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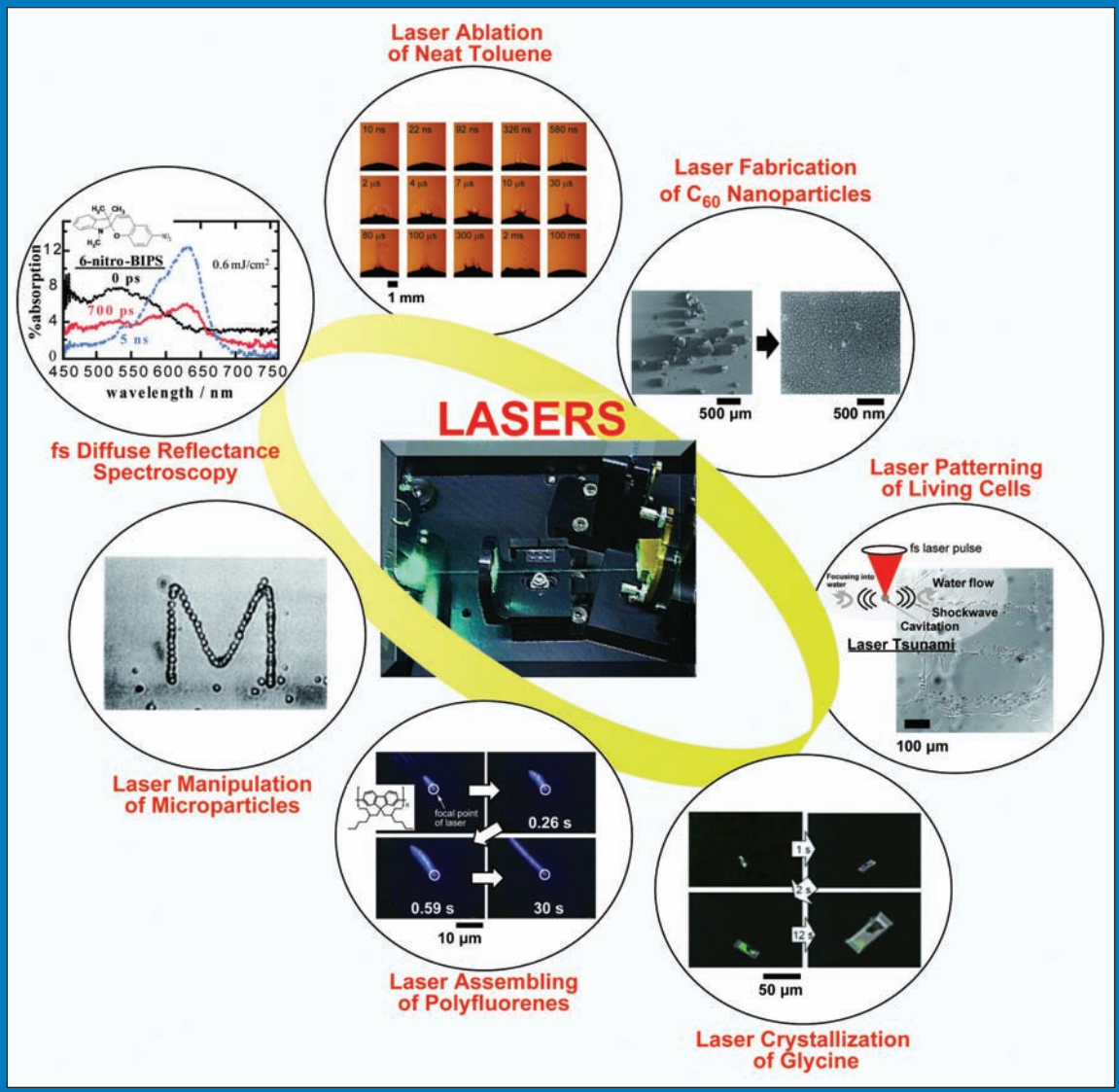

Exploration with Lasers into New Areas of Molecular Photoscience
(see page XXX)

Hiroshi Masuhara Festschrift

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Preface to the Hiroshi Masuhara Festschrift: Exploration with Lasers into New Areas of Molecular Photoscience

This issue of the *Journal of Physical Chemistry C* is dedicated to Hiroshi Masuhara, Chair Professor of National Chiao Tung University, Guest Professor of Nara Institute of Science and Technology, and Professor Emeritus of Osaka University. Masuhara's many outstanding scientific accomplishments, especially his contributions toward the exploratory research on molecular photoscience utilizing lasers, have been recognized in this issue by many of his colleagues, collaborators, friends, and students.

Hiroshi Masuhara was born in Tokyo, Japan and grew up in Izumi-Ohtsu, Osaka. He earned a B.Sc. degree in chemistry from Tohoku University in 1966 and participated in the laboratory of Professor Masao Koizumi, during his fourth undergraduate year and two years during his Masters program at Tohoku University, where he was engaged mainly in the study of molecular orbital calculations of transient species. In 1968, as a Ph.D. student at Osaka University, he worked in the Department of Chemistry at the Graduate School of Engineering Science, where he began constructing an apparatus for nanosecond laser spectroscopy in the laboratory of Professor Noboru Mataga.

During experiments using a Q-switched ruby laser, he discovered that the fluorescence spectrum of weak charge transfer (CT) complexes, such as tetracyanobenzene (TCNB)$^-$ benzene derivatives, under the laser excitation was different from those obtained by the steady-state light irradiation. Particularly, a strong dip was observed near 465 nm in its broad fluorescence spectrum. As the output of the Q-switched ruby laser was intense, a large number of the ground-state CT complexes were pumped up into the excited state. Consequently, the fluorescence from the excited state produced by the laser excitation was partly absorbed by the excited-state CT complex itself. This laserinduced phenomenon was not observed under the steady-state light irradiation and was the probable impetus for his exploration with lasers. Through the analysis of the fluorescence spectra with and without the additional laser excitation, Masuhara deduced the transient absorption spectrum of the weak CT complex in the excited state. The shape of this absorption band was similar to those of the anion and cation radicals of the electron acceptor and the donor, respectively (the dip at 465 nm was the absorption maximum of the anion radical of TCNB). His analysis led to the first measurement of the electronic absorption spectra of the CT complex in its excited state, and also provided information on the electronic structure of the excited CT complex.

After receiving his Ph.D. from Osaka University, Masuhara became a postdoctoral fellow and then a member of university staffs when he was appointed as a research associate at the laboratory of Professor Mataga. As a research associate, and with the help of Professor Mataga and several students, he conducted systematic studies on the dynamics and mechanisms of electron-donor−acceptor systems, polymers in solutions and solids, and molecular assemblies, using nanosecond and picoseconds laser photolysis methods. In 1981, his research on the precise kinetics and dynamics of basic photochemical processes and ionic dissociation were presented in *Accounts of Chemical Research*. Masuhara's innovative use of laser-induced phenomena for the time-resolved detection of photochemical reactions extended to the investigation of molecular systems, for example, estimation of energy migration rates in aromatic polymer system through the detection of S_1−S_1 annihilation and the use of laserinduced multiphoton excitation to create higher excited states in solution. In the same year, Masuhara spent several months in Leuven, Belgium and performed research in Professor Frans C. De Schryver's laboratory as a Visiting Scientist. This stay was the starting point of a long-standing collaboration and interchange of personnel and ideas between

these two laboratories as well as a strong friendship between two families, which continues to this day. Masuhara learned a lot about European science, culture, society, and even family, which no doubt contributed to flourishing his scientific carrier.

In 1984, Masuhara became a full professor at the Kyoto Institute of Technology and set up a new laboratory in the Department of Polymer Science and Engineering, where he began research with lasers on photochemical dynamics in the solid state. He also began to explore lasers as a tool for manipulation and fabrication in the solid-state. Four years later (in 1988), he was appointed as leader of a renowned project, Masuhara Microphotoconversion Project for Exploratory Research for Advanced Technology (ERATO) of Japan Research and Development Corporation (JRDC, which has more recently become the Japan Science and Technology Agency, JST). In this project, Masuhara and his team of more than 20 scientists explored new photochemical and photophysical phenomena by developing ps-total internal reflectance (evanescent wave) fluorescence spectroscopy, fs-grating spectroscopy, various microspectroscopies, and laser manipulation (One example is a letter “M” in Cover Illustration; Sasaki et al., *Jpn. J. Appl. Phys.* **1991**, *30*, L907) and patterning methods. These pioneering studies led to the exploration of several new interdisciplinary areas in molecular photoscience as well as the development of microchemistry (i.e., space-resolved laser chemistry), which was created by combining laser and microscopy techniques. This innovative approach was the outcome of the icrophotoconversion project, and was summarized as a first book on Microchemistry. Since then, Masuhara’s science has grown in breadth, encompassing several new fields of molecular photoscience and the importance of his work is reflected in its citation by many photoscientists.

In 1991, while working on the Microphotoconversion project, Masuhara moved back to Osaka, as a Professor in the Department of Applied Physics at Osaka University, where he conducted groundbreaking research on the novel applications of spectroscopy in several research fields, including as materials science, physics, optics, and most recently bioscience. In the field of laser nano spectroscopy and nano photochemistry, Masuhara and his colleagues developed various time-resolved reflection spectroscopies, including ps- and fs-diffuse reflectance (in Cover Illustration; Suzuki et al., *Phys. Chem. Chem. Phys.* **2002**, *4*, 185), ps- and fs-regular reflectance spectroscopies. By applying these methods to the investigation of photophysical and photochemical dynamics of nancrystals, nm-thin films and nm-surface/interface layers of solids, Masuhara and his colleagues demonstrated the importance of these detection methods through a series of seminal papers on the time- and spaceresolved measurements of solid systems. In addition, they also studied individual nanoparticles as functions of their shape, size, morphology, internal structure, and environment, by combining optical microscopy and AFM. Through the application of these techniques, the structural confinement was revealed namely, the size-dependence of crystal lattice softening, molecular packing, and polymer conformation, which are characteristic to molecular materials, and completely different from well-known nm size effects in semiconductors and metals. This single nanoparticle spectroscopy is highly complementary to single molecule spectroscopy and can bridge the gap in understanding the relationship between properties of molecules and bulk materials.

Masuhara and his group also explored the field of the photon pressure (radiation pressure) with lasers. By the mid-1980s, optical trapping studies had been conducted by physicists, though its extension to chemistry had not yet begun. Consequently in the ERATO project Masuhara applied optical trapping to chemistry to induce the aggregation of molecules, polymers (in Cover Illustration; Masuo et al., *J. Phys. Chem. B* **2005**, *109*, 6917), and micelles on the nanoscale. These studies demonstrated successive one-by-one trapping of a nanometer sized particles resulting in photon-force-assisted aggregation and the 3-dimensional fabrication of nanoparticles. Masuhara utilized this technique to align and fix nanoparticles on a surface with precision of a few tens nm. Although the spatial resolution of the patterning in solution is less than that attained by the 2-dimensional surface manipulation by a STM tip at low temperature under vacuum, a broader applicability such as in biological materials and cells, and recently crystallization of amino acid is achieved (in Cover Illustration; Sugiyama et al., *Chem. Lett.* **2007**, *36*, 1480). The demonstration and analysis of the above-mentioned phenomena is nowadays referred to as “chemistry of photon force”.

Masuhara and his group also explored the physics and chemistry induced by intense laser excitation for nano droplets, aggregates, crystals, powders, and films, from a fundamental viewpoint. They developed time-resolved imaging methods to probe laser-induced morphological dynamics and combined

them with time-resolved spectroscopy (in Cover Illustration; Hatanaka et al., *J. Phys. Chem. B*, **2002**, *106*, 3049) to elucidate the dynamics and mechanisms of ns-, ps-, and fs-laser ablation and related phenomena such as expansion, surface roughening, and contraction. These studies demonstrated how electronic excitation of molecules in solids evolves in time into morphological changes and established the molecular mechanisms of laser ablation, i.e., a cyclic multiphoton absorption mechanism in the case of ns-excitation and for fs-excitation a transient pressure mechanism due to rapid photothermal conversion. More recently, Masuhara and co-workers have extended these studies to nano particle fabrication (in Cover Illustration; Sugiyama et al., *J. Photochem. Photobiol. A: Chem.* **2009**, in press) and to applications in biological molecules and even living cells. For example, Masuhara and his group were able to successfully crystallize proteins by introducing fs-pulse into supersaturated protein solutions, thereby demonstrating they could control of the direction of the crystal growth with fs-multiphoton excitation. In addition, the Masuhara group achieved the alignment of living cells onto a substrate in water (in Cover Illustration; Hosokawa et al., *Biomed. Microdevices* **2007**, *9*, 105) by using fs laser-induced impulsive force due to shockwave propagation, the generation and contraction of cavitation bubbles, and the resulting convection flow (Masuhara calls this force phenomenon "Laser Micro/Nano Tsunami"), which has promising applications in biotechnology.

From 2004−2007, he led the Grants-in-aid program in the Ministry of Education, Culture, Science, Sports, Science and Technology, Japan. He managed a project called a "Molecular Nano Dynamics" which included 86 research groups and yielded numerous results originating from the seminal works of Masuhara and his co-workers. This active team of excellent researchers conducted advanced studies to develop new methodologies of time- and space-resolved measurements of chemical reactions of inhomogeneous systems, including single living cells, solid−liquid interfaces, catalysts, and molecular crystals. Various methodologies clarifying reactions not only in the time domain but also as a function of position, have been developed and will contribute not only to chemistry but also to scientific instrumentation, and materials and life sciences.

After retiring from Osaka University in March 2007, Masuhara continued doing research with lasers (especially in the area of bio/nano science), at the National Chiao Tung University in Taiwan and the Nara Institute of Science and Technology.

In recognition of his scientific achievements Professor Masuhara has received many awards including, the Vinci d'Excellence Trophy in the LVMH Moet Hennessy-Louis Vuitton Science for Art Competition in 1993, the Award of Chemical Society of Japan in 2006, the Porter Medal in 2006, Doctor Honoris Causa de Ecole Nomale Superier de Cachan, France in 2006, and the Purple Ribbon Medal from the Japanese Government in 2008. He also serves as a Foreign Member of Royal Flemish Academy of Belgium for Science and the Arts since 1998 and as an IUPAC Fellow since 2007. He has not only contributed to physical chemistry and photochemistry but also participated in several associations, editorial boards of journals such as *J. Phys. Chem.* (1999−2004) and organized many international conferences.

During his academic carrier, Masuhara has trained 37 Ph.D students and 84 Master students. Moreover more than 50 doctors from his research group are now working in universities and National Institutions around the world.

It has been an honor for us to be included among the friends, colleagues, and students of Hiroshi Masuhara. We dedicate this special issue of The *Journal of Physical Chemistry C* to him with great pleasure.

Paul F. Barbara
University of Texas at Austin

Johan Hofkens
Katholieke Universiteit Leuven

Hiroaki Misawa
Hokkaido University

Kei Murakoshi
Hokkaido University

Hiroshi Miyasaka
Osaka University

Curriculum Vitae of Hiroshi Masuhara

Education

Ph.D., in chemistry, Osaka University (1971) with Noboru Mataga

Mc.D., in chemistry, Tohoku University (1968) with Masao Koizumi

B.A., in chemistry, Tohoku University (1966)

Academic Nominations

Chair Professor, National Chiao Tung University (2008 to present)

Appointed Guest Professor, Nara Institute of Science and Technology (2008 to present)

Chief Scientist, Hamano Life Science Research Foundation (2007-2008)

Professor Emeritus, Osaka University (2007 to present)

Professor, Osaka University (1991-2007)

Director of Masuhara Microphotoconversion Project, Exploratory Research for Advanced Technology Program, Research and

Development Corporation of Japan (1988-1994)

Professor, Kyoto Institute of Technology (1984-1991)

Research Associate, Osaka University (1972-1984)

Postdoctoral Fellow, Osaka University (1971-1972) with Noboru Mataga

Guest Academic Nominations

2008 Guest Professor, Ritsumeikan University

2007-present Guest Professor, Osaka University

2007-2009 Guest Professor, Kwansei Gakuin University

2006-present Guest Professor, Technical Institute of Physics and Chemistry, Chinese Academy of Science

2006 Guest Professor, University of Paris 6 (Universite Pierre & Marie Curie), France

2005 Guest Professor, Ecole Normale Superier (Paris), France

2004 Guest Professor, National Yang-Ming University, Taiwan

2002 Guest Professor, Katholieke Universiteit Leuven, Belgium

2000-2002 Guest Professor, Nagoya University

1998-2000 Guest Professor, Ecole Normale Superier (Cachan), France

1995 Guest Researcher, National Institute of Materials and Chemistry

1994-1999 Guest Researcher, Japan Atomic Energy Research Institute

1994 Guest Professor, Katholieke Universiteit Leuven, Belgium

1993-1999 Fundamental Research Advisor of JRDC/JST, Japan

1991 Guest Professor, Tohoku University

1986 Summer Faculty Fellow, IBM Almaden Research Center, USA

1985 Guest Professor, Tokyo Institute of Technology

1981 Visiting Scholar, Katholieke Universiteit Leuven, Belgium

Awards

2008 Outstanding Scholar Award (Foundation for the Advancement of Outstanding Scholarship, Taiwan)

2008 The Purple Ribbon Medal (Japanese Government)

2007 IUPAC Fellow

2006 Doctor Honoris Causa de Ecole Nomale Superier de Cachan, France

2006 Spectroscopic Society of Japan Award

2006 Porter Medal

2006 The Chemical Society of Japan Award

2005 Optical Industrial Technology Development Association: Kenjiro SAKURAI Memorial Award

1998 Foreign Member of Royal Flemish Academy of Belgium for Science and the Arts

1994 Osaka Science Prize

1994 Divisional Award of the Chemical Society of Japan

1993 Moet Hennessy Louis Vuitton International Prize “Science for Art” Excellence de Da Vinci, France

1989 Japanese Photochemistry Association Award

Honors

2007 to present Committee Member of INPAC Program, Katholieke Universiteit Leuven

2007 to present IUPAC fellow

2003 Committee Member of Nano Program, Royal Dutch Academy

2002-2004 President of Asian and Oceanian Photochemistry Association

2000-2001 President of Japanese Photochemistry Association

1998-2001 Member of IUPAC Photochemistry Commission

1997-2001 Executive Committee Member of Japanese Applied Physics Society

1992-1995, 1998-2000 Executive Committee Member of Japanese Photochemistry Association

1996 to present Committee Member of IUAP Program, Belgium

Editorial Boards

J. Photochem. Photobiol. A. Chem. (Asian Editor, 1997 to present)

*J. Photochem. Photobiol. C. Photochem. Re*V. (Associate Editor, 2000-2004, Editorial Board 2005 to present)

Chem. Rec. (2007 to presesnt)

Bull. Chem. Soc. Jpn. (2005 to present)

Acc. Chem. Res. (2003-2007)

ChemPhysChem (2000 to present)

J. Phys. Chem. (1999-2004)

Phys. Chem. Chem. Phys. (1999-2002)

J. Photosci. (1997-2006)

Sci. Prog. (1997 to present)

*Re*V. *Laser Eng.* (1994-2002)

Laser Chem. (1993-1996)

Res. Chem. Intermed. (Guest Editor, 2001)

Mol. Cryst. Liq. Cryst. (Guest Editor, 1997)

J. Photochem. Photobiol. A. Chem. (Guest Editor, 1996)

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