RESEARCH ACTIVITIES I
Department of Theoretical Studies

I-A  Theoretical Study and Design of Functional Molecular Systems: New Bonding, Structures, and Reactions

It is an important subject to develop functional molecules with novel bonding and structures from theoretical and computational points of view. Thus, novel bonds and structures provided by heavier atoms are investigated, which are expected to serve as new building blocks for the design of functional molecules. In addition, unique spaces and flexible structures provided by large molecules and clusters are highly emphasized to develop functional molecular systems by modulating the electronic properties. Efficient computational methods are also investigated to perform reliable quantum chemistry calculations of large molecular systems.

I-A-1  Spherical Sila- and Germa-Homoaromaticity

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There has been considerable progress in investigating the effects of silicon and germanium substitution on the aromaticity of arenes with 4n+2 π electrons. However, homoaromaticity, well-established in organic chemistry, has received much less attention in silicon and germanium counterparts. Guided by the 2(N+1)^2 electron-counting rule, we have designed various spherical sila- and germa-homoaromatic systems rich in group 14 elements. Their significant homoaromaticity is demonstrated by structures and nucleus-independent chemical shifts calculated using density functional theory. The novel homoaromatic systems with well-delocalized electrons in the heavier group 14 elements present new synthetic targets, in particular, the spherical homoaromaticity-stabilized silicon and germanium clusters Si8 M 2 and Ge 8 M 2 (M = Li and Na). Besides the formally used endohedral inclusion strategy, spherical homoaromaticity is another way to stabilize silicon and germanium clusters.

I-A-2  Synthesis and Characterization of Tetrakis-Silylated C60 Isomers

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(1 Univ. Tsukuba; 2 Univ. Electron-Communications; 3 Niigata Univ.)


It is demonstrated that the tetrakis-silylation of C60 takes place readily by generating photochemically a silyl radical from disilane to afford tetrakis-isomers, (t-BuPh2Si)4C60. The relative energies and structures of tetrakis isomers as well as addition positions are revealed by molecular orbital calculations. The redox properties of C60 can be controlled not only by the electronegativity of substituents and regiochemistry of its functionality but also by the number of substituents. Thus, the tetrakis-adducts (t-BuPh2Si)4C60 has lower oxidation and higher reduction potentials than C60 and the bis-adducts (t-BuPh2Si)2C60.

I-A-3  Silylation of Fullerenes with Active Species in Photolysis of Polysilanes

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(1 Univ. Tsukuba; 2 Univ. Electron-Communications)


Organosilicon compounds represent unique features of materials. A combination of organosilicon compounds and fullerenes forms new classes of organic compounds and open a new field in materials science. Thus, derivatization of fullerenes by the addition of active silicon species generated in the photolysis of polysilanes is developed from the experimental and theoretical points of view, which leads to several new materials. In addition, we summarize recent advance in the chemistry of mono- and bis-silylation of fullerenes with silylenes and silyl radicals to afford new fullerene-based organosilicon materials.

I-A-4  Syntheses and Structures of Silicon Analogues of Cyclopropabenzenes

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The reaction of an overcrowded diaryldilithiosilane, Tbt(Dip)SiLi2 (Tbt = 2,4,6-tris[bis(trimethylsilyl)]-
methyl]phenyl; Dip = 2,6-diisopropylphenyl), with o-dibromobenzene and 1,2,4,5-tetrabromobenzene results in the synthesis and isolation of the first stable silacyclopropabenzenes and bis(silacyclopropa)benzences, respectively. The crystallographic analyses and theoretical calculations reveal that the lengths of the junction carbon–carbon bonds of the mono- and bis(silacyclopropa)benzences are marginally in the range of carbon–carbon bond lengths of usual benzene rings. It is shown that the structural feature is attributable to a decrease in the strain energy of silacyclopropabenzenes relative to the corresponding cyclopropabenzenes, and the strain energy is a simple additive function of the number of the fused three-membered rings involving Si atom.

I-A-5 The Effect of Substituents on the Thermal Decomposition of Diazirines: Experimental and Computational Studies

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The photochemical bis-silylation of N@C60 with disilirane is successfully performed. Based on control experiment and laser flash photolysis, it is considered that the bis-silylation reaction proceed by electron transfer from disilirane to 3C60* via an exciplex. A noticeable finding is that N@C60 has a lower photochemical reactivity toward disilirane than C60, although N@C60 does not differ from C60 in its thermal reactivity. This important difference in the photochemical reactivity of N@C60 and C60 may be ascribed to the different excitation energies of N@C60 and C60 or the faster quenching of the triplet N@3C60* state. Theoretical calculations reveal that N@C60 and C60 have the same orbital energies, suggesting that they have very similar excitation energies. It is likeliest that the three parallel spins on the N atom play an important role in the decay of N@3C60*.

I-A-7 A Comparison of the Photochemical Reactivity of N@C60 and C60: Photolysis with Disilirane

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The photochemical bis-silylation of N@C60 with disilirane leads to the so-called nanopeapod, in which fullerences self-assemble into a linear chain by weak interactions. By using first-principle calculations, we found that the electronic structures near the Fermi level of the nanotubes rigidly filled by a loose-packed fullerene chain can be approximated by a sum of those of the two constituents that are rigidly relatively shifted.
tending this rigid band shift approximation to the \((n,0)\) nanotubes rigidly filled by a close-packed \(C_{60}\) chain, a dramatic change in electronic properties from semiconductor \((n = 17)\) to metal \((n = 18\) and 19) is seen, and the recently observed fine double peak structure on the conduction band of the semiconducting nanotube induced by \(C_{60}\) encapsulation is well reproduced. The theoretical smallest diameter of a nanopeapod is 10.64 Å.

I-A-9 A Density Functional Theory Study Applied for Carbon Isotope Effects in the Non-Aqueous \([Cu(CO)]^+\,/CO\) System

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Density functional theory calculations are performed on the carbon isotopomers of CO and CO-complexes \([Cu(NH_2CH_2CH_2OH)_3(CO)]^+, \[Cu(CH_3OH)_3(CO)]^+\). The results are compared with the experimental results on the carbon isotope exchange equilibrium between CO and CO-copper complexes. The gas-phase model is used even for calculating the isotope effects involving the solutes of solutions. Contributions of the extra-molecular motion of the solute molecule to the reduced partition function ratios are responsible for the steep slope of \(ln\alpha\) vs. \(-1/T\) plots of the experimental data, where \(\alpha\) is the isotope separation which is identical to the equilibrium constant in the present exchange system. The calculated results agree well with the experimental data.


CAO, Baopeng\(^1\); WAKAHARA, Takatsugu\(^1\);
MAEDA, Yutaka\(^1\); HAN, Aihong\(^1\); AKASAKA, Takeshi\(^1\); KATO, Tatsuhisu; KOBAYASHI, Kaoru; NAGASE, Shigeru

\(^{(1)\text{Univ. Tsukuba}}\)


Two lanthanum endohedral fulleropyrrolidines are produced, isolated, and characterized. Addition of an azomethine ylide to \(La@C_{82}\) is very efficient and, to some extent, regioselective. Introduction of pyrrolidines to the endohedral metallofullerene \(La@C_{82}\) cannot alter the octet EPR and endohedral character of the encapsulated metal atom but varies the electronic structure of the metallofullerene. The Prato reaction is also a valuable and versatile functionalization methodology for endohedral metallofullerenes, which could afford various endohedral metallofulleropyrrolidines with diversity of functions.


CHEN, Zhongfang; NAGASE, Shigeru; HIRSCH, Andreas\(^1\); HADDON, Robert C.\(^2\); THIEL, Walter\(^3\); SCHLEYER, Paul von Rague\(^4\)

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Since single-walled carbon nanotubes (SWCNTs) have unique properties, chemical modifications of the exohedral surfaces is currently of considerable interest for promising applications to functional materials. At present, a vexing problem is ascertaining the detailed structures of nanotube derivatives after their preparation; all experimental attempts to determine the precise location and mode of addition of newly attached groups have failed. Thus, we have performed density functional B3LYP calculations on the \(O, CH_2, NH_2, \text{and SiH}_2\) nanotube derivatives for both (5,5) armchair and (8,8) zigzag SWCNTs. The (5,5) and (8,8) SWCNT derivatives have opened structures instead of three-membered rings (3MRs). Since armchair and zigzag tubes are two extremes for SWCNT structures, evidently the side-wall of SWCNTs can be opened by chemical modification. It is pointed out that the often-used ONIOM approach is not appropriate for the systems studied here and has serious limitations to computational nanotube chemistry. The present computational results, that SWCNT derivatives favor opened rather than 3MR structures, may be verified experimentally with new advances in SWCNT solubilization and spectroscopic analysis.

I-A-12 Ca@C_{82} Isomers: Computed Temperature Dependence of Relative Concentrations

SLANINA, Zdenek\(^1\); KOBAYASHI, Kaoru; NAGASE, Shigeru

\(^{(1)\text{IMS and Academia Sinica}}\)


Calcium is a relatively common element in formation of endohedral metallofullerenes. Among the calcium endohedrals, \(Ca@C_{82}\) exhibits the richest isomerism. For some cases, it is found that a structure that is not the lowest in potential energy is the most populated at higher temperatures and other higher-energy structures undergo stability interchanges with changing temperatures. Thus, relative concentrations of nine isomers of \(Ca@C_{82}\) derived from the isolated-pentagon-rule-satisfying cages of \(C_{82}\) are computed in a wide temperature range. The computations are based on the Gibbs free energies constructed from partition functions with molecular parameters from density functional theory calculations. Five isomers show significant populations at higher temperatures: \(C_{3v}\) > \(C_6\) > \(C_2\) > \(C_3\) > \(C_1\). These computed relative populations agree well with available observations.

I-A-13 \(C_{72}\) Isomers: The IPR-Satisfying Cage is Disfavored by Both Energy and Entropy
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(¹IMS and Academia Sinica)


C72 has been counted as a “missing fullerene.” As C72 could only be recorded in mass spectroscopic data, its structure is still unknown. Relative concentrations of seven isomeric C72 cages (a cage with isolated pentagons, two cages with a pentagon-pentagon junction, a cage with a heptagon, a cage with two heptagons, and two cages with two pentagon-pentagon fusions) are computed using the Gibbs free energies in a broad temperature interval. It is found that the IPR (isolated pentagon rule)-violating C2v cage with one pentagon-pentagon junction prevails at any relevant temperature. Although the IPR-satisfying cage is the second lowest in energy, it is disfavored by entropy so that several cages still higher in energy are in fact more populated at higher temperatures.

I-A-14 How Is the CH/π Interaction Important for Molecular Recognition?
RE, Suyong; NAGASE, Shigeru

[Chem. Commun. 658–659 (2004)]

Attractive CH/π interactions have received considerable attention as a principal factor governing molecular recognition and self-assembly, as accumulated in the database on CH/π proximate arrangements in crystal structures of host-guest complexes. To address the role of CH/π interactions in molecular recognition, a resorcinol cyclic tetramer is considered as a typical host and its interactions with alcohols are theoretically investigated with the Hartree-Fock (HF) and second-order Møller-Plesset perturbation (MP2) methods. The major source of CH/π attraction is due to the dispersion force (electron correlation). It is pointed out that CH/π attraction significantly contributes to host-guest complexation, but is not always a direct factor in molecular recognition.

I-A-15 A Bowl-Shaped Fullerene Encapsulates a Water into the Cage
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(¹Nagoya Univ.)


In recent years, the controlled carbon–carbon cleavage of fullerene cages has attracted much attention, because the resulting open-cage derivatives allow small molecules to enter the internal cavities. Thus, a novel bowl-shaped fullerene cage with a large hole is synthesized by the regioselective multiple cage scissions of C60. It is demonstrated from the observed 1H NMR chemical shifts and theoretical calculations that one water molecule is encapsulated inside the bowl-shaped cage through the open hole, as the first example of the endohedral water complex of C60.

I-A-16 Ca@C74 Isomers: Relative Concentrations at Higher Temperatures
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Relative concentrations of six isomers of Ca@C74 are evaluated: one species with isolated pentagons, three isomers with a pentagon-pentagon junction, two structures with one pentagon-pentagon pair and one heptagon. In a broad temperature interval, Gibbs energies are calculated using density functional theory. It is shown that the endohedral species derived from the C74 cage with isolated pentagons prevails throughout. Two structures with a pentagon-pentagon junction come as minor isomers at higher temperatures while the remaining three species are always negligible. For the domain species, a kinetic barrier of less than 9 kcal/mol is computed for autoisomerizations mediated by motion of the encapsulated Ca atom.

I-A-17 Computed Temperature Development of the Relative Stabilities of La@C82 Isomers
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(¹IMS and Academia Sinica)


Relative concentrations of four selected isomers of La@C82 are computed from the Gibbs energy derived from partition functions supplied with parameters from density functional theory calculations. An agreement with experiment can be reached for temperatures roughly from 1000 to 1300 K when the C2v species is the major isomer followed by an isomer that undergoes C3v/Cs symmetry reduction while the intrinsically Cs species comes as a still less populated third product. It is suggested that the C3v isomer can be suppressed in the condense phase because of its higher reactivity.

I-A-18 Characterization of Ce@C82 and Its Anion
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[J. Am. Chem. Soc. 126, 4883–4887 (2004)]
The cage symmetry of Ce@C\textsubscript{82} is determined as C\textsubscript{2v} by measuring the \textsuperscript{13}C NMR spectra of its anion, as theoretically predicted for M@C\textsubscript{82} (M = Sc, Y, and La). The \textsuperscript{13}C NMR peaks of [Ce@C\textsubscript{82}]\textsuperscript{-} show temperature-dependent shifts ascribed to the f electron remaining on the Ce atom. This kind of temperature-dependent shifts is the first example for the M@C\textsubscript{82} system. Both Ce@C\textsubscript{82} and [Ce@C\textsubscript{82}]\textsuperscript{-} are ESR silent because of the highly anisotropic g matrix as well as the fast relaxation process originating from the orbital angular momentum of the f electron remaining on the Ce atom. This is the complementary relationship to the observation of the paramagnetic shift in \textsuperscript{13}C NMR. In air, the stability of Ce@C\textsubscript{82} is lower than that of La@C\textsubscript{82}.

I-A-19 Isolation and Characterization of a Carbene Derivative of La@C\textsubscript{82}

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The addition of 2-admantane-2,3-[3H]-diazirine (Ad) to La@C\textsubscript{82} proceeds in a regiospecific way to afford one single isomer that is isolable. As the first example of the crystallographic study of paramagnetic endohedral metallofullerenes derivatives, structural determination of the enantiomeric isomer, La@C\textsubscript{82}:Ad, is carried out. The bond lengths and angles in the X-ray structure are in good agreement with the values obtained from density functional theory calculations. From the X-ray data observed at 90, 213, and 293 K, it is suggested that the La atom in La@C\textsubscript{82}:Ad is located at one single site. The selective formation of La@C\textsubscript{82}:Ad is explained by calculating charge densities and pyramidalization angles (local strain on the C atoms). The redox potentials of La@C\textsubscript{82}:Ad are cathodically shifted, indicating that the introduction of an Ad group results in decreasing the electron-accepting power, as confirmed by the calculated electron affinity.

I-A-20 Isolation, Characterization, and Theoretical Study of La\textsubscript{2}@C\textsubscript{78}

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A new endohedral metallofullerene, La\textsubscript{2}@C\textsubscript{78}, is isolated and characterized. For the C\textsubscript{78} fullerene, there are five isomers (D\textsubscript{3}, C\textsubscript{2v}(a), C\textsubscript{2v}(b), D\textsubscript{3h}(a), D\textsubscript{3h}(b)) that satisfy the isolated pentagon rule. The first three isomers ((D\textsubscript{3}, C\textsubscript{2v}(a), C\textsubscript{2v}(b)) have been isolated up to now for the empty C\textsubscript{78}. Interestingly, a total of eight lines (five lines with full intensity and three lines with half intensity) is observed in the \textsuperscript{13}C NMR spectrum, which shows that La\textsubscript{2}@C\textsubscript{78} has D\textsubscript{3h} symmetry. From theoretical calculations, it is verified that the La atom is encapsulated inside the D\textsubscript{3h}(a) isomer, as a result of three-electron transfer from each La to C\textsubscript{78}.


LU, Jing\textsuperscript{1}; NAGASE, Shigeru; ZHANG, Shuang\textsuperscript{2}; PENG, Lianmao\textsuperscript{2} (\textsuperscript{1}IMS and Peking Univ.; \textsuperscript{2}Peking Univ.)


The energetic, geometric, and electronic evolutions of a K-doped single wall (10,10) carbon nanotube rope with K intercalation concentration are systematically investigated by using first principle calculations. The existence of a stable intermediate phase (K\textsuperscript{exo}C\textsubscript{13.3}) before saturation (K\textsuperscript{exo}C\textsubscript{6.7}) for exohedral K-doping is first theoretically confirmed. The optimum K-intercalation density in single-wall carbon nanotube ropes with open ends is predicted to be as high as about KC\textsubscript{4.2}, nearly twice the well-known value in graphite. The simple charge transfer model is applicable only in the low K-doping level regime. The nearly free electron states of the nanotube couple with the 4s orbital on K, and the lower hybridized states do cross the Fermi level as the exohedral and endohedral K-doping densities exceed K\textsuperscript{exo}C\textsubscript{20} and K\textsuperscript{endo}C\textsubscript{80}, respectively. The saturation phase of K-doped open-ended single-wall nanotube ropes is a conductor with three channels: one along the tube wall and the other two along the inside and outside of the tube wall, respectively.