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Noboru Mataga: Fifty Years of Research on Chemistry with Light

This issue of *The Journal of Physical Chemistry A* is dedicated to Noboru Mataga, Professor Emeritus of Osaka University and Fellow of the Institute for Laser Technology, on the occasion of his 50th year of scientific activities. This collection of articles—from many of his students, collaborators, friends, and colleagues—is contributed in recognition of Mataga's many outstanding scientific accomplishments, and especially in honor of his contributions toward the elucidation of many of the central issues in molecular spectroscopy, photochemistry, photophysics, and the study of molecular interactions. The articles collected here reflect the broad range of scientific interests of Mataga, and in no small way, reflect the great enthusiasm for fundamental research that he has inspired in his colleagues and co-workers over these 50 years.

Noboru Mataga was born in Masuda, Shimane Prefecture, Japan, on May 20, 1927. He attended primary and secondary schools in Shimane Prefecture and high school in Yamaguchi Prefecture. In 1948, he entered the University of Tokyo to study chemistry, and performed undergraduate research in the group of Professor San-Ichiro Mizushima, a leader in the fields of molecular structure and spectroscopy. In 1951 he graduated from the University of Tokyo and joined the research group of Professor Masao Koizumi in Osaka City University as a research associate.

At Osaka City University, Mataga's seminal research on the interaction of an excited polar solute molecule with a polar solvent led in 1955 to the first quantitative theoretical formula for fluorescence solvatochromism. This conceptually simple formulation has been widely used to study the solvation and dipole moments of exited polar solutes and excited CT complexes, and continues today to influence research on ultrafast solvation dynamics and polar solution photochemistry. The experimental proof for Mataga's equation was given by himself- and by Lippert who independently proposed the same equation at the same time. At Osaka City University, Mataga and co-workers also performed pioneering studies on excited-state hydrogen-bonding interactions (1955), intermolecular excited-state proton-transfer reaction in hydrogen bonding complexes (1962−1964), and fluorescence quenching in hydrogen-bonded complexs of π-aromatic systems(1955−1962). In Osaka City University, Mataga and co-workers engaged in molecular orbital (MO) calculations on the relationship between electronic spectra and molecular interaction, resulting in the Mataga-Nishimoto approximation (1957) for the two center electron repulsion integral for PPP type MO calculations. This equation profoundly and broadly contributed to the investigation of aromatic molecules in biochemical and photochemical problems.

In 1964, Mataga was promoted to a full professor of chemistry at Faculty of Engineering Science in Osaka University, which was established in 1961 in order to promote the fusion of basic science and engineering. One of Mataga's main focus in the new laboratory was the development of more precise tools and methodologies for the elucidation of basic elementary processes in solution photochemistry, including the addition of pulsed laser systems in the late 1960s allowing for direct time domain measurements of reaction dynamics. The other main focus of the Mataga laboratory was the investigation of the photochemical processes and molecular interaction in molecular aggregates and assemblies, such as polymer solids, liquid crystals, membranes, and proteins. The many exciting and influential results from the Mataga laboratory during the period from its establishment in 1964 until his retirement in 1991 are too numerous to treat in detail in this format. We will attempt instead to just the scratch the surface of a small selection of the some of the most influential work.

A major portion of the body of work of the Mataga group at Osaka University was the investigation of the microscopic mechanistic details of fast and ultrafast electron transfer reactions in solution. This work has been extremely influential on the contemporary understanding of many aspects of electron-transfer reactions in solution. These studies include: the investigation of the energy gap (or driving force) dependences of charge separation (CS) and charge recombination (CR) in solution, and more generally, the apparent absence of the Marcus inverted regime in certain cases; the role of solvent dynamics on electron-transfer reaction; the mechanism of photoinduced ET coupled with proton transfer; the photophysics of intramolecular exciplex systems and related photosynthetic reaction center models; the electron ejection process of solutes in polar solvents; and the role of intramolecular twisting motion in electron-transfer reactions, just to name a few. In the course of these studies the Mataga group pioneered the application of time-resolved spectroscopy to these various photochemical systems on the nanosecond, picosecond, and ultimately, femtosecond time scales.

In the end of 1960s and in the beginning of 1970s a major focus of the laboratory was the investigation of molecular complexes appearing in photochemical processes such as the exciplex and the excited-state CT complex. Mataga and co-workers used nanosecond laser spectroscopy to the measure the

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transient absorption spectrum of a CT complex (between 1,2,4,5-tetracyanobenzene and toluene) and revealed that the absorption spectra of the excited CT complex was close to the summation of anion and cation spectra of the components. This revealed that ion pair character was the major contribution to the electronic structure of this excited CT complex. Mataga and co-workers also published pioneering studies on solvent polarity effects on fluorescence spectra, yields and lifetimes of exciplex systems (1966−67) and CT complexes (1969), which led to the concept that their electronic and geometrical structures are strongly dependent upon solvent polarity. This work demonstrated that the structures of exciplex systems are dependent on such factors as solvent polarity, the driving force for charge separation, and the magnitude of the electronic interaction between exciplex components (1975). These effects could be understood in terms of a nonlinear interaction between solvent polarization and solute charge distribution, leading to a nonlinear wave equation for solute electronic states. In later years these concepts greatly aided the understanding of photochemical reactions of complexes via exciplex and/or charge-separated states.

Ultimately, this work formed the foundation of extensive studies on the dynamics of the charge-transfer processes, leading to important new insights on the role of energetics, reactant diffusion, and solvation dynamics on electron-transfer reactions in solution. This important body of work allowed for an unraveling of the complex interplay of charge separation, charge recombination, and other photophysical process. A key component of Mataga's elucidation of this system is the nature of the charge transfer complex in a particular systems with respect to whether the complex is a "contact ion pair" or a "loose ion pair".

A related and particularly important research thrust in the Mataga group was a pioneering time-resolved spectroscopy study of electron donor (D)−acceptor (A) systems linked by flexible methylene chains (1972) of varying length. These results on linked D−A systems indicated that a compact sandwich-like conformation is required for the intramolecular charge separation (CS) in nonpolar, while in polar solution CS can occur for a less-compact conformation. These authors clearly elucidated the role and relationship of the many important factors in the CS process, including solvent polarity, conformational rearrangements, donor−acceptor electronic coupling along the methylene chain, and the driving force for the CS process. This work is also a foundation for many recent studies from many laboratories on CS in chained molecules linked with flexible, semirigid, and rigid spacers; CS in photofunctional supramolecular systems; and organic photochemical reactions via exciplex states.

Mataga and co-workers also extensively investigated the photophysics of *intramolecular* CT process in bichromophoric molecules directly linked by a covalent bond. These studies were the first to apply picosecond time-resolved spectroscopy to several important prototypical intramolecular charge-transfer compounds. For example, in 1976 they published a pioneering study of solvent induced symmetry breaking in the key symmetric intramolecular charge-transfer compound bianthryl. This paper and many subsequent papers involving picosecond and femtosecond spectroscopy on various intramolecular charge-transfer compounds have led to a detailed understanding of the role of energetics, solvation dynamics, and solute structure on the dynamics of charge transfer.

Due to the short format of this article we have only been able to briefly mention a small portion of the extensive body of work from the Mataga group. The interested reader is referred to the accompanying complete list of publications of Prof. Mataga for more topics and references to articles that present this work in a more in depth treatment.

After retiring from Osaka University in 1991 Mataga has been continuing to actively pursue his research interests in the Institute for Laser Technology. He is extending his investigations on excited-state molecular interactions and reaction dynamics to the protein environments (protein nanospace, PNS) by employing photoresponsive proteins. He and co-workers have investigated the effects of PNS on the photoinduced ultrafast twisting of the chromophore in the photoactive yellow protein (PYP) of a photoresponsive bacteria, and the femtosecond time-resolved fluorescence dynamics of bovine rhodopsin (Rh), and other biological systems.

Over his twenty-seven years in Osaka University, Mataga has trained more than eighty graduate students, almost twenty of which are working in universities and National Institutes.

It has been a great honor for us to be included among friends, colleagues, and the students of Noboru Mataga. It is with great pleasure that we dedicate this special issue of *The Journal of Physical Chemistry A* to him.

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