

Preface: 25th Austin Symposium on Molecular Structure and Dynamics

This special issue of *The Journal of Physical Chemistry A* is devoted to the 25th Austin Symposium on Molecular Structure and Dynamics (ASMD@D) that took place in Dallas, Texas, U.S.A., in the first week of March 2014. During the time period of 1966–2014, James (Jim) E. Boggs organized 23 times the ASMD in Austin, Texas, basically as a one-man enterprise. This sometimes led people to speak of the “Austin Symposium” as the “Boggs Symposium”. Jim Boggs passed away a couple of days before his 92nd birthday and just shortly after he had arranged the future of ASMD by passing its organization into the hands of the authors of this Preface. He attended the 24th ASMD, which took place for the first time in Dallas (ASMD@D), and he was very pleased that the basic approach that he had invented more than 40 years ago, to make the ASMD a very special symposium, was and will be maintained in the future. Unfortunately, he could not attend the 25th ASMD (ASMD@D) in 2014, and therefore, these lines are also in honor of his legacy as an outstanding scientist who did not just publish more than 400 peer-refereed articles on structure determination and related topics and organize the ASMD but was also instrumental in bringing together scientists from West and East, from the Free World and those from behind the Iron Curtain, and scientists from different disciplines devoted to structure determination and molecular dynamics.

■ HISTORY OF THE AUSTIN SYMPOSIUM

The first Austin Symposium in 1966 was planned as a one-time event in the form of a special session of the *Annual Meeting of the American Crystallographic Association*. Two professors of the University of Texas at Austin were the initiators and organizers of this special session, Jim E. Boggs, Professor of Physical Chemistry and a microwave (MW) spectroscopist, and Harold P. Hansen, Professor of Physics, who was about to introduce gas-phase electron diffraction (GED) as a new technique at the University of Texas at Austin. Jim Boggs and Harold Hansen were exponents of two groups of researchers who used diverging methodologies of molecular structure determination in the gas phase.

MW spectroscopy reached back to the year 1934 when Cleeton and Williams (University of Michigan) had studied the 1.26 cm inversion line of NH_3 and provided a new way of analyzing the inversion process of this pyramidal molecule. The technology of using MW radiation in molecular structure determination was significantly improved in the 1940s as it benefitted from the development of MW radar by the Allies during World War II. In the 1950s, MW spectroscopy was applied to the study of simple gas-phase molecules with spectra in the centimeter wavelength region. At the same time, coherent sources of radiation in the centimeter, millimeter, and sub-millimeter wavelength ranges were explored so that MW spectroscopists could aspire to for the investigation of larger molecules in the gas phase and determine molecular geometries by deriving effective bond lengths (r_0 values) from rotational constants. By the 1960s, these developments led to an increasing

community of MW spectroscopists devoted to structure determination of molecules in the gas phase to which Jim Boggs belonged.

Harold Hansen, apart from the fact that he was working in physics, belonged to a different breed of scientists devoted to structure determination. He, who was of Norwegian descent, had spent 1960–1961 as a Fulbright Fellow in Norway. There, he had been exposed to the Norwegian School of GED run by Odd Hassel in Oslo, with an offshoot in Trondheim headed by Otto Bastiansen. Both Norwegian scientists were widely recognized for their GED work, and therefore, it was not a surprise that Odd Hassel was honored with the 1969 Nobel Prize in Chemistry. GED is based on the wave nature of the electrons as reflected by the Schrödinger equation (1925) and as verified by the electron beam experiments of C. Davisson and L. Germer in 1927 (the beam showed a similar diffraction pattern as that caused by X-rays when fired on a crystalline nickel target). In the year 1930, Mark and Wierl carried out the first GED experiment at the Badische Anilin- and Soda-Fabrik (BASF) in Ludwigshafen, Germany. Hassel, who knew Mark from his studies in Berlin, was invited to Ludwigshafen. He quickly realized the potential of this new electron diffraction method for the determination of molecular geometries and therefore brought the GED technology to Oslo, where a new GED group grew out of the existing X-ray diffraction group.

At the time of Harold's stay in Norway, GED was, despite many setbacks during and shortly after the war, well-established in Oslo and Trondheim and already had its impact within and beyond Scandinavia. After his stay, Harold was determined to bring GED to Austin, spurred by a \$10 million Center of Excellence grant that the University of Texas at Austin's Physics Department just had obtained and the fact that he, in absentia, had been chosen as the new Chair of the Department. This was an excellent setup to start GED in Austin.

In the 1960s, MW spectroscopists and GED researchers had little interaction, did not understand each other's work, and had a tendency of looking down on the research of their counterparts. There was a controversy on who was measuring the more relevant and reliable molecular geometries. MW spectroscopy led to effective geometrical parameters (r_0), derived from the rotational constants (not always corresponding to those associated with the zero-vibrational level), and these values differed significantly from the average distances r_g at a temperature T that GED provided.

Therefore, in the mid-1960s, Jim and Harold were working in opposing scientific fields pursuing the same objectives (structure determination) but producing deviating results. For lack of a systematic approach relating r_0 and r_g structures, members of the different groups simply claimed the superiority and proven

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accuracy of their own approach. Jim and Harold realized that the origin of the controversy was a lack of constructive communication between the two groups. They got together to find ways out of the deadlocked situation between the practitioners of MW spectroscopy and GED and to overcome the tendency of treating each other with some scorn. Methods that could be used for relating structural parameters, differently obtained, were lacking, and therefore, a common effort of the two groups of structural chemists to connect MW and GED data was needed.

Because of this, Jim and Harold set up a 2-day session called the Austin Symposium on Gas Phase Molecular Structure at the 1966 meeting of the *American Crystallographic Association* that took place in Austin on March 1–3. They invited the most prominent scientists involved in either MW spectroscopy or GED with the intention of forcing them to listen to each other. Harold Hansen gave the welcoming address, and Jim Boggs chaired the first session with contributions from Ken Hedberg (Oregon State University, a GED specialist, with Norwegian background and close ties to Odd Hassel and Otto Bastiansen), William D. Gwinn and David R. Lide (well-known MW spectroscopists from Berkley and the NBS in Washington), and a number of other prominent speakers. Simon H. Bauer (Cornell) chaired the second session. The opening lectures were given by Larry S. Bartell (U Michigan, Ann Arbor, GED) and C. C. Costain (NRC of Canada, Ottawa, MW). The constructive and relaxed atmosphere during the 2 days of lectures and discussions made the first ASMD in 1966 a convincing success in terms of attendance (2 out of the 25 participants later became Nobel Laureates) and in the quality of interactions that were fostered during the meeting.

The second Austin Symposium took place in 1968, attracted 86 participants, and was again organized by Jim Boggs and Harold Hanson, but now as an independent symposium. The NSF and the University of Texas supported the ASMD with small grants that helped to bring colleagues from Europe and Asia to Texas. On February 26, the who-is-who in MW spectroscopy and GED gathered in Austin; Y. Morino and K. Kuchitsu (Tokyo, MW), O. Bastiansen (Oslo, GED), H. Dreizler (Freiburg, MW), R. A. Bonham (Indiana, GED), W. D. Gwinn (Berkley, MW), L. S. Bartell (Ann Arbor, GED), K. Hedberg (Oregon State, MW), W. Zeil (Ulm, GED and MW), S. H. Bauer, C. C. Costain, and D. W. J. Cruickshank (Manchester, GED), H. D. Rudolph (Freiburg, MW), B. Bak (Copenhagen), and E. B. Wilson Jr. (Harvard) were among the participants.

The second ASMD included two discussion sections. The first section (chaired by Y. Morino and K. Kuchitsu) was entitled “How can data obtained by electron diffraction and by MW spectroscopy be compared? How can the two techniques complement each other?” The second section (chaired by B. Bak and E. B. Wilson, Jr.) was entitled “What are the major remaining unsolved problems in structural studies and what prospects are there for their solution?” In these sections, the gap between MW and GED researchers was closed, and the problem of structure determination was approached in a joint and mutually supportive rather than a diametrical fashion.

■ FROM MW AND GED TO MOLECULAR STRUCTURE

The third ASMD took place in 1970 without Harold Hansen, who had moved to Florida. He had been nominated as Dean of the Graduate School at the University of Florida, and later he continued as Provost at Boston University (1978–1979) and then as Executive Director, Committee on Science, Space, and

Technology, U.S. House of Representatives (1980–1982, 1984–1990), just interrupted by a position as Provost of Wayne State University (1982–1984). Apart from that, he became known for the translation of the work of Norway's winner of the Nobel Prize for Literature in 1928, Sigrid Undset, into English. He received in recognition of the work he had done for Scandinavia the prestigious St. Olaf Medal from the King of Norway and the Order of the North Star (Knight) from Sweden. Therefore, Harold was lost for the ASMD at an early stage and never returned. In the 40 years from 1970–2010, Jim Boggs organized the ASMD by himself with some help from the University of Texas and especially with the help of his family members. In this way, it is fully justified to speak of the “Boggs Symposium” and honor him as an outstanding scientist who, through all the years, succeed in bringing scientists from different fields to Austin and having them discuss their research.

■ THE ENTRY OF QUANTUM CHEMISTRY TO THE ASMD

The third ASMD was memorable for two reasons: The symposium was extended to 3 days, and it opened its doors for the first time to quantum chemists who at that time were trying to remedy the mean-field simplification of Hartree–Fock theory and calculating molecules with more than just 5 or 10 atoms. Robert Mulliken (University of Chicago) chaired the opening session, and Enrico Clementi (IBM, Research Laboratories) delivered the first plenary lecture of the symposium, which was entitled “Current Status of Computation of Molecular Structure”. This lecture was timely as in the previous year (1969), Peter Pulay (University of Arkansas) had published a basic paper on the calculation of the analytical energy gradient with regard to the nuclear coordinates of a molecule. The energy gradient defines the forces exerted on the nuclei, and a vanishing gradient indicates that the equilibrium geometry of the molecule has been obtained. The Pulay paper was a landmark paper as it provided the platform for the routine calculation of molecular geometries with quantum chemical methods.

Jim Boggs started a long-lasting collaboration with Peter Pulay, who developed the quantum chemical program TEXAS for the routine calculation of molecular geometries. More and more experimentalists applied quantum chemical methods themselves. The ASMD changed its nature from a meeting between different experimental groups to one between experimental and computational chemists. At one point, the number of quantum chemical contributions increased to the extent that they were about to take over the ASMD. This went against the original idea of the ASMD: to have a meeting place for various experimental methods of structure determination, possibly welded together by theory and quantum chemical calculations.

Jim Boggs managed to keep the balance between experimental and computational contributions to the ASMD, and this balance will be maintained in the future although two quantum chemists have taken over the organization of the ASMD. Experimental work will drive the Symposium (the upper “globe” of the cover of this issue, which does not exclude that much of this work will provide a theoretical and computational basis in the lower globe on the cover).

■ INTRODUCTION OF THE “D” INTO ASMD

Over time, the experimental methods presented at the Symposium changed with increasing numbers of publications on time-dependent measurements out of the field of molecular

dynamics. Accordingly, "Dynamics" was added to the title of the symposium, leading to the D in ASMD. In the last 2 decades, presentations at the ASMD have been focused on novel experimental setups, leading to novel information about structures as well as the change of structure during chemical reactions. The ASMD was and still is a sensitive indicator for new scientific developments reaching from femtosecond laser spectroscopy to nanotechnology.

■ THE UNIQUE NATURE OF THE ASMD

During the last 48 years, the ASMD has maintained its special atmosphere as a meeting of friendly connected scientists brought together not to boast of their achievements but to listen to each other and to learn from each other, particularly from colleagues using different methods and theoretical constructs to pursue a deeper understanding of molecular structure and dynamics, which play a central role in much of chemistry and physics.

In this spirit, the organizers of the ASMD@D have tried to arrange a symposium in an urban environment with a clustering of universities and research entities (first Austin and later Dallas) while keeping the nature of a Gordon Conference where the participants enjoy common meals and where there is ample time for discussions in smaller or larger groups. In this way, the ASMD has been the incubator for many collaborations and common research projects. In his memories about the ASMD, Jim Boggs narrates the following anecdote: *"(One of the collaborations) involved Harry Kroto. I was impressed by his ability as a young spectroscopist and was able to furnish minor support for him to come to the Symposium from time to time. At the 1984 meeting, Bob Curl was also here from Rice, and the two found many common interests. Bob invited Harry to stop in at Rice on the way home, which he did. While he was there, Bob took him to meet Rick Smalley and see an experiment he was doing. The three of them hatched up the idea of doing a similar experiment with carbon, which they accomplished in September of 1985. The result was the discovery of fullerenes and Nobel prizes for all of them, followed by the discovery of related nanotubes and all the subsequent nano-science and nanotechnology that have created such a revolution in modern science."* This is certainly a convincing example for the fruitful and collaborative way Jim Boggs arranged the ASMD meetings. It challenges us to continue its organization in the same spirit in the future.

■ WHY IS THE SPECIAL ISSUE BEING ASSEMBLED NOW?

The 25th ASMD meeting was the first meeting without Jim Boggs, who passed away June 2, 2013. He definitely would have enjoyed the meeting, which brought 108 participants from 22 different countries together, who could listen to a large variety of high-quality contributions from spectroscopy, molecular dynamics, and computational chemistry. Harold Kroto shared with the ASMD participants in his dinner talk his memories about the 1984 meeting, his special relationship with Jim Boggs, and the discovery of the fullerenes. Many new research results were presented during the 25th ASMD, and new scientific ideas emerged, some of which are summarized in this special issue.

Dieter Cremer

Elfi Kraka

Computational and Theoretical Chemistry Group
(CATCO), Southern Methodist University, Dallas, Texas,
United States