My Scientific Journey and Colleagues

From Nanosecond Photochemistry to Optical Force Chemistry

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Hiroshi Masuhara
National Yang Ming Chiao Tung University,
1001 Ta Hsueh Rd., Hsinchu 30010, Taiwan
E-mail: masuhara@masuhara.jp

ABSTRACT

Laser was invented in 1960 and soon introduced to chemistry research. We started time-resolved spectroscopy and photochemistry and initial trial was focused to nanosecond and then picosecond electronic absorption spectroscopy for studying molecular electronic excited states, charge separation in molecular complexes, and intermolecular electron transfer in solution. We considered that not only time-resolved but also space-resolved chemistry would be important for future laser-based chemistry and combined pulsed lasers with optical microscopes. Further we shifted from micro to nano and opened a new field of laser nanochemistry consisting of spectroscopy, manipulation, crystallization, and ablation of organic molecules, proteins, nanoparticles, and so on. Then we have explored many chemical phenomena induced by laser irradiation at solution surfaces, which has opened a unique seminal study on optical force chemistry.

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1. Starting Chemistry in Sendai, Japan

I entered Tohoku Univ. in 1962 and joined the laboratory of Prof. Masao Koizumi (Late Emeritus Prof. of Tohoku Univ.) of Physical Chemistry and Photochemistry in the fourth year of undergraduate. I think the reason why I participated in the Lab of Prof. Koizumi was that I was trying to read “The Nature of the Chemical Bond” written by Linus Pauling and translated into Japanese by Prof. Koizumi, and his large book “Survey of Photochemistry” (Figure 1). At that time, Profs. Tetsuo Nozoe and Koji Nakanishi were two giants in organic chemistry in Tohoku Univ. and had a strong presence in the field of Natural Products Chemistry. However, I thought that_the intermediate between physics (research on the theory of things) and chemistry (research on the abundance of things) was very interesting, and it fitted me. That is the reason I choose physical chemistry and I felt Prof. Koizumi was a sincere scientist and real gentleman, However, his research life was more than what I, a vague young man, had thought. Every morning, he walked from his home in Yagiyama to the Faculty of Science in Katahira and worked on a well-defined schedule, while he sometimes rushed to the toilet with his shirt outside on his back. I remember, like as if it were just yesterday, that I had a strong impression from him about what research is and what research life is.

After that, I went on to a doctoral program at the Faculty of Engineering Science, Osaka Univ., and decided to try to get a Ph.D. degree under the supervision of Prof. Noboru Mataga (Late Emeritus Prof. of Osaka Univ.). That was in 1968. In front of the nanosecond ruby laser installed in that year, Prof. Mataga told me, “Lasers will replace all light sources in the future, and photochemical research using lasers will have unlimited possibilities.” I was so excited with his words. I became the first graduate student at Mataga Lab who obtained a degree in laser-based research. My first work was to oscillate a nanosecond ruby laser stably. I realized I could be awarded to Ph.D. if I could write papers unique to nanosecond lasers. So, I was very free to choose a theme. At this time, I think that I enjoyed the real (true) fun of exploratory research. Since then, I have been studying molecular systems unique to lasers and working in the so-called interdisciplinary area, belonging to the departments of chemistry, synthetic chemistry, polymer science, applied physics, life science, materials science, and applied chemistry. However, my research has been consistently laser-based molecular science and photochemistry. I think that there is no other field that enables pioneering research and the real thrill of physics and chemistry as much as physical chemistry.

In 2021 I turned 77 years old. I am still conducting exploratory research using lasers and microscopes at the National Yang Ming Chiao Tung Univ. (NYCU) in Hsinchu, Taiwan.

Figure 1

(Left) L. Pauling, “The Nature of the Chemical Bond”

(Translated to Japanese by M. Koizumi), Kyoritsu Shuppan, Tokyo, **1962**

(Middle) M. Koizumi, “Survey of Photochemistry” (in Japanese), Asakura Shoten, Tokyo, **1963**

(Right upper) N. Mataga, “Introduction to Photochemistry” (in Japanese), Kyoritsu Shuppan, Tokyo, **1975**

(Right lower) N. Mataga, T. Kubota, “Molecular Interactions and Electronic Spectra”, Marcel-Dekker, **1970**

2． Dye Photochemistry and Flash Photolysis Method at Koizumi Lab, Tohoku University (1965-1968)

Japanese lost many things during the World War II and we started almost from zero. I heard that Prof. Koizumi considered on critical energy problem of future Japan, as we had and have no natural resource, and decided to study photo-oxidation and reduction reactions of dye molecules aiming solar energy utilization. In 1965 when I joined his laboratory, two methods were introduced and utilized to identify photochemical intermediates directly; one was rigid matrix isolation method and the other was flash photolysis method. The former method was carried out with ESR spectroscopy by Prof. Michio Okuda (Late Director of the Inst. of Environmental Science, Environment Agency, Japan) and Dr. Shigeru Niizuma (Emeritus Prof. of Iwate Univ.). Prof. Okuda gave me the theme of stably capturing and spectroscopy of the pi-radical of the dye intermediate and assigning its electronic absorption spectrum. At that time all computer programs calculating for molecular electronic structure and electronic transition must be developed by ourselves. Nobody in the Department of Chemistry in Sendai had any experience in molecular electronic structure calculation at that time. Learning a lot from the books and reviews written by Saburo Nagakura, Kenichi Fukui, and Haruo Hosoya groups and being helped by Yuji Mori, Kichisuke Nishimoto, and Shigeyuki Aono. develop a program for calculating the open-shell electronic structure of the Pariser-Parr-Pople method. I truly understood my situation and high potentiality of the Nagakura and the Fukui Groups in the theoretical chemistry in Japan. Then, while saying that the middle of physics (research on the theory of things) and chemistry (research on the abundance of things) is interesting, I wanted to shift toward the study of abundance of things.

The second method of flash photolysis was made possible by utilizing home-made flash lamp and pulse circuit using vacuum tubes. In 1959, Drs. Shunji Kato (Late Emeritus Prof. of Osaka Univ.), Kengo Uchida (Emeritus Prof. of Hirosaki Univ.) and Masao Koizumi reported the first transient absorption spectra of dyes intermediates

in Nature[1] In the flash photolysis where the first flashlight forms excited states of dyes and the second flashlight monitors the induced photoreaction. It was proposed by Late Dr. Ronald George Wreyford Norrish and Late Dr. George Porter in England during the Second World War much long before the 1960s when the laser was born (Figure 2), and they were awarded the Nobel Prize in 1967 together with Late Dr. Manfred Eigen, the developer of the stopped flow method. In late 1960' Dr. Yoshiharu Usui (Emeritus Prof. of Ibaragi Univ.), Mr. Akira Kira (Emeritus Researcher of RIKEN, Former Director of Japan Synchrotron Radiation Research Inst. (JASRI)), Mr. Masaharu Morita (Late Prof. of Matsumoto Dental College), and Mr. Koichi Kikuchi (Emeritus Prof. of Kitasato Univ.) were engaged in the flash photolysis studies. It was developed to a luminescence-absorption-flash method (named by Prof. Koizumi),[2] which was a simultaneous measurement of delayed fluorescence and absorption. According to Dr. Keitaro Yoshihara (Emeritus Prof. of Inst. for Molecular Science),[3] the flash photolysis system was in operation in the Laboratory of Prof. Saburo Nagakura (Late Emeritus Prof. of the Univ. of Tokyo, Former director of Inst. for Molecular Science) at the Inst. for Solid State Physics, the Univ. of Tokyo, led by Dr. Hiroshi Tsubomura (Late Emeritus Prof. of Osaka Univ.) in 1966. In the early days, time-resolved spectroscopy was technically possible only for the molecular electronic spectral measurement in the visible wavelength, although it is now commonplace in all wavelength regions from X-rays to terahertz spectroscopy.

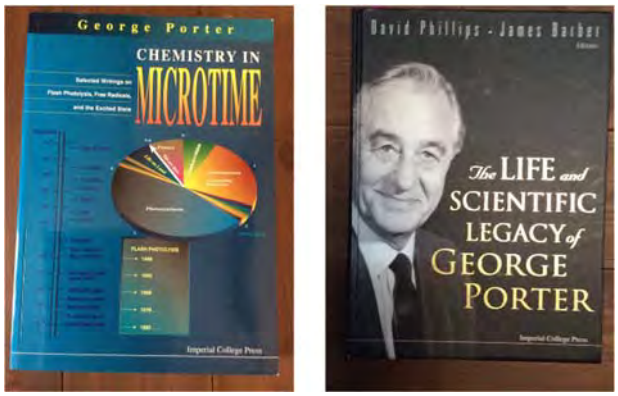

Figure 2

(Left) G. Porter, "Chemistry in Microtime: Selected Writings on Flash Photolysis, Free Radicals, and the Excited State", Imperial College Press, London, **1977**

(Right) D. Phillips, J. Barber, "The Life and Scientific Legacy of George Porter", Imperial College Press, London, **2006**

3. Nano-picosecond Laser Photochemistry at Mataga Laboratory, Osaka University (1968-1984)

Prof. Mataga became a Professor of the newly established Faculty of Engineering Science of Osaka University when he was already known worldwide as the proposer of the Mataga-Lippert formula[6] and the Mataga-Nishimoto approximation[7] at that time. Two reports on these works were later cited in Iwanami's "50 Years of Japanese Scientific Papers" (Iwanami Shoten, Publishers.),[8] which summarizes typical postwar research examples. In addition, Prof. Mataga published a famous paper in 1968 that proposed the concept of molecular ferromagnetism. [9] I consider these three papers the most notable works by Prof. Mataga before entering the brilliant laser photochemistry era. A little bit later two books on the state and photochemistry of molecules were written by Prof. Mataga and published (Figure 1).

In 1968 I started working as a Ph.D. student at the Mataga Lab after obtaining the Master Degree from the

Koizumi Lab. My work was to operate the laser and enable the nanosecond time-resolved spectroscopy first in Japan. I started experimenting with making and running the equipment from scratch. We managed to operate a ruby laser to measure nanosecond transient absorption spectra while learning vacuum tube circuits from Mr. Tadashi Okada (Emeritus Prof. of Osaka Univ.). After that, a picosecond ruby laser was introduced to the Mataga Lab. by Mr. Nobuaki Nakashima (Emeritus Prof. of Osaka City Univ.). These ruby lasers could oscillate every 3 min, we adjusted the optical system without a viewer to look at the beam, and we measured absorption spectra using photographic film and ran into a dark room for developing the film. After that, we could know whether or not it worked well, and we performed this procedure for more than 10 hours every day.[13] However, Windsor, Albrecht, and Porter et al. had internationally reported the development of the spectroscopy, so that we chose charge transfer and electron transfer molecular systems as the target, that is, Mataga's specialty. Their fluorescence is wide covering all the visible wavelength and it was not easy to measure the absorption spectra of the fluorescent state. Proposing re-absorption method, we successfully measured a S_1-S_n absorption of charge-transfer complex of s-tetracyanobenzene and toluene, and proved that its excited-state absorption is very similar to the anion of the electron acceptor s-tetracyanobenzene.[10] We were surprised to see that Michael Ottolenghi also reported the similar spectra in the same volume of Chem. Phys. Lett. in 1970. This direct indication that the excited state of charge transfer complex is an electronic state similar to an ion pair received much attention, and the result became one of the topics at that time.

Sincere discussion was extended in Japan and abroad, including exciplexes that form a charge-transfer complex only in an excited state. (At the time, it was called hetero-excimer at the Mataga Lab, while excimers were formed for the same molecules). Mataga considered that electronic structure of donor-acceptor system is determined by interaction with solvent and the charge transfer degree gradually changing depending solvent polarity. Albert Weller proposed that the electron transfer and non-radiative relaxation compete with each other and its ration depends on solvent polarity. This discussion was developed from initial intermolecular to intramolecular systems, namely, twisted intramolecular charge transfer dynamics. I remember there were sometimes intense debates among N. Mataga, S. Nagakura, A. Weller, M. Ottolenghi, Z. Grabowski, K. Zachariasse, Frans C. De Schryver, J. Verhoeven, W. Rettig, T. Okada, N. Nakashima, S. Iwata, H. Hayashi, T. Kobayashi et al.[11,12]

In the early 1980s, we were able to install a Nd^{3+}: YAG laser at Mataga Lab with Kakenhi (JSPS) grants. With the laser oscillating at 10 Hz, streak cameras and diode array detectors, we were a bit relieved that we had finally reached some level in front of these modern advanced laser systems. Its optical set up for picosecond transient absorption spectroscopy,[14] was introduced as a representative in the textbook written by Fleming.[15] Many researchers not only in physical chemistry but also in organic chemistry, polymer chemistry, photobiology, and solid state physics highly evaluated the research of the electron transfer dynamics and the excited state dynamics of charge transfer complexes. They developed collaborative studies with Mataga Lab. I realized that something between physics (research on the theory of things) and chemistry (research on the abundance of things) is so attractive. I think Prof. Mataga has just proved this proverb: the peach and the plum do not speak and try hard to appeal to people, yet a path is born beneath them because of their flower and fruit.[16]

Prof. Mataga did not say anything about my research trial, but when I came to his office with the data, Prof.

Mataga always discussed them with me for hours. After explaining and discussing the experiment results, I had more time to talk with Prof. Mataga about what to do next and what might be the future of this research. Prof. Mataga was often silent for a while. Still, on the other hand, the conversation with Prof. Mataga flourished, and I was sometimes moved to tears. I think that this discussion-style with the manuscript that was turned red by Prof. Mataga became the basis for my research life. His seminal work was highly evaluated and he was awarded the Purple Ribbon Medal in 1995, Porter Medal in 1996 (Figure 3), Japan Academy Prize in 2006, and many others.

Separately from Mataga's charge transfer and electron transfer studies, I had not found a possible subject enough convincing me. I studied photochemistry using a laser of the micellar solution and polymer solution, considering the development to a higher-order assembly system. However, Prof. Mataga had written about six papers in that direction in the mid-1950s while working at Koizumi Lab at Osaka City Univ. I felt I was on the palm of a giant. I thought that studying the excited state dynamics and reactions of solid molecular systems using time-resolved reflection spectroscopy with a pulsed laser would be a good idea. I tried total internal reflection fluorescence spectroscopy of organic thin films, and my funding on the application on this method was approved, making my feeling positive.

Figure 3

Profs. Noboru Mataga and George Porter at IUPAC Symposium on Photochemsitry in Helsinki in 1996.

Prof. Mataga (left) was awarded the Porter Medal directly from Prof. Porter (right). The photo was taken by Prof. Iwao Yamazaki (Emeritus Prof. of Hokkaido Univ.).

4. Time-resolved Reflection Spectroscopy of Organic Solids at Kyoto Institute of Technology (1984-1991)

I was appointed a Prof. of the Department of Polymer Science, Faculty of Textile Science, Kyoto Inst. of Tech., which was reorganized in April 1984. I started studying polymer solids by time-resolved solid-state spectroscopy. Since I could buy a nanosecond excimer laser, I used this laser to come up with many student themes. I asked Profs. Iwao Yamazaki and Keitaro Yoshihara of the Inst. for Molecular Science to conduct collaborative research for single-photon counting fluorescence spectroscopy and picosecond transient absorption spectroscopy, respectively. I asked them to allow us to use their lasers. As a young Prof. at a local university, I was very grateful to have collaborated with the Inst. for Molecular Science. Furthermore, Inst. for Molecular Science could afford to pay for our experiments and travel expenses. It was impossible to follow up with the development of transient

absorption spectroscopy to picoseconds and femtoseconds with my research funding. Also, I could not compete with the laboratories by Profs. Saburo Nagakura, Noboru Mataga, Ikuzo Tanaka, and Keitaro Yoshihara. So, I decided to shift more and more towards the study of the abundance of things between physics (research on the theory of things) and chemistry (research on the abundance of things). In the summer of 1985, Dr. Hiroyuki Hiraoka of the IBM (IBM Almaden Research Center) in the United States invited me as a Summer Faculty Fellow for three months, recommended by Prof. Haruo Shizuka (Emeritus Prof. of Gunma Univ.). I thought that I could study anything freely, so I decided to try a spectroscopic study of polymer laser ablation as new nonlinear photochemical processes for my future. Ablation itself was famous in Japan for the work of Dr. Susumu Namba (Late Emeritus Researcher of RIKEN and Late Emeritus Professor of Osaka University). R. Srinivasan of the IBM (IBM Thomas J Watson Research Center) wrote a famous paper in 1982. Many researchers have been working on developing optical lithography techniques, but there had been no fundamental examinations of the molecular or electronic aspects. During my stay at IBM, I studied the ablation of polymer films doped with aromatic molecules that could lead to spectroscopic research. I posted the results to Prof. Mitsuo Ito (Late Emeritus Prof. of Tohoku Univ.),[17] who was editing Chem. Phys. Lett. I wondered if this was not physical chemistry and would be refused by Prof. Ito. However, he accepted this as being new physical chemistry. I think that my research attitude may have been more conservative if Prof. Ito refused at that time. At Kyoto Inst. of Tech., Prof. Akira Itaya (Emeritus Prof. of Kyoto Inst. of Tech.), Dr. Noriaki Ikeda (Emeritus Prof. of Kyoto Inst. of Tech.), and Dr. Hiroshi Fukumura (Emeritus Prof. Tohoku Univ.) greatly assisted me for developing research on time-resolved reflection spectroscopy and ablation dynamics.

5. Laser Microchemistry at Masuhara ERATO Project, JST (1988-1994)

In 1984, JST (at that time, Research Development Corporation of Japan (JRDC)) invited me to apply for research supervision of the Exploratory Research for Advanced Technology (ERATO) project, which aims to create new science and technology. Because they are hoping for “picosecond chemistry” and preparing their budget, they suggested me to write such a proposal. I argued with them that although raising the time resolution from picosecond to femtoseconds was necessary, already being challenged. I did not think this could be an exploratory subject for creative science and technology trials. I proposed to pursue the “Microphotoconversion” project aiming at reaction control. To start from the research of spectroscopy and photochemistry using a microscope, it was common knowledge at the time to adopt a micrometer for spatial resolution, and microchemistry using a laser and a microscope was an issue for the project. The chief coordinator of the council to decide who should be the ERATO Project leaders and promote the research was Prof. Saburo Nagakura, and later replaced to Prof. Ikuzo Tanaka (Emeritus Prof. of Tokyo Inst. of Tech., Former president of Tokyo Inst. of Tech.). With the understanding and support by these two Profs., I significantly advanced my research. I was given two billion JPY research funds and was able to hire 15 postdocs in five years. It was an exceptional project. Also, I was asked to get a research place outside the university. Researchers of our project were a full-time researcher and could not concurrently hold other jobs. At that time, excellent researchers such as Profs. Junichi Nishizawa, Tsuyoshi Masumoto, Osamu Hayaishi, and Chikara Hayashi were the leaders. On the other hand, I was only 44 years old and had been studying fundamental research fields until then. It was like walking in the dark. My ERATO research begun with young researchers such as Noboru Kitamura (at that time, Assistant Prof. at Tokyo Inst. of Tech., present Emeritus

Prof. of Hokkaido Univ.), Hiroaki Misawa (at that time, Assistant Prof. of Tsukuba Univ., present Prof. of Hokkaido Univ.), Keiji Sasaki (at that time, Assistant Prof. of Tokushima Univ. present Prof. of Hokkaido Univ.), Naoto Tamai (at that time, Assistant Prof. of Hokkaido Univ., present Prof. of Kwansei Gakuin Univ.), Nobuyuki Ichinose (Prof. of Kyoto Inst. of Tech.), and U. Pfeifer-Fukumura (Prof. of Univ. of Applied Sciences Wiesbaden). Drs. Hiroyuki Sugimura (Prof. of Kyoto Univ.), Kiyoharu Nakatani (Prof. of the Univ. of Tsukuba), Nobuyuki Ichinose (Prof. of Kyoto Institute of Technology), Atsushi Sekiguchi (Kogakuin Univ.), Tatsuya Uchida (Prof. Tokyo University of Pharmacy and Life Sciences), Kenji Kamada (Senior Researcher of AIST), Sanyo Hamai (Akita University), Nobuo Shimo (Idemitsu Kosan Co.,Ltd.), Masatoshi Yanagimachi (Mitsui Chemicals, Inc.), and Seiji Funakura, (DIC Corporation) were also tremendous. They contributed very much to our project.

The results of this Masuhara ERATO Microconversion project include the development of a three-dimensional spatial and time-resolved spectroscopy system, the development of transient grating diffraction spectroscopy, the spectroscopy and photochemistry of single micrometer microparticle, the solid/solid and solid/liquid interface layers. Characterization, electrochemistry of single microdroplets, electrochemistry on microarrays, dynamics of photoresponsive polymer microgels, optical assembly, and optical drive of microparticle structures were also topics. To develop a method to create a field that makes these possible, we also worked on surface micromachining and modification by laser, electrochemical surface micromachining by scanning microscope, and micropatterning by CVD. The research on space- and time-resolved chemistry, which is now a major trend, using a combination of laser and microscope began with our ERATO project. A series of achievements was published in Japanese in 1993 and English in 1994, respectively, as the world's first books entitled "Microchemistry" (Figure 4). Since then, many researchers around the world have followed us. We pride ourselves on being ahead of microchemistry flow as a new area of science and technology along with microelectronics, micromachines, and microoptics. To confirm this research results, we organized an international conference on microchemistry in Brussels in 1993 with excellent cooperation by Prof. Frans C. De Schryver. Profs. G. Whiteside (Harvard), M. S. Wrighton (MIT), A. J. Bard (Texas Austin), J. Klafter (Tel Aviv), R. Srinivasan (IBM), D. D. Dlott (Illinois), Ikuzo Tanaka, Kenichi Honda (Late Professor of Univ. of Tokyo), et al. presented their advanced progress and supported this organization. We could launch a new research stream of time- and space-resolved chemistry to the world.

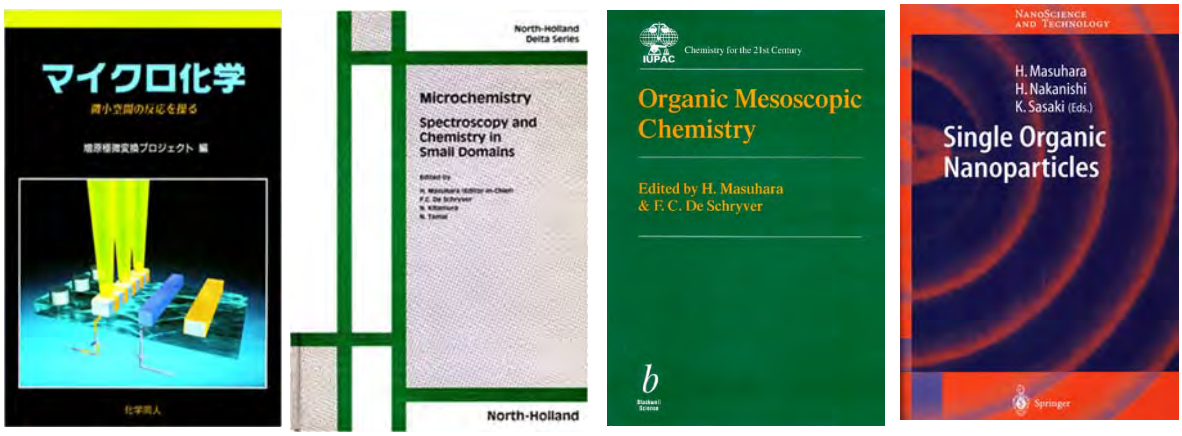

Figure 4

(Left) H. Masuhara, N. Kitamura, H. Misawa, N. Tamai, K. Sasaki, “Microchemistry” (in Japanese), Kagaku Dojin, Kyoto, 1993

(Middle left) H. Masuhara, F. C. De Schryver, N. Kitamura, N. Tamai (Eds.), “Microchemistry: Spectroscopy and Chemistry in Small Domains”, North Holland, 1944

(Middle right) H. Masuhara, F.C. De Schryver (Eds.), “Organic Mesoscopic Chemistry (IUPAC 21st century chemistry monograph)”, Blackwell Science, 1999

(Right) H. Masuhara, H. Nakanishi, K. Sasaki (Eds.), “Single Organic Nanoparticles”, Springer, 2003

6. Laser Nanochemistry at Osaka University (1991 – 2007)

During the development of ERATO research, Prof. Shigeo Minami of the Department of Applied Physics, Osaka Univ., invited me to have a laboratory there. I again thought that between physics (research on the theory of things) and chemistry (research on the abundance of things) was interesting. Still, I was hesitant about whether I could live in the Department of Applied Physics. When I looked at departments at major universities across Japan, there were some instances where physicists moved to the chemistry department. I could not find any cases where chemists became Professors in the physics department. The Department of Applied Physics of Osaka Univ. was known to be strong in optics and microscopy. Profs. Yoshiki Ichioka and Shinichiro Nakajima (both Emeritus Prof. of Osaka Univ.) were there in addition to Prof. Minami (Emeritus Prof. of Osaka Univ.). If I moved to Osaka University, my lab would be the fourth lab related to light. Prof. Satoshi Kawata (Emeritus Prof. of Osaka Univ.) was an Assistant Prof. of Prof. Minami’s laboratory at that time, while he was already prominent. If I participated, the laboratory's name in charge was Applied Physics 2nd Laboratory “Applied Optics/Applied Spectroscopy.” The lecture in charge was “Analytical Instruments and Applied Spectroscopy”. Prof. Hiroshi Yoshinaga, who started this course during the 2nd World War, was an authority on far-infrared spectroscopy and had been collaborating on amino acids with Profs. Sanichiro Mizushima and Akiko Hirakawa of the Univ. of Tokyo.[18] His research results had been known around the world. Also, Prof. Minami said, “Applied physics is changing rapidly. Many people are now studying physics and spectroscopy of semiconductors, but in the future, research on the organic matter using lasers will become the mainstream.” Before that, I remembered many research stories by Profs. Koichi Shimoda, Shigeo Shionoya, Susumu Namba, Chiyoe Yamanaka, Tatsuo Yajima, et al. through the laser conferences and workshops. There were in principle physicists but show their deep understanding on chemistry and materials. The spirit of exploration and research had since revived within me, and I decided to move to the Department of Applied Physics. I thought it was an opportunity to explore new research by putting myself in a different environment from others.

In the ERATO project, we studied microchemistry. On the other hand, we developed laser-based spectroscopy and reaction in the small domains from micro to meso, and meso to nano at Osaka Univ. I wanted to open up a new research area in laser nanochemistry, which would significantly change the conventional framework of light and chemistry. Regarding the development of nanospectroscopy and the study of reaction dynamics, I continued my work focusing on time-resolved reflection spectroscopy, which had been the theme since my research at Kyoto Inst. of Tech. I have also developed femtosecond specular/regular reflection spectroscopy for solid nano surfaces and interface layers and femtosecond diffuse reflection spectroscopy for nanoparticle powders. We have

paved the way to analyze the photoreaction of a heterogeneous molecular solid system at exactly the same level as the solution. With the leadership of Assistant Prof. Hiroshi Fukumura (Emeritus Prof. of Tohoku Univ.), Mr. Musubu Ichikawa (Prof. of Shinshu Univ.), Kazuya Watanabe (Prof. of Kyoto Univ.), Akihiro Furube (Prof. of Tokushima Univ.), and Mototsugu Suzuki (the Metropolitan Police Agency) had grown up as researchers. Prof. Shuichi Hashimoto (Emeritus Professor of Tokushima Univ.) Regarding subsequent nanospectroscopy, Prof. Asahi launched a single nanoparticle spectrometer combining a microscope and AFM and clarified the correlation between the shape of the nanoparticles and fluorescence and light scattering spectroscopic data to which Dr. Victor Volkov (Prof. of Nottingham Trent Univ.) and Hideki Matsune (Prof. of Miyazaki Univ.) contributed.[19)] These data were valuable, indicating the size effect of the electronic spectrum of organic solids. At that time, graduate student Mr. Tamitake Itoh (Senior Researcher of Advanced Inst. of Science and Technology) developed the femtosecond single nanoparticle spectroscopy and clarified the relaxation dynamics of single gold nanoparticles.

In the field of nanomanipulation and photon pressure chemistry, we have systematically clarified the dynamics in which various molecular aggregates, polymers, and nanoparticles in a solution at room temperature were captured at the focal position by the optical pressure of a focused laser beam under a microscope. In the early years, Prof. Keiji Sasaki constructed a new system and started new research. Then, Mr. Hiroyuki Yoshikawa (Prof. of Hiroshima Institute of Tech.) continued Prof. Sasaki's research and presented unique results one after another under top-notch ideas and guidance. From this trend, Mr. Junichi Hotta (Prof. of Yamagata Univ.), Mr. Syoji Ito (Prof. of Osaka Univ.), Mr. Sadahiro Masuo (Prof. of Kwansei Gakuin Univ.), Mr. Yu Nabetani (Prof. of Miyazaki Univ.), Ms. Chie Hosokawa (Prof. of Osaka City Univ.), Mr. Yoshito Tanaka (Prof. of the Univ. of Tokyo) and Ms. Yuriko Matsumura from Nara Women’s University (Prof. of Tokyo Healthcare University) have grown up as professors. The seminal work of optical trapping in chemistry received much attention and Drs. Johan Hofkens (Prof. of Katholieke Universiteit Leuven (KUL)), Trevor Smith (Prof. of Univ. of Melbourne), and Dr. Pawel Borowicz (former Polish Academy of Science) joined us as postdocs, and Ms. Rachel Miallet-Renault (Prof. Univ. Paris-Saclay Univ.) and Mr. Michel Sliwa (CNRS Lille) also joined us as graduate exchange students of Ecole Normale Supérieure Cachan. Some results are included in the books in Figure 4.

Prof. Hiroshi Fukumura initially studied the dynamics and mechanism of nano laser ablation. Mr. Yasuyuki Tsuboi (Prof. of Osaka City Univ.), Mr. Hisashi Fujiwara (Prof. of Hiroshima City Univ.), Mr. Hiroshi Furutani (Prof. of Osaka Univ.), and Koji Hatanaka (Researcher, Academia Sinica, Taiwan) were the students of this group. One of nonlinear optical absorptions we proposed is cyclic multiphotonic absorption of the excited singlet state during its lifetime,[20)] which can now explain laser ablation, single molecule photoacoustic behavior, and optical resonance effect in optical trapping. After he moved to Tohoku Univ. with a student, Mr. Hiroshi Uji-I (Prof. of Hokkaido Univ. & KUL), Prof. Tsuyoshi Asahi proceeded as a leader in research on laser ablation dynamics and mechanism. Mr. Yoichiroh Hosokawa (Prof. of Nara Inst. of Science and Tech. (NAIST)) extended their research as graduate students. As a fundamental study, we proved that abrupt temperature rise in nanosecond excitation and local transient pressure in femtosecond excitation are the keys to understanding the ablation mechanism and dynamics of organic materials.[21.22)] In particular, we succeeded in clarifying the process in which the electronic excitation of molecules evolves into the ablation of solids using a femtosecond laser. I like this work very much as a bridge between physics (research on the theory of things) and chemistry (research on the abundance of

things). This result, led by Yoichiroh Hosokawa, resulted in a method that attracted widespread attention, such as non-invasive and non-destructive manipulation of living cells. Dr. Yuqiang Jiang (Chinese Academy of Science, China), Dr. Tsuyoshi Ohmoto (Private Sector), Dr. Atsushi Yamaguchi, Mr. Takahiro Kaji (Researcher of NICT), and Mr. Ryohei Yasukuni (Prof. of NAIST) have worked along this line. These achievements were also drawing attention from the bioscience field. For example. Mr. Hiroshi Yoshikawa (Prof. of Osaka Univ.) was playing an active role in femtosecond application to protein crystallization.

Laser ablation of organic crystals results in formation of fragmented crystals which are usually dispersed in vacuum chamber in air. However, we carried out nanosecond laser ablation in solution, then the ejected particles were dispersed homogeneously as they are charged more or less. We confirmed their size distribution from a few tens to a few hundreds of nanometer, namely, solution ablation is a best laboratory scale fabrication method of organic nano crystals.[19] Dr. Teruki Sugiyama (Prof. of NYCU) and Mr. Yoshiaki Tamaki (Prof. of Univ. of the Ryukyus), intensively studied the fundamental mechanism and explored the application. Based on this activity, a venture business (AB Size Co. Ltd.) was started by Dr. Isamu Oh and Mr. Sen-ichi Ryu in 2007. The application of solution laser ablation to molecular electronics was also started by Prof. Asahi and Mr. Hyeon-Gu Jeon (Prof. of Ehime Univ.) This experimental study convinces us a high potential of laser ablation in solution.

The stream of my research is often regarded as one of nanoscience and nanotechnology research. Still, nanotechnology began to gain social attention because the US President Clinton issued a textbook in 2000[23] and invested in research. Because I was heading toward nano by focusing on high potential of lasers and the research of molecular nanos with light earlier than the 2000s, I could create a unique stream as laser nanochemistry. At Osaka Univ., Profs. Satoshi Kawata, Toshio Yanagida, and Tomoji Kawai were playing leading roles in the world of nanoscience and nanotechnology. On the other hand, I could demonstrate my uniqueness by focusing on lasers and molecular systems. Prof. Kawata and I organized a series of Meetings on Nanophotonics, demonstrated high activity of Department of Applied Physics, Osaka University in 2004-2006, and published their proceedings (Figure 5). Also based on these achievements, I organized a JSPS research project named "Molecular Nano Dynamics" with Profs. Hiroyasu Iwasawa, Masahiro Irie, Kohei Uosaki, and Hiroshi Fukumura, and worked with many researchers. Fortunately, I was able to summarize those three years' activities as "Molecular Nano Dynamics" (Figure 5). For celebrating my activity, a special issue for my 60 years birthday was edited by Profs. Frank Wilkinson and Hiroshi Fukumura, and published in Photochem. and Photobiol. Sci. in 2005.These research developments had been evaluated, and Prof. G. Schatz, P. Kamat, Editor-in-Chief of J. Phys. Chem. invited Profs. P. F. Barbara, J. Hofkens, Kei Murakoshi, Tsuyoshi Asahi, Hiroshi Miyasaka, and Hiroaki Misawa as Guest Editors, and published my Festschrift in December 2009 (Figure 6). I read J. Phys. Chem. at Chemistry Department of Tohoku Univ. in Sendai Katahira campus during my master's degree in 1960’s. At that time, I wondered if I could submit a paper to this journal in the future. I clearly remembered that time.

Figure 5

(Upper) H. Masuhara, S. Kawata (Eds.), "Nanophotonics", Elsevier, **2004**

S. Kawata, H. Masuhara (Eds.), "Nanoplasmonics: From Fundamentals to Applications", Elsevier, **2006**

H. Masuhara, S. Kawata, F. Tokunaga (Eds.), "Nano Biophotonic: Science and Technology", Elsevier, **2007**

(Lower) H. Fukumura, M. Irie, Y. Iwasawa, H. Masuhara, K. Uosaki (Eds.), "Molecular Nano Dynamics Vol. 1 & 2", VCH-Wiley, Berlin, **2009**

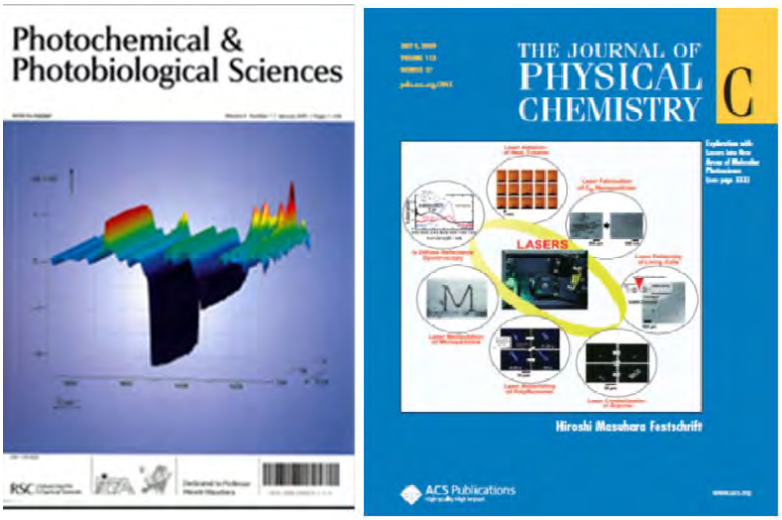

Figure 6

(Left) H. Fukumura, F. Wilkinson, "Special Issue of Life and Research of Prof. Hiroshi Masuhara", Photochemical and Photobiological Sciences, Royal Society of Chemistry, **2005**, 4, 1-164.

(Right) P. F. Barbara, J. Hofkens, H. Misawa, K.Murakoshi, T. Asahi, and H. Miyasaka, "the Hiroshi Masuhara Festschrift: Exploration with Lasers into New Areas of Molecular Photoscience", J. Phys. Chem. C, American Chemical Society, **2009,** 113 (27), 11425-11974

7. Optical Force Chemistry at National Yang Ming Chiao Tung University, Taiwan (2008-present)

Fortunately, even after retirement, I have been developing my research activities by holding a laboratory. In 2007, I established the Laser Bio-Nano Science Laboratory in the 21 Life Science Research Inst. of the Hamano Life Science Research Foundation in Kobe, together with Drs. Yoichiroh Hosokawa, Teruki Sugiyama, Takayuki Uwada (Prof. of Josai Univ.), Kazunori Okano (NAIST) and others. Since the foundation set up a three-year donation course at the Graduate School of Material Science of NAIST in 2008, we all moved to Nara. Although it was relatively a short term, we succeeded in demonstrating laser trapping-induced crystallization in 2007. In Nara, Drs. Ken-ichi Yuyama (Osaka City Univ.), Yasuyo Maezawa (private sector), and Takanori Iino (private sector) graduated the Ph D. course of NAIST. At the same time, Prof. Y.-P. Lee of NCTU offered me a laboratory with two staffs. I accepted his offer and was assigned with Drs. Atsushi Miura (Prof. of Hokkaido Univ.) and Takayuki Uwada. Regarding these assignments, I am very grateful to Prof. Soji Tsuchiya (Emeritus Prof. of the Univ. of Tokyo). At the School of Science of NCTU, famous Japanese Profs. Takayoshi Kobayashi and Hiro-o Hamaguchi had their labs. Also, Profs. M.-C. Lin and S.-H. Lin had shifted from the USA, participated in research activities, and cooperated to globalize NCTU. Following them, Profs. Hiroki Nakamura (the Inst. for Molecular Sciences), Koichi Narasaka (the Univ. of Tokyo), Hiroyuki Matsui (the Univ. of Tokyo), Nobuhiro Ohta (Hokkaido Univ.), Ilhyong Ryu (Osaka Prefecture Univ.), Yoshito Tobe (Osaka Univ.), Yasuki Endo (the Univ. of Tokyo), and Takayuki Ebata (Hiroshima Univ.) joined there.

NCTU and Prof. Lee have been allowing me do my research freely without placing any orders for my research subjects. Furthermore, like the Japanese course system, one laboratory was started to create a research team consisting of one Professor, one Associate Professor, and one Assistant Professor. Under that condition, the successive presidents of NCTU also allocated me special budgets to buy new instruments and devices. I think my laboratory is now one of the most cohesive laboratories globally, with a theme focused on optical force chemistry. In addition to numerous CW lasers and femtosecond lasers, seven microscopes and their associated optics are located on five vibration isolation tables. When I arrived in 2008, it had already been decided that the donation course at NAIST would end after 2011. Therefore, I developed my original research in Taiwan while proceeding research of the same theme at the same time both in Japan and Taiwan, which was extremely efficient to start bridging Japanese and Taiwanese collaboration.

The first theme is related to "bio-application of lasers", especially with a femtosecond laser. This research topic was initially developed in my laboratory in Osaka University, developed in NAIST, and partly shifted to NCTU. Prof. Fu-Jen Kao of National Yang-Ming Univ. strongly supported us in Taiwan. Femtosecond laser irradiation produces bubbles and causes the local convection flow and shock waves due to the multiphoton absorption, which was successfully applied to amyloid fibril formation of insulin, which was demonstrated by Mr. Tsung-Han Liu (Prof. of Kwansei Gakuin Univ., Japan). More extensively this bubbling phenomenon is utilized to manipulate the single cell in solution. Since the cells are not illuminated directly by light, they do not undergo photo decomposition, which is extremely useful for manipulating bio-samples. First, proteins and macromolecules are patterned on a glass substrate. Then heterologous cells are arranged with a femtosecond laser one by one while manipulating them in a non-contact and non-destructive manner. Dr. Okano joining us in Taiwan from NAIST

demonstrated a research approach to measure various functions of cells using the spatial arrangement. Based on this, we finally set the goal of producing biosensors and biodevices in which living cells are placed. Based on these results, we were able to summarize a review on our progress in NCTU in J. Photochem. Photobiol. C.[24)]

The second theme is the study of “molecular crystallization by trapping at the solution surface”. In 2007, Prof. Sugiyama and Prof. Takuji Adachi (currently Prof. of Univ. of Geneva) succeeded in molecular crystallization with trapping for the first time in the world. This crystallization is commonly observed when amino acids are optically captured at the solution surfaces. More interestingly, we found that even unsaturated solutions crystallize.[25)] The optical force acts in the space where the light is focused and irradiated, and the molecules gather and crystallize even under unsaturated solution conditions. We have proposed a mechanism in which focused trapping light is scattered by the crystals. The scattered light causes the molecules to assemble and grow at the crystal edge even though it is an unsaturated solution. Ms. Jing-Ru Tu, Mr. Chi-Shiun Wu, and Mr. Gino George (Indian Institute of Science Education and Research, Mohali, India) joined this study. It was in 2013 that Dr. Kenichi Yuyama was able to demonstrate that idea directly. Recently, Prof. Sugiyama has been developing this molecular crystallization research for introducing plasmons to lower the threshold of laser power required for crystallization, arranging gold nanostructures in a chiral manner for chiral crystallization, controlling crystal morphologies.[26)] In particular, this chiral crystallization is a significant chemical problem. This was carried out by Ms. An-Chieh Cheng (Prof. Hokkaido Univ.). I think it is an excellent opportunity to demonstrate that optical trapping can be a new methodology for opening new chemistry. Chiral crystallization is one of the projects that Prof. Sugiyama is currently focusing on most.

The third theme is the “optically evolving assembling and swarming of nanoparticles at the solution interfaces”. We investigated polystyrene nanoparticles of 200 nanometers at the same solution surface. Dr. Wang Shun-Fa (NYCU) succeeded in proving that the aggregate spreads out of focus and has an array using the Bragg reflection. In addition, although the focal point of 1 micrometer is irradiated, a structure corresponding to it can be formed even outside the 8 micrometers. To prove this in a more visible form, Dr. Tetsuhiro Kudo (Currently Lecturer of Toyota Technological Inst.) experimented to capture light using polystyrene particles of 500 nanometers at the solid-liquid interface that highlights the excellent points of the interface. It was actually observed that the polystyrene particles were arranged on the glass substrate reflecting the deflection direction of the laser, and further arranged in a horn shape to propagate the light to the outside. After that, Dr. Kudo found that when gold nanoparticles are used, the scattering is very strong, so the gold nanoparticles interact with each other to form a periodic structure, which works like the Yagi-Uda antenna and scatters light far away, and then many gold nanoparticles gathered and moved like a group of bees. We named this "optically evolved swarming”, and we have been researching its dynamics and mechanism.[27)] Now optically evolved assembling studies are being extended to proteins and related systems at their solution surface by Drs. Shuich Toyouchi and Roger Bresoli-Obach.

The fourth theme is "femtosecond laser trapping of nanoparticles in solution ". Dr. Anwar Usman (Prof. of Universiti Brunei Darussalam) explored a new and unique optical tweezers phenomenon. He worked with Mr. Wei-Yi Chiang (Rice Univ.) to study the femtosecond trapping phenomenon in solution, a phenomenon in liquids.

Nanoparticles gather only in the irradiated space, but gradually form an assembly. When they exceed a specific size, they are released in one direction. Dr. Masayasu Muramatsu participated from Osaka Univ. to this femtosecond trapping and ejection research. We characterized a femtosecond repeating pulse, in which trapping and de-trapping are repeated. Early papers stated that femtosecond laser light and CW laser light trapping had the same result. But that is the case when the subject is a microparticle. The nanoparticles are captured by light and form an assembly by optical force. The assembly grows asymmetrically and is finally pushed out by the force of femtoseconds. The femtosecond pulse exerted optical force on nanoparticles, leading to assembling and the following dynamics completely different way from CW laser irradiation.[28] Trapping and assembling of quantum dots were also tried by Drs. Tetsuhiro Kudo, Wei-Yi Chiang, and Morihiko Hamada.

The study of optical trapping at NYCU in Taiwan is still very unique in the world, while our laboratory would be the one of the largest in the world as a group studying chemistry utilizing optical manipulation (Figure 7). We have reached the point where we have discovered a new phenomenon of optical trapping from the material research side. I have gone back and forth between physics (research on the theory of things) and chemistry (research on the abundance of things). Our present research on optical force chemistry is exactly the research of exploration and elucidation of new molecular phenomena between them. Many excellent researchers in molecular science, photochemistry, and boundary areas have come from this field, and we expect many more in the future.

Figure 7

Group photo of Masuhara - Sugiyama joint laboratory in August 2020. The author and Prof. Sugiyama are the 1st and the 2nd from the left on the top row, respectively. Dr. Kudo is the 4th from the left on the middle row. Dr. Shun-Fa Wang is the far right on the back row.

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Chair Professor Hiroshi MASUHARA
Department of Applied Chemistry
Center for Emergent Functional Matter Science
National Yang Ming Chiao Tung University
Ta Shueh Road 1001, Hsinchu City 30010, Taiwan

増原　宏
講座教授、工学博士
国立陽明交通大學　理学院応用化学系
国立陽明交通大學　新世代功能性物質研究中心
〒30010　台湾新竹市大學路 1001
masuhara@masuhara.jp
https://masuhara.lab.nycu.edu.tw/
http://www.masuhara.jp/
+886-(0)983-811-798