Available online at www.sciencedirect.com
ScienceDirect
International Journal of Mass Spectrometry 265 (2007) 75–79
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Foreword

Jean H. Futrell

This special issue of the *International Journal of Mass Spectrometry* honors Dr. Jean H. Futrell for his broad contributions to the field of mass spectrometry that extend over nearly half a century.

Jean is recognized for his pioneering research in several key areas of mass spectrometry, particularly his seminal contributions to tandem mass spectrometry, ion–molecule reaction chemistry and physics, and the fundamentals of collisional ion activation. He is a past president of the American Society of Mass Spectrometry, past Chair of the Council of Chemical Research, Fellow of the American Association for the Advancement of Science and the American Physical Society, and recipient of the 2007 F.H. Field and J.L. Franklin Award for Outstanding Achievement in Mass Spectrometry from the American Chemical Society. International recognition includes the Shrodinger medal of the Austrian Society for Atomic and Surface Physics and the Wolfgang Paul Lectureship of the German Mass Spectrometry Society.

I met Jean 36 years ago at the University of Utah when I became one of his many graduate students. As I recall, there were about eight other graduate students and somewhere around four or five post docs in his lab during that period. Our working relationship and friendship have grown over the years, and today we are both Battelle Fellows at the Department of Energy's Pacific Northwest National Laboratory (PNNL). I took a direct route to PNNL following a post-doctoral position at the Naval Research Laboratory, while Jean's career followed a far more circuitous path.

After graduating from high school in rural Louisiana, Jean attended Louisiana Polytechnic Institute, where he majored in chemical engineering and graduated *summa cum laude* in 1955. He then won a National Science Foundation graduate fellowship that enabled him to pursue his strong interest in chemistry at the University of California at Berkeley. Working in the nuclear chemistry division under the direction of the late Nobel Laureate Glenn Seaborg, Jean investigated the radiation chemistry of symmetrical dichoroethylenes, using mass spectrometry to identify the major reaction products, including radiation and free radical initiation generated oligomers.

This brief exposure to analytical mass spectrometry stimulated Jean's interest in the exciting new developments rapidly occurring in this area. Noteworthy contemporary developments were the first satisfactory theory of mass spectrometry – the Absolute Rate Theory formulation of a statistical model for ion fragmentation – and the first reports that ion–molecule reactions occurred at every collision in mass spectrometer ion sources. Drawing on this knowledge, Jean presented in his dissertation defense an original research proposal that the fragmentation of molecular ions was the inverse of an ion–molecule reaction and that attractive ion-induced dipole forces would overpower any activation energy barrier for dissociation. It follows that an accurate measurement of the appearance potential for simple fragmentation reactions is an accurate measurement of the thermochemicnl bond strength for that ion.

After receiving his Ph.D. in Physical Chemistry in 1958, Jean worked briefly at Humble Oil and Refining Company in Baytown, Texas in a research group that included Joe Franklin, Fred Lampe, and Frank Field—all pioneers in the field of ion–molecule reactions. Since many ion–molecule reactions occur at every collision and are two orders of magnitude faster than neutral collisions, they play a dominant role in gas phase radiation chemistry. Jean's first single author publication submitted only 3 months after joining the research center established a quantitative mechanistic framework for radiation chemistry of gaseous hydrocarbons. He also obtained a discarded mass spectrometer, but before he could set it up for experiments, he was called to active duty in the U.S. Air Force (Fig. 1).

Jean was stationed at Wright Patterson Air Force Base in Dayton, Ohio from 1959–1961 and assigned to the Aerospace Research Laboratory (ARL). When his military tour of duty was completed in 1961, he established his own research group at ARL that specialized in photochemistry, radiation chemistry, and mass spectrometry. In these first years of his independent research career Jean developed new flash photolysis and gas chromatography methods for studies of rare gas sensitized radiation chemistry. He was the first to use electron multiplier signal amplification for pulse counting with a commercial mass spectrometer, thereby increasing its sensitivity by over three orders of magnitude. Additionally, he was the first to measure thermal energy rate coefficients for ion–molecule reactions, and the first to measure the effect of ion kinetic energy on reaction rates.

Several of Jean's major instrumental innovations during this period markedly advanced mass spectrometry as a method for studying ion chemistry, an area that became a hallmark of his

1387-3806/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.ijms.2007.06.022

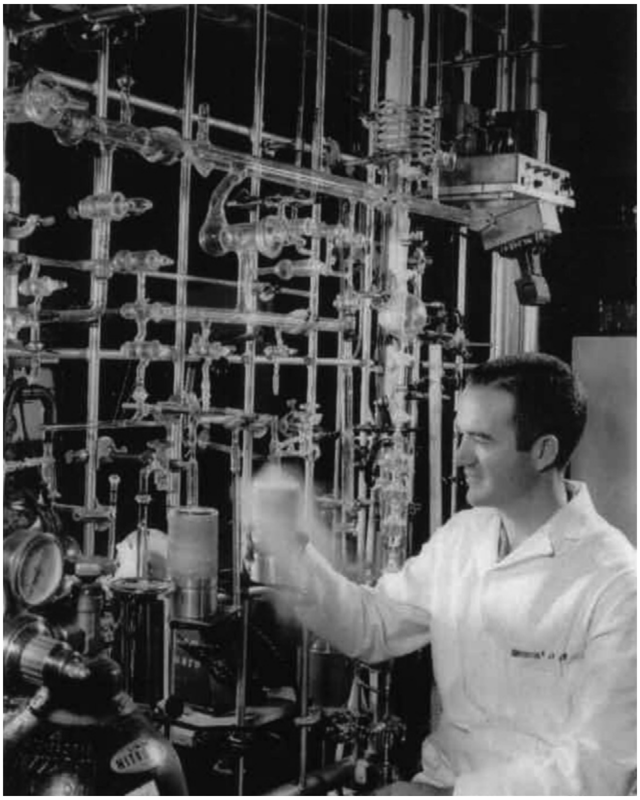

Fig. 1. Pictured here as a first year graduate student, Jean is applying then state-of-the art separations methods – bulb to bulb distillation under vacuum with flasks held at several fixed temperatures – to isolate fractions of radiolysis products as simplified mixtures for analysis. He later used a home built gas chromatograph – well before commercial instruments were available – to isolate single component fractions that were readily identified by mass spectrometry.

career. No project was too large or difficult as long as it would enable measurements that could lead to new insights into ion chemistry and physics! Driven by this passion, he developed a range of early tandem mass spectrometers that were the forerunners of the tandem and hybrid mass spectrometers that we use today, and that have made mass spectrometry the most powerful tool available for making sophisticated chemical and biological measurements.

A milestone achievement at ARL was his development of a five sector tandem mass spectrometer with ion optics that decelerated ions to kinetic energies two orders of magnitude lower than had been previously possible with ion beam experiments. But more importantly, this was the first multi-sector tandem mass spectrometer with high transmission optics that allowed energy selection of ions and effectively collected and refocused the reaction products into a second stage high resolution mass spectrometer. The new capabilities of this tandem mass spectrometer enabled Jean and his coworkers to access the thermal energy regime with a mass and energy selected ion beam and to vary collisional energy in a quantitative and systematic manner. Over a period of about a year, they established the “ground rules” for ion–molecule reaction kinetics of charge transfer, proton-transfer, hybrid transfer, and condensation reactions. They made the first estimates of lifetimes of ion–molecule collisional complexes, and defined the pressure regime where three-body stabilization is effective. They also defined the basic experimental methods for investigating unimolecular decomposition and bimolecular collisional processes in specific time and space domains that remains in use today.

In 1968 Jean moved to academia as Associate Professor of Chemistry at the University of Utah. Here, he established a large and dynamic research group that allowed him to develop new instruments and explore increasingly broad areas of chemistry and physics. Jean’s research mainly focused on probing the details of kinetics and dynamics of low-energy ion–molecule reactions, but also included applications of mass spectrometry, such as the first sequencing of peptides by chemical-ionization mass spectrometry. He explored ion-cyclotron resonance (ICR) mass spectrometry for its applicability to the study of ion–molecule reactions, and in the early 1970s developed a crossed ion beam neutral supersonic jet apparatus, a triple-quadrupole mass spectrometer (with photodissociation between MS1 and MS3!) and a hybrid tandem Dempster-ICR MS with an external high-pressure chemical-ionization source (an instrument constructed primarily by then post doc David L. Smith that I used after David’s departure for the latter part of my thesis research) (Fig. 2).

Jean’s intellectual ability, honor, and his cultivation and appreciation of quality in research (and indeed all aspects of his life) had profound impacts on his many students. When I entered graduate school in the fall of 1971, I knew I was going to be “activated” for 6 months service in the Army reserve the following spring, so my goal was to choose a research advisor as soon as possible. What could have been a daunting task turned out to be easy! A short scheduled meeting with Jean transformed into an extended discussion that was followed by a tour of his labs – a truly impressive display of complex hardware being developed and deployed by an obviously bright, diverse, and driven research group – and descriptions of a range of fascinating projects. Based on Jean’s reputation and the nature of the research in his group, I signed on to work with the new ICR instrumentation (this was “pre-FT” days). An added benefit was the interactions I was privileged to experience with the exceptionally talented individuals Jean attracted and cultivated, who also shared his insistence on scientific rigor and passion for science. For me, 1972–1975 was an enormously enlightening time, and also great fun. The appreciation I developed for instrumentation that embraced new types of measurements lead to 25 first author papers with Jean, and to this day still influences my approach to research.

Over the next decade Jean’s research focused on the reaction dynamics of elementary ion–molecule reactions. This work was facilitated by a unique supersonic jet ion-neutral crossed beam apparatus developed by Marvin Vestal as part of his Ph.D. thesis research with assistance from an equally talented postdoctoral fellow Calvin Blakely. This apparatus enabled detailed studies of the reaction mechanisms and dynamics at low collision velocities. For a number of experiments this apparatus provided focused ion beams moving more slowly than their neutral collision partners that were accelerated by supersonic jet expansion. Measurements of the velocity vectors of reactants and products as collision energy was varied clearly established

Fig. 2. The Futrell group in the Chemistry Department at the University of Utah in 1973. Standing are graduate students Bob Odom, Dave Herold, Leonard Wojcik, postdoc David Smith, graduate student Tony Taylor, visiting Professor Russ Bjorklund, postdoc Calvin Blakley, graduate student Fred Hileman, Jean's secretary, graduate student Richard (Dick) Smith and Professor Austin Wahrhaftig. Seated are postdocs Paul Abegglan and Tom Elwood, an undergraduate research student, graduate student Marvin Vestal and Jean. Not shown in this picture is postdoc Andre Fiaux.

the dynamics of ion–molecule reactions. These studies facilitated detailed descriptions of the mechanisms of simple classes of such reactions as proton-transfer, hydride-transfer, charge exchange and bond formation. During this period, Jean also expanded his interest in mass spectrometry applications (and research administration) as Associate Director and later Director of the NSF-sponsored Flammability Research Center in the Colleges of Engineering and of Medicine. Signature strengths of this interdisciplinary research center included applications of gas chromatography–mass spectrometry, atmospheric sampling instruments, and pyrolysis mass spectrometry for identifying toxic and neurotoxic chemicals generated by smoldering and combustable materials. Among other noteworthy achievements was orders of magnitude increase in sensitivity of a commercial double focusing instrument that allowed them to perform the first isotope-specific identification (at sub-toxic levels) of the potent dioxin 2,3,7,8 TCDD in a human tissue sample.

In 1986, Jean moved his research group across the country to the University of Delaware, where he was appointed the Willis F. Harrington Professor of Chemistry and Chair of the Department of Chemistry and Biochemistry. At the same time, he changed his research focus from low-energy ion–molecule reactions to high-energy ion collisions. The ability to accelerate ions to much higher energies than achievable in neutral collisions enabled the discovery of reaction mechanisms not yet demonstrated for neutrals. Noteworthy examples of his high-

Fig. 3. The Futrell group in the Chemistry Department at the University of Delaware, 1996. Shown are Research Professor Anil Shukla, graduate student Rahul Chawla, postdoc Ron Tosh, MS specialist Gordon Nichol, visiting Professor Eugene Nikolaev, graduate students Sergey Rakov and Xuedong Zhou, and Jean.

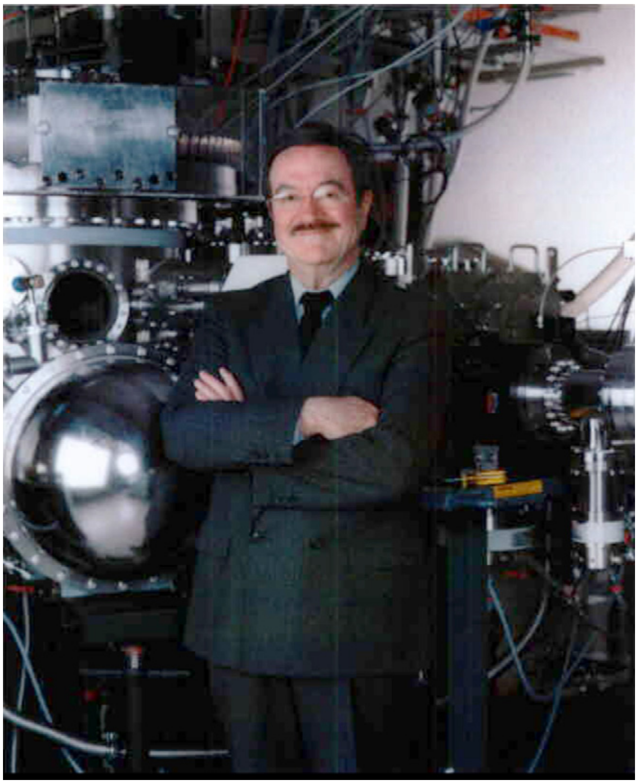

Fig. 4. As Director of the William H. Wiley Environmental Molecular Sciences Laboratory, a Department of Energy national scientific user facility at PNNL, Jean retained his commitment to experimental laboratory science.

energy dynamics research included discovery of the role that impulsive collisions played in relaxing long-lived excited states and the inverse reaction that promoted electronic excitation in recoil collisions. His group also demonstrated the spherical spatial distribution of products that resulted from collision-induced Coulomb explosion of metastable multiply charged cations. At this time Jean also re-entered the field of ion-cyclotron resonance – now Fourier Transform Mass Spectrometry – by developing the first external ion source for FTMS that utilized standard non-RF optics to inject ions through the fringe field of a superconducting magnet. He also initiated his first studies to contrast ion gas phase collisional activation and surface-induced dissociation (Fig. 3).

The diverse nature of the contributions to this special issue is an indicator of the range of important contributions from Jean's long academic and now national laboratory career. Although too numerous to list in their entirety, an especially noteworthy contribution was the first experimental mapping of ion–molecule reaction dynamics from thermal to high energies through definitive studies of kinematics of this class of reactions. Jean and coworkers were the first to experimentally demonstrate "stripping" reactions, displacement reactions, collisional-induced electronic transitions, and scattering resonances. On sabbatical leaves in Boulder and Berlin, he accomplished the first infrared spectroscopy of ions and the first demonstration of ion–molecule reactions in clusters, respectively. All the while I continued to regularly call upon Jean's expertise and meet with him during his numerous visits to PNNL during the early developmental stages of the Environmental Molecular Sciences Laboratory (EMSL), a Department of Energy national scientific user facility. Jean was an advisor to the EMSL's mass spectrometry program and a participant in a 1990 workshop on high magnetic field FTICR mass spectrometry (Fig. 4).

When Jean's tenure as Department Chair at Delaware concluded in 1997, PNNL presented him with an attractive opportunity to assume leadership of the Environmental Molecular Sciences Laboratory as its first permanent Director, a position he accepted in 1998. Despite his demanding management responsibilities as EMSL Director, Jean remained actively engaged in research, shown symbolically in his "official" PNNL photograph as EMSL Director shown in Jean is now Director Emeritus of EMSL and Battelle Fellow at PNNL. He is coordinator for mass spectrometry in our basic sciences separations and analysis research program and a member of Julia Laskin's

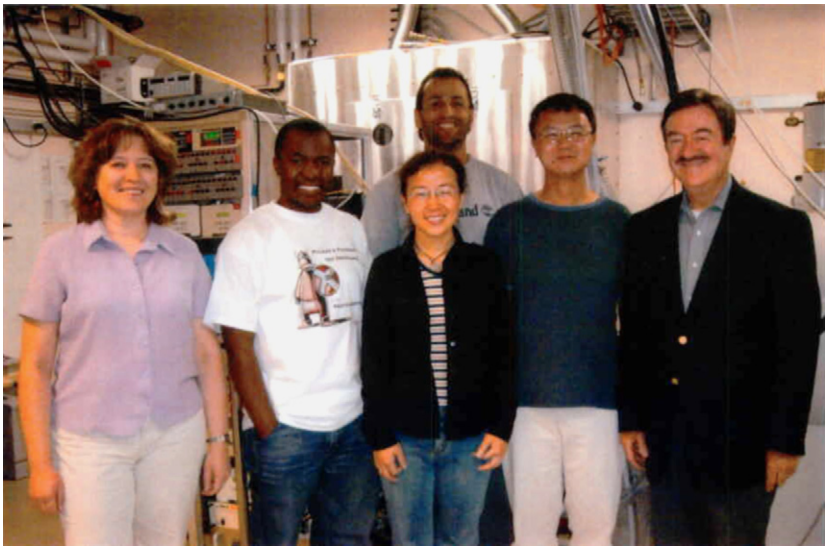

Fig. 5. The 2007 Laskin research group at PNNL includes Senior Scientist Julia Laskin, (EMSL user) graduate student Leonard Nyadong, post docs Peng Wang, Omar Hadjar, Zhibo Yang, and Jean.

research group (Fig. 5) in that program. The surprising recent discovery made by this group that complex ions can be "soft landed" as intact ions at high ion impact energies—is leading to fundamental discoveries in interfacial science. Interestingly, simple collision models from gas phase collision theory both rationalizes these results and provides guidance for tailoring such surfaces to emphasize capture of ions through non-covalent interactions and/or forming covalent bonds—e.g., to position-specific ion-surface reactions. Not-yet published work will report real-time SIMS-based kinetics measurements of charge reduction and neutralization reactions of soft landed ions.

To a remarkable degree, Jean's research interests have been driven by his desire to quantitatively understand fundamental ionic phenomena: charge exchange of atomic ions early on, collisional activation in mid-career, and most recently, processes by which ions interact with surfaces. In these pursuits he has proven to be an exceptionally gifted instrumentalist who has provided new insights into the fundamental processes of ions and their reactions. His passion over the years for science and for developing tools to answer scientific questions has inspired numerous students, including me. In appreciation of this inspiration, we honor Jean with this special issue in which the diversity of topics only samples the breadth of contributions Jean has made in pursuit of his particular passion.

Richard Smith
Pacific Northwest National Laboratory,
3335 Q Avenue-MSIN K8-98 Richland,
WA 99354, United States

E-mail address: dick.smith@pnl.gov