RESEARCH ACTIVITIES I
Department of Theoretical Studies

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

In theoretical and computational chemistry, it is an important goal to develop functional molecules with novel bonding and structures before or in cooperation with experiment. Thus, novel bonds and structures provided by heavier atoms are investigated. In addition, unique spaces and flexible structures provided by large molecules and clusters are investigated. Efficient computational methods are investigated to perform reliable quantum chemistry calculations of large molecular systems.

I-A-1 Effect of the Axial Cysteine Ligand on the Electronic Structure and Reactivity of High-Valent Iron (IV) Oxo-Porphyrins (Compound I): A Theoretical Study

CHOE, Yoong-Kee[1]; NAGASE, Shigeru
([1]AIST)

[*J. Comput. Chem.* **26**, 1600–1611 (2005)]

The effects of axial ligands on the alkane hydroxylation of high-valent iron (IV) oxo-porphyrins (Compound I) are investigated using hybrid density functional theory at the B3LYP kevel. As axial ligands, thiolate, imidazole, phenolate, and chloride anions are invetigated; the first three are the models of cysteinate, histidine, and tyrosinate, respectively. The alkane hydroxylation proceeds *via* several steps. A remarkable effect of axial ligands is found in the final product release step. The thiolate ligand weakens a bond between heme and an alcohol. In contrast, the imidazole ligand significantly increases the interaction between heme and an alcohol, which causes the catalytic cycle to be less efficient.

I-A-2 $Sc_3N@C_{80}$: Computations on the Two-Isomer Equilibrium at High Temperatures

SLANINA, Zdenek; NAGASE, Shigeru

[*ChemPhysChem* **6**, 2060–2063 (2005)]

The relative concentrations of the two isomers (I_h and D_{5h}) of $Sc_3N@C_{80}$, are investigated by calculating Gibbs free energies at the B3LYP level. When a relatively free motion of Sc_3N inside C_{80} is allowed, the observed populations of 10 and 17% for the minor D_{5h} isomer are reached at 2100 and 2450 K, respectively. The entropy term plays an essential role, since, if it is neglected, the D_{5h} population at 2100 K is only 1%, owing to the relatively large interisomeric separation potential energy of 19 kcal/mol.

I-A-3 The Aromacity of the Stannole Dianion

SAITO, Masaichi[1]; HAGA, Ryuta[1]; YOSHIOKA, Michikazu[1]; ISHIMURA, Kazuya; NAGASE, Shigeru
([1]Saitama Univ.)

[*Angew. Chem., Int. Ed.* **44**, 6553–6556 (2005)]

Neither monoanions nor dianions of stannoles have been well characterized, unlike the cases of the silole and germole anions. Thus, the lithium salt of a stannole dianion is isolated and investigated by NMR, X-ray crystal analysis, and theoretical calculations as the first tin-containing carbocyclic aromatic compound. The aromaticity of the stannole dianion is characterized by calculating charge delocalization and NICS (nucleus-indepenndent chemical shift) values.

I-A-4 Reversible and Regioselective Reaction of $La@C_{82}$ with Cyclopentadiene

MAEDA, Yutaka[1]; MIYASHITA, Jun[1]; HASEGAWA, Tadashi[1]; WAKAHARA, Takatsugu[2]; TSUCHIYA, Takahiro[2]; NAKAHODO, Tsukasa[2]; AKASAKA, Takeshi[2]; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru; KATO, Tatsuhisa[3]; BAN, Noritaka[4]; NAKAJIMA, Hiroshi[4]; WATANABE, Yoshihito[4]
([1]Tokyo Gakugei Univ.; [2]Univ. Tsukuba; [3]Josai Univ.; [4]Nagoya Univ.)

[*J. Am. Chem. Soc.* **127**, 12190–12191 (2005)]

The reversible and regioselective reaction of $La@C_{82}$ with cyclopentadiene is demonstrated in comparison with the corresponding reaction of C_{60}. Theoretical calculations show that $La@C_{82}$ reacts faster with cyclopentadiene than C_{60}, because $La@C_{82}$ has a lower LUMO than C_{60}. The low yield of the adduct of $La@C_{82}$ and cyclopentadiene is due to the presence of the fast retro-reaction. The rate constant for the consumption of $La@C_{82}$ is 2200 times slower than that of C_{60} at 293 K.

I-A-5 Structural Determination of Metallofullerene Sc_3C_{82} Revisited: A Surprising Finding

IIDUKA, Yuko[1]; WAKAHARA, Takatsugu[1]; NAKAHODO, Tsukasa[1]; TSUCHIYA, Takahiro[1]; SAKURABA, Akihiro[2]; MAEDA, Yutaka[3]; AKASAKA, Takeshi[1]; YOZA, Kenji[4]; HORN, Ernst[5]; KATO, Tatsuhisa[6]; LIU, Michael T. H.[7]; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Niigata Univ.; [3]Tokyo Gakugei Univ.; [4]Bruker AXS K.K.; [5]Rikkyo Univ.; [6]Josai Univ.; [7]Univ. Prince Edward Island)

[*J. Am. Chem. Soc.* **127**, 12500–12501 (2005)]

It is widely accepted that the maximum-entropy-method (MEM)/Rietveld analysis of synchrotron X-ray powder diffraction data is powerful for structural determination of endohedral metallofullerenes. For example, the MEM/Rietveld analysis of Sc_3C_{82} has shown that three Sc atoms are encapsulated inside a C_{3v} isomer of C_{82} as a trimer with extremely short Sc–Sc distances. For Sc_3C_{82}, however, theoretical calculations reveal that two C atoms as well as three Sc atoms are encapsulated inside the I_h-C_{80} (not C_{82}) fullerene, this $Sc_2C_2@C_{80}$ structure being much more stable than the $Sc_3@C_{82}$ structure determined by MEM/Rietveld analysis. The $Sc_2C_2@C_{80}$ structure is also verified by the NMR analysis of the anion and X-ray crystal analysis of a $Sc_2C_2@C_{80}$ derivative. It is suggested that the widely used MEM/Rietveld analysis is not reliable enough to determine the structures of endohedral metallofullerenes.

I-A-6 Electronic Structures of Semiconducting Double-Walled Carbon Nanotubes: Important Effect of Interlay Interaction

SONG, Wei[1]; NI, Ming[1]; LU, Jing[1]; GAO, Zhengxiang[1]; NAGASE, Shigeru; YU, Dapeng[1]; YE, Hengqiang[1]; ZHANG, Xinwei[2]
([1]Peking Univ.; [2]Inst. Appl. Phys. Comput. Math.)

[*Chem. Phys. Lett.* **414**, 429–433 (2005)]

Electronic structures of zigzag (7, 0)@(15, 0), zigzag (7, 0)@(18, 0), zigzag (8, 0)@(16, 0), and chiral (4, 2)@(10, 5) double-walled carbon nanotubes (DWNTs) are investigated by using first-principle calculations. The π and π^* states of inner (7, 0) and (4, 2) single-walled carbon nanotubes (SWNTs) exhibit a larger downward shift with respect to those of the outer (15, 0), (18, 0) and (10, 5) SWNTs. For (7, 0)@(15, 0), (8, 0)@(16, 0), and (4, 2)@(10, 5) DWNTs, it is notable that the inter-layer π-π stacking interaction causes a significant band reconstruction of the inner SWNT.

I-A-7 Positional Control of Encapsulated Atoms inside a Fullerene Cage by Exohedral Addition

YAMADA, Michio[1]; NAKAHODO, Tsukasa[1]; WAKAHARA, Takatsugu[1]; TSUCHIYA, Takahiro[1]; MAEDA, Yutaka[2]; AKASAKA, Takeshi[1]; KAKO, Masahiro[3]; YOZA, Kenji[4]; HORN, Ernst[5]; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Univ. Electro-Communications; [4]Bruker AXS K.K.; [5]Rikkyo Univ.)

[*J. Am. Chem. Soc.* **127**, 14570–14571 (2005)]

Theoretical calculations shows that the three-dimensional random motion of two La atoms in La_2C_{80} can be restricted to the circular motion in a plane by attaching an electron-donating molecules such as disilirane on the outer surface of the C_{80} cage. Thus, the exohedral chemical functionalization of $Ce@C_{82}$ by disilirane is performed to fix the random motion of two Ce atoms at specific positions. The exohedral attachment of disilirane regulates the Ce positions under the equator of the C_{80} cage.

I-A-8 A Singly Bonded Derivative of Endohedral Metallofullerene:La@ $C_{82}CBr(COOC_2H_5)_2$

FENG, Lai[1]; NAKAHODO, Tsukasa[1]; WAKAHARA, Takatsugu[1]; TSUCHIYA, Takahiro[1]; MAEDA, Yutaka[2]; AKASAKA, Takeshi[1]; KATO, Tatsuhisa[3]; HORN, Ernst[4]; YOZA, Kenji[5]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Josai Univ.; [4]Rikkyo Univ.; [5]Bruker AXS K.K.)

[*J. Am. Chem. Soc.* **127**, 17136–17137 (2005)]

A novel singly bonded derivative of $La@C_{82}$ is obtained by the reaction with diethyl bromomalonate. Theoretical calculations show that the reaction center of $La_2@C_{82}$ is most positively charged and has the second largest local strain, which is most reactive toward a nucleophilic attack. This suggests that a nucleophlic reaction takes place at the first step, followed by the oxidation of an intermediate, $[La@C_{82}CBr(COOC_2H_5)_2]^-$, to afford the singly-bonded adduct.

I-A-9 S-Heterocyclic Carbene with a Disilane Backbone

NIKAWA, Hidefumi[1]; NAKAHODO, Tsukasa[1]; TSUCHIYA, Takahiro[1]; WAKAHARA, Takatsugu[1]; RAHMAN, G. M. Aminur[1]; AKASAKA, Takeshi[1]; MAEDA, Yutaka[2]; LIU, Michael T. H.[3]; MEGURO, Akira[4]; KYUSHIN, Soichiro[4]; MATSUMOTO, Hideyuki[4]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Univ. Prince Edward Island; [4]Gunma Univ.)

[*Angew. Chem., Int. Ed.* **44**, 7567–7570 (2005)]

Heterocyclic carbenes have attracted considerable interest as ligands, catalysis, abd spin sources. It is found that S-heterocyclic carbene can be generated by the [2 + 3] addition of cyclotetrasilene with CS_2, which is trapped by C_{60} as a chemical probe. The structure and electronic state of the S-heterocyclic carbene are determined by density functional calculations. It is calculated that the singlet state is 23.4 kcal/mol stable than the triplet state, and has a high nucleophlicity.

I-A-10 Ab Initio and DFT Study of the ^{29}Si NMR Chemical Shifts in RSi≡SiR

KARNI, Miriam[1]; APELOIG, Yitzhak[1]; TAKAGI, Nozomi; NAGASE, Shigeru
([1]Technion-Israel Inst. Tech.)

[*Organometallics* **24**, 6319–6330 (2005)]

The first DFT and ab-inito calculations of the ^{29}Si NMR chemical shifts of triply bonded silicon atoms are reported for RSi≡SiR (R = H, CH_3, SiH_3, $SiMe(SiH_3)_2$, $SiMe(SiMe_3)_2$, SiMe(Si*t*Bu$_3$)$_2$, and Si*i*Pr[CH(SiMe$_3$)$_2$]$_2$. Small changes in geometries (the central Si–Si bond distance, the RSiSi bond angle and the RSiSiR twisting angle) strongly affect the chemical shifts. Inclusion of electron correlation by using MP2 and CCSD methods is found to be very important for reliable chemical shift calculations of RSi≡SiR. The chemical shifts calculated using the HCTH407 GGA functional are in good agreement with those calculated at the MP2 and CCSD levels. In contrast, a poor agreement is obtained when the popular B3LYP functional is used. The chemical shift of the triply-bonded silicon atoms in RSi≡SiR (R = SiMe (Si*t*Bu$_3$)$_2$) is calculated to be in the range of 88 ± 5 ppm, this agreeing well with the observed chemical shift.

I-A-11 A New Parallel Algorithm of MP2 Energy Calculations

ISHIMURA, Kazuya; PULAY, Peter[1]; NAGASE, Shigeru
([1]Univ. Arkansas)

[*J. Comput. Chem.* **27**, 407–413 (2006)]

A new parallel algorithm is developed for second order Møller-Plesset perturbation theory (MP2) energy calculations. Its main projected applications are for large molecules, for instance for the calculation of dispersion interaction. Tests on a moderate number of processors (2-16) show that the program has high CPU and parallel efficiency. Timings are presented for two relatively large molecules, taxol ($C_{47}H_{51}NO_{14}$) and luciferin ($C_{11}H_8N_2O_3S_2$), the former with the 6-31G* and 6-311G** basis sets (1032 and 1484 basis functions, 164 correlated orbitals), and the latter with the aug-cc-pVDZ and aug-cc-pVTZ basis sets (530 and 1198 basis functions, 46 correlated orbitals). An MP2 energy calculation on $C_{130}H_{10}$ (1970 basis functions, 265 correlated orbitals) completes in less than 2 hours on 128 processors.

I-A-12 Synthesis and Properties of a New Kinetically Stabilized Digermyne: New Insights for a Germanium Analogue of an Alkyne

SUGIYAMA, Yusuke[1]; SASAMORI, Takahiro[1]; HOSOI, Yoshinobu[1]; FURUKAWA, Yukio[2]; TAKAGI, Nozomi; NAGASE, Shigeru; TOKITOH, Norihiro[1]
([1]Kyoto Univ.; [2]Waseda Univ.)

[*J. Am. Chem. Soc.* **128**, 1023–1031 (2006)]

The reduction of an overcrowded (E)-1,2-dibromodigermene, Bbt(Br)Ge=Ge(Br)Bbt [Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl], with KC_8 affords a stable digermyne, BbtGe≡GeBbt. The Ge–Ge triple bond distance of BbtGe≡GeBbt is significantly shorter than that in the previously reported digermyne, Ar’Ge≡GeAr’ (Ar’ = 2,6-Dip$_2$C$_6$H$_3$, Dip = 2,6-diisopropylphenyl). The nature of the Ge–Ge triple bond in BbtGe≡GeBbt is disclosed by density functional calculations with large basis sets.

I-A-13 Computational Modelling for the Clustering Degree in the Saturated Steam and the Water-Containing Complexes in the Atmosphere

SLANINA, Zdenek; UHLIK, Filip[1]; LEE, Shyi-Long[2]; NAGASE, Shigeru
([1]Charles Univ.; [2]Natl. Chung-Cheng Univ.)

[*J. Quant. Spectrosc. Radiat. Transfer* **97**, 415–423 (2006)]

Recent computational findings of temperature increase of clustering degree in several different saturated vapors are analyzed further. A thermodynamic proof is presented, showing that this event should be rather common, if not general. Illustrations are based on the saturated steam and consequences for the atmosphere are discussed with both homo- and hetero-clustering. The best stabilization energies of $H_2O{\cdot}N_2$, $H_2O{\cdot}O_2$, and $(O_2)_2$ are reported. The water-dimer thermodynamics is recomputed in an anharmonic regime and a remarkable agreement with experiment is found. The results have some significance for the atmospheric greenhouse effect.

I-A-14 Analysis of Lanthanide-Induced NMR Chemical Shifts of the Ce@C_{82} Anion

YAMADA, Michio[1]; WAKAHARA, Takatsugu[1]; LIAN, Yongfu[1]; TSUCHIYA, Takahiro[1]; AKASAKA, Takeshi[1]; WAELCHLI, Markus[2]; MIZOROGI, Naomi; NAGASE, Shigeru; KADISH, Karl M.[3]
([1]Univ. Tsukuba; [2]Bruker Biospin K.K.; [3]Univ. Houston)

[*J. Am. Chem. Soc.* **128**, 1400–1401 (2006)]

From paramagnetic NMR spectra analysis and density functional calculations, it is found that the Ce atom in Ce@C_{82} as well as [Ce@C_{82}]$^-$ is located at an off-centered position near a hexagonal ring of the C_{2v}-C_{82} cage along the C_2 axis, as found for M@C_{82} (M = Sc, Y, and La). This is in sharp contrast with the Eu and Gd positions determined recently by the MEM/Rietveld method for Eu@C_{82} and Gd@C_{82}.

I-A-15 Synthesis and Structural Characterization of Endohedral Pyrrolidinodimetallofullene: $La_2@C_{80}(CH_2)_2NTrt$

YAMADA, Michio[1]; WAKAHARA, Takatsugu[1]; NAKAHODO, Tsukasa[1]; TSUCHIYA, Takahiro[1]; MAEDA, Yutaka[2]; AKASAKA, Takeshi[1]; YOZA, Kenji[3]; HORN, Ernst[4]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Bruker AXS K.K.; [4]Rikkyo Univ.)

[*J. Am. Chem. Soc.* **128**, 1402–1403 (2006)]

The reaction of $La_2@C_{82}$ with 3-triphenylmethyl-5-oxazolidinone leads to the 6,6- and 5,6-adducts, $La_2@C_{80}(CH_2)_2NTrt$ (Trt = triphenylmethyl). The structure of the 6,6 adduct is determined by X-ray crystal structure and density functional calculations. As suggested by the electrostatic potential maps calculated for $[C_{80}(CH_2)_2NH]^-$, the two La atoms in $La_2@C_{80}(CH_2)_2NTrt$ are fixed, unlike the random motion in $La_2@C_{80}$, and can be regulated by addition positions.

I-A-16 $La_2@C_{72}$ and $Sc_2@C_{72}$: Computational Characterizations

SLANINA, Zdenek; CHEN, Zhongfang[1]; SCHLEYER, Paul v. R.[1]; UHLIK, Filip[2]; LU, Xin[3]; NAGASE, Shigeru
([1]Univ. Georgia; [2]Charles Univ.; [3]Xiamen Univ.)

[*J. Phys. Chem. A* **110**, 2231–2234 (2006)]

The $La_2@C_{72}$ and $Sc_2@C_{72}$ metallofullerenes are characterized by systematic density functional computations. On the basis of the most stable geometry of 39 C_{72} hexaanions and the computed energies of the best endofullerene candidates, the experimentally isolated $La_2@C_{72}$ has the structure coded #10611 that invalidates the so-called isolated pentagon (IPR) rule. The good agreement between the computed and the experimental ^{13}C chemical shifts for $La_2@C_{72}$ further supports the literature assignment. The geometry, IR vibrational frequencies, and ^{13}C chemical shifts of $Sc_2@C_{72}$ are predicted to assist its future experimental characterization.

I-A-17 Reactivity of 1-Hydro-5-Carbaphosphatrane Based on Tautomerization between Pentavalent Phosphorane and Trivalent Cyclic Phosphonite

KOBAYASHI, Junji[1]; GOTO, Kei[1]; KAWASHIMA, Takayuki[1]; SCHMIDT, Michael W.[2]; NAGASE, Shigeru
([1]Univ. Tokyo; [2]Iowa State Univ.)

[*Chem. Eur. J.* **12**, 3811–3820 (2006)]

Several reactions of 1-hydro-5-carbaphosphatrane based on tautomerization to the trivalent *t* cyclic phosphonite, not definitively observed by spectroscopic methods, are investigated experimentally and analyzed by ab initio theoretical calculations. The calculated potential energy surfaces (reaction intermediates and transition states) provide insight into the reaction mechanism.

I-A-18 Evolution of the Electronic Properties of Metallic Single-Walled Nanotubes with the Degree of CCl_2 Covalent Functionalization

LU, Jing[1]; WANG, Dan[2]; NAGASE, Shigeru; NI, Ming[1]; ZHANG, Xinwei[3]; MAEDA, Yutaka[4]; WAKAHARA, Takatsugu[5]; NAKAHODO, Tsukasa[5]; TSUCHIYA, Takahiro[5]; AKASAKA, Takeshi[5]; GAO, Zhengxiang[1]; YU, Dapeng[1]; YE, Hengqiang[1]; ZHOU, Yunsong[2]; MEI, W. N.[6]
([1]Peking Univ.; [2]Capital Normal Univ.; [3]Inst. Appl. Phys. Comput. Math.; [4]Tokyo Gakugei Univ.; [5]Univ. Tsukuba; [6]Univ. Nebraska)

[*J. Phys. Chem. B* **110**, 5655–5658 (2006)]

The changes in energetic, structural, and electronic properties of the metallic (5, 5) single-walled carbon nanotube (SWNT) with the degree of sidewall covalent functionalization of CCl_2 are investigated by using density functional calculations. The saturation concentration of CCl_2 covalent functionalization is predicted to be 33.3%. The cycloadducts always adopt an open structure. A band gap opens as the functionalization concentration reaches 11% and then basically increases with increasing functionalization concentration. These results are in agreement with available experiments and can be applied to predict the band gap of metallic SWNTs produced by the HiPco method at a given CCl_2 functionalization concentration.

I-A-19 Stability Computations for $Ba@C_{74}$ Isomers

SLANINA, Zdenek; NAGASE, Shigeru

[*Chem. Phys. Lett.* **422**, 133–136 (2006)]

Relative concentrations of six isomers of $Ba@C_{74}$ are evaluated: one cage with isolated pentagons, three isomers with a pentagon–pentagon junction, two structures with one pentagon–pentagon pair and one heptagon. The density functional calculations of Gibbs free energies show that $Ba@C_{82}$ has a D_{3h}-C_{74} cage that satisfies the isolated pentagon rule. The stability computations are in agreement with recent observations.

I-A-20 Comment on Disproving a Silicon Analog of an Alkyne with the Aid of Topological Analyses of the Electronic Structure and Ab Initio Molecular Dynamics Calculations

FRENKING, Gernot[1]; KRAPP, Andreas[1]; NAGASE, Shigeru; TAKAGI, Nozomi; SEKIGUCHI, Akira[2]
([1]Philipps-Univ.; [2]Univ. Tsukuba)

[*ChemPhysChem* **7**, 799–800 (2006)]

As the first example of the silicon analoges of alkynes, RSi≡SiR (R = Si*i*Pr[CH(SiMe$_3$)$_2$]$_2$) has been isolated. From the topological analysis of electron density distributions, it is recently claimed that only two electron pairs participate in the Si–Si bonding. In view of donor-acceptor interactions, however, it is commented that the Si–Si bond can be described as a triple bond.

I-A-21 Selective Interaction of Larger or Charge-Transfer Aromatic Molecules with Metallic Single-Wall Carbon Nanotubes: Critical Role of the Molecular Size and Orientation

LU, Jing[1]; NAGASE, Shigeru; ZHANG, Xinwei[2]; WANG, Dan[3]; NI, Ming[1]; MAEDA, Yutaka[4]; WAKAHARA, Takatsugu[5]; NAKAHODO, Tsukasa[5]; TSUCHIYA, Takahiro[5]; AKASAKA, Takeshi[5]; GAO, Zhengxiang[1]; YU, Dapeng[1]; YE, Hengqiang[1]; MEI, W. N.[6]; ZHOU, Yunsong[3]
([1]Peking Univ.; [2]Inst. Appl. Phys. Comput. Math.; [3]Capital Normal Univ.; [4]Tokyo Gakugei Univ.; [5]Univ. Tsukuba; [6]Univ. Nebraska)

[*J. Am. Chem. Soc.* **128**, 5114–5118 (2006)]

Using first principles calculations, we report for the first time that large nearly neutral aromatic molecules, such as naphthalene and anthracene, and small charge-transfer aromatic molecules, such as TCNQ and DDQ, interact more strongly with metallic single-walled carbon nanotubes (SWNTs) *vs.* their semiconducting counterparts as the molecular orientation of DDQ is taken into account. Two new mechanisms for separating metallic and semiconducting SWNTs *via* noncovalent π-π stacking or charge-transfer interaction are suggested.

I-A-22 Excited Electronic States and Relative Stabilities of C$_{80}$ Isomers

SLANINA, Zdenek; LEE, Shyi-Long[1]; UHLIK, Filip[2]; ADAMOWICZ, Ludwik[3]; NAGASE, Shigeru
([1]Natl. Chung-Cheng Univ.; [2]Charles Univ.; [3]Univ. Arizona)

[*Int. J. Quantum Chem.* **106**, 2222–2228 (2006)]

The synthesis of fullerenes at very high temperatures allows for a significant population of excited electronic states and thus for non-negligible electronic partition functions. This issue is studied for seven isomers of C$_{80}$ that satisfy the isolated pentagon rule. It is calculated that the effects of electronic excited states are larger than those in the previously tested examples. For the special conditions of fullerene synthesis/isolation, the electronic partition function based on the singlet excited states only reflect better the experimental population findings.

I-A-23 Synthesis and Characterization of a Bisadduct of La@C$_{82}$

FENG, Lai[1]; TSUCHIYA, Takahiro[1]; WAKAHARA, Takatsugu[1]; NAKAHODO, Tsukasa[1]; PIAO, Qiuyue[1]; MAEDA, Yutaka[2]; AKASAKA, Takeshi[1]; KATO, Tatsuhisa[3]; YOZA, Kenji[4]; HORN, Ernst[5]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Josai Univ.; [4]Bruker AXS K.K.; [5]Rikkyo Univ.)

[*J. Am. Chem. Soc.* **128**, 5990–5991 (2006)]

Up to now, no direct evidence has been reported for the dimerization of endohedral metallofullerenes. By synthesizing the bisadduct of La@C$_{82}$, it is demonstrated that the bisadduct forms a dimer in the single crystal. From the density functional calculations, it is evaluated which carbons in the bisadduct have large spin densities and POAV (p orbital axis vector) values to predict the most favorable position for dimerization. The intermolecular C–C distance of 1.635 Å calculated at the B3LYP level for the dimer agrees very well with the value of 1.638 (9) Å determined by the X-ray crystal analysis.

I-A-24 ^{13}C NMR Spectroscopic Study of Scandium Dimetallofullerene, Sc$_2$@C$_{84}$ *vs.* Sc$_2$C$_2$@C$_{82}$

IIDUKA, Yuko[1]; WAKAHARA, Takatsugu[1]; NAKAJIMA, Koji[1]; TSUCHIYA, Takahiro[1]; NAKAHODO, Tsukasa[1]; MAEDA, Yutaka[2]; AKASAKA, Takeshi[1]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.)

[*Chem. Commun.* 2057–2059 (2006)]

It has been widely believed that the typical dimetallofullerene, Sc$_2$C$_{84}$, takes the form of Sc$_2$@C$_{84}$ in which two Sc atoms are encaged inside the C$_{84}$ fullerene. However, it is found that the endohedral structure is not Sc$_2$@C$_{84}$ but Sc$_2$C$_2$@C$_{80}$. This finding is in sharp contrast with the previous NMR and power X-ray MEM/Rietvelt analysis.

I-A-25 H$_2$, Ne, and N$_2$ Energies of Encapsulation into C$_{60}$ Evaluated with the MPWB1K Functional

SLANINA, Zdenek; PULAY, Peter[1]; NAGASE, Shigeru
([1]Univ. Arkansas)

[*J. Chem. Theory Comput.* **2**, 782–785 (2006)]

The recently suggested MPWB1K functional is tested on H$_2$@C$_{60}$, Ne@C$_{60}$, and N$_2$@C$_{60}$ as a tool for evaluations of stabilization energies upon encapsulation of nonmetallic species into fullerenes. It is found that the MPWB1K (modified Perdew-Wang and Becke functionals) values can be within a few kilocalories per mole from the MP2 or SCS-MP2 (spin-component scaled MP2) values so that further applications of the functional are clearly encouraged. The best estimates of the encapsulation-energy gains found for H$_2$@C$_{60}$, Ne@C$_{60}$, and N$_2$@C$_{60}$ are at least 4 kcal/mol, slightly less than 4 kcal/mol, and about 9 kcal/mol, respectively.

I-A-26 Host-Guest Complexation of Endohedral Metallofullerene with Azacrown Ether and Its Application

TSUCHIYA, Takahiro[1]; SATO, Kumiko[1]; KURIHARA, Hiroki[1]; WAKAHARA, Takatsugu[1]; NAKAHODO, Tsukasa[1]; MAEDA, Yutaka[2]; AKASAKA, Takeshi[1]; OHKUBO, Kei[3]; FUKUZUMI, Shunich[3]; KATO, Tatsuhisa[4]; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Osaka Univ.; [4]Josai Univ.)

[*J. Am. Chem. Soc.* **128**, 6699–6703 (2006)]

Complexation of La@C_{82}-A with macrocyclic compounds, such as 1,4,7,10,13,16-hexaazacyclooctadecane, 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16,-hexaazacyclooctadecane, mono-aza-18-crown-6 ether, 18-crown-6 ether, and p-*tert*-buthylcalix[*n*]arenes (n = 4–8) is investigated.

I-A-27 Synthesis of Stannaindenyl Anions and a Dianion

SAITO, Masaichi[1]; SHIMOSAWA, Masakazu[1]; YOSHIOKA, Michikazu[1]; ISHIMURA, Kazuya; NAGASE, Shigeru
([1]Saitama Univ.)

[*Organometallics* **25**, 2967–2971 (2006)]

Reduction of 1,1-diphenylstannaindene with lithium gives the 1-phenyl-1-stannaindenyl anion, which is further reduced to provide the 1-stannaindenyl dianion. The remarkable upfield ^{7}Li NMR resonance in the dianion and theoretical calculations suggest that the 1-stannaindenyl dianion has considerable aromatic character, as is observed in the sila- and germaindenyl dianions. The structure, charge distribution, NMR chemical shifts of the unsolvated and solvated 1-stannaindenyl dianion are calculated at the B3LYP level.

I-A-28 The Bingel Monoadducts of La@C_{82}: Synthesis, Characterization, and Electrochemistry

FENG, Lai[1]; WAKAHARA, Takatsugu[1]; NAKAHODO, Tsukasa[1]; TSUCHIYA, Takahiro[1]; PIAO, Qiuyue[1]; MAEDA, Yutaka[2]; LIAN, Yongfu[1]; AKASAKA, Takeshi[1]; HORN, Ernst[3]; YOZA, Kenji[4]; KATO, Tatsuhisa[5]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Rikkyo Univ.; [4]Bruker AXS K.K.; [5]Josai Univ.)

[*Chem. Eur. J.* **12**, 5578–5586 (2006)]

The reaction of La@C_{82} with diethyl bromomalonate provides five monoadducts. Four of the five adducts are ESR inactive and singly bonded regioisomers, while the remaining adduct is ESR active and possesses a cyclic moiety between the malonate group and the C_{82} cage. Addition sites, thermal stabilities, and electrochemical properties are investigated with the help of density functional calculations.

I-A-29 Syntheses, Structures, and Reactions of Heptacoordinate Trihalogermanes Bearing a Triarylmethyl-Type Tetradentate Ligand

IWANAGA, Kohei[1]; KOBAYASHI, Junji[1]; KAWASHIMA, Takayuki[1]; TAKAGI, Nozomi; NAGASE, Shigeru
([1]Univ. Tokyo)

[*Organometallics* **25**, 3388–3393 (2006)]

Heptacoordinate trihalogermanes are synthesized by the reaction of the (triarylmethyl)lithium species and with tetrachlorogermane. The bonding nature of the central heptacoordonate Ge atom and the surrounding O atoms is investigated by the AIM (atoms-in-molecules) analysis at the B3PW1 level. The small electron density ($\rho(r_c)$) value and the small positive Laplacian ($\nabla^2\rho(r_c)$) value at the bond critical point (r_c) value suggest that the Ge–O bonds are weak and have ionic character.

I-A-30 Structural and Electronic Properties of Fluorinated Boron Nitride Nanotubes

LAI, Lin[1]; SONG, Wei[1]; LU, Jing[1]; GAO, Zhengxiang[1]; NAGASE, Shigeru; NI, Ming[1]; MEI, W. N.[2]; LIU, Jianjun[2]; YU, Dapeng[1]; YE, Hengqiang[1]
([1]Peking Univ.; [2]Univ. Nebraska)

[*J. Phys. Chem. B* **110**, 14092–14097 (2006)]

The effects of F doping on the structural and electronic properties of the (5,5) single-walled boron nitride nanotube (BNNT) are investigated by using the density functional theory method. The chemiadsorption of F maintains the hexagonal BN network, increases the lattice constant, and introduces acceptor impurity states. On the other hand, substitutional doping of F destroys the hexagonal BN network, decreases the lattice constant, but does not alter the insulating feature of the BNNT. The observed insulator-to-semiconducting transition, a lattice contraction, and a highly disordered atom arrangement in the sidewall of BNNTs upon F doping are most reasonably attributed to a codoping of dominating substitutional F over chemiabsorbed F, which can induce deep donor impurity states, a lattice contraction, and a destruction of the hexagonal BN network simultaneously.

I-A-31 Characterization of the Bis-Silylated Endofullerene Sc_3N@C_{80}

WAKAHARA, Takatsugu[1]; IIDUKA, Yuko[1]; IKENAGA, Ozora[1]; NAKAHODO, Tsukasa[1]; SAKURABA, Akihiro[2]; TSUCHIYA, Takahiro[1]; MAEDA, Yutaka[3]; KAKO, Masahiro[4]; AKASAKA, Takeshi[1]; YOZA, Kenji[5]; HORN, Ernst[6]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Niigata Univ.; [3]Tokyo Gakugei Univ.;

[4]Univ. Electro-Communications; [5]Bruker AXS K.K.;
[6]Rikkyo Univ.)

[*J. Am. Chem. Soc.* **128**, 9919–9925 (2006)]

The photochemical reaction of $Sc_3N@C_{80}$ with 1,1,2,2-tetramesityl-1,2-disilirane affords the bis-silylated adduct. This adduct was characterized by NMR spectroscopy and single-crystal X-ray structure analysis. The dynamic behavior of the disilirane moiety and the encapsulated Sc_3N cluster were also investigated. The unique redox property of the adduct is reported by means of CV and DPV. Experimental results were confirmed by density functional calculations.

I-A-32 Synthesis and Characterization of Dimetallostannafluorenes

SAITO, Masaichi[1]; SHIMOSAWA, Masakazu[1]; YOSHIOKA, Michikazu[1]; ISHIMURA, Kazuya; NAGASE, Shigeru
([1]Saitama Univ.)

[*Chem. Lett.* 940–941 (2006)]

There has been considerable interest in the chemistry of anions and dianions of group 14 metalloes as heavier congeners of cyclopentadienyl anions. The reaction of 9,9-bis(*p*-methoxyphenyl)-9-stannafluorene with lithium or potassium gives the corresponding dimetallostannafluorene. The structure and aromaticity are characterized by density functional calculations.

I-A-33 Carbon Monoxide inside an Open-Cage Fullerene

IWAMATSU, Sho-ichi[1]; STANISKY, Christopher M.[2]; CROSS, R. James[2]; SAUNDERS, Martin[2]; MIZOROGI, Naomi; NAGASE, Shigeru; MURATA, Shizuaki[1]
([1]Nagoya Univ.; [2]Yale Univ.)

[*Angew. Chem., Int. Ed.* **45**, 5337–5340 (2006)]

It is of considerable interest to store a molecule inside cage molecules by making an orifice on the cage surface. Thus, an orifice is made on C_{60} by chemical modification, which is the largest known to date for fullerenes, and CO is inserted through the orifice. The binding energy and dynamic behaviors are investigated by density functional calculations. It is suggested that the stored CO molecule rotates rapidly on the NMR time scale but not on the IR time scale.