determined. Interestingly, the endohedral C_{2v} structure determined by MEM/Rietveld analysis of the X–ray powder data [*Nature* **408**, 426 (2000)] does not correspond to an energy minimum but collapses with no barrier. Instead, a much more stable C_{2v} structure with two pairs of three-fold fused pentagons is found, which satisfies the observed ^{13}C NMR spectrum. Two Sc atoms are highly stabilized in the non-classical C_{66} cage by electrostatic interactions induced by electron transfer from Sc to C_{66}.

I-A-10 Theoretical Study of the Cations and Anions of La_2@C_{80} and Sc_3N@C_{80}

MAYER, Bodo[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]IMS and TU-Darmstadt)

Theoretical calculations are performed for the neutral, anionic, and cationic states of La_2@C_{80} and Sc_3N@C_{80}. It is found that added electrons are localized on the encapsulated metal atoms while electron removal takes place from the carbon cage. As the number of added electrons increases, the spherical carbon cage transforms to an ellipsoid structure and the metal positions is changed. The electron density difference maps reveal the important changes in electronic structures upon reduction and oxidation.

I-A-11 Theoretical Identification of the Structures of C_{20}: Prevalence of the Monocyclic Isomer and Existences of the Smallest Fullerene and Bowl Isomers

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* submitted]

Free energies, electron affinities and vibrational modes of C_{20} isomers are theoretically investigated. The major C_{20} isomer generated by vaporizing graphite has a monocyclic ring, followed by a tadpole (a short chain attached to a monocyclic ring), chain, and a bicyclic ring. On the other hand, the two C_{20} isomers synthesized recently [*Nature* **407**, 60 (2000)] have fullerene and bowl structures.

I-A-12 The Size of Silicon Clusters Suitable for Endohedral Metal-Doping

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

Structures and electronic properties of metal-doped silicon clusters $M\mathrm{Si}_n$ (M = W, Zr, Os, Pt, and Co; n = 8–20) are theoretically investigated. In contrast to a recent experiment [*Phys. Rev. Lett.* **86**,1733 (2001)] suggesting that a metal atom is encapsulated inside the Si_n cluster, formation of endohedral structures depends strongly on the size of silicon clusters. In addition, several novel stable endohedral structures are found. The size of stable endohedral forms is predicted to be in the range $10 \le n \le 16$.

I-A-13 What is the Smallest Metal-Encapsulated Germanium Clusters?

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

Metal-doped germanium clusters $M\mathrm{Ge}_n$ (M = Hf, W, Os, Ni, and Zn) are investigated using density functional calculations. The smallest metal-encapsulated germanium cluster contain 13 germanium atoms and takes a distorted hexagonal prism structure ($\mathrm{W@Ge}_{12}$ and $\mathrm{Os@Ge}_{12}$). These size and shape differ from those of the smallest metal-encapsulated silicon cluster that contains 11 silicon atoms and has a basketlike structure. The stable ZnGe_{12} structure is exohedral, although an endohedral icosahedral structure is suggested in a recent theoretical study [*Appl. Phys. Lett.* **80**, 859 (2002)].

I-A-14 Host-Guest Interaction in Molecular Capusule Formation

RE, Suyong; NAGASE, Shigeru

It is of current synthetic interest to develop functional molecular capsules. Carceplex is a complex in which guest molecules are entrapped by a container host molecule. Although it is known that guest molecules act as a template, the encapsulation mechanism is not fully understood. Small changes in the size and shape of guest molecules lead to remarkable changes in the yield of carceplex. Since the efficient synthesis of carceplex depends strongly on the type of guest molecules, host-guest interactions are systematically investigated by theoretical calculations to reveal the details of formation mechanism.

I-A-15 Does the Axial Ligand of Iron (IV)-Oxo-Porphyrin Affect the Reactivity of Cytochrome P450?

CHOE, Yoong-Kee; NAGASE, Shigeru

Hemoenzymes play versatile roles in living organisms. However, the origin of their various functions has not been fully understood. Among these, alkane hydroxylation by cytochrome P450 has been a subject of intense studies because the reaction intermediates have not been captured experimentally. It has been considered that the coordination of cystein to heme is responsible for the catalytic action of cytochrome P450. However, there has been much debate on the role of the axial cysteine ligand. Therefore, density functional calculations have been carried out to investigate the roles of the axial cysteine ligand of the iron (IV)-oxo-porphyrin intermediate (compound I) that is generated in the alkane hydroxylation catalyzed by cytochrome P450. The ligand effects are compared with those in enzymes such as tyrosine and hitidine.

I-A-16 A Nonspectroscopic Method to Determine the Photolytic Decomposition Pathways of 3-Chloro-3-Alkyldiazirine; Carbene, Diazo and Rearrangement in Excited State

WAKAHARA, Takatsugu[1]; NIINO, Yasuyuki[2]; KATO, Takashi[2]; MAEDA, Yutaka[1]; AKASAKA, Takeshi[1]; LIU, Michael T. H.[3]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Niigata Univ.; [3]Univ. Prince Edward Island)

[*J. Am. Chem. Soc.* **124**, 9465 (2002)]

The C_{60} fullerene acts as a mechanistic probe for the formation of carbene, diazo compound, and for the rearranged product via the excited state in the photolysis of 3-chloro-3-isopropoly-diazirine and 3-chloro-3-chloromethyldiazirine. The carbene adds to C_{60} to form methanofullerene, whereas the diazo compound adds to C_{60} to form fulleroid. The olefin product arises as a result of the rearrangement in the excited state

I-A-17 Prediction of Molecular Crystal Structures by an Ab Initio Pair Potential Method

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

It is an important subject to predict the structures of molecular crystals from the component molecules. Therefore, several methods have been suggested to predict crystal structures using empirical atom-atom potentials. However, these empirical methods are not sufficiently reliable to be widely applicable. Instead, we developed an efficient method to predict lattice constants using ab initio pair potentials. It is the advantage that lattice constants can be calculated without empirical parameters, even if crystals contain any atoms. To realize high-speed calculations, a parallel computing program is developed on PC clusters.