# 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 $4n+2$ $\pi$ 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 $Si_8M_2$ and $Ge_8M_2$ (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 $C_{60}$ Isomers

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[*J. Org. Chem.* **68**, 6791–6794 (2003)]

It is demonstrated that the tetrakis-silylation of $C_{60}$ takes place readily by generating photochemically a silyl radical from disilane to afford tetrakis-isomers, ($t$-$BuPh_2Si)_4C_{60}$. The relative energies and structures of tetrakis isomers as well as addition positions are revealed by molecular orbital calculations. The redox properties of $C_{60}$ 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 ($t$-$BuPh_2Si)_4C_{60}$ has lower oxidation and higher reduction potentials than $C_{60}$ and the bis-adducts ($t$-$BuPh_2Si)_2C_{60}$.

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

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[*J. Organomet. Chem.* **685**, 177–188 (2003)]

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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[*J. Organomet. Chem.* **686**, 118–126 (2003)]

The reaction of an overcrowded diaryldilithiosilane, $Tbt(Dip)SiLi_2$ (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 silacyclopropabenzene and bis(silacyclopropa)benzenes, respectively. The crystallographic analyses and theoretical calculations reveal that the lengths of the juncture carbon–carbon bonds of the mono- and bis(silacyclopropa)benzenes 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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[*J. Org. Chem.* **68**, 7471–7478 (2003)]

The thermal decomposition of phenylchlorodiazirine (**1**), phenyl-*n*-butyldiazirine (**2**), and 2-adamantane-2-3’-[3*H*]diazirine (**3**) is studied in solution in the presence of $C_{60}$. The $C_{60}$ probe technique indicates that in the decomposition diazirine **1** yields exclusively phenylchlorocarbene, diazirine **2** yields mainly a diazo intermediate, and diazirine **3** yields a mixture of carbene and diazo compound. In the case of diazirine **2**, 13% of (*E*)-1-phenyl-1-pentene results from the direct thermal rearrangement of diazirine without the participation of a carbene. As well, the thermal decomposition of these diazirines is theoretically invetigated with ab initio molecular orbital and density functional methods at the CASSCF and B3LYP levels, respectively. The experimental results are broadly in agreement with the theoretical prediction. In addition, the theoretical calculations indicate that the rebound reaction between carbene and molecular nitrogen leading to the formation of a diazo intermediate is an important reaction in the gas-phase decomposition of diazirine.

### I-A-6 Temperature Development in a Set of $C_{60}H_{36}$ Isomers

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[*Chem. Phys. Lett.* **382**, 211–215 (2003)]

Relative stabilities of $C_{60}H_{36}$ isomers are evaluated using both enthalpy and entropy terms, *i.e.*, the Gibbs free energies. The set consists of eight low energy isomers known from previous calculations and a new $C_1$ species, topologically equivalent to the recently isolated $C_1$ isomer of $C_{60}F_{36}$. The PM3 and B3LYP/6-31G* methods are applied, and in both treatments the new $C_1$ species is located 7 kcal/mol below the previous best $C_1$ structure. The treatments differ in the lowest energy isomer but they place the new $C_1$ isomer as the second most populated species at higher temperatures owing to its entropy enhancement.

### I-A-7 A Comparison of the Photochemical Reactivity of N@$C_{60}$ and $C_{60}$: Photolysis with Disilirane

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[*Chem. Commun.* 2940–2941 (2003)]

The photochemical bis-silylation of N@$C_{60}$ 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 $^3C_{60}{}^*$ *via* an exciplex. A noticeable finding is that N@$C_{60}$ has a lower photochemical reactivity toward disilirane than $C_{60}$, although N@$C_{60}$ does not differ from $C_{60}$ in its thermal reactivity. This important difference in the photochemical reactivity of N@$C_{60}$ and $C_{60}$ may be ascribed to the different excitation energies of N@$C_{60}$ and $C_{60}$ or the faster quenching of the triplet N@$^3C_{60}{}^*$ state. Theoretical calculations reveal that N@$C_{60}$ and $C_{60}$ 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@$^3C_{60}{}^*$. In fact, preliminary calculations of spin orbit coupling between the excited $\Psi$(N@$^3C_{60}{}^*$) and ground $\Psi$(N@$C_{60}$) states is larger than the corresponding coupling between $\Psi(^3C^*_{60})$ and $\Psi(C_{60})$, suggesting that N@$^3C_{60}{}^*$ has a shorter lifetime than $^3C_{60}{}^*$.

### I-A-8 Strongly Size-Dependent Electronic Properties in $C_{60}$-Encapsulated Zigzag Nanotubes and Lower Size Limit of Carbon Nanopeapods

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[*Phys. Rev. B* **68**, 121402 (4 pages) (2003)]

Encapsulation of fullerenes into single-wall carbon nanotubes leads to the so-called nanopeapod, in which fullerenes 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. Extending 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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[*Chem. Phys. Lett.* **390**, 71–78 (2004)]

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.

### I-A-10 Lanthanum Endohedral Metallofulleropyrrolidines: Synthesis, Isolation, and EPR Characterization

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[*Chem. Eur. J.* **10**, 716–720 (2004)]

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 functinalization methodology for endohedral metallofullerenes, which could afford various endohedral metallofulleropyrrolidines with diversity of functions.

### I-A-11 Side-Wall Opening of Single-Walled Carbon Nanotubes (SWCNTs) by Chemical Modification: A Critical Theoretical Study

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[*Angew. Chem., Int. Ed.* **43**, 1552–1554 (2004)]

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, $CH_2$, $NH_2$, 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

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[*J. Chem. Phys.* **120**, 3397–3400 (2004)]

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 supplied with molecular parameters from density functional theory calculations. Five isomers show significant populations at higher temperatures: $C_{2v} > C_s > C_2 > C_{3v} > C_s$. 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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[*Chem. Phys. Lett.* **384**, 114–118 (2004)]

$C_{72}$ has been counted as a “missing fullerene.” As $C_{72}$ could only be recorded in mass spectroscopic data, its structure is still unknown. Relative concentrations of seven isomeric $C_{72}$ 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 $C_{2v}$ 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 ?

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[*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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[*J. Am. Chem. Soc.* **126**, 2668–2669 (2004)]

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 $C_{60}$. It is demonstrated from the observed $^1$H 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 $C_{60}$.

### I-A-16 Ca@$C_{74}$ Isomers: Relative Concentrations at Higher Temperatures

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[*Chem. Phys.* **301**, 153–157 (2004)]

Relative concentrations of six isomers of Ca@$C_{74}$ 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 $C_{74}$ 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@$C_{82}$ Isomers

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[*Chem. Phys. Lett.* **388**, 74–78 (2004)]

Relative concentrations of four selected isomers of La@$C_{82}$ 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 $C_{2v}$ species is the major isomer followed by an isomer that undergoes $C_{3v}/C_s$ symmetry reduction while the intrinsically $C_s$ species comes as a still less populated third product. It is suggested that the $C_{3v}$ isomer can be suppressed in the condense phase because of its higher reactivity.

### I-A-18 Characterization of Ce@$C_{82}$ and Its Anion

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[*J. Am. Chem. Soc.* **126**, 4883–4887 (2004)]

The cage symmetry of Ce@$C_{82}$ is determined as $C_{2v}$ by measuring the $^{13}$C NMR spectra of its anion, as theoretically predicted for M@$C_{82}$ (M = Sc, Y, and La). The $^{13}$C NMR peaks of [Ce@$C_{82}$]$^-$ 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@$C_{82}$ system. Both Ce@$C_{82}$ and [Ce@$C_{82}$]$^-$ are ESR silent because of the highly anisotopic **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 $^{13}$C NMR. In air, the stability of Ce@$C_{82}$ is lower than that of La@$C_{82}$.

## I-A-19 Isolation and Characterization of a Carbene Derivative of La@$C_{82}$

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[*J. Am. Chem. Soc.* **126**, 6858–6859 (2004)]

The addition of 2-admantane-2,3-[3*H*]-diazirine (Ad) to La@$C_{82}$ 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@$C_{82}$·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@$C_8$·Ad is located at one single site. The selective formation of La@$C_{82}$·Ad is explained by calculating charge densities and pyramidalization angles (local strain on the C atoms). The redox potentials of La@$C_{82}$·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 $La_2$@$C_{78}$

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[*J. Am. Chem. Soc.* **126**, 9164–9165 (2004)]

A new endohedral metallofullerene, $La_2$@$C_{78}$, is isolated and characterized. For the $C_{78}$ fullerene, there are five isomers ($D_3$, $C_{2v}$(a), $C_{2v}$(b), $D_{3h}$(a), $D_{3h}$(b)) that satisfy the isolated pentagon rule. The first three isomers (($D_3$, $C_{2v}$(a), $C_{2v}$(b)) have been isolated up to now for the empty $C_{78}$. Interestingly, a total of eight lines (five lines with full intensity and three lines with half intensity) is observed in the $^{13}$C NMR spectrum, which shows that $La_2$@$C_{78}$ has $D_{3h}$ symmetry. From theoretical calculations, it is verified that the La atom is encapsulated inside the $D_{3h}$(a) isomer, as a result of three-electron transfer from each La to $C_{78}$.

## I-A-21 Energetic, Geometric, and Electronic Evolutions of K-Doped Single-Wall Carbon Nanotube Ropes with K Intercalation Concentration

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[*Phys. Rev. B* **69**, 205304 (4 pages) (2004)]

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 ($K^{exo}C_{13.3}$) before saturation ($K^{exo}C_{6.7}$) 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 $KC_{4.2}$, 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 4*s* orbital on K, and the lower hybridized states do cross the Fermi level as the exohedral and endohedral K-doping densities exceed $K^{exo}C_{20}$ and $K^{endo}C_{80}$, 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.