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Autobiography of Sheng Hsien Lin

National Taiwan University

I was born in Taiwan to a poor family and grew up during the Second World War. My parents and grandparents believed that only engineers and medical doctors could improve our living conditions. Naturally, I was urged to study chemical engineering when I was admitted to National Taiwan University (NTU) in 1954. During the college time, in a major course, transport phenomena, we were taught that these processes could only be treated by using empirical or semiempirical methods. I was not satisfied by this nonrigorous approach, because I had excellent high school teachers in mathematics and physics who showed us rigorous and logical ways to explain various scientific phenomena. A slide rule was then a commonly used computational tool for students. Since I could not afford to buy a slide rule, I had to train myself not only to be fast, but also to be accurate in numerical calculations so that I could compete with other students who used slide rules; I also constantly tried to find new and efficient methods to improve the speed of my numerical computations.

When I graduated from NTU in 1958, my parents finally agreed to let me choose a major that I really wanted to study in graduate school. I was very happy when I passed the entrance examination to enter the Chemistry Department of NTU as a graduate student.

For my M.S. work, I chose to work with Prof. K. Pan, a distinguished physical chemist in Taiwan at that time and the first Taiwanese academician of Academia Sinica. His main expertise was in electrochemistry, especially polarography. Being a chemical engineering graduate without any training in experimental physical chemistry, I did not have any knowledge of polarography; so in the laboratory I felt completely out of space. Luckily not long after I joined Prof. Pan's group, his laboratory purchased a Beckman DU spectrophotometer, and I was asked to employ it to study reaction kinetics in aqueous solution and determine the formation constants of inorganic complexes.

While working on the reaction kinetics, I had to study Eyring's transition state theory and was fascinated by the theory and decided to do my Ph.D. work with him after the M.S. studies. Because my research work involved spectrophotometric measurement, I was very much interested in the spectral band shapes of different molecular systems and wanted to know the nature of their band shapes. So I first asked other graduate students trained in physical chemistry and then the physical chemistry professors in NTU, but it seemed that nobody could provide me a satisfactory answer. Therefore, I made up my mind to find the answer to this question someday, and years later I did find the answer I was searching for.

Prof. Pan was a very kind person. Knowing that I had to do a tutoring job to finish my undergraduate studies, he offered me a tutoring job to help his children. Since his children were very bright, usually it would take only 1 hour to finish the teaching. In addition, he would invite me to have supper with his family before tutoring. So, I was able to have a second tutor job right after this one. The economic condition in Taiwan in 1950−1960 was quite poor. I made about 8 USD per month for tutoring 2 h per week. After obtaining my M.S. degree, I did military service (ROTC) for 1 year, serving as an instructor at the Chinese Air Force Academy. Even though Prof. Eyring already offered me a research fellowship, to save enough money to buy an airline ticket to the U.S., I had to take up a research assistantship at Prof. Pan's laboratory for 1 year plus two tutorial jobs.

During the year of my military service and the year of assistantship, I had plenty of time to read various reference books on quantum mechanics, statistical mechanics, and spectroscopies. By that time I realized that it would be hard for me to become a respectable experimental chemist. Therefore, I was really looking forward to working with Prof. Eyring to become a theoretical chemist.

University of Utah

In the first quarter (i.e., fall quarter of 1962) at the University of Utah, Prof. Eyring asked me to work on the quasi-equilibrium theory (later called the RRKM theory) of unimolecular reactions. At that time the accurate evaluations of the total number of states and the density of states were important problems in unimolecular reactions. In the first quarter, I took four courses: quantum chemistry, statistical mechanics, thermodynamics, and analytical chemistry. Prof. Eyring taught the first two courses. In the statistical mechanics class, he discussed the Darwin−Fowler method as a possible approach for the development of equilibrium statistical mechanics. I quickly noticed that I could use this method to calculate the total number of states and the density of states. By the end of the first quarter, Prof. Eyring and I finished a paper on this subject. After the first quarter at Utah, Prof. Eyring practically left me alone to work on any research problems I chose. Taking advantage of this special treatment, I worked on liquid theories, transition state theory, and the Faraday Effect. My Ph.D. thesis work was on the calculations of the magnetic optical rotation of transition metal complexes. In this work, I had to learn the theory of the Faraday effect and the crystal field theory. At that time, this type of work was considered to be original. I learned while I worked; in this way I not only earned knowledge in various areas but also learned Prof. Eyring's attitude toward science. He was interested in all important scientific problems. He had an extraordinary ability to understand the nature of problems and to provide the answers to the problems. In my mind, he was a real giant in chemistry. In the 2 years of my studies at Utah, Prof. Eyring was the Dean of Graduate School and also directed the Institute for the Study of Rate Processes and had a group of 40 people working for him. When he was not out of town, we used to spend Saturday afternoons together to discuss various scientific problems. We became very good friends. After I joined Arizona State University as a faculty member, he used to invite me to spend a period of two weeks every year to work on various research projects. I stayed at his house every time I visited Salt Lake City. This collaboration continued until the week before he passed away in December of 1981. In my last visit, we were working on the mechanism of cancer; he had had cancer for more than 10 years.

In the 1960s, to obtain a Ph.D. in chemistry at Utah, a student was required to have a major program and a minor program and to pass the preliminary examinations in these programs. But before taking the preliminary examinations, he/she had to

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pass examinations for two foreign languages (native language being excluded). I majored in physical chemistry and minored in physics, and for the foreign languages I chose Japanese and German. I was lucky to obtain my Ph.D. in less than 24 months.

Columbia University

Before I received my Ph.D. in the summer of 1964, I began to look for a postdoctoral position. Since, in my graduate work, I had to be mainly concerned with research projects related to the ground electronic state surface, I decided to do postdoc work on research problems entirely different from my Ph.D. work. Luckily, I was accepted by Prof. Richard Bersohn of Columbia University. At the time, one of the most popular and important problems was theoretical studies of radiationless transitions in photochemistry. Richard asked me to work on this problem and told me that his funding situation only allowed him to support me for 1 year. So, being a thoughtful person, he gave me another straightforward problem, that is, the calculation of the quintet state lifetime of the carbon atom in case I could not get any results from the studies on radiationless transitions. At that time, Richard was on a sabbatical leave at Bell Lab and only came back to Columbia once a week or once in two weeks. This allowed me time to go through the literature to find and study various models proposed by various groups so that I could present these models to Richard and discuss them with him. In the early 1960s, Wilse Robinson and his group (notably Frosch) were the most active group in the area of radiationeless transitions. So, naturally, Richard and I went through their papers very carefully. We felt that there was room for more theoretical work in this area. Richard suggested that I should carefully study the Born−Oppenheimer approximation, vibronic coupling, and spin−orbit coupling.

By the spring of 1965, Richard and I came to conclude that for the case in which the B−O basis set was used for treating radiationless transitions, the breakdown of the B−O approximation was probably the most reasonable choice as the perturbation to calculate the rate of radiationless transitions. In the process of writing a paper, Richard not only corrected my English but also made numerous corrections and suggestions, and he also suggested the title of the paper as “Rate of Interconversion of Electronic and Vibrational Energy”. In this theory, the B−O approximation was used as a basis set for internal conversion, and thus the B−O coupling (i.e., mainly vibronic coupling) was responsible for this radiationless transition. This theory takes into account the temperature effect, selection rule, and the role of the Franck−Condon factor that describes the vibrational distribution in the final electronic state after IC. At that time I could not appreciate the profound implication of the title because in 1965 the reverse process of a radiationless transition could only be accomplished by temperature, which was nearly impossible experimentally. However, 20 years later this reverse process became possible by employing an IR laser to pump the molecule in a collision-free environment. When we were ready to submit the paper to *The Journal of Chemical Physics*, being a generous and thoughtful person, Richard suggested that I should be the single author for this publication but he would take care of the paper charge and the publication cost. Because of his sabbatical leave, he felt that he did not make sufficient contribution to this work. The “quintet state of the carbon atom” project was also finished at about the same time. So the two papers were submitted to JCP at the same time. Both Richard and I were relieved that satisfying results were obtained in both projects. At the end of the spring of 1965, Richard asked me if I could join him at Woodshole to continue the research work for the summer.

Around the same time, Prof. Henry Eyring’s youngest brother, Prof. LeRoy Eyring came to Columbia to see me and ask me if I would like to join Arizona State University because he was responsible for starting a Ph.D. program there. After talking to Henry and some consideration, I decided to accept the offer as an assistant professor, which started in the September of 1965.

The Woodshole Oceanographic Laboratory had one of the best libraries and they welcomed researchers to use the library. But to regularly occupy a desk, it was necessary to pay a rent. Richard and I spent the mornings during that period for scientific discussions. At that time we chose to investigate the effect of radiation damping on various optical spectroscopies. This work led me to my later work on the density matrix treatment of vibrational relaxation and vibrational dephasing and their effect on time-resolved and/or steady state band-shape functions. The Woodshole collaboration continued for two more summers. In the summer of 1966, Richard showed me a set of triplet lifetime data of benzene molecules, which exhibited a distinguished feature of the isotope effect. In the process of working on this problem, Richard proposed the terminology of “failure of the B−O approximation”, which results in radiationless transitions; it later became the “breakdown of the B−O approximation”. He also classified the vibrational modes involved in radiationless transitions into “promoting modes” and “accepting modes”.

In the summer of 1967, Richard and I decided to work on a general and systematic treatment of the anisotropic effect induced by beam excitation. This project was motivated by the work of Zare and Herschbach on the anisotropic angular distribution induced by beam excitation.

After 1970, Richard’s research interests began to focus on reaction dynamics. So we only saw each other in conferences occasionally till 1995 when the Institute of Atomic and Molecular Sciences (IAMS) became a formal institute. IAMS invited Richard to be a member of the advisory committee for the reactive scattering group. After that, we saw each other when he visited IAMS once a year till he became ill.

Arizona State University

I joined Arizona State University in the fall of 1965. Prof. LeRoy Eyring was the Department Chairman recruited for establishing a respectable Ph.D. program at ASU. In addition to myself, two other senior members, Prof. G. R. Petite and C. H. Liu were recruited. LeRoy was a well-known solid state chemist and a very nice person. At that time, he was preparing a proposal to NSF for establishing a solid state science center that included eight members from the Chemistry and Physics Departments. The grant application was successful and the center was formally established in 1966 and the Solid State Science (SSS) Center under the Directorship of Prof. LeRoy Eyring became well-known in a short time. In addition to attracting famous visiting scholars in solid state chemistry and physics, he recruited a number of established solid state scientists: for example, Prof. J. M. Cowley specialized in high-resolution electron microscopy, Prof. Sumio Iijima, a pioneer in carbon nanotubes, etc. Being a member of the SSS Center, I naturally got involved in the solid state science research, mainly collaborating with LeRoy’s experimental group working on the phase transitions of nonstoichiometric rare earth oxides, the hystereis in their phase transitions, their spectroscopic properties, oxygen transport and kinetics of oxidation of rare earth oxides, photoacoustic spectroscopy of rare earth oxides, and time-resolved X-ray diffraction to study the kinetics of solid state reactions and the thermal decomposition of $CdCO_3$ powder.

In 1968, I met a bright and attractive female student, Hsiu-Ping (Pearl) Pi, majoring in botany at NTU. She came to ASU for her graduate studies. We got married in 1970 after she received her MS degree. Our older son, Huie was born in 1974, a medical doctor now, and our second son, Bing, was born in 1983, now a Ph.D. student studying industrial psychology. Pearl received her Ph.D. degree in 1977, and is now a program director at the Development Center for Biotechnology in Taipei.

Another co-worker in the SSS Center that I collaborated closely wtih was Prof. I. S. T. Tsong, an experimentalist, working on the nature and mechanism of the sputtering process, which plays a crucial role in secondary ion mass spectrometry. We believed that after energetic ions impact on solid surfaces, except for a minor amount of sputtered particles (molecules or ions) due to direct inelastic collisions, most particles were desorbed after the incident energetic ions transferred the excitation energy into local energetic vibrations that rapidly vibrationally relaxed and created the local heating. The desorption took place afterward due to the local heating and could be described by a statistical theory, for example, the RRKM theory. Using this theory, the mass spectra could be calculated.

At the SSS Center I also collaborated with another colleague, Prof. R. W. Carpenter, an experimental materials scientist, to work on microelectron energy loss spectra of Si core edge fine structure in an oxidation series of silicone compounds, and silicone refractory compounds, and the theoretical study of the solid−solid interfacial concentration profile of two component systems.

Regarding the photophysical research that became my main research interest, I applied the formalism and theoretical technique of radiationless transitions to develop the vibronic theory of spectral band shape for absorption and emission of molecules in dense media, and the effect of heavy atoms and paramagnetic species on the phosphoscience of molecules in rigid media. I continued to work on the problems related to radiationless transitions such as temperature effect, high-pressure effect, delayed fluorescence and radiationless transitions in isolated molecules.

In 1972, I spent my first sabbatical leave on a Guggenheim fellowship in England for 1 year, working mainly with Prof. George Porter's group at the Royal Institution, in particular with Graham Fleming (then a graduate student) and O. L. J. Gijzeman (a postdoctoral fellow from The Netherlands). We worked on the calculation of the lifetimes of single vibronic states, theories of time-resolved absorption spectroscopy and emission spectroscopy, and theoretical treatment of intramolecular vibrational relaxation by using the density matrix method. It was a very exciting and stimulating collaboration. The time-resolved absorption work led to the pressure-induced band-narrowing observed in time-resolved absorption spectra by Schlag's group. The IVR work provided the foundation of my later work on the application of the density matrix method to relaxation and dephasing processes, kinetics of phase transitions, and nonlinear spectroscopy.

In the electronic excitation energy transfer between the donor and acceptor either in the dense media or in the intramolecular condition, the Förster and Dexter theories are commonly used, which express the transfer rate in terms of the spectral overlap between the emission spectra of the donor and the absorption spectra of the acceptor. Using the radiationless transition formalism, I reformulated these theories in terms of the properties of potential surfaces of the donor and acceptor involved in energy transfer so that the effect of energy gap, temperature and isotope could be explicitly treated. Later this theory was extended to the case of the vibrational excitation energy transfer in the dense media. In collaboration with Tsen's experimental group from the Physics Department of ASU, we applied the electronic excitation energy transfer theory to study spectroscopies and excited state dynamics of color centers.

In 1976, Dr. Y. Fujimura, a young assistant professor from Prof. Nakajima's group at Tohoku University, Japan, came to work with me. He originally planned to work on radiationless transitions but was inspired by the experimental results on resonance Raman scattering of Prof. Ito's group (also at Tohoku University) and thus decided to work on the theory of resonance Raman scattering. At that time the rigorous vibronic theory of RRS was not yet developed, although Albrecht had already provided an important theoretical foundation in this area. In eighteen months Fujimura formulated a vibronic theory of RRS based on the use of the B−O approximation as a basis set and expressed the RRS cross section in terms of the three time integrals. As applications, the multimode effect and temperature effect on RRS were treated. Later he applied this theory to analyze the RRS spectra of pyrazine resonant to the S_2 state experimentally obtained by Prof. Ito's group and to β-carotene by Hanson's group at ASU studying the high-pressure effect on RRS spectra. Dr. Fujimura also compared resonance fluorescence with resonance Raman scattering. After going back to Japan, Fujimura continued to collaborate with me on molecular theories of multiphoton processes such as two-photon absorptions, multiphoton ionization of molecules, three-photon absorption, and two-photon magnetic circular dichroism. Another of Fujimura's expertises was in the theories of radiationless transitions. Jointly we published papers on the calculation of rates of radiationless transitions in matrix-isolated CN, the magnetic field effect on radiationless transitions, the time evolution of the triple state after a radiationless transition, and the density matrix treatment of quantum beats. In the paper on the theory of time-resolved absorption, Fleming, Gijzeman, and Lin predicted that the time-resolved spectra after radiationless transitions in the presence of molecular collisions would exhibit pressure-induced narrowing. Motivated by this work, Prof. E. W. Schlag's group measured the time-resolved spectra for the triplet−triplet absorption of naphthalene after intersystem crossing. We successfully performed a theoretical simulation on these observed time-resolved spectra. For the purpose of the simulation, it was necessary to have a proper theoretical model of the vibronic-level populations after ISC.

Not long after I joined ASU, Prof. Henry Eyring began to invite me to visit him to set up collaboration with his group. Prof. Eyring was a pioneer in molecular optical activity (including optical rotation and circular dichroism). So when the magnetic optical activity facilities became available, Prof. Eyring's group naturally acquired them. My role in this area was to develop a molecular theory for MCD by modifying the theories of absorption and emission spectra and those of ORD and CD that my group developed. This vibronic theory for MCD helped Prof. Eyring's group analyze their MCD experimental data. Prof. Eyring's other major research interest was the molecular basis of macroscopic biology; some joint work on ion flow through membrane and anesthesia was published. I did not fully appreciate Prof. Eyring's profound knowledge in science till we began to continue our collaboration after I joined ASU. Our collaborative work covered numerous research areas. Normally, he would suggest a problem and I would carry out theoretical derivations. We would then discuss the outcome of the work together.

I was very fortunate to have Fujimura as a co-worker, because he encouraged his co-workers and/or young Ph.D. graduates to come to work with me. After him, I had Nishikawa, Kono, Sugawara, Ohtsuiki, Kato, and Hayashi coming to work in my group.

After Dr. Fujimura left ASU in 1978, another Tohoku University graduate, Dr. H. Kono, joined my group in 1980. In collaborating with Dr. Fujimura, we finished a few papers on the master equation approach (i.e., density matrix method) of quantum beats, in addition to RRS. And in collaboration with Prof. Schlag's experimental group, we also studied the rotational effect on single ro-vibronic level lifetimes of formaldehyde, in which the effect of Coriolis coupling, ro-vibrational coupling due to the vibrational dependence of moments of inertia, and level line width had been taken into consideration. Experimentally, the dramatic rotational effect on single ro-vibronic level lifetimes was observed by Schlag's group for formaldehyde. For aromatic molecules in collision-free conditions, it was observed that beyond the excess vibrational energy of 3000 cm^{-1}, the rates of radiationless transitions increased dramatically. Kono applied the microcanonical theory of radiationless transitions to interpret this excess energy dependence. He also pointed out that the potential surface crossing of distorted surfaces could make significant contributions to radiationless transitions. In the 1970s, the investigations of spectroscopic properties and vibrational dynamic behaviors of diatomic impurity molecules in solids attracted considerable attention. Until that time, in theoretical treatments of this problem, only qualitative or semiquantitative models had been developed. As a typical Tohoku University theorist, Kono not only could formulate an analytical theory but also could perform numerical computations. In this problem, he first constructed a reasonably good potential surface for the system, and then employed the adiabatic approximation as a basis set to develop the theory of molecular spectroscopy and vibrational dynamics of an impurity molecule in solids. We then carried out numerical computations to compare with experimental results.

I first met Prof. Schlag in 1972 when he came to visit Prof. Porter at RI where I was on a sabbatical leave, but our real collaboration did not start until 1976 when I spent the summer with his group at the Technical University of Munich. I was very impressed by his research activities, which were divided into high-resolution molecular spectroscopy, photophysical processes, and synchrotron radiation research, and by the number of distinguished scholars visiting his institute. At that time, I was fascinated by the time-resolved spectra of naphthalene after intersystem crossing measured by Schröder and Neusser. These spectra exhibited the pressured-induced spectral band-narrowing. This phenomenon was predicted by the work of Fleming et al. As mentioned above, the theoretical analysis of their experimental results was carried out by Fujimura. After 1976, I became a regular visitor of Schlag's group once a year usually in summers except the year 1979−1980 when I spent my second sabbatical leave with Schlag's group on the Alexander von Humbolat US Senior Scholarship. Our collaboration covered the collision-induced ISC and magnetic quenching, vibrational relaxation in isolated molecules, time-resolved level anticrossing, quantum beat in polyatomic molecules, rotational fine structures in photophysical processes, resonance multiphoton absorption and ionization, spectroscopies and dynamics of molecular clusters, laser-induced desorption of molecules, dynamics and spectroscopies of ZEKE states, biological electron transfer, and high-power ionization of molecules.

In the summer of 1980, Prof. Voltz of Louis Pasteur University invited me to visit his institute after I concluded my sabbatical leave at Schlag's institute. That was when I had opportunity to work with Prof. A. Villaeys and Alex Boeglin. Alex was still a student then. We jointly studied the dynamical effect of vibrational relaxation on electronic relaxation. Later Alex came to ASU to work in my group as a postdoc. He first attacked the problem of the viscosity effect on photoisomerization and electronic relaxation and then worked with Prof. B. Fain on density-matrix treatment of multiphoton processes in molecules and on laser-stimulated desorption of molecules and phase transition kinetics in solids. He found a position at CNR and went back to Strasbourg in 1986, but my collaboration with Villaeys continued. Our interest turned to the susceptibility treatment of nonlinear optics, transient hole burning, molecular theory of second-harmonic generation, sum-frequency generation, third-harmonic generation, and degenerate four-wave mixing in molecules.

In 1982, Prof. B. Fain of Tel Aviv University spent 1 year with me at ASU. At that time, experimentally IR laser-stimulated desorption of molecules from solid surfaces attracted a great deal of attention. He first developed a general theory of IR laser stimulated processes (including desorption and diffusion) by using the density matrix method. He then became a regular visitor of ASU after 1982 and then studied the effect of vibrational energy transfer on laser-induced desorption, instability of desorption mode in laser-stimulated desorption, laser-stimulated desorption spectroscopy, and laser-stimulated desorption of molecules via electronic excitation of adsorbed molecules. His work covered almost all aspects of laser-stimulated desorption of molecules.

Fain is an eminent expert in quantum optics. He assisted us in developing a density matrix method to treat the multiphoton processes due to intense lasers and the band-shape of autoionization of molecules. Femtosecond (fs) time-resolved experiments became an important experimental technique to study ultrafast processes in the 1980s. Again it was Fain who helped us entering the area of fs time-resolved spectroscopies. We developed a theory of fs pump−probe experiments by formulating the generalized linear response theory in which the time-dependent behaviors of population and coherence (or phase) were considered and we then calculated the generalized linear time-dependent susceptibility for the probing laser with the dynamical initial conditions determined by the pump laser. Theories of ultrafast time-resolved fluorescence and resonance Raman scattering were also developed. The collaboration between Fain and our group continued till he retired from Tel-Aviv University in 2000.

Supported by DOE, NSF and Department of Agricultures, the "Center for the Studies of Early Events in Photosynthesis" was established in 1986 at ASU. It was a joint effort of the Departments of Chemistry and Botany and initiated by Prof. R. E. Blankenship who naturally became the first director of the Center. Being the only theorist in the Center, I spontaneously began to undertake the theoretical investigations of photoinduced electron transfer between donor and acceptor because it was an early event involved in bacterial reaction centers. Because two potential surfaces are involved in this process, it was natural to employ the radiationless transition formalism to study this electron-transfer process. We showed that the Marcus equation could be obtained for the displaced harmonic surfaces and the displaced-distorted surfaces for the strong coupling case in the high-temperature range (that is, the classical condition). For the harmonic mixed-mode surfaces (i.e., the Duschinsky effect), although in the high-temperature condition the Arrhenius form can be obtained, it does not exhibit the Marcus equation form. The anharmonic effect on photoinduced electron transfer was also studied. In photoinduced electron transfer, the bridge groups between donor and acceptor often exhibit the so-called the bridge effect, which can be treated by using the second order perturbation method. For the case in which the electronic states of the bridge group are higher than the photoexcited state of the donor, one has the so-called superexchange ET (or the ET through the bridge group or indirect ET). However, for the case in which an electronic state of the bridge group is lower or in resonance with the photoexcited state of the donor, one would have the sequential ET and/or the resonance Raman type of ET. This was also treated by us.

In resonance electronic excitation energy transfer between donor and acceptor, as in the case of photoinduced electron transfer between donor and acceptor, the bridge group may also affect the rate of the energy transfer and can be treated in the same manner as that in the electron transfer. It was shown that the spectral overlap relation holds even for the case of single vibronic-level energy transfer (that is, the nonrelaxed energy transfer).

To analyze the experimental results of the femtosecond time-resolved spectra involved in the ultrafast photoinduced electron transfer in bacterial reaction centers, it was necessary to combine the theory of femtosecond pump−probe experiments and theories of photoinduced electron transfer. For this purpose, it was natural to employ the density matrix method. We then pointed out the importance of the role played by vibrational relaxation and vibrational dephasing (that is, quantum beats) in the femtosecond time-resolved pump−probe experiments of reaction centers and showed that the vibrational mode involved has the frequency of $\sim 10^2$ cm^{-1} with the rate of vibrational relaxation of 0.3−0.5 ps. The smallness of the vibrational frequency explains the observation that the bandwidths of the P-band, B-band, and H-band are of only several hundred wavenumbers (i.e., 400−500 cm^{-1}). Although the 100 cm^{-1} mode plays an important role in absorption spectra, due to the fact that the energy gap (or free energy change) involved in the photoinduced electron transfer is much bigger than 100 cm^{-1}, the major accepting modes have much larger frequencies but with small Huang−Rhys factors (i.e., coupling constants), which explains the weak or inverse temperature dependence of the electron-transfer rate. By a careful analysis of steady state absorption spectra and ultrafast measurements of electron transfer in reaction centers, a detailed energy-level scheme had been proposed to describe the electron-transfer process involved in bacterial reaction centers.

Institute of Atomic and Molecular Sciences

In the spring of 1993 when I was planning to spend the fall semester of my sabbatical leave at National Sun Yet-Sen University in Taiwan, the founding director, Dr. C. T. Chang of the Institute of Atomic and Molecular Sciences, Academia Sinica, passed away unexpectedly. I was on the advisory committee of IAMS since when it was in the planning stage. Prof. Yuan T. Lee, who is the founding father of IAMS, urged me to take the director position. Without any administrative experience, I told him that I would try my best. IAMS was only about 10 years old then. Yuan became the president of Academia Sinica in January of 1994. With Yuan's help, the funding for research was not a problem. So my duty was trying to improve the quality and quantity of IAMS's research. From my experience with the experimentalists at ASU and TU of Munich, I decided to establish a strong collaboration between experimentalists and theorists. At that time, the area of light-emitting polymers (e.g., poly(*p*-phenylenevinylene), PPV) attracted considerable attention and a young colleague at IAMS, Dr. W. S. Fann, and his co-worker Prof. S.-A. Chen made a series of PPV-related polymers and measured absorption and photoluminescence spectra. Meanwhile, the soliton theory was proposed to treat the photophysics of light-emitting polymers, but we felt that in polymers the molecular excitons should play a very important role in the absorption and PL spectra of PPV and its related polymers and proceeded to perform molecular orbital calculations to determine the electronic states of monomers and then applied the molecular exciton theory to determine the excited states of PPV and its related polymers. The experimental absorption and PL spectra were analyzed. We also performed the MO calculations to examine the effect of polymer chain length and exciton interactions between polymers on absorption and PL spectra. The temperature effect on steady state spectra was also measured and theoretically analyzed and the spectroscopic band shapes were calculated. We undertook the investigations of the ultrafast dynamical behaviors of the exciton states of PPV and the experiment of photocurrent versus laser excitation wavelengths.

It was Dr. M. Hayashi who made my transition from ASU to IAMS smooth. He is another Tohoku University product from Fujimura's group, who joined my group at ASU in 1993 and was willing to come to Taiwan with me. Dr. Hayashi had excellent training in theoretical chemistry but he is also capable of doing numerical computations. He was involved in ultrafast electron transfer in photosynthesis, photophysical processes in light-emitting polymers, molecular spectroscopies and radiationless transitions, nonlinear optics and high-power laser ionization, and dissociation of molecules. Dr. Hayashi is an excellent theoretical chemist with a very profound knowledge in quantum chemical calculations and has a nice personality, which makes him an extremely valuable co-worker.

Dr. A. M. Mebel joined IAMS in 1995 as a senior postdoc. He is an excellent quantum chemist with good backgrounds in molecular spectroscopies, photophysical processes, and reaction kinetics and has a very friendly personality—easy to work with colleagues. He was a very valuable addition to IAMS and opened up a new era in the collaboration between experimentalists and theorists. Without his quantum chemical calculations, numerical analysis and interpretation of experimental results would not have been possible. Jointly with Hayashi, Mebel quickly established collaboration with Prof. Y.-T. Chen, a molecular spectroscopist, on the investigations of $\pi-\pi^*$ vibronic spectra of ethylene using the ab initio surfaces (including the Duschinsky effect) to show the observed dramatic spectral width and vibronic spectra of other molecular systems like methyl radical, vinyl radical, and acetone. They also worked on photoluminescent properties of silica-based mesoporous materials and nanoscale materials.

In the 1990s, Yuan had several groups of principal investigators such as Prof. X.-M. Yang, Prof. H.-C. Chang, Prof. C.-K. Ni, and Dr. R. I. Kaiser working with him at IAMS. In addition to reactive scattering, photodissociation of molecules attracted their attention considerably. At that time, Prof. Rex Skodjie was a regular visiting scholar of IAMS and he worked with Yuan's group and Prof. Kopin Liu's to interpret and analyze their experimental data on reactive scattering.

Because I had considerable experience in the transition state theory of unimolecular reactions, Mebel and I developed a program of an *ab initio* quantum mechanical calculation of the RRKM theory and analyzed the experimental data of Yang, Kaiser, and Ni. The program contains the calculation of the rate constants based on the use of *ab initio* calculated results of the reactant and activated complex, the solution of unimolecular rate equations and the determination of branching ratios. The calculation of energy distribution in products is also included in this program. Another important contribution to IAMS made by Mebel was that he introduced a number of established scientists from Russia and Ukraine (i.e., the Charkins, the Zyubins, Rozenbaum, and Makhnovskii) to visit IAMS regularly (2−3 months each year). They had strengthened our ongoing research or helped us move into new research areas. In addition, they formed important bridges between two different research groups of IAMS to work together, for example, Dr. D.-Y. Yang's group and mine.

In the same period, Prof. H.-C. Chang's group was investigating the spectroscopy and structure of various sizes of protonated water clusters. Quantum chemical calculations play a very important role in understanding the structure of these clusters. Dr. J.-C. Jiang, a postdoc in my group then, was very enthusiastic to collaborate with Chang's group to perform this type of calculations. A number of different kinds of protonated water clusters were then studied.

High-power laser ionization of atoms and molecules became an important area, and J. P. Wang's group at IAMS planned to build up a high-power laser laboratory. In collaboration with Hayashi, we generalized the Keldysh theory (originally developed for the high-power ionization of the 1s state of hydrogen atoms) so that it could be applied to study molecular systems by combining the molecular orbital theory and the Born−Oppenheimer approximation. In this way we could treat the high-power laser ionization and dissociation of molecules and effect of molecular vibrations on molecular ionization. High harmonic generation by a high-power laser was also treated in this frame work.

In 1997, Prof. Sunney Chen joined Academia Sinica, first as the director of Institute of Chemistry and then as a vice president of Academia Sinica, and organized a group project on protein folding. I was invited to participate in this project, which started in 1999. Through the regular group meetings of the PIs in this project and Prof. R. W. Woody's lectures on protein folding, we developed a mean field theory to treat the thermodynamics and kinetics of protein folding, which can be used to interpret and analyze experimental results. According to this theory, a protein consists of a number of units (e.g., foldons), which can be described by a two-state model, and the interactions between these units are treated in a mean-field manner. We pointed out that different experiments like absorption and emission spectra, CD, calorimetric measurements, NMR, atomic force microscopy, small-angle X-ray scattering, etc., can provide information on the protein folding−unfolding behaviors either of different units (by absorption, emission, and CD spectroscopies) or of the whole protein (by NMR, AFM, calorimetry, X-ray scattering).

Prof. Y. R. Shen has been on the advisory committee of IAMS since 1993. Through association with him, Hayashi has worked on sum-frequency generation related to the experimental results obtained by his group, for example, the first-principle calculation of IR-UV SFG spectra of acetone by combining the molecular dynamics calculations (to determine structures of the surface) and quantum chemistry calculations (to determine dipole derivatives and polarizability derivatives). We formulated a vibronic theory for the doubly resonant IR−UV SFG developed by Shen's group. The theory can provide the selection rule for the vibrational mode active in this type of SFG, and we have showed that, at a fixed UV (or visible) laser wavelength, the IR spectra can be obtained and, at a fixed vibrational IR laser wavelength, the excitation spectra can be obtained. The IR−UV SFG optical activity in bulk solution was observed by Shen's group. The conventional dipole approximation clearly breaks down in this case. We proposed several mechanisms for this, for instance, the breakdown of the B−O approximation, the improved Hertzberg−Teller approximation, and the inclusion of magnetic-dipole or quadruple interactions. Shen's group has recently succeeded in developing a femtosecond time-resolved IR−UV SFG to study the vibrational dynamics of surface water molecules. A vibronic theory was developed by Hayashi that includes a general theoretical treatment of time-resolved SFG, mechanisms of vibrational relaxation and energy transfer, and quantum chemistry calculation of water clusters.

On October 1, 2007, I will retire from the Institute of Atomic and Molecular Sciences and move to Chiao-Tung University. This move will give me a nice opportunity to actively continue my scientific research work. I sincerely hope that I can still make some useful contributions to the scientific community.

Sheng H. Lin