Autobiography of Max Wolfsberg

Emigration

I was born in Hamburg, Germany on May 28, 1928 in the Jewish Hospital, which was located a couple of blocks from St. Pauli, the famous red light district of the port of Hamburg. The obstetrician who delivered me was named Dr. Stork. A couple of years ago, I met a lady, who upon finding out that I came from Hamburg, told me that she had an uncle there who was an obstetrician and had a curious name. I immediately told her that he delivered me. I grew up in a part of the city known as Uhlenhorst and was aware of the rise to power of Adolf Hitler during the 1930s. When the time came for me to start elementary school, my parents enrolled me in a private school rather than a public school to avoid difficulties. I only remember one instance during my four years in this school in which one of my fellow students made a nasty remark about my being Jewish. After completing the four years of elementary school in Germany in those days, one continued to a university preparatory high school or to a less academic high school, depending on performance on a special examination. By the time I finished elementary school in 1938, Jewish children were no longer permitted to attend public university preparatory schools nor universities. Hence, my parents enrolled me in a Jewish school, the Talmud Torah School, and moved to a section of Hamburg close to this school, where I started the fifth grade, and my brother Kurt, who had been born in 1932, started the first grade in 1938. I remember well that there was about one hour of instruction in Hebrew every day, a subject in which I was very deficient compared to my classmates who had been in this school for four years. My parents hired Mr. Hamburger, an elementary school teacher, to give me special Hebrew lessons. Sadly, I learned later that Mr. Hamburger died in a concentration camp in Poland when he chose to accompany a group of Jewish orphans to this camp. By the winter of 1938, more German Jews were beginning to realize that their future in Germany looked pretty bleak, and consequently, some students and teachers started to disappear from school. My parents also set in motion an attempt to obtain permission to enter the United States. My father, who was a lawyer in his forties, could no longer carry out his profession. In November 1938 came the so-called Krystall Nacht, which is often taken as the date of the beginning of the holocaust. Many Jewish men were arrested, windows of Jewish owned stores were broken, and buildings of Jewish organizations were smashed. I heard the Gestapo men coming to our apartment to arrest my father. My mother talked them out of it by showing them a certificate signed by a Nazi physician that his physical condition was such that he had to remain in bed. From my bedroom, I heard the Nazi's smash the dishes in the Jewish Community Center, which was adjacent to the house in which we lived. By early summer 1939, my family obtained permission to enter the U.S.A. and made preparations to leave Germany. As a condition for obtaining German passports for leaving, the Gestapo made my father book passage to New York on a German boat sailing at the end of August. As the summer progressed, it became obvious that war would start very soon. When German boats were ordered to return to their home ports in Germany, my family was in the position of having a visa to enter the U.S.A. but had no way of getting there. Luckily, there was a Swedish boat scheduled to sail from Göteborg to New York in the middle of September, and some very generous Swedes lent my parents the money to pay for the tickets. We flew from Hamburg to Göteborg two days before the German army entered Poland, thereby starting World War II. In the middle of September, we sailed to New York on a very northerly route to try to avoid meeting any war ships. The boat was packed with people fleeing a war in Europe, arriving in New York on September 20.

We spent about four months in New York City before moving to Galveston, Texas, on the advice of Jewish relief agencies, which advised that New York was too crowded with Jewish refugees. While in New York, my brother and I attended P.S.7 Bronx in the second and sixth grades, respectively. Early in 1940, I started attending the sixth grade of a newly opened junior high school in Galveston, S. F. Austin School, a school with grades 6 through 8. Under the 11 year Texas school system, the eighth grade was the first year of high school. Enrolling in this school had a very profound effect on my life. The school had four classes which were called grade 6, with the students apportioned in the four classes on the basis of an examination, with all of the best students in class 1 and all of the least promising students in class 4. I was given an exam to take when I appeared at the office of the principal. My knowledge of the English language was such that I had no idea what was going on. Not unexpectedly, I ended up in class 4. In this class, I excelled. While in Germany, I had been a fair student, I suddenly found myself in a position where I was by far the best student in the class. This gave me a fantastic self-confidence. I started tutoring my fellow students and found that such tutoring could raise their grades drastically. I started a debating club and invariably won my debates. I now suspect that my great skill in debating was the result of the fact that the debate judges chose not to embarrass me by telling me that they could not understand my heavily accented English. I was very active on the editorial board of the school newspaper. After a year in this class, I was promoted to a class with more intelligent students. However, by this time, I had sufficient experience as a good student and enjoyed school so that, subsequently, I was always among the better students in all of my classes in any school that I attended. In the eighth grade, we started foreign languages. Latin became my favorite subject and remained that for a few years. When I informed a Latin teacher that I intended to become a Latin teacher, she counseled me that this was a poor career choice. I then did switch my career choice to science. I started my second year of high school at Ball High School in Galveston in the fall of 1942. In the meantime, my Father had been unable to start a new career in Galveston. My Mother, who had not worked outside of the home in Germany, started working as a clerk in an insurance company. As it was, she was the main supporter of her family until my brother and I graduated from college. In order to help my Father, the family decided to move to St. Louis in the winter of 1943. I finished the second year of high school at Soldan High School in St. Louis in 1943. I established a reputation at Soldan by winning a city-wide Latin contest, which was usually won by a student from a Catholic school. I stayed at Soldan for the next two years and graduated in the spring of 1945. It was my great luck that Washington University announced a new competitive scholarship program for St. Louis students in 1945, under which 10 full-tuition four

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year scholarships would be awarded. I won one of these scholarships, which enabled me to attend Washington University.

Washington University

I enrolled at Washington University in the Fall of 1945 as a chemistry major. The second World War had ended during the summer. A. H. Compton left the Manhattan Project to become Chancellor at Washington U. He soon announced that he had recruited six new chemistry faculty members from Los Alamos, J. W. Kennedy, A. C. Wahl, S. I. Weissman, L. Helmholz, H. Potratz, and D. Lipkin. Kennedy and Wahl had been a postdoctoral student and a doctoral student, respectively, of G. Seaborg at Berkeley and are recognized together with Seaborg as the co-discoverers of the first transuranic elements plutonium and americium. Weissman and Lipkin had both been in the laboratory of the great American physical chemist G. N. Lewis. L. McMaster, who had been chairman of the department and who was my first year chemistry teacher, died soon after Compton's announcement, and Kennedy became the chairman. Kennedy became my first undergraduate advisor. Weissman, my hero, was my undergraduate physical chemistry teacher. I must have spent almost an hour a day in his office when I was taking physical chemistry. He never protested this invasion of his research time. Helmholz was my undergraduate research advisor as well as my graduate school mentor. He too was very generous with his time. He even permitted me to share his office with him. I was a very demanding student, and he never complained. Over time, he became a parent-figure and a friend. He had been a graduate student of J. E. Mayer and a postdoctoral student of L. Pauling. It was during my freshman year that I found my future Ph.D. thesis topic. In a prelaboratory lecture, the instructor showed us a test tube containing a solution of potassium permanganate; I do not recall what the context was. However, after the lecture, I went up to his desk and asked him "Why is permanganate purple?". His answer was "Because God made it so." I then decided that I would try to study this problem. Several years ago, the chemistry department undergraduate chemistry club at Irvine commemorated this occasion by wearing purple T-shirts inscribed with the question "Why is permanganate purple?". I mentioned my interest to Professor Helmholz a couple of years later, and he replied that this topic was of great interest to him also and that, in fact, he had recently discussed this question with Linus Pauling. He showed me some resonance structures that Pauling had scribbled for permanganate.

During my second year at Washington U., I recognized that our family finances were such that I should try to obtain my undergraduate degree as soon as possible. Having taken qualitative analysis in summer school, I determined that, if I obtained two years of credit by examination for my knowledge of German, I could graduate after a total of three years. I proceeded to do so. In my senior year, I enrolled in undergraduate research with Helmholz. At the same time, I was enrolled in undergraduate p-chem with Weissman and in the graduate-level course that Weissman taught on quantum chemistry. In research, I looked at the absorption spectra of many transition-metal—halide complexes using a Beckman spectrophotometer. In the quantum chemistry course, I wrote a term paper on molecular orbital theory based on the classic paper by Van Vleck and Sherman and decided that I should further study molecular orbital theory if I wished to understand the absorption spectra which I was obtaining in the laboratory as well as the spectrum of the permanganate ion. When I told my mentors that I wished to go to graduate school at Washington U. and that I certainly wanted to emphasize theory in this study, they all discouraged me, saying that I should go to a school where there were people who considered themselves theoretical chemists. Weissman told me that he would, under no circumstances, be willing to have a graduate student who specializes in theoretical chemistry. Helmholz, who also encouraged me to go elsewhere, was not quite as adamant about not taking a theoretical student. I went ahead and applied for admission to graduate school in chemistry at Washington U. and was turned down within couple of weeks with the statement that the department would not accept its own undergraduates. I had been taking some advanced math courses, which I had greatly enjoyed. I went to the mathematics department at Washington U. and asked if they would accept me as a student for graduate study. I received an affirmative answer. I promptly went back to Kennedy in the chemistry department and told him that I would go to grad school in mathematics unless the chemistry department accepted my application for graduate study. I pointed out that, while I understood the reasoning for not considering my application, I could not leave St. Louis for graduate school because my Father had died the previous year and I could not leave my Mother and brother alone, especially since even my small salary contribution to the household income would ease my Mother's financial burden somewhat. I was then accepted for graduate study in chemistry in Fall 1948.

I chose Professor Helmholz as my graduate research advisor. We agreed that I should work on the theory of the spectra of transition-metal complexes, in particular, permanganate and chromate. Professor Helmholz had discovered low-temperature spectral measurements by K. H. Hellwege in Goettingen of permanganate ions imbedded in perchlorate crystals of different site symmetries at the position of the perchlorate ion (and therefore of the permanganate ion). The polarization of the permanganate absorption and the splittings of the permanganate lines in the crystals should give information about the excited permanganate states. Thus, the ground electronic state of the permanganate ion is almost certainly described as a singlet A1 state. The excited state of allowed dipole transitions must be a singlet T2 state. Hellwege attempted no explanation of his observations. However, the triplet degeneracy of the excited electronic state was clearly visible in all of the spectra with sufficiently low site symmetries at the permanganate ion. Professor Helmholz agreed to a detailed study of the Hellwege spectra while I would try to work out the molecular orbital theory of permanganate. While chemists in 1948 were already using Huckel molecular orbital theory for studying conjugated hydrocarbons, the preferred theory for looking at chemical bonding was valence bond theory because valence bond theory yields in first order a much better binding energy for the hydrogen molecule than does first-order molecular orbital theory. My studies of R. S. Mulliken's series of papers published in the 1930s largely in the *Journal of Chemical Physics* had convinced me that we should try the molecular orbital approach in studying permanganate. I then set up the appropriate atomic orbital symmetry orbital combinations for symmetric molecules RX2, RX3, RX4 (tetradral and square planar), and RX6 (octahedral). I used atomic s, p, and d orbitals on R atoms and s as well as p atomic orbitals on X atoms. This work differed from earlier work of Mulliken in that d orbitals on R were included. We then used hand-waving arguments similar to arguments used previously by Mulliken for molecules involving no d atomic orbitals to explain bonding in transition-metal complexes. These arguments were purely qualitative. We recognized that the alphas of Huckel theory were related to the valence-state ionization potentials of the various different orbitals in the transition-metal complexes and that the betas of Huckel theory needed replacement by quantities which reflect pi and sigma bonding and also overlap integrals between atomic orbitals. As it was, our arguments were purely qualitative. This situation changed during my second year in graduate school when I opened the December issue of the *Journal of Chemical Physics* and found the famous paper by Mulliken, Rieke, Orloff, and Orloff on overlap integrals between s and p atomic orbitals. I immediately ran to Professor Helmholz and proposed to extend the Mulliken et al. paper to include overlap integrals involving d orbitals. The next problem that arose was that, while the Slater rules for effective nuclear charges and effective *n* values work reasonably well to construct atomic orbitals which are close to Hartree−Fock atomic orbitals of the first two long rows of the periodic table, these rules do not work well for d orbitals. I hence fitted most of the Hartree−Fock functions in the literature to linear combinations of Slater-type functions and used these to calculate the overlap integrals that I needed to apply what is now known as the Wolfsberg−Helmholz approximation.

We wrote up my thesis publication for the *Journal of Chemical Physics* and sent it off to J. E. Mayer. In a signed referee report, Maria Goeppert Mayer approved our paper and obviously told R. S. Mulliken about the paper because an invitation followed from Mulliken to Helmholz to present a seminar in Chicago. Helmholz asked me to accompany him, saying that he would pay for my trip from his own pocket. Likewise, he paid for my trip to the Ohio State Symposium in 1951. I was a pretty innocent 20 year old at the time, and I well remember Mulliken inviting me to have a beer with him in a bar in Columbus, the first beer I ever drank.

I finished up my Ph.D. requirements with the final exam in August 1951 and left to take up a position at the newly created Brookhaven National Laboratory in Upton, NY. In applying there, I had stated that I wished to do spectroscopy on the transuranic elements in various crystal environments to prove the hypothesis that the transuranic elements contained 5f electrons. While I did not see the letters of recommendation from my Washington U. mentors, it is quite clear that they did not sing about my laboratory skills. R. W. Dodson, the department chairman, informed me that Brokhaven was following a university type of employment system with short-term contracts followed after six years, subject to research excellence, by the award of a tenure position. They were in the process of hiring in these tenure track positions. They were interested in hiring in a theoretical position on the basis of my recommendations, while on the other hand, they were also quite sure that they did not want a chemical theoretician on their permanent staff. Hence, they offered me a nontenure track position in which they expected me to take an interest in applications of theory to ongoing research projects in the chemistry department.

Brookhaven

Brookhaven was a very exciting place. I will just point out a few of the research efforts. J. Bigeleisen was working on the observation and elucidation of the effect of isotopic substitution on chemical and thermodynamic properties. R. Davis was beginning his work on neutrinos, attempting to determine their mass. This work eventually led to his winning the Nobel Prize. J. Hastings and L. Corliss were beginning to study magnetic scattering from lattices by use of neutron diffraction. It was a very intense research environment. I became seminar chairman soon after I arrived. One typically had to warn seminar speakers that the department members were quite aggressive in their questioning of speakers. I did follow the instructions that I was given when I had been offered the position. I soon did start working with Bigeleisen on isotope effects, in particular, kinetic isotope effects. This led to our joint paper in the first volume of *Advances in Chemical Physics*. My major interest in isotope effects over the last 50 years, much of it in collaboration with Bigeleisen and also his former students, can be traced to this beginning. The close personal relationship with both Grace and Jake has been another “bonus”. I also became interested in the excitation of extra nuclear electrons in atoms following nuclear decay processes such as beta decay or K-capture. In connection with an experiment of R. Wolfgang, I studied the probability of bond rupture following nuclear decay. Together with M. L. Perlman and J. P. Welker, I worked on the theory of the ratio of K-capture to positron emission in nuclear decay. This work occurred during the time when the world of physics was being turned upside-down by the work of Lee and Yang on parity nonconservation; my work on beta decay enabled me to understand what was going on in physics, although I certainly made no contribution to the revolution in physics. Over the years, I had spent much time talking to L. Friedman, a pioneer in many areas in modern mass spectrometry, about mass spectral patterns. Friedman was one of the very first people who recognized that mass spectral dissociation patterns appear to be driven strongly by the energetics rather than by random dissociation. At the time, Friedman had a very active collaboration with F. A. Long at Cornell University. I joined this collaboration for a couple of years in exploring the application of the statistical theory of mass spectra, which had been proposed by H. Eyring and his co-workers. While the Eyring group had looked at the mass spectra of alkanes, in particular, propane, we studied the mass spectra of the lower aliphatic alcohols. The alcohols, by virtue of the presence of an oxygen atom, had a much “richer” mass spectrum. Our studies confirmed Friedman’s ideas of the importance of energetics as the basis of the observed mass spectral patterns.

At a chemistry department holiday party in December 1955, I met a biology graduate student from NYU who had just started doing her graduate research laboratory work at Brookhaven. She came as the guest of one of my colleagues. I did talk to her briefly, and I thought that she was very interesting. It took me a couple of months to get up the courage to ask her to have dinner with me at the Three Village Inn in Stony Brook on the last day of the Jewish festival of Passover. I still have a date with that girl on the same date in the Jewish calendar every year. Our romance was carefully watched by my elder colleagues in the chemistry department, who considered me to be their child that needed someone to take care of him. They all loved Marilyn Fleischer and so did I. After dating almost a year, we announced that we would get married in June (1957). In 1956, I had started to realize that my six years at Brookhaven would finish pretty soon and that it was time to make plans for my future employment. Before acting on this thought, I had casually passed Richard Dodson, the department chairman, in the hall one day; he stopped and informed me that he had just passed the department’s decision to give me a tenure appointment to the Laboratory director. This came as a complete surprise to me. After discussing our future at Brookhaven, Marilyn and I decided that it was reasonable after six years at Brookhaven to request a sabbatical. I was probably one of the first Brookhaven staff members who made such an application. After talking this matter over with the chemistry department, I applied for a NSF Senior Postdoctoral Fellowship. The application was successful. The stipend was $10000 (plus travel expenses), higher than my annual Brookhaven salary. The fellowship enabled me to spend the year in three places, Oxford (with R. P. Bell), Copenhagen (with C. Ballhausen), and Upsala (with P. O. Loewdin). At the end of the fellowship, the Weizmann Institute invited me to spend a month in Rehovot (with F. S. Klein). I returned to Brookhaven with new perspectives.

Much of the work on isotope effect theory at Brookhaven had been based on the classic paper by J. Bigeleisen and M. G. Mayer (BM) on the reduced isotopic partition function ratio and by approximations introduced by them. In the BM formulation, thermodynamic isotope effects (including rate isotope effects in a transition-state theory formulation) depend on knowing harmonic molecular vibrational frequencies and the isotope effects on these frequencies. The approximations required by the theory came about, in part, because the determination of these isotope effects in large (unsymmetric) molecules would require the diagonalization of large matrices, involving major computational effort. However, already in the late 1950s and early 1960s, computer programs existed that enabled the ready diagonalization of relevant large matrices. One such program was written, at my request, by W. Givens when be visited NYU in about 1958. When J. Ibers came to Brookhaven, he pointed out to me that his former colleagues J. H. Schachschneider and R. G. Snyder had a program for calculating harmonic vibrational frequencies of a molecule by the GF matrix method of Wilson which combines a matrix diagonalizer with a program for constructing G matrices, and he volunteered to ask them to make this program available to me. I still feel a deep debt to Ibers and his former colleagues. Our new computational abilities completely changed the isotope theory game. An early application of the programs, which still required a knowledge of isotope-independent harmonic force constants and geometry, was the work on isotope effects on the vapor pressures of the ethylenes, which I carried out with M. J. Stern and A. Van Hook, who worked as postdocs of Bigeleisen on measurements of experimental vapor pressure isotope effects. When Bigeleisen left on sabbatical leave before their postdoctoral appointments expired, I had "inherited" them. We decided to apply a statistical mechanical cell model of the liquid which had been proposed by Bigeleisen but which had not been completely applied before. This model worked quite well in rationalizing the ethylene vapor pressure isotope effects and has become the standard theoretical model for such work, especially in the research of Van Hook, who moved to the University of Tennessee. My collaborations on isotope effect calculations with Stern went on until his untimely death. My collaborations with Van Hook are still ongoing after more than 40 years. I thank both of them for making science "fun".

Over the next couple of years, while Stern was a Professor at the Columbia College of Pharmacy and at the Belfer Graduate School of Science of Yeshiva University, he and I carried out many calculations on equilibrium and kinetic isotope effects (transition-state theory) to test whether some of the simple qualitative arguments about isotope effects which followed from the approximate equations developed by Bigeleisen and Mayer had meaning when one calculates isotope-dependent frequencies using the programs derived from the Schachtschneider/Snyder programs. Thus, the Bigeleisen Mayer approximations lead to the conclusion that at higher temperature, an isotope effect on an equilibrium constant implies that the Cartesian force constants must change at the position of isotopic substitution to produce any isotope effect except a trivial one. We did extensive numerical calculations that indeed this high temperature result still makes sense for room-temperature effects for both equilibria and rate constants (within a transition-state formulation). Thus, it makes sense to say that isotope effects reflect force constant changes at the position of isotopic substitution. This is important in considering secondary isotope effects. A secondary isotope effect is one where the isotopic atom is not directly involved in the bond making or the bond breaking of the reaction. When I first learned about the secondary kinetic isotope effects which were being measured by V. J. Shiner, E. S. Lewis, and A. Streitwieser, it was my feeling that the coupling of vibrations in molecules might be such that the observation of an isotope effect might not really tell you very much about what is happening in a reaction. The extensive calculations demonstrated that this "feeling" was wrong. This conclusion extends further. The English physical organic chemist C. Ingold proposed the existence of a substituent effect in chemical reactions that he called a ponderal effect, which only depends on the shape and distribution of mass introduced by the substituent. I was able to show that a ponderal effect as proposed by Ingold would be equivalent to a no force constant change isotope effect. It does not contribute significantly to a substituent effect even at room temperature.

My interest in computer calculations on isotope effects made me interested in other theoretical studies which require large digital computers. At this time, both D. Bunker, then at Los Alamos, and M. Karplus were beginning to study simple elementary reactions by carrying out classical trajectory calculations, which lead to the calculations of rate constants by the use of Monte Carlo averaging. D. Kelly and I decided to do fairly extensive calculations on translational to vibrational energy transfer in collinear collisions of an atom and a diatomic molecule. These calculations showed that some simple approximations that had been reasonably made in both classical and quantum mechanical calculations on these systems can be quite erroneous.

V. J. Shiner from Indiana University visited Brookhaven for a couple of months during a sabbatical to talk with me about secondary deuterium isotope effects. He also was interested in solvent isotope effects of H_2O versus D_2O and also mixed H_2O/D_2O solvent isotope effects. The organic chemists had used the mixed solvent isotope effects to draw mechanistic conclusions about reactions. These reasonings required a knowledge of the equilibrium constant for the reaction of H_2O and D_2O to form HDO. The crude Bigeleisen Mayer harmonic frequency approximation for the equilibrium constant yielded a value of exactly 4 for this equilibrium constant, and this value was often used by the organic chemists. Shiner measured this equilibrium constant at Brookhaven together with L. Friedman and determined a value considerably below 4. An exact Bigeleisen Mayer type of calculation with the frequencies calculated with our programs yielded a value below 4 but not as low as the experimental measurements. This led me to the $G0$ factor, an isotope-dependent correction to the zero-point energy term of a rotating−vibrating molecule which does not arise from terms which involve $(n + 1/2)$ or powers of $(n + 1/2)$, where n refers to the vibrational quantum number. When I talk about crude Bigeleisen Mayer calculations above, I am in no way implying any error in the calculation of isotope effects in using the BM approach, but I am talking about approximations that some people have introduced into applications of this theory. I started exploring the $G0$ term at Brookhaven and later continued this exploration at Irvine.

In 1962, my colleague F. A. Long, with whom I had been working on mass spectra, asked me to spend a semester at Cornell to teach the undergraduate physical chemistry course.

A year later, V. J. Shiner, with whom I had started extensive discussions on secondary isotope effects, invited me to spend a semester at Indiana University to teach a quantum chemistry course and for further discussions on isotope effects with him and his group. I enjoyed my teaching experiences but not sufficiently so that I was willing to think about leaving all my "parents" at Brookhaven for a university professorship. Yet, when talking with Francis Bonner, the chairman of the chemistry department at the new campus of the State University of New York at Stony Brook, I did express a great interest in teaching one course each semester at Stony Brook, which is located about 20 min by car from Brookhaven After much negotiation between the University and Brookhaven, I did start teaching at Stony Brook "on a part-time leave of absence from Brookhaven" in 1966. A couple of years later, F. S. Rowland, who was creating a new chemistry department at the new campus of the University of California in Irvine, invited me to spend a month as a Regents' Lecturer to lecture on isotope effects. I traveled to Irvine with Marilyn and our two year old daughter Tyra in January 1968. This led to an offer from Rowland to join the faculty at Irvine. I had decided by this time that the joint appointment between Brookhaven and Stony Brook created difficulties of divided loyalties. On the other hand, I also wanted to live in an environment with students. After innumerable discussions with Rowland about my move to Irvine, which must have led him to regret ever broaching my move, Marilyn and I decided to leave the East Coast. Being part of a new and hopefully growing institution seemed very exciting. We arrived in Irvine in Spring, 1969.

Irvine

(In looking over my notes discussing my early years, I realize that this biographical discussion will grow far too long if I discuss my life in Irvine in the same detail. I apologize to colleagues with whom I have enjoyed collaborations but whose contributions are being omitted.) By the time I arrived at the University of California, Irvine, for the Spring Quarter 1969, I joined a faculty of about 10 other chemists in the School of Physical Sciences, whose dean was the physicist F. Reines. At the time of this writing, the chemistry department faculty size has expanded by a factor of approximately four. The Spring of 1969 coincided with greater U.S. involvement in the war in Vietnam and was a time of great unrest at many college campuses in this country. UCI was spared much of this unrest, in part, because it was a new campus and, in part, because many of the students had grown up in Orange County, traditionally a conservative part of California. I immediately started teaching the one-quarter graduate course in thermodynamics, an assignment I kept for many years since no one else had any interest in teaching this course. F. S. Rowland had taken a leave from the university, and D. L. Bunker was the acting chairman. When Rowland returned to campus the following year, he soon resigned his chairmanship, and H. Moore became the second chairman of the department.

Many of my research activities in isotope effects grew out of my interests in comparing precise experimental measurements of equilibrium isotope effects with theory. Standard theoretical work on isotope effects was based on the Born−Oppenheimer (BO) approximation, in which isotope effects result from the effect of different mass atomic nuclei moving on identical potential energy surfaces, the surfaces being the respective isotope-independent electronic energy surfaces as a function of nuclear geometry. The previously mentioned Bigeleisen Mayer formulation of isotope effects, as well as most considerations of isotope effects, was based on the BO approximation. It is within the BO approximation that the statistical mechanical formulation of isotope effects leads to the statement that isotope effects (whether observed on equilibria or on rate constants within transition-state theory) are probes for force constant changes at the position of isotopic substitution between reactants and products (or transition states). Prior to 1952, almost all full (a priori) calculations of electronic wave functions of molecules (always within the BO approximation) had involved the hydrogen molecule. By the middle and late 1950s, there were sufficient advances in computers as well as in theory so that Hartree−Fock functions of molecules containing larger numbers of electrons were becoming available. Such wave functions are a necessity if one wants to evaluate corrections to the Born−Oppenheimer approximation. The adiabatic correction is the first-order correction to the isotope-independent electronic potential energy surface of the BO approximation. Adiabatic correction calculations were undertaken by postdocs L. I. Kleinman (now at Brookhaven) and R. D. Bardo. While the effect of these corrections on equilibrium isotope effects are not huge, they are sufficiently large that they should be detectable when accurate experiments are compared with full theoretical calculations (see later discussion).

For the readers not acquainted with the details of how calculations on isotope effects are carried out, it is necessary to comment briefly on these details. For the usual calculations of isotope effects in the harmonic approximation within the BO approximation, one needs an expression for the electronic energy of the molecular system as a quadratic expression of the displacement of the nuclei from the equilibrium configuration (often in terms of valence coordinate stretches, bends, and torsions). The coefficients of the various terms are known as (harmonic) force constants. If cubic and quadratic terms are included, then the calculations include anharmonicity. How were the harmonic and anharmonic force constants determined?

Until quite recently, the usual (only) method for determining the vibrational force constants was the substitution of the expression for the electronic energy into a quantum mechanically derived expression for the rotational−vibrational energy levels of the system to calculate therefrom an expression for these energy levels of the system in terms of molecular parameters including the vibrational force constants. One then obtains the force constants of the system by fitting the force constants to yield spectroscopic values. Since the electronic energy is independent of isotopic substitution, isotopic spectra often played a major role in determining the force constants. This situation has changed considerably over the last 20 years or so with the availability of large digital computers and the programs which enable the calculation of the electronic energy of molecules as a function of geometry. In fact, these programs usually calculate harmonic force constants in Cartesian displacement coordinates as well as the equilibrium geometry of the molecule corresponding to the minimum electronic energy. Some 20 years ago, I had the pleasure of meeting M. Saunders when he visited Irvine on a sabbatical from Yale. After he returned to Yale, we started a collaboration with K. Laidig, his graduate student, by rewriting our old programs from Brookhaven so that they would accept directly as input the harmonic Cartesian force constants and equilibrium geometry of relevant molecules and enable the calculation of equilibrium isotope effects in the BO approximation and the harmonic approximation. The most recent instance of my collaboration with Saunders just appeared in the *Journal of the American Chemical Society* quite recently. Agreement with experiment in all of these endeavors was quite good. Those who have enjoyed collaborations with Saunders will appreciate my statement that I enjoy late night telephone conversations. Many is the time when I have talked with him after midnight. (Who knows what time it was in New Haven?) We investigated further the effect of the previously mentioned $G0$ term on the molecular partition functions of molecules as well (and found a general expression for it) as well as the anharmonic correction to the zero-point energy. In fact, of all of the corrections that one can apply to calculations in the harmonic approximation/BO approximation, these tend to be the largest correction factors. The Irvine version of the program that evaluates isotopic partition function ratios directly from quantum mechanical calculations of the electronic energy does include this correction in the evaluation of isotopic partition function ratios.

When one studies the literature on measured equilibrium isotope effects, one finds that the most studied system over a wide range of temperature is the equilibrium $H_2O + HD = HDO + H_2$. On the cover of this issue of the journal, there is one graph in the lower right hand corner of the cover art which is reproduced from a communication by R. D. Bardo and myself (*J. Phys. Chem.* **1976**, *80*, 1068) and which shows three curves of plots of ln K versus $1000/T$. The highest lying curve (dash−dot−dash) is a plot of theoretical values including corrections for vibrational anharmonicity, vibrational−rotational interaction, and non-classical rotation. There is no correction to the Born−Oppenheimer approximation. The lowest of the curves (dash−dash) corresponds to a least squares plot of the experimental data obtained by J. R. Rolston and his coworkers (*J. Phys. Chem.* **1976**) over the temperature range of 280−475 K. The middle curve, the solid line, is the plot which contains all of the correction factors noted above for the (dash−dot−dash) curve plus the correction to the Born−Oppenheimer approximation (the adiabatic correction). The K values differ from those without the adiabatic correction by a factor of $\exp(-5.8/T)$, about 0.98 at $T = 298$ K. The ratio of K with the adiabatic correction to the experimental value is 1.003 at 273 K, reaches a maximum 1.007 at 330 K, and then decreases to 1.001 at 480 K. The agreement between theory including the correction to the BO approximation and experiment is very good.

It has already been mentioned earlier here that the low value measured for the equilibrium constant for the self-exchange of water in the gas phase, $H_2O + D_2O = 2HDO$, led us to look carefully at corrections to this equilibrium constant arising from vibrational anharmonicity and, in particular, led to the G0 correction. While the original calculations seemed to show that there was an effect, it turned out that this result arose from an algebraic error. As it is, the value calculated for the equilibrium constant without any corrections at 298 K is 3.85, fairly independent of which harmonic force field deduced from spectroscopic measurement is used. The various corrections from anharmonicity, from quantum rotation, from rotational−vibrational interaction, as well as from the adiabatic correction make little or no contribution. There is no doubt that the result of the effect, to first order, has a $1/m$ dependence in the atomic masses and therefore vanishes. The lowest value that we have obtained for the equilibrium constant at 298 K is 3.84. On the other hand, the experimental value obtained at this temperature in the original experiments was 3.76, while the latest measurement by J. W. Pyper and co-workers yielded 3.81 ± 0.06. Thus, within the experimental error limits, experiment and theory agree. Note that the theoretical considerations on the two equilibria just discussed were based on force fields derived from spectroscopic data. Many colleagues were involved in these calculations, including R. A. Bardo, P. Bopp, J. Bron, C. F. Chang, C. L. Chen, M. J. Huang, B. Maessen, A. W. Raczkowski, and F. Webster.

In 1973, I became chair of the Irvine chemistry department. This was an interesting experience for me. It was a very difficult time financially for the state of California, and there was some doubt at some point if the smaller campuses of the university could survive. Irvine was one of those. We did all survive, but there was very little growth of the department during my tenure. While I was chair, I started an active collaboration with D. Thompson (now at the University of Missouri), who had been a postdoc with D. Bunker at Irvine and had moved on to Los Alamos. I did spend some summer months at Los Alamos with Thompson. I used the Los Alamos computers to do classical mechanical studies in which the Monte Carlo methods for averaging the trajectories to obtain results to be compared with experiment were replaced by nonrandom numerical integrations. Graduate students V. Cheng (actually at Stony Brook) and H. Suzukawa were involved in these calculations. I also used the Los Alamos computer facilities to do calculations in connection with our studies of the adiabatic correction.

In 1977, I received an invitation from A. Klemm and K. Heinzinger at the Max Planck Institute for Chemistry in Mainz, Germany. I also received an Alexander von Humboldt Award from the similarly named Foundation to support my stay in Germany. The award program, which is still ongoing today, was basically a gesture by the German state in gratitude for the American Marshall Plan, which saved a starving Europe from disaster after World War II. I applied for a sabbatical leave from Irvine for the year 1978/79 and was persuaded also only to take a leave of absence from being chair rather than resigning this position. (I did finally quit the position in 1980.) Klemm was (is) editor of the *Zeitschrift fur Naturforschung*. Heinzinger, his former Ph.D. student, had been a postdoc at Brookhaven. The p-chem world was still trying to digest the pioneering molecular dynamics (MD) calculations of Rahman and Stillinger of liquid water. To everyone's surprise, they had a model of water which reproduced the properties of water without explicitly requiring the formation of water polymers. Heinzinger was not a theoretician, but he had great interest in ionic solutions. He decided to carry out MD calculations on ionic solutions in Rahman−Stillinger water. The general opinion of my colleagues in the U.S. was that these calculations would be a complete failure. Heinzinger undertook these calculations together with C. Vogel, whom I had met at Indiana University when I was visiting V. J. Shiner there and whom I had recommended to Heinzinger; he was not a theoretical chemist.

By the time I got to Mainz, Heinzinger and Vogel had published their first papers, and Heinzinger had gathered a fairly large group of graduate students and postdocs. While I did not join in the MD calculations, I watched the evolving field of MD calculations of aqueous ionic solutions with great interest. I was especially drawn to the work of a young Ph.D. student, P. Bopp. Bopp eventually joined me as a postdoc at Irvine for a couple of years as a Lynen Fellow (again with the generous support of the Humboldt Foundation). Bopp worked at Irvine on the spectrum of ammonia as well as on MD calculations. In fact, L. X. Dang, a guest editor of this volume, got his training in MD calculations from P. Bopp who is now at Bordeaux.

I knew that my trip to Germany would involve some personal difficulties for me because of my memories of my early years in Germany. H. Pfeiffer, the secretary general of the Humboldt Foundation, literally spent hours with me to ease my personal distress caused by being in Germany. Both Heinzinger and

Klemm were marvelous hosts. Since I was in Germany in 77/78, I have made many trips to Germany, including the former East Germany. Thus, I spent a sabbatical leave as a German National Science Foundation Pofessor in Ulm with W. Witschel, whom I met first during the year in Mainz. I also spent a very exciting one month sabbatical as a National Research Council Fellow during the East German revolution in October 1989. Leipzig was, in some ways, the birthplace of that revolution. Revolution took place only on Monday evenings when we all marched around the town square and shouted "Die Mauer muss weg" ("The wall must go"). I enjoyed a couple of stays in Germany on reinvitations of the Humboldt Foundation in Mainz, Ulm, and Leipzig. My Leipzig visits led to a prolonged collaboration on MD calculations of diffusion in zeolites with S. Fritzsche, R. Haberlandt, and others.

During my stay in Mainz, I became acquainted with the nuclear chemist H. O. Denschlag, who had actually been a postdoc with my colleague E. K. C. Lee in Irvine before I moved to Irvine and who had hosted my brother Kurt's year in Mainz the year before I was in Mainz. German undergraduate students typically spend 6 months away from their home campus during their third university year. Denschlag proposed that six or so Mainz students spend half of a year in Irvine under a program financed by DAAD (German Academic Exchange Service). During the 10 or so years of this program, the Irvine chemistry department hosted some very bright undergraduates who typically enrolled in first-year graduate school courses and also undertook some research projects. A high percentage of these students have ended up in European academic positions. Among these students were two authors whose work I have been told is included in this volume, E. Spohr (Essen) and D. Marx (Bochum). Both Spohr and Marx did undergraduate research in my group in Irvine. They both returned to Mainz to do undergraduate research with Heinzinger on water MD calculations. Spohr also did his Ph.D. with Heinzinger, while Marx did his Ph.D. on Monte Carlo calculations in Mainz. Spohr came back to Irvine as a postdoc, and Marx went to work with M. Parrinello and consequently started applying Car−Parrinello molecular dynamics to aqueous systems. Spohr and I have enjoyed a multiyear research relationship on MD calculations.

Among recent isotope effect work, I mention work with Van Hook and L. Rebelo on isotope effects on second virial coefficients and also on liquid−vapor equilibrium. Also, Van Hook, Rebelo, P. Paneth, and I have been recently trying to write a graduate-level text on isotope effects. For many years, my office neighbor at Irvine has been P. Rentzepis. We do talk about many things including even research. These discussions have recently taken me back to the beginnings of my research career, namely, the so-called charge-transfer bands of transition-metal complexes. Rentzepis and his group have carried out a unique time-resolved XAFS study of the reduction of Fe(III) oxalate after photon absorption in the electron-transfer band. We have discussed this work in a paper.

Finally, some family remarks. Marilyn received her Ph.D. in biology from NYU on the basis of her Brookhaven research. She then did postdoctoral work at Brookhaven on a NIH postdoctoral fellowship with H. Quastler. After the arrival of our daughter Tyra, she retired from active research. Tyra went to school at Princeton and received her Ph.D. in molecular biology from UC San Francisco. She did a postdoc at the National Medical Library at NIH and is now Associate Director of Informatics at NHGRI, NIH. She is married to Eric Francis and has one son Nathaniel. My brother Kurt did his undergraduate work at St. Louis University and his graduate work at Washington University, working with A. C. Wahl in fission chemistry. He spent his scientific career at Los Alamos and died sadly in a snorkeling accident on a trip celebrating his 50th wedding anniversary.

Max Wolfsberg

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