



Laboratory for Physical Chemistry 2: Molecular Spin Science

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1. Current Research and Principal Research Interests

Major research interests in our group fall into over ten areas and categories of chemistry and materials science, centering on the advancement of molecular spin science and on the significant contribution to the conceptual and material advance in organic molecule-based magnetism and magnetics. A major goal of our study on molecular spin science is to develop spin-mediated molecular devices in terms of novel functionality concepts and materials challenge, stimulating actual molecular designing and organic syntheses of component key-molecules. Both molecular spin science and organic molecule-based magnetics are underlain by high-spin chemistry and material development in novel open-shell molecular systems and magnetic molecular assemblages. Molecular design and synthetic challenges for chemically stable and genuinely organic open-shell systems have particularly been emphasized in our recent research efforts. Our principal interests focus on not only the fundamental understanding of spin alignment in organic high-spin systems and the establishment of conceptual advance in molecule-based magnetics, but also search for novel quantum phenomena and molecular functionalities derived from genuinely organic open-shell molecular systems. A novel concept, “Molecular Spinics” termed by us includes redox-based spin electronics underlying molecular organic charge storage devices. These new molecular quantum functionalities are based on quantum chemical considerations and methodology developed in high-spin chemistry and genuinely organic molecule-based magnetics. Our recent findings of redox-based spin diversity provide us with not only a new field of chemistry and related molecular spin science, but also material and technological advance such as organic molecular batteries. The spin diversity originates in “molecular diversity” intrinsic to molecular systems, not appearing in atomic ones alone. In this context, the spin diversity is a quantum aspect of molecular diversity. Our long-standing expertise in these particular fields since 1970 has been utilized to search for such novel molecular functionalities.

Our sixteen principal research interests are as follows:

(1) Molecular spinics underlain by organic high-spin chemistry and organic molecule-based magnetics: Theory and Applications.

Our current interests include superparamagnetic nanochemistry and magnetic quantum-well effects as well as molecular spin quantum tunneling which has been shown in the study of polyanionic C₆₀ fullerene in the high-spin and low-spin states. The C₆₀ polyanionic systems with high molecular symmetry have shown dynamic Jahn-Teller assisted molecular hot-phonon bottleneck phenomena, which is the first example of phonon bottleneck phenomenon for organic systems. The findings of the dynamic Jahn-Teller effects have given for the first time an

experimental evidence for the occurrence of dynamic Jahn-Teller effects responsible for high- T_c superconductivity in alkaline-doped C_{60} molecular crystalline systems, which has been predicted by physicists from the theoretical side. Our current interests include also to find novel quantum modes originating in semi-microscopic superlattices such as periodically fine-structured ferromagnetic thin films of one- or two-dimension (see Figure 1). We have for the first time shown the occurrence of lateral “Walker modes” (spin-waves standing along the y-direction) from the superlattices on a micron scale in terms of ferromagnetic resonance spectroscopy (see Figure 2).

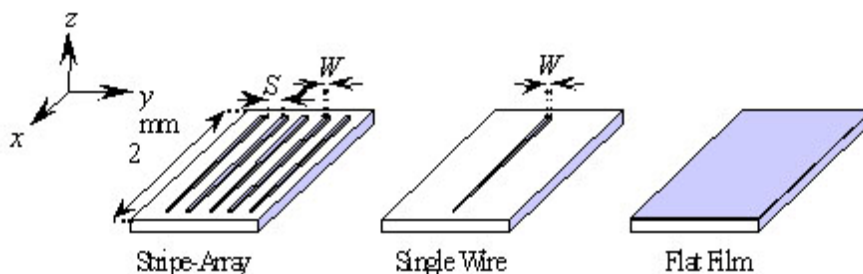


Figure 1. 2D Superlattice composed of ferromagnetic thin films on a micron scale used for ferromagnetic resonance spectroscopy; Thin film width = 50 nm and $W = S = 2 \mu\text{m}$.

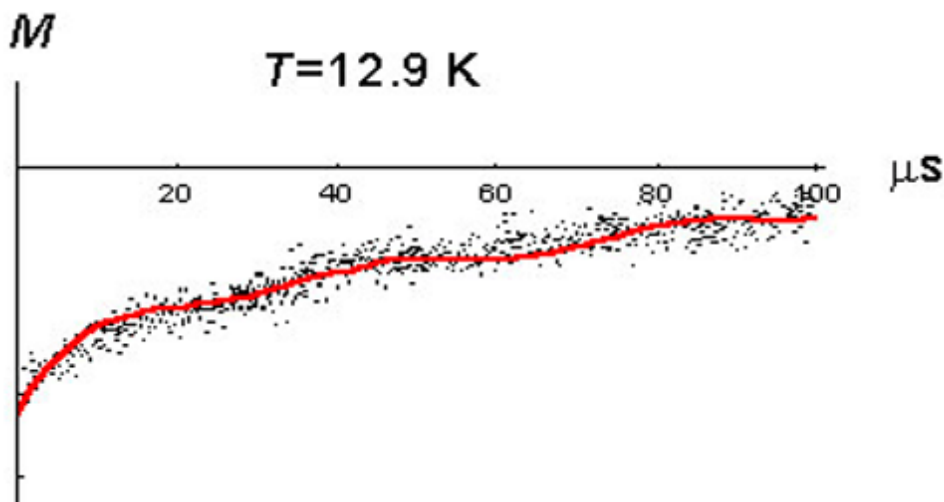


Figure 2. Observed ferromagnetic resonance spectra from the 1d superlattice of $n = 100$ with $B_0 // y$ and theoretically calculated stick spectra for lateral Walker mode spin waves and spin dipolar spin waves.

(2) Nonlinear oscillations of gigantic spin-magnetic moments in artificial superlattices on a semi-microscopic scale.

Nonlinear oscillation phenomena from the one- and two-dimensional superlattices with microwave field B_1 parallel to B_0 have been observed at certain conditions, illustrating the possible device of self-oscillation in microwave frequency range. The two-dimensional tiled superlattices show group-theoretical pseudo-degeneracy in a semi-microscopic scale.

(3) New trend in high spin chemistry: electronically ground and excited high-spin states from π -conjugated oligocarbenes and oligonitrenes.

Oligocarbene-based high-spin chemistry has been a well established area in molecule-based magnetics. High spin chemistry has underlain molecule-based magnetism, bringing about conceptual advances such as π -topologically controlled spin polarization (π -topology rule in spin alignment). A New trend in high spin chemistry includes detection and characterization of excited states of open-shell oligocarbenes. Various excited states with different spin multiplicities are located close to the high spin ground states, generating salient features for high-spin open-shell molecular systems. Their electronic spin structures are particular interests and have drawn general attention from both theoretical and experimental sides. We have studied absorption and emission spectra from typical triplet and quintet carbenes and have made efforts to identify electronic transitions by invoking the latest and most reliable *ab initio* quantum-chemical computations.

The new trend also includes advance in oligonitrene chemistry. Referred to the electronic and molecular structures of high-spin oligonitrenes, documentation so far since 1967 has been misleading and most of the reported fine-structure parameters have never reproduced the corresponding observed fine-structure spectra in non-oriented media. We have solved this long-standing issue from both theoretical and experimental sides, establishing molecular design for stable oligonitrenes of desired fine-structure tensors.

(4) New π -topology-controlled high-spin hydrocarbons: development of polynuclear benzenoid high-spin chemistry.

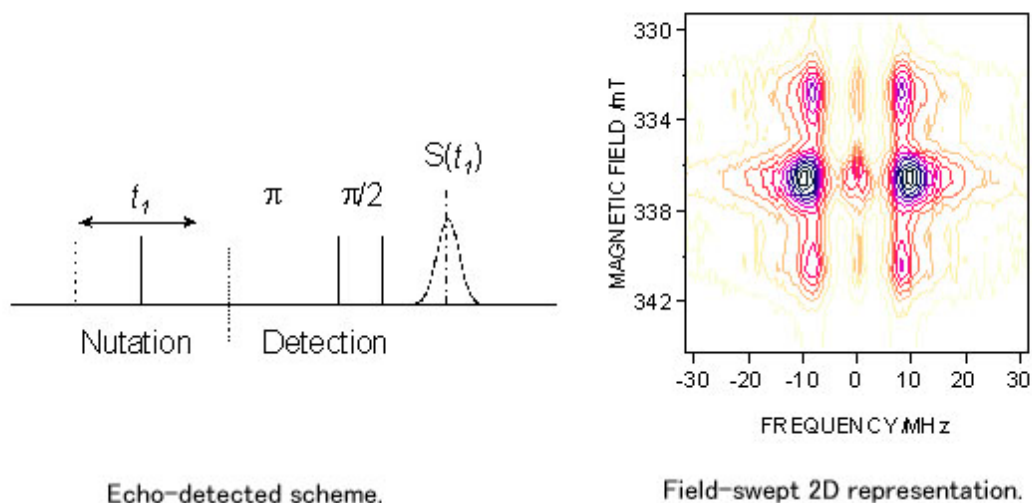
Besides well established π -topology rule, we have proposed new types of π -topology-controlled molecular design for super high-spin and ferromagnetic hydrocarbons of one- or two-dimension from theoretical side. One of such molecular designs is triangulene-based. During the course of this project, we have synthesized, detected and characterized stabilized triangulene (Clar's hydrocarbon) in the triplet ground state, for the first time. The molecular design has been based on new molecular diversity of hydrocarbons of π -conjugation. The project has been run in collaboration with the group of Professors K. Nakasuji and Y. Morita, Osaka University.

(5) Development of new methodology and experimental techniques in pulsed electron spin resonance spectroscopy: Transition moment spectroscopy as a novel spectroscopy.

Our particular interests focus on establishment and a wide variety of applications of two-dimensional (2D) electron spin transient nutation spectroscopy as new transition moment spectroscopy (see Figures below for an echo-detected scheme and for a field-swept 2D representation). We have already made quite a number of applications in high-spin chemistry, illustrating that the pulse-based nutation spectroscopy is facile and powerful in straightforwardly identifying spin multiplicities as well as ESR transition assignments involved under study. The ESR transition assignments include both fine-structure allowed and forbidden transitions in non-oriented media and hyperfine allowed and forbidden ones in single crystals in terms of corresponding nutation frequencies appearing in the rotating frame of microwave irradiation.

Inversion recovery methods applied to the trianionic C60 fullerene systems have given evidence for the occurrence of such quantum spin tunneling between the doublet-quartet states for the trianionic case as is assisted by spin-vibronic dynamic Jahn-Teller interactions and hot-phonon bottleneck phenomena (see Figure 3 for the triplet-singlet resonant spin tunneling occurring in the dianionic C60 fullerene system). The tunneling frequencies and sizes of

responsible nuclear displacements have quantum-mechanically been derived in terms of dynamic treatments with nuclear kinetic energies. The results have given a rationale for the occurrence of the dynamic Jahn-Teller mechanism in the high T_c superconducting states of alkaline-doped C_{60} molecular crystals, which has been predicted by theoretical physicists.



(6) Parametric (parallel polarization) excitation spectroscopy: general theory and applications.

In high-spin chemistry in terms of spin identification, parametric excitation of microwave irradiation gives ample information on fine-structure terms. We have frequently applied the parametric excitation spectroscopy to molecular magnetic systems which have large fine-structure interactions, in some cases to high-spin systems characterized by non-vanishing large orbital angular momenta. The data derived from the parametric excitation spectroscopy have been complementary to those acquired by highfield/highfrequency ESR spectroscopy in some cases. General exact analytical solutions for the motion of spin magnetization in parametric excitation spectroscopy have been obtained by invoking exponential operator techniques, emphasizing that the general exact analytical solutions predict the occurrence of multiple-harmonic frequency oscillations in parametric excitation spectroscopy. General theory for the motion of any spin magnetization in the presence of static and oscillating irradiation fields of various types gives new aspects and physical pictures in magnetic resonance spectroscopy.

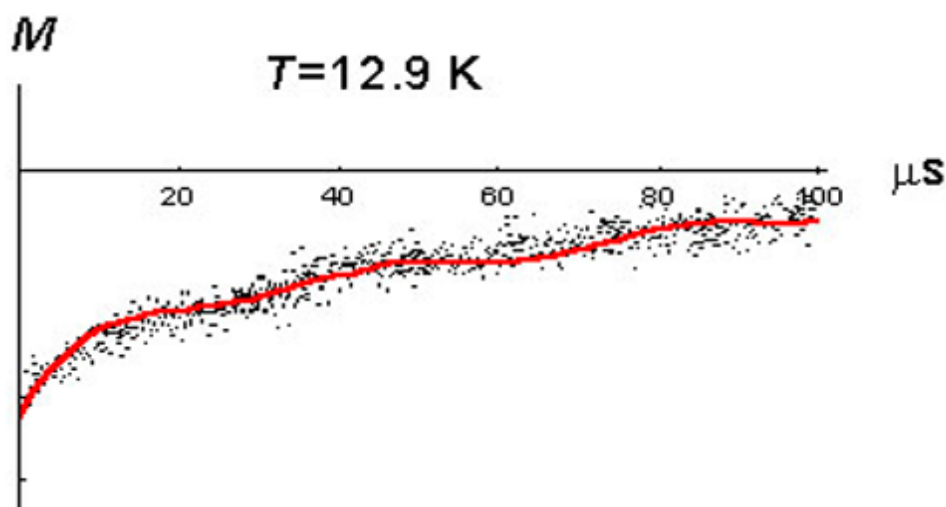


Figure 3. Spin relaxation curves for the annealed C_{60}^{2-} with the triplet state at 12.9K. The solid curve represents the theoretical curve derived from the modified Scott-Jeffries equation combined with a sine curve with the

frequency of 30 kHz.

(7) General theory of magnetic resonance spectroscopy.

Our current interests focus on the development of fine-structure spectral simulation methods which execute facile and fast simulation processes. Fine-structure spectral simulations have enjoyed “notorious drawbacks” for a long time. A remarkable advance in highfield/highfrequency ESR spectroscopy has decreased crucial needs for sophisticated fine-structure spectral simulations, which gives straightforward transition assignments for many cases. Nevertheless, recently non-ESR-specialist chemists or materials scientists working in interdisciplinary fields often need reliable X-band ESR fine-structure spectral simulations and methodology to understand magnetic properties and electronic spin structures of a variety of high-spin systems. We have appreciated the eigenfield approach introduced by Belford et al. in 1970's. Owing to ultrafast computer facilities, sizable computations based on numerical matrix diagonalization for the simulation seem feasible. Speaking exactly, this is still not the case for high-spin fine-structure chemistry. We have made efforts to develop much more reliable and fast-access approach termed “hybrid eigenfield approach” devoted to high-spin chemistry and high-spin ESR spectroscopy. Program softwares have been distributed on request for chemists and materials scientists working in the fields of molecule-based magnetism and high spin chemistry.

(8) Paramagnetic metalloporphyrin chemistry related to biological implications: Jahn Teller interactions in low symmetry.

The overall goals of our current research programs are to elucidate electronic structures and distorted molecular geometries of ferric iron porphyrin in the sextet ground state and cobalt(II)porphyrin in the low-spin doublet state. Both systems undergo sizable static Jahn-Teller distortions at liquid helium temperatures. Single-crystal ESR and ENDOR spectroscopy has been applied to identify distorted molecular structures and to elucidate peculiar electronic structures. Concepts of nuclear spin degenerate state ENDOR have frequently used to understand complicated ^{14}N -ENDOR spectra. It has shown for the first time that referred to the electronic structure of fifth-ligand non-coordinated cobalt(II)porphyrin frequently applied Magarvey's model breaks down.

(9) Electron-nuclear multiple resonance in organic high-spin chemistry and paramagnetic metal complexes.

(10) Crystal Engineering for purely organic high-spin molecular crystals.

Genuinely organic molecule-based ferrimagnetics is the focus of our current issues in this particular area, simply because genuinely organic ferrimagnets have not been documented yet. Organic ferrimagnetics also gives new aspects in the research field of magnetism as well as chemistry. A concept of “magnetic supramolecule” has been proposed in magnetic molecular crystals and molecular crystal engineering.

(11) VB theory for charge fluctuation vs. spin polarization in high-spin polyanionic and polycationic systems.

(12) Chemometric 2D electron spin resonance spectroscopy.

(13) Molecularinformatics and chemoinformatics.

(14) Chemometrics for environmental radiation damages.

These projects (12)-(14) have recently launched for biologically important metal complexes and medical applications, and several issues are underway for generalization. The issues under

study are categorized into generalized two-dimensional correlation spectroscopy handling experimental data in a sizable scale.

(15) Photo-storage molecular materials luminescence spectroscopy and molecular batteries.

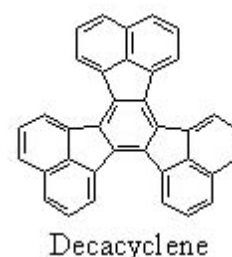
Our group strives to develop molecular spin science, understanding electronic structures and magnetic properties of novel high-spin molecular systems underlying molecule-based magnetic materials. On the basis of the electronic structures we have developed the theory of molecular design of molecule-based high-spin systems. Molecular systems applied are in a wide range from organic high-spin systems to inorganic polynuclear complexes. The organic systems include polyradicals, high-spin oligocarbenes and oligonitrenes, and in addition, the polyionic states of the organic molecules. All compounds possess a high-spin ground or thermally accessible excited states. The inorganic systems include not only magnetically coupled transition metal systems but also rare earth metals. One of the rare earth metal systems which we are currently interested in is europium(II)-doped aluminates which are remarkably long-lasting phosphors. The aluminate is free of hazardous and radioactive substances, and has been attracting interest because of its potential for a variety of applications. In order to elucidate the long-lasting mechanisms, we have applied highfield/highfrequency ESR spectroscopy to the systems in collaboration with Professor T. Kato, IMS and with Professor W. Lubitz, TU in Berlin.

(16) Quantum chemistry of fine-structure interactions in high-spin systems with high molecular symmetry.

Polyionic states of highly symmetric molecules have been attracting interest with respect to symmetry-lowering distortions by the Jahn-Teller effect in degenerate electronic states such as polyanionic decacyclene. Preference for the high-spin ground states resulting from the robust dynamic spin polarization has been a long-standing issue for trianionic decacyclene. In terms of spin correlation in the open-shell systems, our current research efforts are directed toward quantum chemical calculations of the fine-structure terms in highly symmetric π conjugation systems. Recently, we have detected for the first time a Clar's hydrocarbon in the triplet ground state. The Clar's hydrocarbon is neutral and triangular molecule with a highly delocalized π -system.

Referred to highly symmetric molecules of π -spin delocalization, we have reported high-spin states of polyanionic C_{60} fullerene and decacyclene prepared by chemical reduction with alkali metals. As described above, we have found the anomalous spin relaxation due to phonon bottleneck and quantum-mechanical tunneling phenomena in the polyanionic C_{60} fullerene. In the case of the highly symmetric molecule in the high spin state, the pseudo Jahn-Teller interaction is responsible for the occurrence of the quantum tunneling phenomena.

Noticeably, the Jahn-Teller assisted quantum spin tunneling observed in polyanionic C_{60} fullerene supports a theoretical model proposed for high-temperature superconductivity in fullerides with alkali metals. On the other hand, decacyclene with three-fold symmetry has two degenerate LUMOs and a pseudo-degenerate MO above the LUMOs in the neutral molecule. It has been well known that the trianionic state of decacyclene is spin-doublet in the ground state. Theoretical calculations considering configuration interaction also supported the doublet ground state for the trianionic state. Nevertheless, detection of the quartet state has been a long-standing issue because knowledge of this state is important for understanding of the Jahn-Teller effect in the high-spin state. On the contrary to the documentation, we have recently detected the quartet state using fine-structure ESR spectroscopy for random orientation. Our hybrid eigenfield approach has successfully reproduced the observed spectra with all the forbidden transitions. It is concluded that the



trianionic state of decacyclene is in the quartet ground state, contrary to the previously documented results, indicating that highly sophisticated quantum chemical calculations incorporating vibronic and spin-orbit interactions are required.

Both polyanionic C₆₀ fullerene and decacyclene possess two or three delocalized π -spins in the high-spin states. Spin-spin interaction in the three-spin system includes a fundamental issue for establishing the ground-state electronic structure of the delocalized high-spin system. The spin-spin interaction has been understood based on two-body interaction. Recently, we have noticed that three-body interactions are essential for the understanding of spin-spin interactions in the three spin systems. This issue has been overlooked for a long time even in high spin chemistry. Our findings contribute to the understanding and theoretical considerations of the spin-spin interaction in terms of the three-body quantum-mechanical problem. Quantum chemical approach to fine-structure terms in terms of spin pair functions is underway.

2. Selected Publications

1. "Detection of an aromatic hydrocarbon in its septet electronic ground state by electron spin resonance", T. Takui, K. Itoh, *Chem. Phys. Lett.*, **19**, pp. 120-124 (1973).
2. "General description of multiple-modulation effects and sideband production in magnetic resonance", H. Sakamoto, T. Takui, K. Itoh, *Can. J. Chem.*, **66**, pp. 3077-3082 (1988).
3. "Design, preparation, and electron spin resonance detection of a ground-state undecet ($S = 5$) hydrocarbon", I. Fujita, Y. Teki, T. Takui, T. Kinoshita, K. Itoh, *J. Am. Chem. Soc.*, **112**, pp. 4074-4075 (1990).
4. "Novel organic ions of high-spin states. 2. Determination of the spin multiplicity of the ground state and ¹H-ENDOR study of the monoanion of m-phenylenebis(phenylmethylene)", M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita, K. Itoh, *J. Am. Chem. Soc.*, **114**, pp. 7470-7475 (1992).
5. "Polycationic high-spin states of one- and two-dimensional (diarylamino)benzenes, prototypical model units for purely organic ferromagnetic metals as studied by pulsed ESR/electron spin transient nutation spectroscopy", K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma, Y. Shirota, *J. Am. Chem. Soc.*, **119**, pp. 6607-6613 (1997).
6. "Persistent high-spin polycarbene. Generation of polybrominated 1,3,5-tris-[2-[4-(phenylcarbeno)phenyl]thynyl]benzene ($S = 3$) and spin identification by two-dimensional electron spin transient nutation spectroscopy", H. Tomioka, M. Hattori, K. Hirai, K. Sato, D. Shiomi, T. Takui, K. Itoh, *J. Am. Chem. Soc.*, **120**, pp. 1106-1107 (1998).
7. "Electronic quartet and triplet states of polyanionic C-60 fullerene and their anomalous spin relaxation as studied by cw-ESR/2D-Electron spin transient nutation spectroscopy", M. C. B. L. Shohoji, M. L. T. M. B. Franco, M. C. R. L. R. Lazana, S. Nakazawa, K. Sato, D. Shiomi, T. Takui, *J. Am. Chem. Soc.*, **122**, pp. 2962-2963 (2000).
8. "Evidence for the breakdown of simple classical pictures of organic molecule-based ferrimagnetics: Low-temperature crystal structure and single-crystal ESR studies of an organic heterospin system", M. Nishizawa, D. Shiomi, K. Sato, T. Takui, K. Itoh, H. Sawa, R. Kato, H. Sakurai, A. Izuoka, T. Sugawara, *J. Phys. Chem. B*, **104**, pp. 503-509 (2000).
9. "Single-component molecule-based ferrimagnetics", D. Shiomi, T. Kanaya, K. Sato, M. Mito, K. Takeda, T. Takui, *J. Am. Chem. Soc.*, **123**, pp. 11823-11824 (2001).

10. "The first detection of a Clar's hydrocarbon, 2,6,10-tri-tert-butyltriangulene: A ground-state triplet of non-Kekule polynuclear benzenoid hydrocarbon", J. Inoue, K. Fukui, T. Kubo, S. Nakazawa, K. Sato, D. Shiomi, Y. Morita, K. Yamamoto, T. Takui, K. Nakasuji, *J. Am. Chem. Soc.*, **123**, pp. 12702-12703 (2001).

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学歴 昭和 42 年 3 月 大阪大学基礎工学部卒業

昭和 45 年 3 月 大阪大学大学院基礎工学研究科修士課程修了

昭和 48 年 3 月 大阪大学大学院基礎工学研究科博士課程修了

職歴	昭和 48 年 4 月から 昭和 49 年 3 月まで	日本学術振興会	奨励研究員
	昭和 49 年 4 月から 昭和 49 年 9 月まで	大阪大学基礎工学部	研究生
	昭和 49 年 9 月から 昭和 51 年 8 月まで	ブリティッシュコロンビア大学	博士研究員
	昭和 51 年 9 月から 昭和 53 年 3 月まで	ブリティッシュコロンビア大学	ティーチング 博士研究員
	昭和 53 年 4 月から 昭和 61 年 3 月まで	大阪市立大学 理学部	助手
	昭和 61 年 4 月から 平成 1 年 9 月まで	大阪市立大学 理学部	講師
	平成 1 年 10 月から 平成 4 年 9 月まで	大阪市立大学 理学部	助教授
	平成 4 年 10 月から 平成 13 年 3 月まで	大阪市立大学 理学部	教授
	平成 13 年 4 月から 平成 14 年 3 月まで	大阪市立大学 理学部・大学院理学研究科	教授
	平成 14 年 4 月から 平成 18 年 3 月まで	大阪市立大学 大学院理学研究科・理学部	教授

在職中の
主な役職 なし

学位 工学博士 (昭和 48 年 3 月 24 日 大阪大学)