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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[*J. Am. Chem. Soc.* **125**, 15507–15511 (2003)]

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 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

WAKAHARA, Takatsugu[1]; MAEDA, Yutaka[1]; KAKO, Masahiro[2]; AKASAKA, Takeshi[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
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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

LIU, Michael T. H.[1]; CHOE, Yoong-Kee; KIMURA, Masahiro; KOBAYASHI, Kaoru; NAGASE, Shigeru; WAKAHARA, Takatsugu[2]; NIINO, Yasuyuki[3]; ISHITSUKA, Midori O.[2]; MAEDA, Yutaka[2]; AKASAKA, Takeshi[2]
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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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([1]IMS and Academia Sinica)

[*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

WAKAHARA, Takatsugu[1]; MATSUNAGA, Yoichiro[1]; KATAYAMA, Akira[2]; MAEDA, Yutaka[1]; KAKO, Masahiro[3]; AKASAKA, Takeshi[1]; OKAMURA, Mutsuo[2]; KATO, Tatsuhisa; CHOE, Yoong-Kee; KOBAYASHI, Kaoru; NAGASE, Shigeru; HUANG, Houjin[4]; ATA, Masafumi[4]
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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 Ψ(N@$^3C_{60}$*) and ground Ψ(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 α 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

SLANINA, Zdenek[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
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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

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

[*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 ?

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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([1]Nagoya Univ.)

[*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

SLANINA, Zdenek[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
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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

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

[*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

WAKAHARA, Takatsugu[1]; KOBAYASHI, Jun-ichi[1]; YAMADA, Michio[1]; MAEDA, Yutaka[1]; TSUCHIYA, Takahiro[1]; OKAMURA, Mutsuo[2]; AKASAKA, Takeshi[1]; WAELCHLI, Markus[3]; KOBAYASHI, Kaoru; NAGASE, Shigeru; KATO, Tatsuhisa; KAKO, Masahiro[4]; YAMAMOTO, Kazunori[5]; KADISH, Karl M.[6]
([1]Univ. Tsukuba; [2]Niigata Univ.; [3]Bruker Japan; [4]Univ. Electro-Communications; [5]Japan Nuclear Fuel Cycle Development Inst.; [6]Univ. Houston)

[*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}

MAEDA, Yutaka[1]; MATSUNAGA, Yoichiro[2]; WAKAHARA, Takatsugu[2]; TAKAHASHI, Satomi[3]; TSUCHIYA, Takahiro[2]; ISHITSUKA, Midori O.[2]; HASEGAWA, Tadashi[1]; AKASAKA, Takeshi[2]; LIU, Michael T. H.[4]; KOKURA, Kisato[5]; HORN, Ernst[5]; YOZA, Kenji[6]; KATO, Tatsuhisa; OKUBO, Shingo; KOBAYASHI, Kaoru; NAGASE, Shigeru; YAMAMOTO, Kazunori[7]
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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}

CAO, Baopeng[1]; WAKAHARA, Takatsugu[1]; TSUCHIYA, Takahiro[1]; KONDO, Masahiro[2]; MAEDA, Yutaka[1]; RAHMAN, G. M. Aminur[1]; AKASAKA, Takeshi[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru; YAMAMOTO, Kazunori[3]
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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

LU, Jing[1]; NAGASE, Shigeru; ZHANG, Shuang[2]; PENG, Lianmao[2]
([1]IMS and Peking Univ.; [2]Peking Univ.)

[*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.

I-B Prediction of Protein Tertiary Structures and Protein Folding Problem

Prediction of the three-dimensional structures of protein molecules by computer simulations is a very challenging problem in theoretical molecular science. The difficulty of the problem lies in two facts: (1) the inclusion of accurate solvent effects is non-trivial and time-consuming (2) there exist a huge number of local minima in the energy function, forcing conventional simulations to get trapped in states of energy local minima. We have been exploring the strategies that allow us to overcome these difficulties and to study the protein folding mechanism by directly folding proteins.

I-B-1 Optimization of Protein Force-Field Parameters with the Protein Data Bank

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([1]GUAS)

[*Chem. Phys. Lett.* **382**, 626 (2003)]

We propose a novel method to optimize existing force-field parameters for protein systems. The method consists of minimizing the summation of the square of the force acting on each atom in the proteins with the structures from the Protein Data Bank. We performed this optimization to the partial-charge and torsion-energy parameters of the AMBER parm94 force field, using 100 molecules from the Protein Data Bank. We then performed folding simulations of α-helical and β-hairpin peptides. The optimized force-field parameters gave structures more consistent with the experimental implications than the original AMBER force field.

I-B-2 Prediction of Transmembrane Helix Configurations by Replica-Exchange Simulations

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([1]GUAS)

[*Chem. Phys. Lett.* **383**, 397 (2004)]

We propose a method for predicting helical membrane protein structures by computer simulations. Our method consists of two parts. In the first part, amino-acid sequences of the transmembrane helix regions are obtained from one of existing WWW servers. In the second part, we perform a replica-exchange simulation of these transmembrane helices with some constraints and identify the predicted structure as the global-minimum-energy state. We have tested the second part of the method with the dimeric transmembrane domain of glycophorin A. The structure obtained from the prediction was in close agreement with the experimental data.

I-B-3 Free Energy Calculations for DNA Base Stacking by Replica-Exchange Umbrella Sampling

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[*Chem. Phys. Lett.* **385**, 1 (2004)]

We have investigated the free energy change of the stacking process of DNA dimers using molecular dynamics simulations based on replica-exchange umbrella sampling. Pairs of replicas with different umbrella potentials are exchanged in this method, which allows the simulation to sample much wider conformational space and, therefore, to yield more accurate free energy profiles than by the conventional umbrella sampling. From the free energy profiles, we observed good stacking for all DNA dimers and sequence-dependent stacking stability. This sequence dependence of the stacking free energy is in accord with the experimental results.

I-B-4 Comparisons of Force Fields for Proteins by Generalized-Ensemble Simulations

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[*Chem. Phys. Lett.* **386**, 460 (2004)]

Secondary structural characteristics of six commonly used force fields for protein systems developed by different research groups have been compared. We performed molecular dynamics simulations of an α-helical polypeptide and a β-hairpin polypeptide with explicit water molecules. Two generalized-ensemble algorithms, replica-exchange multicanonical algorithm and multicanonical replica-exchange method, for efficient sampling of configurational space have been employed. Comparisons of the secondary structure content of polypeptides for different force fields highlighted differences of their structural tendency. The results imply that α-helix is favored for AMBER94 and AMBER99 and that β-hairpin is favored for GROMOS96, while CHARMM 22, AMBER96, and OPLS-AA/L have intermediate tendency.

I-B-5 Prediction of Membrane Protein Structures by Replica-Exchange Monte Carlo Simulations: Case of Two Helices

KOKUBO, Hironori[1]; OKAMOTO, Yuko
([1]GUAS)

[*J. Chem. Phys.* **120**, 10837 (2004)]

We test our prediction method of membrane protein structures with glycophorin A transmembrane dimer and analyze the predicted structures in detail. Our method consists of two parts. In the first part, we obtain the amino-acid sequences of the transmembrane helix regions from one of existing WWW servers and use them as an input for the second part of our method. In the second part, we perform a replica-exchange Monte Carlo simulation of these transmembrane helices with some constraints that indirectly represent surrounding lipid and water effects and identify the predicted structure as the global-minimum-energy state. The structure obtained in the case for the dielectric constant $\varepsilon = 1.0$ is very close to that from the NMR experiments, while that for $\varepsilon = 4.0$ is more packed than the native one. Our results imply that the helix–helix interaction is the main driving force for the native structure formation and that the stability of the native structure is determined by the balance of the electrostatic term, van der Waals term, and torsion term, and the contribution of electrostatic energy is indeed important for correct predictions. The inclusion of atomistic details of side chains is essential for estimating this balance accurately because helices are tightly packed.

I-B-6 Replica-Exchange Extensions of Simulated Tempering Method

MITSUTAKE, Ayori[1]; OKAMOTO, Yuko
([1]Keio Univ.)

[*J. Chem. Phys.* **121**, 2491 (2004)]

In this article we consider combinations of two well-known generalized-ensemble algorithms, namely, simulated tempering and replica-exchange method. We discuss two examples of such combinations. One is the previously developed replica-exchange simulated tempering and the other is the newly developed simulated tempering replica-exchange method. In the former method, a short replica-exchange simulation is first performed and the simulated tempering weight factor is obtained by the multiple-histogram reweighting techniques. This process of simulated tempering weight factor determination is faster and simpler than that in the usual iterative process. A long simulated tempering production run is then performed with this weight factor. The latter method is a further extension of the former in which a simulated tempering replica-exchange simulation is performed with a small number of replicas. These new algorithms are particularly useful for studying frustrated systems with rough energy landscape. We give the formulations of these two methods in detail and demonstrate their effectiveness taking the example of the system of a 17-residue helical peptide.

I-B-7 Self-Assembly of Transmembrane Helices of Bacteriorhodopsin by a Replica-Exchange Monte Carlo Simulation

KOKUBO, Hironori[1]; OKAMOTO, Yuko
([1]GUAS)

[*Chem. Phys. Lett.* **392**, 168 (2004)]

We examine by a molecular simulation whether or not the transmembrane helices of bacteriorhodopsin have the ability to self-assemble into the native configuration by themselves. Starting from random initial configurations of seven transmembrane helices, the same helix arrangement as the experimental one (PDB code: 1C3W) was obtained by a replica-exchange Monte Carlo simulation. This implies that helix–helix interactions are the main driving force for the native structure formation of bacteriorhodopsin.

I-C Development of Simulation Algorithms for Complex Systems

Developing a powerful simulation algorithm that can alleviate the multiple-minima problem is important in many complex systems. We have been advocating the uses of the so-called generalized-ensemble algorithms such as multicanonical algorithm and replica-exchange method.

I-C-1 New Approach to the First-Order Phase Transition of Lennard-Jones Fluids

MUGURUMA, Chizuru[1]; OKAMOTO, Yuko;
MIKAMI, Masuhiro[2]
([1]Chukyo Univ.; [2]AIST)

[*J. Chem. Phys.* **120**, 7557 (2004)]

The multicanonical Monte Carlo method is applied to a bulk Lennard-Jones fluid system to investigate the liquid-solid phase transition. We take the example of a system of 108 argon particles. The multicanonical weight factor we determined turned out to be reliable for the energy range between 27.0 and 24.0 kJ/mol, which corresponds to the temperature range between 60 and 250 K. The expectation values of the thermodynamic quantities obtained from the multicanonical production run by the reweighting techniques exhibit the characteristics of first-order phase transitions between liquid and solid states around 150 K. The present study reveals that the multicanonical algorithm is particularly suitable for analyzing the transition state of the first-order phase transition in detail.

I-C-2 Molecular Dynamics Simulations in the Multibaric-Multithermal Ensemble

OKUMURA, Hisashi; OKAMOTO, Yuko

[*Chem. Phys. Lett.* **391**, 248 (2004)]

We propose a new generalized-ensemble molecular dynamics simulation algorithm, which we refer to as the multibaric-multithermal molecular dynamics. This is the molecular dynamics version of the recently proposed multibaric-multithermal Monte Carlo method. The multibaric-multithermal simulations perform random walks widely both in the potential-energy space and in the volume space. From only one simulation run, therefore, one can calculate isobaric-isothermal-ensemble averages in wide ranges of temperature and pressure. We test the effectiveness of this algorithm by applying it to a Lennard-Jones 12-6 potential system.

I-C-3 Monte Carlo Simulations in Generalized Isobaric-Isothermal Ensembles

OKUMURA, Hisashi; OKAMOTO, Yuko

[*Phys. Rev. E* **70**, 026702 (2004)]

We present three generalized isobaric-isothermal ensemble Monte Carlo algorithms, which we refer to as the multibaric-multithermal, multibaric-isothermal, and isobaric-multithermal algorithms. These Monte Carlo simulations perform random walks widely in volume space and/or in potential energy space. From only one simulation run, one can calculate isobaric-isothermal-ensemble averages in wide ranges of pressure and temperature. We demonstrate the effectiveness of these algorithms by applying them to the Lennard-Jones 12–6 potential system with 500 particles.

I-D Applications of the Zhu-Nakamura Theory to Electronically Nonadiabatic Chemical Dynamics

I-D-1 Semiclassical Theory of Electronically Nonadiabatic Chemical Dynamics: Incorporation of the Zhu-Nakamura Theory into the Frozen Gaussian Propagation Method

KONDORSKIY, Alexey; NAKAMURA, Hiroki

[*J. Chem. Phys.* **120**, 8937 (2004)]

The title theory is developed by combining the Herman-Kluk semiclassical theory for adiabatic propagation on single potential-energy surface and the semiclassical Zhu-Nakamura theory for nonadiabatic transition. The formulation with use of natural mathematical principles leads to a quite simple expression for the propagator based on classical trajectories and simple formulas are derived for overall adiabatic and nonadiabatic processes. The theory is applied to electronically nonadiabatic photodissociation processes: a one-dimensional problem of H_2^+ in a cw (continuous wave) laser field and a two-dimensional model problem of H_2O in a cw laser field. The theory is found to work well for the propagation duration of several molecular vibrational periods and wide energy range. Although the formulation is made for the case of laser induced nonadiabatic processes, it is straightforwardly applicable to ordinary electronically nonadiabatic chemical dynamics.

I-D-2 Semiclassical Frozen Gaussian Propagation Method for Electronically Nonadiabatic Chemical Dynamics: Møller Operator Formulation and Incorporation of the Zhu-Nakamura Theory

KONDORSKIY, Alexey; NAKAMURA, Hiroki

[*J. Theor. Comput. Chem.* in press]

The title theory is developed by combining the Herman-Kluk semiclassical theory for adiabatic propagation on single potential energy surface and the Zhu-Nakamura theory for nonadiabatic transition. A quite simple expression for the propagator based on classical trajectories is derived using the Møller operator formulation of scattering theory. The theory takes into account almost all quantum effects that occur during nonadiabatic transition, especially at low energies and is expected to be applicable to general chemical dynamics of high dimensions. Application to a two-dimensional model system shows that the theory works well for the propagation duration of several molecular vibrational periods and wide wave packet energy range.

I-D-3 Evaluation of Canonical and Microcanonical Nonadiabatic Reaction Rate Constants by Using the Zhu-Nakamura Formulas

ZHAO, Yi[1]; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki
([1]IMS and Univ. Sci. Tech. China, China)

[*J. Chem. Phys.* in press]

We consider a problem of calculating both thermal and microcanonical rate constant for nonadiabatic chemical reactions. Instead of using the conventional transition state theory (TST), we use a generalized seam surface and introduce a concept of a coordinate dependent effective nonadiabatic transition probability based on the Zhu-Nakamura (ZN) theory which can treat the nonadiabatic tunneling properly. The present approach can be combined with Monte Carlo method so as to be applicable to chemical reactions in complicated systems. The method is demonstrated to work well in wide energy and temperature range. Numerical tests also show that it is very essential for accurate evaluation of the thermal rate constant to use the generalized seam surface and take into account the nonadiabatic tunneling effect.

I-D-4 Trace Formula of Thermal Rate Constant for Multi-Surface Processes

CHIKAZUMI, Shinpei; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

The trace formula for thermal rate constant formulated by W. Miller and co-workers for electronically adiabatic reactions is extended so as to be applicable to multi-potential energy surface processes. A semiclassical theory is formulated with the Zhu-Nakamura theory incorporated to treat the electronically nonadiabatic transition. Adiabatic propagation on the single potential energy surface is treated by the Herman-Kluk type wave packet propagation.

I-D-5 Tragectory Surface Hopping Approach to Electronically Nonadiabatic Chemical Dynamics

OLOYEDE, Ponmile[1]; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki
([1]GUAS)

With use of the Zhu-Nakamura formulas, the TSH method can be generalized so as to treat both classically allowed and forbidden transitions unformly. This new implementation is applicable to both crossing seam type and conical intersection type processes of high dimension.

I-E Theory of Nonadiabatic Transition

I-E-1 Analytic Solution to Wave Packet Dynamics in a Laser Field: The Case of Linear Chirp

NAKAMURA, Hiroki

[*Chem. Phys.* **295**, 269–273 (2003)]

An analytical expression for the nonadiabatic transition probability is derived for the case that two linear potentials in coordinate space are coupled by a linearly chirped time-dependent laser field. This constitutes a solution to the wave packet dynamics in the high energy approximation. Numerical calculations are carried out to demonstrate the applicability of the formula.

I-E-2 Semiclassical Theory of Nonadiabatic Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir[1]; USHAKOV, Vladimir[1]; NAKAMURA, Hiroki
([1]Inst. Problems Chem. Phys., Russia)

[*Russ. Chem. Phys.* **22**, 87 (2003)]

The semiclassical analysis is carried out for a two-state model potential system, in which two asymptotically degenerate Morse type potentials are coupled by an exponential diabatic coupling. Both crossing and non-crossing cases are treated and explicit analytical expressions for the full scattering matrix are obtained. The result can be used in a more general problem involving the present type of asymptotic transitions.

I-E-3 Analytical Treatment of *S-P* Type Collisional Resonant Excitation Transfer

OSHEROV, Vladimir[1]; USHAKOV, Vladimir[1]; NAKAMURA, Hiroki
([1]Inst. Problems Chem. Phys., Russia)

[*Russ. Chem. Phys.* **23**, 103 (2003)]

The analytical solution developed in the previous paper is applied to the *S-P* type collisional resonant excitation transfer between atoms. The corresponding cross-sections are calculated in the high energy approximation. Good agreement is obtained with the results calculated previously by Watanabe with use of the fully numerical integration of the time-dependent coupled differential equations. This indicates usefulness of the present analytical theory developed in our previous papers.

I-E-4 Rabi Dynamics of Coupled Atomic and Molecular Bose-Einstein Condensates

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([1]Engineering Cent. Armenian Natl. Acad. Sci., Armenia; [2]Russian Res. Cent. "Kurchatov institute," Inst. Nuclear Fusion, Russia)

The dynamics of coherent Rabi oscillations in coupled atomic and molecular Bose-Einstein condensates is considered taking into account the atom-atom, atom-molecule and molecule-molecule elastic interactions. The exact solution for the molecule formation probability is derived in terms of the elliptic functions. The 2-dimensional space of the involved parameters is analyzed and divided into two regions where the Rabi oscillations show different characteristics. A resonance curve is found, on which the molecular formation probability monotonically increases as a function of time. The maximum value of the transition probability on this curve is 1 (*i.e.*, total transition to the molecular state) and it is achieved at high field intensities starting from a minimal threshold determined by the inter-species interaction scattering lengths. The explicit form of the resonance curve is determined, and it is shown that the resonance frequency position reveals a nonlinear dependence on the Rabi frequency of the applied field. A singular point is found on the resonance curve, where a power-law time evolution of the system is observed.

I-F Quantum Dynamics of Chemical Reactions

I-F-1 Full Quantum Dynamics of Atom-Diatom Chemical Reactions in Hyperspherical Elliptic Coordinates

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([1]Univ. Tokyo; [2]Russian Res. Cent. "Kurchatov Institute," Russia)

[*J. Phys. Chem.* in press]

Explicit expressions of the full Hamiltonian of tri-atomic system in the hyperspherical elliptic (HSE) coordinates are derived. The derivation is made from the expressions in the Delves coordinates. A numerical algorithm is also presented to evaluate the surface eigenfunctions including all the effects of Coriolis coupling terms. The whole formalism is numerically tested by using the Cl + DH and O(^{1}D) + HCl reacton systems. The HSE coordinate system, which is well-known to be powerful to elucidate reaction mechanisms especially for heavy-light-heavy systems, is now ready to be applied for clarifying full quantum dynamics of such systems.

I-F-2 Quantum Dynamics of O(^{1}D) + HCl Reactions

ZHAO, Yi[1]; NANBU, Shinkoh; NAKAMURA, Hiroki
([1]IMS and Univ. Sci. Tech. China, China)

Quantum dynamics calculations of O(^{1}D) + HCl are carried out with the three potential energy surfaces (1^1A', 2^1A', 1^1A") taken into account. The three accurate potential energy surfaces are already available (*J. Theor. Comput. Chem.* **1**, 263, 275, 285 (2002)).

I-G Theory of Multi-Dimensional Tunneling

I-G-1 On the Determination of Caustics

OLOYEDE, Ponmile[1]; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki
([1]GUAS)

[*J. Theor. Comput. Chem.* **3**, 91 (2004)]

This paper presents a numerical method which locates caustics of classical trajectories on-the-fly. The method is conceptually simple and is applicable to a system of arbitrary dimensions. The efficiency of the method is demonstrated by determining caustics of trajectories in the 2-D Henon-Heiles potential and of trajectories used to simulate a triatomic reaction process for J (total angular momentum) = 0.

I-G-2 Simple and Accurate Method to Evaluate Tunneling Splitting in Polyatomic Molecules

MIL'NIKOV, Gennady V.; YAGI, Kiyoshi[1]; TAKETSUGU, Tetsuya[2]; NAKAMURA, Hiroki; HIRAO, Kimihiko[1]
([1]Univ. Tokyo; [2]Ochanomizu Univ.)

[*J. Chem. Phys.* **120**, 5036 (2004)]

A practical and accurate semiclassical method for calculating the tunneling slpitting of the ground state in polyatomic molecules is presented based on a recent version of the instanton theory [*J. Chem. Phys.* **115**, 6881 (2001)]. The method uses *ab initio* quantum chemical data for the potential energy surface without any concominant extrapolation and requires only a small number of *ab initio* data points to get convergence even for large molecules. This enables one to use an advanced level of electronic structure theory and achieve a high accuracy of the result. The method is applied to the 9-atomic malonaldehyde molecule by making use of the potential energy surface at the level of CCSD(T) with the hybrid basis set of aug-cc-pVTZ (for oxygen atoms and the transferred hydrogen atom) and cc-pVTZ (for other atoms).

I-G-3 Effect of Out-Of Plane Vibration on the Hydrogen Atom Transfer Reaction in Malonaldehyde

YAGI, Kiyoshi[1]; MIL'NIKOV, Gennady V.; TAKETSUGU, Tetsuya[2]; HIRAO, Kimihiko[1]; NAKAMURA, Hiroki
([1]Univ. Tokyo; [2]Ochanomizu Univ.)

Tunneling splitting of the ground vibrational state is calculated for the planar model of malonaldehyde by the instanton method of Mil'nikov and Nakamura with use of *ab initio* potential energy surface. The planar model gives much larger tunneling splitting than the previous full dimensional calculations, indicating a strong effect of the anharmonic coupling between the in-plane and out-of-plane modes of the hydrogen atom. The anharmonicity is related to the Coriolis coupling between the OH stretching vibration and the pseudo-rotation of the hindered rotor. The present results suggest that the multidimensional effects should be carefully taken into account in the tunneling dynamics of polyatomic molecules.

I-G-4 Tunneling Splitting in Vinyl Radical C_2H_3

MIL'NIKOV, Gennady V.; ISHIDA, Toshimasa[1]; NANBU, Shinkoh; NAKAMURA, Hiroki
([1]Shizuoka Univ.)

Tunneling splitting of the ground vibrational state in vinyl radical is calculated with use of our theory developed before (*J. Chem. Phys.* **117**, 9588 (2002)). The potential energy surface is calculated accurately by the CCSD(T)/(aug-)cc-pvTZ method. The splitting obtained (= 0.53 cm^{-1}) is in very good agreement with the recent experiment (= 0.54 cm^{-1}) (*J. Chem. Phys.* **120**, 3604 (2004)).

I-G-5 Semiclassical Theory of Tunneling Splitting of Vibrationally Excited State

MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

The practical implementation of the instanton theory (*J. Chem. Phys.* **117**, 9588 (2002)) is extended so as to be applicable to vibrationally excited states. The effect of multi-dimensionality found before (*J. Chem. Phys.* **102**, 3977 (1995)) can now be nicely interpreted by the analytical expression.

I-H Laser Control of Molecular Processes

I-H-1 Semiclassical Formulation of Optimal Control Theory

KONDORSKIY, Alexey; NAKAMURA, Hiroki

[*J. Theor. Comput. Chem.* in press]

In the present paper semiclassical formulation of optimal control theory is made by combining the conjugate gradient search method with new approximate semiclassical expressions for correlation function. Two expressions for correlation function are derived. The simpler one requires calculations of coordinates and momenta of classical trajectories only. The second one requires extra calculation of common semiclassical quantities; as a result additional quantum effects can be taken into account. The efficiency of the method is demonstrated by controlling nuclear wave packet motion in a two-dimensional model system.

I-H-2 Control of Electronic Transitions of Wave Packet by Using Quadratically Chirped Pulses

ZOU, Shiyang; KONDORSKIY, Alexey; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

We consider an effective scheme for the laser control of the nonadiabatic wave packet dynamics. It is shown that by using specially designed quadratically chirped pulse one can achieve fast and complete excitation of the wave packet without distortion of its shape. The parameters of the laser pulse can be estimated analytically from the Zhu-Nakamura (ZN) theory regardless of the dimensionality of the system. The efficiency of the laser control scheme is demonstrated by several examples: complete $B^1\Pi \leftarrow X^1\Sigma^+$ excitation in LiH, control of the wave packet dynamics in Nak by using pump-dump mechanism and the bond selective photodissociation of H_2O.

I-H-3 Selective Excitation to Closely-Lying Cs ($7D_{3/2}$) and Cs ($7D_{5/2}$) by Femtosecond Laser Pulses

YAMADA, H.[1,2]; YOKOYAMA, K.[1,3]; TERANISHI, Y.[1]; SUGITA, A.[1]; YAMAKAWA, K.[1]; KAWASAKI, M.[2]; YOKOYAMA, A.[3]; NAKAMURA, Hiroki
(*[1]JARI.; [2]Kyoto Univ.; [3]Japan Atomic Energy Res. Inst.)*

Ultrafast selection of closely lying excited states with a broadband light source is reported for a demonstration of precise coherent quantum control based on pulse shaping technique. Transform-limited pulses emitted from a Ti:Sapphire oscillator were shaped to phase-locked pulse pairs by an acousto-optic programmable dispersive filter and focused into cesium vapor to excite the atoms in the ground state to the $Cs(7D_{3/2})$ and $Cs(7D_{5/2})$ states *via* two-photon absorption. The relative excitation probability to each spin-orbit state was measured through the fluorescence to the $Cs(6P_{1/2})$ and $Cs(6P_{3/2})$ states, and was found to exhibit complete modulation with a period of π as a function of the phase-difference between two pulses. At the destructive phase, the fluorescence vanished below the detection limit. The best contrast of the selection ratio exceeded a thousand within 400-fs delay.

I-I Development of New Molecular Functions

I-I-1 Conversion between Cyclohexadiene and Hexatriene as a Model of Photochromism

TAMURA, Hiroyuki; NANBU, Shinkoh; ISHIDA, Toshimasa[1]; NAKAMURA, Hiroki
(*[1]Shizuoka Univ.)*

High level of quantum chemical calculations of potential energy surfaces of the title molecules have been carried out. The conical intersection between 2'A and 1'A states, which is expected to play an important role for the photo conversion, has been found and the previously reported results are found to be not necessarily accurate. The corresponding dynamics calculations will be carried out.

I-I-2 Transmission of Atoms through Ring Molecules as a Model of Encapsulation by Carbon Nanotubes

NANBU, Shinkoh; ISHIDA, Toshimasa[1]; NAKAMURA, Hiroki
(*[1]Shizuoka Univ.)*

The systems composed of ring molecules such as $C_{20}H_{10}$ and atoms such as H, Na, and Li have been studied quantum chemically and dynamically. It is found that in the case that five carbon atoms are replaced by borons nonadiabatic transitions between ground and first excited adiabatic states play a crucial role and hydrogen atom can transmit the ring with high efficiency by appropriately adjusting its translational energy.

I-J Theoretical Studies of Electron Dynamics in Molecular Systems

Electron dynamics in molecular systems is an intrinsic process in a number of interesting phenomena such as linear and nonlinear optical response, electric conduction, and also chemical reaction. Despite the importance, the electron dynamics has not been understood in detail. We have developed a computational method simulating the electron dynamics in real time, and investigated nonlinear optical response and multiple ionization of noble metal clusters.

I-J-1 High-Order Harmonic Generation from Silver Clusters: Laser-Frequency Dependence and the Screening Effect of *d* Electrons

NOBUSADA, Katsuyuki; YABANA, Kazuhiro[1]
([1]Univ. Tsukuba)

[*Phys. Rev. A* **70**, 043411 (7 pages) (2004)]

We present time-dependent density functional studies of harmonic generation from Ag_2 and Ag_8 in pulsed laser fields. The harmonic generation is strongly dependent on the laser frequency. The harmonics are emitted from the clusters much more efficiently when the applied laser field is in tune with the dipole resonance frequency of the system. Such resonance frequency dependence is substantially equal to a resonance phenomenon in a forced oscillator in a sense that the valence *s*-electrons are shaken effectively at the tuned laser frequency and the induced dipole moment continues to oscillate even though the laser field is switched off. Furthermore, we have found that the polarizable core *d*-electrons significantly screen the valence *s*-electrons such that the electron density of the *s* electrons induced in the laser field is canceled out. The screening effect of the *d* electrons becomes more important in the system of Ag_8 than Ag_2.

I-J-2 Multiple Ionization of a Silver Diatomic Molecule in an Intense Laser Field

SHIRATORI, Kazuya[1]; NOBUSADA, Katsuyuki; YABANA, Kazuhiro[2]
([1]Hokkaido Univ.; [2]Univ. Tsukuba)

[*Chem. Phys. Lett.* to be submitted]

Time-dependent density functional studies of multiple ionization of Ag_2 in an intense laser field 10^{14} W/cm^2 are presented. Special emphasis is placed on elucidating frequency dependence and an effect of the *d* electrons on the ionization processes. The multiple ionization occurs depending non-monotonically on the laser frequency. The valence *s* electrons are earlier emitted from the molecules, especially when the applied laser field is in tune with the dipole resonance frequency of the system, and then the *d*-electron emission occurs. Differently from the valence *s*-electrons, the *d* electrons are emitted more efficiently with increasing the laser frequency. We have computationally demonstrated that the *s* and *d* electrons move reciprocally toward the opposite directions such that the *s*-electron density induced in the laser field is cancelled out. This screening effect of the *d* electrons suppresses the multiple ionization in comparison with molecular systems without inner-shell electrons such as alkali metal clusters.

I-K Electronic Structures and Photochemical Properties of Nanometer-Sized Metal Clusters

Nanometer-sized metal clusters provide significantly different physicochemical properties such as optical response, catalysis, and reactivity from corresponding bare metal clusters or bulk metals. We have investigated electronic structures and photochemical properties of monolayer-protected metal clusters with special emphasis on describing metal-molecule interactions.

I-K-1 Electronic Structure and Photochemical Properties of a Monolayer-Protected Gold Cluster

NOBUSADA, Katsuyuki

[*J. Phys. Chem. B* **108**, 11904–11908 (2004)]

The electronic structure of a monolayer-protected gold cluster, $[Au_{13}(SCH_3)_8]^{3+}$, has been investigated by performing density functional calculations. The cluster has a characteristic structure with O_h molecular symmetry and eight (111) facets of a centered cuboctahedral Au_{13} core cluster are fully passivated by eight methanethiolates. The bond distance between two neighboring gold atoms (= 3.673 Å) is much larger than that of the bare Au_{13} cluster (= 2.929 Å), whereas the Au–S bond distance is 2.403 Å. These atomic rearrangement means that the methanethiolates stabilize the enlarged bare Au_{13} cluster by bonding to the (111) hollow sites of the bare cluster. The absorption spectrum of the $[Au_{13}(SCH_3)_8]^{3+}$ cluster is simulated within time-dependent density functional theory. The spectrum shows clear absorption peaks and each peak is assigned to specific excitation processes.

I-L Electronic Structure of a Molecule in Solution

Chemical reaction is undoubtedly the most important issue in the theoretical chemistry, and the electronic structure is a key to solve the problem. As long as molecules in the gas phase are concerned, the theory for the electronic structure has been enjoying its great success. However, when it comes to molecules in solution, the stage of theory is still an infant. We have recently proposed a new method refereed to as RISM-SCF based on the integral equation theory of molecular liquids (RISM) and the ab initio electronic structure theory (SCF).1) The integral equation approach replaces the reaction field in the continuum models by a microscopic expression in terms of the site-site radial distribution functions between solute and solvent.

$$V_{\lambda} = \sum_{j} \int 4\pi r^{2} \frac{q_j}{r} g_{j\lambda}(r)\, dr$$

where *j* and λ specify solvent and solute sites, respectively, and *r* denotes the solvent density. The site-site radial distribution functions $g_{\lambda j}(r)$ can be calculated from the extended RISM equation. Using V_λ the solvated Fock operator is defined as,

$$F^{s} = F^{g} - \sum_{\lambda} V_{\lambda} b_{\lambda}$$

where b_λ is a population operator of solute atoms. The statistical solvent distribution around solute is determined by the electronic structure or the partial charges of solute, while the electronic structure of solute is influenced by the solvent distribution. Therefore, the Hartree-Fock equation and the RISM equation should be solved in a self-consistent manner. It is this self-consistent determination of the solute electronic structure and the solvent distribution around the solute that features the RISM-SCF procedure.

The same Fock operator can be derived from a variation principle.2) Defining the Helmholtz free energy *A* as follows;

$$A = E_{solute} + \Delta\mu$$

where E_{solute} is the energy of solute under solvent influence, and Δμ is the solvation free energy represented in terms of the Singer-Chandler formula. The Fock operator for a solute molecule in solvent as well as the RISM-HNC equations can be obtained as the first order variations with respect to the wave functions and the pair correlation functions under the constraint of the orthonormality to the molecular orbitals. The latest development along this line are reported below.

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I-L-1 A Quantum Solute-Solvent Interaction Using Spectral Representation Technique Applied to the Electronic Structure Theory in Solution

YAMAZAKI, Takeshi; SATO, Hirofumi[1]; HIRATA, Fumio
([1]Kyoto Univ.)

[*J. Chem. Phys.* **119**, 6663–6670 (2003)]

In this paper, we present a new approach to treat the electronic structure of a molecule in solution. Unlike the hybrid-type method such as the reference interaction site model self-consistent-field(RISM-SCF) theory, the new approach describes not only the electronic structure of solute but also solute-solvent interactions in terms of the quantum chemistry based on the Hartree-Fock frozen density formulation. In the treatment, the quantum effect due to solvent, including exchange repulsion, is projected on to the solute Hamiltonian using the spectral representation method. The solvent distribution around the solute is handled by the integral equation theory of liquids. As illustrative applications of the approach, the electronic and solvation structure of noble atoms, neon and argon, in liquid neon are studied. We also investigate the electronic structure of an excess electron in liquid helium. The preliminary results demonstrate that the quantum mechanical effect on the electronic and solvation structure of the solute due to solvent molecules is successfully represented by the new method.

I-L-2 Distortion of Electronic Structure in Solvated Molecules: Tautomeric Equilibrium of 2-Pyridone and 2-Hydroxypridine in Water Studied by the RISM-SCF/MCSCF Method

SATO, Hirofumi[1]; HIRATA, Fumio; SAKAKI, Shigeyoshi[1]
([1]Kyoto Univ.)

[*J. Phys. Chem. A* **108**, 2097–2102 (2004)]

As well recognized, the electronic structure of a molecule in the solution phase is distorted from that in the gas phase. We present a new procedure that enables us to partition the electronic distortion energy caused by solvation into the energy contribution of each atom (or each moiety), with which one can evaluate the atomic-level change of electronic structure. In the present study, we combine the procedure with the RISM-SCF method that can treat solvent molecules explicitly. This method is successfully applied to the tautomerization of 2-pyridone in aqueous solution, whose equilibrium is known to show a marked solvation effect, and provides us a new detailed feature of this equilibrium. (1) As expected, electronic structures of oxygen and nitrogen atoms, which are strongly solvated, are distorted significantly. (2) However, the electronic distortion energies of the oxygen and nitrogen atoms are considerably compensated by the microscopic solvation. (3) One of the determining factors of the equilibrium is the carbon atom, with which the oxygen atom is bound, because the electronic distortion cannot be compensated by the microsolvation due to its rather inside position, and (4) the other factor is the distortion energy of the proton that directly relates to the equilibrium probably because the electronic structure changes too much to be compensated by microsolvation. These new findings lead to deep and correct understanding of this equilibrium.

I-L-3 Theoretical Study on Electronic and Solvent Reorganization Associated with a Charging Process of Organic Compounds: II. A New Decomposition Procedure into Electrostatic and Non-Electrostatic Responses

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[*J. Phys. Chem. B* **108**, 11709–11715 (2004)]

A new procedure, which enables us to decompose the solvent reorganization energy into electrostatic and nonelectrostatic contributions, is proposed. By using the procedure proposed by us very recently (*J. Phys. Chem. A* **106**, 2300–2304 (2002)), the solvent reorganization process and electronic structures of *N*,*N*-dimethylaniline (DMA) and 1,4-dimethoxybenzene (DMB) associated with a charging process in acetonitrile solution are studied at the molecular level on the basis of the ab initio reference interaction site model-self-consistent field (RISM-SCF) method. Differences as well as similarities between the solvation processes of the two molecules are discussed on the basis of the newly proposed method.

I-L-4 Superexchange Electron Tunneling Mediated by Solvent Molecules: Pulsed Electron Paramagnetic Resonance Study on Electronic Coupling in Solvent-Separated Radical Ion

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[*J. Phys. Chem. B* **108**, 10226–10240 (2004)]

Nanosecond pulsed electron paramagnetic resonance spectroscopy is applied to characterize exponential decay constants (β) of the squared electronic coupling matrix element ($V_{DA}{}^2$) in transient, solvent-separated radical ion pairs (RIP) composed of quinone anions and several cation radicals in aprotic liquid solutions of *N*,*N*-dimethylformamide, DMSO, and benzonitrile. The distance dependence of singlet-triplet energy splitting ($2J$) is shown to be described by β in V_{DA} for charge-recombination processes. We show that the radical pair mechanism (RPM) electron spin polarization (P_{RPM}) is quite sensitive to β. The β value is characterized by using the stochastic Liouville equation to fit the experimental P_{RPM} values. The β values (from 0.8 to 1.0 Å^{-1}) manifest that V_{DA} is governed by the superexchange mechanism mediated by the intervening solvent molecules from a result that the β increases with increasing the tunneling energy gap (ΔG_{eff}) for solvent oxidation or reduction in several intermolecular electron-transfer systems. We propose a simple three-dimensional model of V_{DA}, in which the through-solvent tunneling pathways are exponentially increased with the increase in the intermolecular distance in bulk, condensed media. This model explains the ΔG_{eff} dependence of β, including the data previously reported on the charge-transfer reactions both in liquid and frozen (77 K) solutions. Effective solvent-solvent coupling is estimated to be $v_B \approx 850$ cm^{-1} at a mean nearest-neighbor distance of 5.7 Å. This relatively large magnitude of v_B may agree with dynamical amplifications of the effective coupling by low-frequency motions of the mediators as reported in charge-transfer reactions in biological systems. (Balabin, I. A. and Onuchic, J. *Science* **290**, 114 (2000) and Troisi, A. and Orlandi, G. *J. Phys. Chem. B* **106**, 2093 (2002).)

I-M Solvation Thermodynamics of Protein and Related Molecules

Concerning biomolecules such as protein, it is a final goal for the biochemistry and biophysics to explore the relation between conformations and biological functions. The first important step toward the goal would be to explain the conformational stability of biomolecules in terms of the microscopic structure of the molecules in solvent. It is an extremely difficult problem by any means due to the overwhelmingly large degrees of freedom to be handled, including protein and solvent. As long as the small and/or short-time fluctuations of protein around the native structure is concerned, a variety of molecular simulation techniques provides a quite powerful tool to explore the microscopic structure of protein and solvent. However, the techniques are not so effective to characterize stability of the macromolecules in solution, to which the thermodynamic limit ($V \rightarrow \infty$, $N \rightarrow \infty$, with $V/N = const.$) is concerned. In such a case, methods based on the statistical mechanics of liquids should be natural choice for sampling configurations of solvent interacting biomolecules. The extended RISM theory is the most promising candidate of such methods, which provides not only solvation thermodynamics but also microscopic description at the level of the pair correlation functions.1) Obvious technical difficulties which one may face in applying the theory to such a large system are not only the computation time but also the stability of the numerical solution.2)

Here, we present our recent effort to tackle the problem using the two theoretical tools based on the statistical mechanics of liquids: the extended RISM and the scaled particle theories (SPT).3) The studies for the solvation thermodynamics of small molecules such as ions are also included because it is regarded as elementary processes for the solvation of biomolecules, and because it is prerequisite for studying the more complicated molecules.

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1-M-1 Solvation Thermodynamics of Protein Studied by the 3D-RISM Theory

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[*Chem. Phys. Lett.* **395**, 1–6 (2004)]

The partial molar volume and the solvation free energy of five globular proteins in aqueous solutions are calculated by the three-dimensional reference interaction site model (3D-RISM) theory, a modern integral equation theory of molecular liquids.

The partial molar volume calculated by the theory shows quantitative agreement with the corresponding experimental data. Concerning the solvation free energy, the theoretical results are compared with estimations by an empirical method which uses the accessible surface area of atoms, because the corresponding experimental data are not available.

Possible applications of the method to problems related to the solvation thermodynamics of protein are discussed.

I-N Collective Density Fluctuations in Polar Liquids and Their Response to Ion Dynamics

As to the model for molecular diffusion in polar liquids, there are two quite different points of view. One is the conventional rot-translation model, and the other the interaction-site description which sees the diffusion of a molecule as a correlated motion of each atom (site).1) It is clearly advantageous to use the interaction-site description compared to the rot-translation model to account for chemical characteristics of solvent as well as solute dynamics. However, the interaction-site description has its own disadvantage in interpreting physical meaning of the results, since it does not give an explicit picture for the rotational relaxation of molecules, which can be directly probed by many experimental means including the dielectric and NMR relaxation. We have solved the problem by extracting collective modes of the density fluctuation from the site-site density correlation functions. In our recent study for dynamics of molecular liquids based on the interaction-site model, we have succeeded to abstract the collective excitations in liquids, which can be identified as optical and acoustic modes, by diagonalizing the collective frequency matrix appearing in the generalized Langevin equation. The two modes arise essentially from the rotational and translational motions of molecules.2) We applied the method to the ion dynamics in a dipolar liquid, and could have explained successfully the peculiar size dependence of friction of alkali and halide ions in terms of response of the collective excitations in solvent to the solute displacement.3)

In the past year, we have elaborated the memory kernel in our generalized Langevin equation base on the mode coupling theory. We have also extended our treatment to dynamics of water and hydrated ions. Those studies as well as other related topics are reviewed below.

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I-N-1 A Mode-Coupling Analysis of the Translational and Rotational Diffusion of Polar Liquids; Acetonitrile and Water

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[*J. Mol. Liq.* **112/3**, 117–124 (2004)]

The translational and rotational motions of two representative polar liquids,water and acetonitrile, are investigated by the mode-coupling theory for molecular liquids based on the interaction-site model. The diffusive motion of acetonitrile agrees fairly well with that from the molecular-dynamics simulation.The pressure dependence of the translational and rotational diffusion coefficients is also in qualitative agreement with experiments. However, the reorientational relaxation of water is predicted to be much faster than that from experiments or simulations.The agreement between the theory and the simulation is partly improved by using the dynamic structure factor determined by the simulation.The effect of three-site correlation in the mode-coupling expression of the memory function is also examined.

I-N-2 Pressure Dependence of Diffusion Coefficient and Orientational Relaxation Time for Acetonitrile and Methanol in Water: DRISM/Mode-Coupling Study

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[*J. Mol. Liq.* in press]

We present results of theoretical description and numerical calculation of the dynamics of molecular liquids based on the Reference Interaction Site Model/ Mode-Coupling Theory. They include the temperature-pressure (density) dependence of the translational diffusion coefficients and orientational relaxation times for acetonitrile and methanol in water at infinite dilution. Anomalous behavior, *i.e.* the increase in mobility with density, is observed for the orientational relaxation time of methanol, while acetonitrile does not show any deviations from the usual. This efect is in qualitative agreement with the recent data of MD simulation and with experimental measurements, which tells us that presented theory is a good candidate to explain such kind of anomalies from the microscopical point of view and with the connection to the structure of the molecules.

I-O Statistical Mechanics of Interfacial Fluids

Microscopic structure of fluid interfaces has been drawing a lot of attention due to recent development in the experimental techniques devised particularly to probe the interface. However, there are many open questions remained unanswered. For example, how wide is the interfacial region, how does it depend on the chemical species consisting the solution? Is the interface more or less homogeneous in terms of density or concentration of the two fluids, or is it spatially inhomogeneous? If it is inhomogeneous, what is the spatial extent of the inhomogeneity? Answering those questions is the most difficult and challenging tasks for theoretical physics and chemistry, and not much progress has been made in the past, especially from a molecular view point. We have been developing statistical mechanics for two different types of interfacial fluids: fluid-fluid interface and fluids in porous media. Following are the latest achievement in that direction.

I-O-1 Molecular Description of Electrolyte Solution in a Carbon Aerogel Electrode

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[*Cond. Matt. Phys.* **6**, 583–609 (2003)]

We develop a molecular theory of aqueous electrolyte solution sorbed in a nanoporous carbon aerogel electrode, based on the replica reference interaction site model (replica RISM) for realistic molecular quenched-annealed systems. We also briefly review applications of carbon aerogels for supercapacitor and electrochemical separation devices, as well as theoretical and computer modelling of disordered porous materials. The replica RISM integral equation theory yields the microscopic properties of the electrochemical double layer formed at the surface of carbon aerogel nanopores, with due account of chemical specificities of both sorbed electrolyte and carbon aerogel material. The theory allows for spatial disorder of aerogel pores in the range from micro- to macroscopic size scale. We considered ambient aqueous solution of 1 M sodium chloride sorbed in two model nanoporous carbon aerogels with carbon nanoparticles either arranged into branched chains or randomly distributed. The long-range correlations of the carbon aerogel nanostructure substantially affect the properties of the electrochemical double layer formed by the solution sorbed in nanopores.

I-O-2 Microscopic Description of a Liquid-Vapor Interface by an Inhomogeneous Integral Equation Theory

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[*Chem. Phys. Lett.* in press]

We developed an inhomogeneous integral equation theory yielding the inhomogeneous pair correlation functions as well as the density profiles of the liquid-vapor interface of simple fluid. We analytically derived the long-range asymptotics of the inhomogeneous pair distribution along the interface, related to capillary waves. We showed that their physical nature is the same as long-range fluctuations of critical fluid which are restricted to the two-dimensional interfacial region by the external field shaping the interface.

I-P Photoinduced Phase Transitions in Spin-Crossover and Charge-Transfer Complexes

Now a variety of materials show photoinduced phase transitions. Their characters depend much on the relative importance of the interactions inside the system to those between the system and the heat bath. If the former are dominant, the time evolution is deterministic allowing coherent oscillations for instance. If the latter are dominant, the time evolution is stochastic and the efficiency is generally low. These characters depend also on the time scale. For long-time properties, dissipation generally obscures the deterministic evolution. Thus we need to employ both the deterministic approach with the help of the time-dependent Schrödinger equation and the stochastic approach with the help of the master equation. The macroscopic coherent oscillation of the neutral-ionic domain walls in the TTF-CA complex needs to be described by the former approach. Meanwhile, the photoinduced neutral-to-ionic transition accompanied with ferroelectric ordering in the same material by pump light for intra-molecular excitations would be described by the latter approach. Low-spin-to-high-spin transitions in organometal spin-crossover complexes are well described by the stochastic approach because the evolution is governed by thermal processes.

I-P-1 On Thermo- and Photo-Induced Symmetry-Broken Transformation in Spin-Crossover Complex; Cooperative Activation

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[*J. Phys. Soc. Jpn.* **73**, 1237–1243 (2004)]

We study energetics of a cooperative low-spin (L) to high-spin (H) transformation in a crystal with two sublattices, where thermo- and photo-induced symmetry-broken phases have been recently observed. The model takes into account an intra-dimer antiferroic coupling and inter-dimer couplings. Cooperative activation processes for switching between LH and HL states and that from LL to HH states of a dimer are analyzed. It is shown that locally (within a dimer) preferred symmetry-broken, LH and HL, states compete with inter-dimer couplings, which stimulates dynamical disorder *via* a decrease in the energy barrier for a flip between asymmetric configurations. On the other hand, a locally non-preferred symmetric state (HH) is supported by inter-dimer interaction *via* a cooperative activation mechanism. We conclude that symmetry-broken states can form an intermediate thermo-induced phase or can be observed as a photo-induced one at low temperatures as a result of local equilibrium. The global equilibrium follows from cooperative interaction and governs the thermo-induced re-entrant phase transition.

I-P-2 Different Stabilities of the Mixed-Spin Phase in Equilibrium from That in Non-Equilibrium in a Two-Sublattice Classical-Spin Model for Spin-Crossover Complexes

OTSUKA, Yuichi; YONEMITSU, Kenji

Some spin-crossover complexes show two-step transitions by changing temperature between high-spin and low-spin phases in equilibrium. In $[Fe(2\text{-}pic)_3]Cl_2\cdot EtOH$, high-spin-low-spin ordering is recently observed on the 50% plateau of high-spin fraction at intermediate temperatures. However, the time evolution of this material under continuous photoirradiation does not clearly show the high-spin-low-spin-ordered phase even transiently. We employ a two-sublattice classical-spin model, where an intra-dimer inter-sublattice antiferroic coupling prefers the intermediate phase while an inter-dimer intra-sublattice ferroic coupling the uniformly high-spin or low-spin phase. Although an inter-dimer inter-sublattice coupling plays the same role with the intra-dimer inter-sublattice coupling at the mean-field level, we find by Monte Carlo simulations that their effects are different especially when the material is under photoirradiation. The inter-dimer coupling so enhances the short-range spin-spin correlation as to give larger deviation from the mean-field results than the intra-dimer coupling. This effect makes the appearance of the high-spin-low-spin-ordered phase difficult in non-equilibrium conditions.

I-P-3 Inter-Chain Electrostriction and Pressure-Induced Multicriticality in Charge-Transfer Organic Complexes

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[*Proc. Int. Conf. Sci. Tech. Synth. Met.* (2004)]

Pressure-induced multicriticality in the quasi-one-dimensional mixed-stack charge-transfer complex TTF-CA is theoretically explained. We show that the inter-stack electrostriction (Coulomb-lattice coupling) is essential to cause multi-critical phase transitions among the neutral, paraelectric ionic, and ferroelectric ionic phases.

I-P-4 Stochastic Approach to Evolution of Ionicity and Ferroelectricity in Mixed-Stack Organic Charge-Transfer Complexes by the Blume-Emery-Griffiths Model

INOUE, Hitoshi; YONEMITSU, Kenji

Mixed-stack organic charge-transfer complexes show neutral-ionic and dimerization-induced ferroelectric phase transitions. In the most famous TTF-CA complex, they occur simultaneously at ambient pressure but at different temperatures under high pressure. Thus we treat both the ionicity and the dimerization using the Blume-Emery-Griffiths model. Long-time evolution is studied by solving the master equation during and after photoirradiation of the complex. As a first step, we use the mean-field approximation that does not distinguish the intra- and inter-chain couplings. The time evolution of the ionicity and that of the ferroelectricity generally take place on different time scales, allowing the transient appearance of the paraelectric ionic phase. We find photoinduced breaking of the inversion symmetry and spontaneous ordering of electric polarizations leading to the ferroelectric ionic phase after the neutral phase is photoexcited and converted into the paraelectric ionic phase. This would explain the recent experimental findings with intra-molecular excitations.

I-P-5 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: I. Threshold Behavior in Ionic-to-Neutral Transition

YONEMITSU, Kenji

[*J. Phys. Soc. Jpn.* **73**, 2868–2878 (2004)]

Photoinduced dynamics of charge density and lattice displacements is calculated by solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating potentials for the mixed-stack organic charge-transfer complex, TTF-CA. A pulse of oscillating electric field is incorporated into the Peierls phase of the transfer integral. The frequency, the amplitude, and the duration of the pulse are varied to study the nonlinear and cooperative character of the photoinduced transition. When the dimerized ionic phase is photoexcited, the threshold behavior is clearly observed by plotting the final ionicity as a function of the increment of the total energy. Above the threshold photoexcitation, the electronic state reaches the neutral one with equidistant molecules after the electric field is turned off. The transition is initiated by nucleation of a metastable neutral domain, for which an electric field with frequency below the linear absorption peak is more effective than that at the peak. When the pulse is strong and short, the charge transfer takes place on the same time scale with the disappearance of dimerization. As the pulse becomes weak and long, the dimerization-induced polarization is disordered to restore the inversion symmetry on average before the charge transfer takes place to bring the system neutral. Thus, a paraelectric ionic phase is transiently realized by a weak electric field. It is shown that infrared light also induces the ionic-to-neutral transition, which is characterized by the threshold behavior.

I-P-6 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: II. Linear Behavior in Neutral-to-Ionic Transition

YONEMITSU, Kenji

[*J. Phys. Soc. Jpn.* **73**, 2879–2886 (2004)]

Dynamics of charge density and lattice displacements after the neutral phase is photoexcited is studied by solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating potentials. In contrast to the ionic-to-neutral transition studied previously, the neutral-to-ionic transition proceeds in an uncooperative manner as far as the one-dimensional system is concerned. The final ionicity is a linear function of the increment of the total energy. After the electric field is turned off, the electronic state does not significantly change, roughly keeping the ionicity, even if the transition is not completed, because the ionic domains never proliferate. As a consequence, an electric field with frequency just at the linear absorption peak causes the neutral-to-ionic transition the most efficiently. These findings are consistent with the recent experiments on the mixed-stack organic charge-transfer complex, TTF-CA. We artificially modify or remove the electron-lattice coupling to discuss the origin of such differences between the two transitions.

I-P-7 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: III. Interference Caused by a Double Pulse

YONEMITSU, Kenji

[*J. Phys. Soc. Jpn.* **73**, 2887–2893 (2004)]

In order to study consequences of the differences between the ionic-to-neutral and neutral-to-ionic transitions in the one-dimensional extended Peierls-Hubbard model with alternating potentials for the TTF-CA complex, we introduce a double pulse of oscillating electric field in the time-dependent Schrödinger equation and vary the interval between the two pulses as well as their strengths. When the dimerized ionic phase is photoexcited, the interference effect is clearly observed owing to the coherence of charge density and lattice displacements. Namely, the two pulses constructively interfere with each other if the interval is a multiple of the period of the optical lattice vibration, while they destructively interfere if the interval is a half-odd integer times the period, in the processes toward the neutral phase. The interference is strong especially when the pulse is strong and short because the coherence is also strong. Meanwhile, when the neutral phase is photoexcited, the interference effect is almost invisible or weakly observed when the pulse is weak. The photoinduced lattice oscillations are incoherent due to random phases. The strength of the interference caused by a double pulse is a key quantity to distinguish the two transitions and to evaluate the coherence of charge density and lattice displacements.

I-P-8 Theory of Optical Phase Control in Charge-Transfer Complexes

YONEMITSU, Kenji

[*Proc. Int. Conf. Sci. Tech. Synth. Met.* (2004)]

Concerning the paraelectric ionic phase in the mixed-stacked organic charge-transfer TTF-CA complex, which needs high pressure to realize in thermal equilibrium or some particular photoexcitation to transiently realize at ambient pressure and low temperatures, we theoretically point out that photoexcitations with appropriate strength and duration can generally produce this phase. Photoinduced charge-lattice dynamics is calculated in a one-dimensional extended Peierls-Hubbard model with alternating potentials during and after a pulse of oscillating electric field. When the field is so weak and long that the supplied energy does not directly transfer charge in the ionic phase, the dimerization-induced charge polarizations are disordered first to restore the inversion symmetry on average before the neutral phase appears. The interference effect observed after a double pulse due to the charge-lattice coherence is accordingly weakened.

I-P-9 Theory of Photoinduced Phase Dynamics in Organic Charge-Transfer Complexes

YONEMITSU, Kenji

[*J. Lumin.* in press]

In the quasi-one-dimensional mixed-stack organic charge-transfer complex, TTF-CA, photoirradiation is known to trigger transitions between the neutral and ionic phases. Here we use a one-dimensional extended Peierls-Hubbard model with alternating potentials and calculate the mean-field dynamics of charge density coupled with that of lattice displacements. We show qualitative differences between the photoinduced ionic-to-neutral and neutral-to-ionic transitions, which are consistent with recent experimental findings. Namely, the ionic-to-neutral transition proceeds cooperatively, characterized by threshold behavior, while the neutral-to-ionic transition proceeds uncooperatively, characterized by linear behavior. The threshold absorption in the former depends on the strength or the duration of the pulse. The coherence during the transition dynamics is also different between the two transitions. In the ionic-to-neutral transition, a clear interference effect is observed as a function of the interval when the pulse is spilt into two.

I-Q Theoretical Studies on Chemical Reactions and Molecular Dynamics of Polyatomic Molecules in Condensed Systems

In a lot of chemical, biological and environmental phenomena, the chemical reactions and molecular dynamics *in solution* or *across interface* play a very important role, where the microscopic solvation structures of solute molecules offer essential and inevitable information. In this project, to obtain a stationary point on a multi-dimensional free energy surface (FES), *e.g.*, stable state (SS) or transition state (TS) in solution chemical reaction, a new optimization method, *i.e.*, the free energy gradient (FEG) method, has been developed and were applied to obtain the hydrated structure and TS in the ionization process of ammonia molecule in aqueous solution.

I-Q-1 Hydrated Structure of Ammonia-Water Molecule Pair *via* Free Energy Gradient Method: Realization of Zero Gradient and Force Balance on Free Energy Surface

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[*J. Chem. Phys.* **119**, 7972–7978 (2003)]

The hydrated structure of ammonia molecule in aqueous solution was theoretically optimized as an ammonia-water molecule pair ($H_3N\cdots H_2O$) by the FEG method [*J. Chem. Phys.* **113**, 3516 (2000)]. The interaction between the pair and a solvent water molecule (TIP3P) [*J. Chem. Phys.* **79**, 926 (1983)] was described by a hybrid quantum mechanical and molecular mechanical (QM/MM) method combined with a semi-empirical molecular orbital (MO) method at the PM3 level of theory. It is concluded that the present FEG method works quite well in spite of a simple steepest descent optimization scheme equipped with the adaptive displacement vector. The free energy stabilization was estimated –0.3 kcal/mol from the free energy for the same structure as that of the cluster in gas phase. The optimized structure was found to be almost the same as that in the gas phase except a longer OH bond length of the water molecule. However, its realization in aqueous solution is accomplished by virtue of fulfillment of both “zero gradient” and “force balance” conditions. Finally, we discussed also the effect of microscopic “solvation entropy,” compared with the result by the conductor-like screening model (COSMO) method.

I-Q-2 Structure Optimization of Solute Molecules *via* Free Energy Gradient Method

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[*Bull. Korean Chem. Soc.* **24**, 805–808 (2004)]

Fundamental ideas of the free energy gradient method are briefly reviewed with three applications: the stable structures of glycine and ammonia-water molecule pair in aqueous solution and the transition state (TS) structure of a Menshutkin reaction $NH_3 + CH_3Cl \rightarrow CH_3NH_3^+ + Cl^-$ in aqueous solution, which is the first example of full TS optimization of all internal degrees of freedom.

I-Q-3 Slowdown of Water Diffusion around Protein in Aqueous Solution with Ectoine

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[*Chem. Phys. Lett.* **388**, 316–321 (2004)]

Ectoine is one of the most common compatible solutes found in halophilic bacteria, and has an effect to introduce a tolerance to high salt concentration or high temperature. By analyzing 1 ns molecular dynamics simulations at 370 K, we have shown that, in the ectoine aqueous solution, the water diffusion slows down around a protein (chymotrypsin inhibitor 2 (CI2)), keeping the protein hydration structure essentially unchanged. It is concluded that the slowdown of water diffusion around the backbone amide protons must be one of the decisive factors in reducing the exchange rate of the backbone amide protons, whose reduction is experimentally believed closely related to the tolerance effect.

I-R Theory and Applications of Relativistic Quantum-Chemical Methods to Molecular Properties of Compounds Containing Heavy Elements

Accurate quantum-chemical calculations of molecular properties which are concerned with a magnetic field and/or an electron spin distribution are required well-correlated and relativistic quantum-chemical theories, especially when the molecules contain heavy elements. Paramagnetic NMR chemical shifts of Fe-complexes, heavy-element NMR of halogen compounds, and magnetic circular dichroism (MCD) of halogen compounds are listed below. The 2nd-order Douglas-Kroll quantum-chemical theory including a magnetic field is also presented.

I-R-1 Quantum-Chemical Calculations for Para-Magnetic ^{13}C NMR Chemical Shifts of Iron-Bound Cyanide Ions of Iron Porphyrins in Ground and Low-Lying Excited States Containing Ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ Configurations

HADA, Masahiko
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[*J. Am. Chem .Soc.* **126**, 486–487 (2004)]

The objectives of this brief communication are as follows. (i) Using an accurate quantum-chemical method, SAC/SAC-CI, we present accurate energy-levels for ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ in bis (cyanide) porphyrinato Iron(III) [FeP(CN)$_2$], bis (cyanide)(*meso*-tetraethyl) por-phyrinatoIron(III) [FeTEP(CN)$_2$], and (cyanide) (imidazole) porphyrinato-Iron(III) [FeP(CN-Im)]. (ii) We calculate the para-magnetic ^{13}C NMR chemical shifts of iron-bound ^{13}CN of the above three complexes, both in the ground and low-lying excited states including the ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ configurations. Then we show the relations between the calculated ^{13}C chemical shifts, the electronic configurations, and the ruffling of the porphyrin rings.

The trans-ligand effect on the paramagnetic ^{13}C NMR chemical shifts of the iron-bound ^{13}CN$^-$ was well reproduced by the present calculations. Further, in [FeP(CN)$_2$], which has a ruffled porphyrin ring, the $(d_{xy})^1(d_{xz,yz})^4$ configuration is included in the ground state, and the alternative $(d_{xy})^2(d_{xz,yz})^3$ configuration is located closely in energy to the ground state. Ruffling of porphyrin rings extremely affects the ^{13}C chemical shift of iron-bound CN in the $(d_{xy})^1(d_{xz,yz})^4$ configuration but not in the $(d_{xy})^2(d_{xz,yz})^3$ configuration.

I-R-2 Nuclear Magnetic Shielding Constants of Halogens in X$^-$ and XO$_4^-$ (X = F, Cl, Br, I) —Relativistic and Electron-Correlation Effects—

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[*J. Comput. Chem., Jpn.* in press]

A series of calculations of halogen nuclear magnetic shielding constants and chemical shifts in X$^-$ and XO$_4^-$ (X = F, Cl, Br, I) was carried out to discuss the relativistic and electron-correlation effects and, in special, the non-additivity of both the effects. The second-order Douglas-Kroll-Hess (DKH2) method was used as a relativistic hamiltonian, and the Møller-Plesset method was applied to the generalized UHF wave function. The calculated chemical shifts in ClO$_4^-$ and IO$_4^-$ agree reasonably well with the observed ones, though there are no experimental values in FO$_4^-$ and BrO$_4^-$. The relativistic effect was quite large especially in IO$_4^-$ as reported previously, while the electron-correlation effect is significant in both FO$_4^-$ and IO$_4^-$. The non-additivity of the relativistic and the electron-correlation effects in magnetic shielding constants is unexpectedly large in IO$_4^-$, and therefore a relativistic electron-correlated method is crucial for describing accurate heavy-element nuclear magnetic shielding constants and chemical shifts.

I-R-3 Quasi-Relativistic Theory for Magnetic Shielding Constant. I. Formulation of the Douglas-Kroll Transformation with Magnetic Field and Applications to Atomic Systems

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A two-component quasi-relativistic theory based on the Douglas-Kroll-Hess transformation is developed in order to study a magnetic shielding constant. The Hamiltonian that is proposed in this study is considering the relativistic effect on magnetic vector potential with the Douglas-Kroll theory. The present Hamiltonian can be applied to calculation of magnetic shielding constants, without further expansion in powers of c^{-1}. By applying the finite-perturbation theory and generalized-UHF wavefunction to this study, we calculate the magnetic shielding constants of two-electron ions, ten-electron ions, and noble gas atoms. The calculation results with the present theory are compared with the result of the Dirac-Hartree-Fock calculation. The numerical difference of the present theory from the DHF is 3% or less. However, a quasi-relativistic theory that handled the magnetic vector potential at the non-relativistic level largely underestimates the relativistic effect. The picture change effect is quite important for the magnetic shielding constant of heavy elements. The change of orbital picture is significant in the valence orbital magnetic response as well as the core orbital response. The effect of finite distribution of nucleus is also studied with using Gaussian nucleus model. The present theory is able to reproduce the correct behavior of the finite nucleus effect that has been reported in the Dirac theory. However, the non-relativistic theory and quasi-relativistic theory with non-relativistic vector potential underestimate the finite nucleus effect.

I-R-4 Quasi-Relativistic Theory for Magnetic Shielding Constant. II. Gauge Including Atomic Orbital and Applications to Molecules

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We present a relativistic theory of the magnetic shielding constants and the chemical shifts for molecules include heavy elements. The present theory is based on the Douglas-Kroll-Hess quasi-relativistic approximation. The gauge-including atomic orbital method is adapted to the quasi-relativistic Hamiltonian to allow the origin independent calculations. The present theory is applied to the hydrogen and halogen magnetic shielding constants of hydrogen halides and mercury magnetic shielding constants and ^{199}Hg chemical shifts of mercury dihalides and methyl mercury halides. The relativistic correction to the magnetic interaction term little affects the magnetic shielding constant of hydrogen; however, the correction is the dominant origin of the heavy atom shifts of the magnetic shielding constant of the heavy halogens. The basis set dependence of mercury shielding constants is quite large in the relativistic calculation; using the basis function which is optimized by the relativistic method is important to describe the relativistic effect properly. The relativistic correction to the magnetic interaction term is quite important for mercury dihalides in which relativistic effects from mercury and halogen are strongly coupled. Without this correction we obtain quite incorrect results. The origin of the 199Hg chemical shifts in mercury dihalides is the spin-orbit interaction from the heavy halogens. In methyl mercury halides the paramagnetic shielding term as well as the spin-orbit interaction from the heavy halogens dominates the 199Hg chemical shifts.

I-R-5 Theoretical Studies on MCD with Finite Perturbation Method and Relativistic Corrections

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The generalized UHF (GUHF)/SECI method for the MCD Faraday terms with the finite magnetic-field perturbation were presented and compared the results for ethylene, *p*-benzoquinone (BQ), and *o*-BQ with those by the conventional sum-over-states method. Their difference was not negligible, and even the signs were contrary for the lowest π-π* state of ethylene. Quasi-relativistic treatments in the calculations of the Faraday terms were also discussed. The method was applied to the three *n*-π* states ($^3\Pi_{1u}$, $^3\Pi_{0u}$, and $^1\Pi_u$) of I_2, Br_2, Cl_2, and F_2. The relativistic effects become more important as molecule is heavier. The Faraday terms for I_2 and Br_2 were dramatically changed by the relativistic correction from the non-relativistic results, whereas the effects were negligible for Cl_2 and F_2 in contrast. This indicates that the relativistic corrections are essential to the theoretical treatments of MCD for molecules containing heavy atoms.

I-S Molecular Vibrations and Intermolecular Interactions in Condensed Phases

In this project, intermolecular interactions and their effects on molecular vibrations in condensed phases are analyzed theoretically to clarify the relation between the structures and dynamics of the systems and the frequency- and time-domain spectroscopic features. Specifically, (1) the resonant transfer of vibrational excitations, vibrational dephasing, and their competition in liquids and biomolecules and (2) the relation between electronic structural features of molecules and intermolecular interactions are analyzed with great emphasis.

I-S-1 Vibrational Interactions in the Amide I Subspace of the Oligomers and Hydration Clusters of *N*-Methylacetamide

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[*J. Phys. Chem. A* **108**, 7272–7280 (2004)]

The diagonal and off-diagonal vibrational interactions in the amide I subspace are examined for the oligomers and hydration clusters of *N*-methylacetamide (NMA). A method called the average partial vector method is developed for constructing the force constant matrix (F matrix) in the amide I subspace from that in the full Cartesian space. It is shown that the F matrix thus constructed can reproduce quantitatively the vibrational frequencies and vibrational patterns of the amide I modes calculated in the full Cartesian space. For the NMA oligomers consisting of three or more NMA molecules, the cooperative effect on the C=O bond length (and on the diagonal force constant of the amide I mode as well) is seen. Including the values for those oligomers, the shifts in the diagonal terms in the amide I subspace (δk_I) and in the C=O bond length ($\delta S_{C=O}$) of the NMA oligomers and NMA–water clusters from the values of an isolated NMA molecule are approximately proportional to each other. In addition, $\delta S_{C=O}$ is shown to be approximately proportional to the electric field (originating from the other molecules in the NMA oligomer or NMA–water cluster) evaluated at a specified point on the C=O bond, indicating that the origin of the cooperative effect is the enhancement of the electric field operating among the molecules. The effect of mechanical anharmonicity on δk_I is examined by introducing the internal-normal mixed coordinate system representation for the cubic force constants, and is shown to overestimate the variation of δk_I. The partial cancellation by the effect of electrical anharmonicity (dipole second derivative) is also important. For the off-diagonal terms, it is shown that the TDC model provides a good approximation. However, for the (small) coupling constants between distant peptide groups, the effect of the polarization of the intervening peptide group(s) (also called the third-body mediation and may be regarded as a dipole-induced dipole effect) is also recognized.

I-S-2 Atomic Quadrupolar Effect in the Methanol-CCl_4 and Water-CCl_4 Intermolecular Interactions

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[*Chem. Phys. Lett.* **393**, 153–158 (2004)]

The intermolecular interactions in the methanol-CCl_4 and water-CCl_4 systems are examined by carrying out *ab initio* molecular orbital calculations on the 1:1 molecular clusters. It is found that, for both systems, the molecular configuration with the C–Cl···O interaction is the most stable. The two-body electrostatic part, especially the effect of the atomic quadrupoles of the Cl atoms of CCl_4, dominates the interaction energy of this configuration. This result suggests that the atomic quadrupolar effect is significant in the structural formation and energetics in the methanol-CCl_4 and water-CCl_4 systems as well as in other related systems.

I-S-3 Atomic Quadrupolar Effect in Intermolecular Electrostatic Interactions of Chloroalkanes: The Cases of Chloroform and Dichloromethane

TORII, Hajime
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[*J. Mol. Liq.* in press]

The atomic quadrupolar effect in intermolecular electrostatic interactions is studied for chloroform and dichloromethane. From the fitting to the electrostatic potentials around these molecules obtained by *ab initio* molecular orbital (MO) calculations, atomic quadrupoles of the magnitude as large as $\Theta \cong 1.5\ ea_0^2$ are obtained for the chlorine atoms in these molecules. It is shown that a reasonably good fit to the electric field around the molecules can be obtained only by including those atomic quadrupoles, indicating that atomic quadrupoles are essential for correct representation of the intermolecular electrostatic interactions of these molecules. From the calculations of the radial distribution functions (rdfs) of liquid chloroform and dichloromethane by the Monte Carlo and molecular dynamics methods, it is shown that a significant atomic quadrupolar effect is seen in the rdfs of the C···C, C···H, and H···H pairs. The intermolecular distances in the optimized structures of the dimers of chloroform and dichloromethane calculated by the *ab initio* MO method support the new features in the rdfs of the liquids that are seen upon including the effect of atomic quadrupoles. It is suggested that an atomic quadrupole has a significant effect on the angular (rather than radial) component of the location of the atoms of neighboring molecules.

I-T Nonlinear Processes Induced by Ultrafast and Intense Extreme Ultraviolet (XUV) Pulses

Recent technological progress on the generation of intense XUV pulses has opened up a new field on ultrafast and nonlinear optics. At such short wavelength only a gas can be a nonlinear medium. Nonlinear optics in XUV regions is interesting for two reasons. The first one is that the attosecond pulse generation is possible only in the XUV region, simply because an optical cycle of the visible-UV photon is in the time scale of femtosecond. The second one is that nonlinear response of the medium is not yet known at the XUV region. In this project, we have carried out investigation from those two aspects.

I-T-1 Time-Frequency Analysis of High-Order Harmonic Generation

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Recently it has been demonstrated by the group of Krausz (Austria) that it is possible to generate a single attosecond XUV pulse through high-order harmonic generation. Still, there are many things to be understood and clarified on the mechanism and conditions for the attosecond pulse generation. By solving time-dependent Schrödinger equations, we carry out the time-frequency analysis to obtain the temporal profile for each order of harmonic pulses for hydrogen (with a single-active electron) and also for helium (with two-active electrons) at various conditions. When the intensity is low, the temporal peak of harmonics has been found to coincide with the peak of the fundamental pulses. At higher intensity, however, we have found that the peak of the harmonic temporally shifts toward the leading edge of the pulse, and the amount of the shift is smaller for higher order harmonics.

I-T-2 Two-Photon Above-Threshold Ionization Cross Sections of Rare Gases by XUV Photons

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Above-threshold ionization (ATI) is the successive absorption of an additional number of photons more than the minimum required to ionize an atom. For rare gas atoms, ATI by infrared ~ visible photons has been very well studied theoretically as well as experimentally. Due to the recent technological progress in high-order harmonic generation and free-electron lasers, a bright light source is becoming available in the extreme ultraviolet (XUV) wavelength region. Provided with such progress, the time is matured to investigate, theoretically as well as experimentally, ATI in the XUV regime. Furthermore, two-photon ATI has a practical importance since it can be used for the pulse characterization (*i.e.*, autocorrelation) of XUV pulses.

In this work we have developed a theory to calculate two-photon above-threshold ionization cross sections of rare gases by XUV photons in the extended framework of multichannel quantum defect theory (MQDT). The advantage of the use of MQDT is that it automatically incorporates not only the spin-orbit interactions but also configuration mixing to some extent. On the other hand, the limitation of the present approach is that we have included only two lowest core states (two-core model), $p^5[^2P_{3/2}]$ and $p^5[^2P_{1/2}]$. Since free-free dipole moments do not converge in the length gauge, we have made the combined use of the length gauge for small r and the acceleration gauge for large r. The two-photon ATI cross sections for Xe and Ar associated with the $p^5[^2P_{3/2}]$ and $p^5[^2P_{1/2}]$ ionic core states are found to be 1.0×10^{-51} cm^4 s and 2.0×10^{-51} cm^4 s, respectively, for 25 eV photons.

I-U Control of Photoionization Processes Using Lasers

Optical control of various photoabsorption processes are of great interest in recent years. In this project, we have theoretically explored the possibility to control spin degree of freedom of photoelectrons and ejection angle of photoelectrons.

I-U-1 Control of the Spin-Polarization of Photoelectrons/photoions Using Short Laser Pulses

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To establish a method for the control of spin degree of freedom is one of the most important issues in modern technology and science, since highly spin-polarized species such as electrons, ions, and nucleus, *etc.*, are very useful not only to develop a new technology using semiconductors but also to study various spin-dependent dynamics. We theoretically propose a generic pump-probe scheme to control spin-polarization of photoelectrons/photoions by short laser pulses. By coherently exciting fine structure manifolds of a multi-valence-electron system by the pump laser, a superposition of fine structure states is created. Since each fine structure state can be further decomposed into a superposition of various spin states of valence electrons, each spin component evolves differently in time. This means that varying the time delay between the pump and probe lasers leads to the control of spin states. Specific theoretical results are presented for two-valence-electron atoms, in particular for Mg, which demonstrate that not only the degree of spin-polarization but also its sign can be manipulated through time delay. Since the underline physics is rather general and transparent, the presented idea may be potentially applied to nanostructures such as quantum wells and quantum dots.

I-U-2 Control of Photoelectron Angular Distributions Using a Dressing Laser

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Strong dressing laser field can induce various interesting modification in laser-matter interactions. Among them, an interesting modification is observed in the photoionization spectra in the wavelength region at which two-photon near-resonance is satisfied for the initially occupied state by a probe laser and initially unoccupied state by a dressing laser. This is known as laser-induced continuum structure. Related to this, if the ionization processes consists of several channels, it should be possible, in principle, to alter the branching ratio of photoionization into several channels, and if the branching ratio is successfully altered, we may also see the alteration of photoelectron angular distribution. In this work we have theoretically studied the modification of photoelectron angular distributions using a dressing laser. We have found a significant change of photoelectron angular distributions for the K atom, as the probe laser frequency is scanned across two-photon resonance under the presence of dressing laser.