AWARDS

Emeritus Professor Iwamura’s Scientific Achievements

Emeritus Professor Hiizu Iwamura received “The Japan Academy Prize in 2003” for his contribution to the Study of Molecule-based Magnets. The prize was awarded jointly to Profs. Koichi Itoh (Emeritus Professor of Osaka City Univ.) and Minoru Kinoshita (Emeritus Professor of the Univ. of Tokyo).

Iwamura was a faculty member of IMS during1976–1987. It was at IMS in early 80’s when he initiated this scientific area by synthesized linear tetrakis(diazo) and pentakis(diazo) compounds in which all the adjacent diazomethylene units were connected by *m*-phenylene units. The polydiazo compounds were photolyzed under cryogenic conditions to show by EPR and magnetic susceptibility measurements that the tetra- and pentacarbenes have nonet (S = 4) and undecet (S = 5) ground states, respectively. Thus, he constructed for the first time paramagnetic hydrocarbons that have ground-state spins and therefore magnetic moments greater than those of d^5 transition metal ions and f^7 lanthanides. Iwamura’s scientific achievements of excellence are demonstrated by further extension of this work in three directions: 1) extensive search for ferromagnetic coupling units, 2) synthesis of higher analogues of polycarbenes, and 3) synthesis of stable polyaminoxyl radicals and their use for supramolecular hybrid spin magnets.

1. Iwamura demonstrated that there are two series of diradicals, dicarbenes, and dinitrenes that have high-spin and low-spin ground states depending on the connectivity of the two spin centers through π-electron systems. He determined the energy gap of the ground and higher-energy spin states by analyzing the temperature dependence of their EPR fine structures and/or magnetic susceptibility data. The molecular structures of the high- and low-spin species are correlated by resonance structures to “trimethylenemethane” and “tetramethyleneethane,” respectively. These simplest diradicals had been suggested by quantum chemical studies of Wes Borden and others to have triplet and singlet ground states, respectively. Iwamura showed that 1,2-dimethylenecyclohexane-1,2-diyl, a conformationally restricted analogue of the latter does have a singlet ground state, the first conclusive experimental evidence for its ground state.

   Iwamura and coworkers solved a question of how to align electron spins in parallel in the stacking interaction of two π-radical molecules by preparing isomeric [2.2]paracyclophanes in which two diphenylcarbene units are modeled to overlap with the rotation angles of 60, 120 and 180 degrees. The isomers have quintet, singlet, and quintet ground states, respectively (1985), offering the first experimental verification of the theory of Harden McConnell proposed in 1963 and serving as a basis for the crystal design of spin alignment between open-shell molecules.
2. Knowing that the connection of many carbene centers in one dimension is too naïve a prototype for organic magnets, Iwamura synthesized a branched-chain, cyclic and dendritic polydiazo compounds constituting various units of a two-dimensional honey-comb-shaped network structure. A branched chain nonacarbene has a nonadecet (S = 9) ground state, the highest spin ever reported for a well-defined organic molecule. A cyclic hexacarbene derived from a calixarene has a tridecet (S = 6) ground state. However, the expected high spin species were not necessarily obtained upon photolysis of dendritic analogues due to intramolecular dimerization and/or azine formation.
3. In order to overcome these limitations of the polycarbene approach, he turned to stable aminoxyl radicals. A series of bis- and tris(aminoxyl) radicals that have triplet and quartet ground states and are stable under air at room temperature have been synthesized. Again it proved not to be easy to extend the system to higher spin species. Iwamura and Inoue made a major breakthrough by advancing a strategy of making hybrid spin magnets consisting of aminoxyl radials as ligands with magnetic metal ions as linkers. Depending on the disposition of the aminoxyl oxygen atoms in the bis- and tris(aminoxyl) radicals, one-, two- and three-dimensional network structures have been obtained as designed. In many of the resulting mixed ligand complexes with $[\mathrm{Mn(hfac)_2}]$, all the 2*p* spins of the aminoxyl ligand and the 3*d* spins of the Mn^{2+} ordered spontaneously to form ferrimagnets at temperatures below 4–60 K.

   Pursuing the first idea of making photomagnetic materials by using polydiazo compounds, Iwamura and Koga developed polydiazo supramolecules by combining various magnetic metal ions with diazodipyridylmethanes. $[\mathrm{Mn(hfac)_2}]$ and $[\mathrm{Cu(hfac)_2}]$ with diazodi(4-pyridyl)methane, for example, formed well-defined polymer complexes that are dilute paramagnets due to the metal ions. When the diazo groups were photolyzed, the polymer complexes produced ferrimagnetic and ferromagnetic chains, respectively. As a result of the extension of the correlation length, S_{av} in the former approached 300 at 2.0 K. Furthermore the carbene centers formed in the crystal lattice of the complexes were found to be stable up to 240 K.

His important scientific contributions described above are published in about 170 international publications.

Professor Kasai’s Scientific Achievements

Prof. Toshio Kasai at Osaka University, a former visiting professor of the institute, received the Scientific Award of the Chemical Society of Japan in 2002 for his contribution to “Studies on Reaction dynamics Using Oriented Molecular Beams: Discovery of Steric (Molecular Orientation) Effects and Its Application to Surface Reactions.” Prof. Kasai has studied stereo-dynamics in various gas phase reactions by utilizing the advantage of the oriented molecular beam method. Orientation of reagent molecule can be controlled by an electrostatic field after rotational quantum state selection by hexapole electrostatic field. His scientific achievements related to the award are summarized as follows:

1. *Reaction of excited rare gas atoms with oriented halomethane and related simple molecules:*
   On the basis of experimentally observed steric effect for these reaction systems, Prof. Kasai demonstrated how the molecular orientation affects the reactivity. Experimental observation of steric effect also enabled us to make comparison with theoretical study, and this comparison further allows us to find out direct relationship between the steric effect and the spatial distribution of related molecular orbital.
2. *Reaction dynamics study under collision energy and orientation specified condition:*
   Prof. Kasai has developed a reaction apparatus for time of flight measurement with oriented molecular beam, which made it possible to observe two dimensional reaction cross section. Throughout several studies related to Penning ionization reactions, he has ascribed the origin of the steric effect to the interaction potential of the reagent molecules. He has also pointed out that the observable steric effect depended upon collision energy of the reagent. Furthermore, he has found reaction pathways correlated to Feshbach resonance under both collision energy and orientation specified condition. He successfully characterized these reaction dynamics in gas phase collision in detail.
3. *Hexapole application to molecular clusters:*
   Prof. Kasai has successfully demonstrated that size and structure of molecular clusters could be selected by hexapole field. Furthermore, by combining this method with Doppler time of flight mass spectroscopy, the internal state distribution for the transient species in the photo-dissociation reaction of DCl dimer has been elucidated.
4. *Hexapole application to reactions:*
   Prof. Kasai has developed an ultra-high vacuum oriented molecular beam apparatus for studying surface reactions. The reaction dynamics of oriented CH_3Cl molecule with Si{001}surface was studied and results provided indispensable knowledge for surface reaction control at molecular level.

Associate Professor Tanimura’s Scientific Achievements

Associate professor Yoshitaka Tanimura, Department of Theoretical Studies, received the Morino Science Award in 2002 for his contribution to “Studies on Theoretical Bases of Two-dimensional Spectroscopy.” With Prof. Mukamel in Rochester University, he proposed two-dimensional optical spectroscopy method for the first time. This method is called “optical version” of two-dimensional nuclear magnetic resonance method. In particular, they showed that the multi-dimensional spectroscopy is realizable in even more complicated systems with the observables such as polarizability and dipole moment than those only with spin angular momenta. This theoretical approach invited the experimental studies on two-dimensional Raman and infrared spectroscopy by Prof. Fleming and Prof. Hochstrasser and can be evaluated as a pioneering work in the field of optical spectroscopy. Prof. Tanimura has been developing analytical methods for studying inhomogeneity in solution, anharmonic oscillators, and non-linear polarizability by using the extended quantum Fockker-Planck equation.

Research Associate Matsuo’s Scientific Achievement

Research Associate Dr. Tsukasa Matsuo of Coordination Chemistry Laboratories has been selected to receive the 2002 Chemical Society of Japan Award for Young Chemists for his contribution entitled “Studies on Anion Species of Silyl-Substituted π-Electron System Based on 4- and 5-Membered Rings.” One of most remarkable achievements relevant to the award is the investigation of cyclobutadiene dianions. Hückel’s rule predicts the cyclobutadiene dianion to be aromatic. However attempts to prepare the planar cyclobutadiene dianion itself and its derivative with D_{4h} symmetry have been failure due to electronic repulsion originating from the large negative charge density per atom. Dr. Matsuo succeeded in synthesizing a dilithio salt of tetrakis(trimethylsilyl)cyclobutadiene dianion by taking advantage of electronic and steric effects of the silyl groups. X-ray crystallographic analysis and NMR spectroscopic studies confirm the aromatic nature of the 6 π-electron cyclobutadine dianion. In addition, since this dianion is a rare example of aromatic organic molecules with degenerate HOπMOs and a nondegenerate LUπMO, he elucidated this type of unusual electronic structure by the simultaneous use of UV-visible absorption and magnetic circular dichroism spectroscopies. This is the first demonstration of a negative Faraday A term for an aromatic organic compound for the first time.

Mr. Kenji Suzuki's Scientific Achievement

Mr. Kenji Suzuki of Yakushi Group, the student of the Graduate University for Advanced Studies, received the Student Award for the Most Impressive Presentation in 83rd Annual Meeting of the Chemical Society of Japan for his contribution "Charge Separation of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ under High Pressure." This student award was initiated from 83rd Annual Meeting, and two students were selected in the field of solid state chemistry. His achievement is the drawing of the electronic phase diagram of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ in the pressure and temperature space using Raman spectroscopy.