

## Focus in Honor of Dr. Julia Laskin, Recipient of the 2008 Biemann Medal

It is a pleasure to introduce a special focus of the *Journal of the American Society for Mass Spectrometry* to celebrate the accomplishments of the 2008 Biemann Medalist, Dr. Julia Laskin. This issue contains a total of eleven papers, devoted to two themes of special interest to Julia: peptide radicals and ion-surface collisions. We thank all the authors, reviewers, and Professor Veronica Bierbaum, who handled the reviewing process as Associate Editor, for helping this issue come to fruition. Finally, we decided on an "interview" format so that readers can learn about Julia's background and motivation.

### Interview with Julia Laskin

*Q: Many of Us were Inspired to Pursue Science by Our High School Teachers. What were Your Chemistry Teachers Like at School?*

*Julia's answer.* I had one chemistry teacher at school. She was a great person and a very good teacher. It is hard for me to say now what had greater influence on me, her personality or professionalism, but I loved chemistry at school. I grew up in Russia in a school system that was very different from the American system. We studied chemistry for four years starting from the seventh grade, which allowed us to make a strong connection with the teacher. Chemistry and math were my favorite subjects at school, but to my own surprise I went to study physics in college. I was looking for a major that would involve a lot of math and I was told that this was it. The general chemistry class that we took as freshman students was the highlight of the entire program because it was given by an outstanding lecturer. It started early in the morning at 8 am, although all the students were always awake. Unfortunately, this class was the only exposure to chemistry for physics majors.

*Q: What Made You Choose Science for Your Tertiary Education?*

*Julia's answer.* The short answer is, I do not know. Somehow I always knew that this was what I wanted to do in my life. Before we immigrated to Israel we thought that we would do PhD studies at Technion in



Haifa. However, other circumstances brought us to Jerusalem. We showed up at the Hebrew University a few days after we crossed the border. Russian was the only language that we spoke fluently at that time. We were lucky that the immigration ministry covered our salaries for the first two years of our PhD studies. This gave us enough time to demonstrate ourselves. Interestingly, our PhD advisors were also a couple. My husband joined the group of Prof. Assa Lifshitz to work on kinetics of radical reactions in shock tubes, whereas I worked with Chava Lifshitz on gas-phase ion chemistry and mass spectrometry of cluster ions. This was a dramatic transition for both of us. We had to take several basic and advanced chemistry courses. All of them were excellent. I was impressed with the quality of higher education in Israel. However, most of the courses were taught in Hebrew, although by the time we started our studies, we were barely ready to communicate in the supermarket. In the beginning

it was not clear whether we would make it through the first semester. I think both our advisors were a bit worried. However, we successfully passed our first exams and started getting more involved in research.

*Q: What was Your First Research Experiment in Chemistry?*

*Julia's answer.* Shortly after I joined Chava's group, I participated in several photoionization experiments. The instrument was quite simple but very large and messy. It was equipped with a discharge lamp and a monochromator for generating tunable VUV light. Ions were produced by photoionization inside the cylindrical ion trap and analyzed using a quadrupole mass spectrometer. Because of the low signals, each experiment took several days to weeks. The entire system was operated by an ancient computer. My first real project involved automation of the instrument using the new PC-426 still operated under DOS. This was a good challenge for me, in that it taught me a lot about the architecture of the instrument. I had to learn how to establish communication between different devices and the computer. However, the bulk part of the project involved developing a graphical interface, which I did not enjoy that much. My first scientific project was focused on the famous question of tropylium versus benzyl ion formation from toluene. We conducted the first time-resolved experiments in a sector instrument to determine the dependence of the branching ratio of these two products on the reaction time. Our theory collaborators, Alexander Ioffe and Sason Shaik, calculated the potential energy surface for this system, and we used Rice–Ramsperger–Kassel–Marcus (RRKM) to model the experimental results. We showed that tropylium is not formed from toluene at its thermochemical threshold. This was a great experience for me not only because the experiments were quite tricky, but I also got a very clear understanding of the RRKM theory.

*Q: You Moved from Russia to Israel to Pursue Your PhD Studies. Tell us Something About What Motivated You to Make Such a Move and How You Managed Starting Out Afresh.*

*Julia's answer.* During my college studies in Leningrad, Russia, I got some idea of the type of work that awaited me after getting my masters degree and I was not thrilled by the options. In the end of the 1980s, *perestroika* opened the borders and allowed people to leave the country. Many people were talking about emigration. My husband and I were among them. We left Russia briefly after we graduated from college. Our son just turned one. It was the most challenging and the most exciting time in our lives. Both of us went through a very steep learning curve. Everything was so different. For example,

there was no banking system in Soviet Russia, so even opening a bank account was a new experience for us. Looking back I think it was an absolutely crazy move, but I do not regret we made it.

*Q: Its Sounds Like the Move was a Great Success, in Part Due Your PhD Supervisors. The Scientific Community was Saddened by the Loss of Chava Lifshitz in 2005. What Do You Miss About Her?*

*Julia's answer.* Chava was a great scientist and a patient teacher. She shaped me as a scientist and influenced me as a person. I particularly appreciated her thoroughness, her knowledge and curiosity, and her enthusiasm for new ideas. I also learned from her that you can be a mother of three children and have a successful career in science. I came to Chava's group knowing nothing about mass spectrometry—and only a little about scientific research—and left it as an independent scientist. It was interesting to see how our relationship evolved with time from the initial teacher–student stage to the point when we became colleagues. After I left her group we wrote a review article on kinetic energy release distributions and co-edited a book *Principles of Mass Spectrometry Applied to Biomolecules*. We could always contact each other with questions, ideas, and even vague thoughts.

*Q: What is Your Favorite Piece of Work in Which You were Involved?*

*Julia's answer.* This is a difficult question because I am excited about many things. However, I am particularly proud of a paper that describes the relationship between the Arrhenius activation energy and the dissociation threshold. This work started from a surprisingly unexpected experimental result and led to some interesting discoveries. I was doing surface-induced dissociation (SID) experiments with protonated des-Arg<sup>9</sup>-bradykinin. Based on the existing literature data, there were two possible outcomes of these experiments. To my great surprise, I obtained a completely unexpected result. Because I was comparing 0 K threshold energies obtained from modeling the SID data with Arrhenius activation energies derived from blackbody infrared radiative dissociation (BIRD) experiments, I had to be able to convert threshold energies into Arrhenius energies. I was sure that the difference between the two energies is very small (close to  $k_B T$ ). However, when I applied Tolman's equation to this system, I realized that this is true only when the Arrhenius pre-exponential factor for reaction is in the range  $10^{10}$ – $10^{15}$  s<sup>-1</sup>. Gas-phase fragmentation of protonated peptides and proteins is commonly characterized by very large or very small pre-exponential factors. In such cases the difference between the Arrhenius activation energy and the dissociation threshold can be substantial. Moreover, the order of Arrhenius activation energies for different

systems relative to the order of the corresponding threshold energies may be reversed. This was an exciting result that was later confirmed for competing low-energy reaction channels of the singly protonated leucine enkephalin.

*Q: Talking About SID, We Know it is a Subject Dear to Your Heart. Could You Tell Us a Bit More When You First Started Working on SID?*

*Julia's answer.* You're correct that surface-induced dissociation of complex ions has been a focus of my research for many years. When I joined Jean Futrell's group at the University of Delaware, I started exploring the energetics, dynamics, and energy transfer in multiple-collision activation experiments of peptide ions. I developed an RRKM-based approach for modeling both SID and multiple-collision CID (collision-induced dissociation) experiments. Two other group members, a graduate student Sergey Rakov and a postdoc Eduard Denisov, were working on implementation of SID on a commercial Bruker FT-ICR mass spectrometer. Our first comparison of SID and SORI-CID convinced me that SID is a preferred method for studying the energetics and dynamics of dissociation of complex ions.

A few months after I joined the group, Jean announced that he was taking a position as the director of the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL) and invited Eduard and me to move to the Pacific Northwest. I have to say that Jean is another person who has played an important role in my life. I appreciate his giving me the opportunity to work at the national laboratory and creating an enjoyable work environment. At PNNL, Eduard and I designed and built a new FT-ICR machine configured for SID studies based on the prior experience of modifying the commercial apparatus and the most recent technology developments at PNNL. Discussions with Steve Barlow, Mike Belov, Dick Smith, Harold Udseth, Anil Shukla, and Gordon Anderson were extremely helpful for converging on the design of the new instrument.

From our earlier studies it was clear that because of the uncertainty in the internal energy deposition function in ion-surface collisions it is difficult to obtain a unique RRKM-based description of the experimental data. The new instrument allowed us to conduct the first time- and collision-energy resolved SID experiments. Adding another dimensionality to the SID data helped us to fix several parameters in the data fitting. However, we had to study fairly large ions, for which the fragmentation pattern changes significantly from the several milliseconds to several seconds sampling time of the FT-ICR instrument. I was particularly interested in systems that are difficult to identify using conventional methods of tandem mass spectrometry. For example, poor fragmentation of singly protonated tryptic peptides presents a significant challenge for

protein identification using MALDI. Together with Eduard and a graduate student Tom Bailey we studied several model peptides characterized by very selective fragmentation behavior in CID experiments. A surprising finding in these studies was a very sharp transition between slow low-energy dissociation and high-energy SID characterized by formation of a large number of fragments via fast kinetics that is adequately described using the "sudden death" approximation. We attributed this fast fragmentation to "shattering" of ions on surfaces—fragmentation taking place on or very near the surface. Shattering of peptides has been predicted by QM/MM calculations performed by Bill Hase and coworkers but never observed experimentally.

*Q: Reading Your Papers, We Couldn't Help but Come Up with the Impression that You Like Doing Challenging Experiments, Don't You?*

*Julia's answer.* We liked playing and having fun, testing new ideas, and designing new experiments. In addition to understanding ion activation following collisions with surfaces, we pursued RRKM modeling of SID data, which provides information on threshold energies and activation entropies of dissociation pathways of complex ions. We used this methodology for studying cleavages of covalent bonds in gas-phase fragmentation of a variety of complex ions and, more recently, used it to quantify the strength of non-covalent interactions. Many of these studies involved collaborations with excellent scientists, which made this work even more enjoyable for me. Most notably we studied dissociation of protonated peptides, peptides modified by ozonolysis (in collaboration with Jeff Spraggins, Murray Johnston, and Doug Ridge from the University of Delaware), and post-translationally modified peptides (with Hadi Lioe and Richard O'Hair from the University of Melbourne). We performed the first determination of the Mo···OX bond strengths in oxomolybdenum model complexes involved in oxygen atom transfer reactions (with Victor Namykin and Partha Basu from Duquesne University).

More recently, we conducted first studies focused on dissociation of peptide radical cations and anions (in collaboration with Corey Lam and Ivan Chu from the University of Hong Kong; and with Andy Siu and Michael Siu from York University). Studies of non-covalent interactions in model complexes of vancomycin with peptide ligands performed by Zhibo Yang in my group were particularly challenging because he combined experimental work with high-level computational studies. I was excited with an opportunity to visualize the structure of such complex systems and understand the origin of fairly strong binding between the peptide and the vancomycin cage.

Another interesting and challenging experiment focused on understanding soft- and reactive landing phenomena that we conducted several years ago opened a



new area of research in my group that I am very excited about. It started as collaboration with Jormarie Alvarez and Graham Cooks (Purdue University) and was continued by two excellent postdocs, Peng Wang and Omar Hadjar, in my group. We developed instrumentation for selective deposition of complex ions on substrates and studied both physical phenomena (charge-transfer, trapping efficiency and its dependence on experimental parameters, etc.) and chemistry on substrates. We showed that reactive landing of peptides onto self-assembled monolayer surfaces may result in formation of a covalent bond between the molecule and the substrate. Surface modification using beams of mass-selected ions delivers 100% pure reagent to the surface and is characterized by similar or higher efficiency than that of the solution-phase reaction. Subsequently, we demonstrated that polyalanine peptide present in a  $\beta$ -sheet conformation in solution can be immobilized on the surface in a stable helical conformation generated during the electrospray ionization process.

*Q: Which Scientist from History would You Like to Meet?*

*Julia's answer.* Richard Feynman is one of my favorite figures in science. I love his sense of humor and his ability to explain difficult things in simple terms.

*Q: You Have a Lovely Family and a Productive Scientific Career. How Do You Balance them All?*

*Julia's answer.* Of course, I am very busy. Our son was a baby when we started graduate studies. We did not have a family that could help us nor did we have money to hire a babysitter. So I had to learn how to manage my time to make it work. Our middle daughter was born at the time I was writing my PhD thesis. She was a fairly quiet baby and I am grateful to her for letting me finish my writing. I was also busy writing after my youngest daughter was born. However, this time I was writing papers. I do not want to give the impression that I work all the time. When I come home, I try to spend as much time as I can with my kids. I enjoy every moment spent with my family. I have three wonderful kids who keep

me busy and happy. I also have a very special relationship with my husband. We have many things in common. During our graduate studies we shared an office and taught the same class. For some time, we were looking for some scientific topic that we could explore together and recently we started collaborating on characterization of atmospheric aerosols using high-resolution mass spectrometry.

*Q: If You were to Condense Your Advice to a Fresh PhD Graduate About Science and Research in Three Sentences, What Will they Be?*

*Julia's answer.* You are asking me for words of wisdom that I do not have. However, let me try. I think passion, focus, and persistence are the pillars of success in science. It is also important to be adventurous enough to be able to explore new directions that are often beyond your comfort zone. Finally, communication and networking are essential for publicizing your findings and building collaborations.

*Q: What are the Ultimate Goals for Chemists?*

*Julia's answer.* I think the goals are similar for all scientists and engineers. Progress in science and technology moves the existing boundaries in all areas of our life. Science should help solve challenges faced by society. Chemists should get a sufficient understanding and control of chemical processes to start designing smart materials and systems. We should also continue developing analytical instrumentation that will be used by other scientific disciplines. Although all these efforts should in the long-term translate into useful applications, it is important to keep a balance between basic and applied science. I am a strong advocate of basic research that provides a solid foundation for applied chemistry.

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