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Biography of Chava Lifshitz

Our colleague, mentor, and friend Professor Chava Lifshitz died on March 1, 2005. Chava was one of the pioneers of the field of gas phase ion chemistry and fundamental mass spectrometry. Her death is a great loss to the mass spectrometry community and to the chemical community in Israel.

Chava Lifshitz was born (née Eva Wolf) in Vienna, Austria, in 1936 and immigrated to Israel with her family in 1938. She studied chemistry at The Hebrew University of Jerusalem where she obtained her Ph.D. in radiation chemistry with Professor Gabriel Stein in 1961. She worked as a postdoctoral fellow (1961−1963) at Cornell University with Professor Franklin A. Long on mass spectrometry and unimolecular fragmentations of polyatomic ions with application of RRKM/QET. She returned to The Department of Physical Chemistry of The Hebrew University in 1963 as a lecturer, became full professor in 1976, and was awarded the Archie and Marjorie Sherman chair in Chemistry established in 1990. She was a visiting scientist at several institutes, including Argonne National Laboratory in 1965, working on VUV photoionization mass spectrometry with William Chupka and Joe Berkowitz. She was a visiting scientist at Cornell University in 1969, working on RRKM/QET of large species with Professor Fred McLafferty, and at Wright Patterson Air Force Base, Ohio, in 1969−1970 and 1972, working on ion−molecule reactions and tandem mass spectrometry with Dr Tom Tiernan. In 1986, she was a Brotherton Research Professor at the University of Leeds, U.K. Her major research interests were mass spectrometry, gas phase ion chemistry, reaction dynamics, photoionization, clusters, fullerenes, and small biomolecules. She was a member of editorial advisory boards of several of the major mass spectrometry journals including *Mass Spectrometry Reviews*, *International Journal of Mass Spectrometry and Ion Processes*, and *Journal of Mass Spectrometry*.

Chava Lifshitz authored and coauthored over 260 scientific papers and received numerous awards, including the Kolthoff Prize (1985, Technion, Haifa), The Max Planck Research Award of the von Humboldt Foundation together with her friend and colleague Prof. Helmut Schwarz (1991), and the Erwin Schrödinger Medal (1998). In 1997, she was honored with a special issue of the *International Journal of Mass Spectrometry* edited by Professors Robert Dunbar and Tilmann Märk on the occasion of her 60th birthday. In 2003, she was awarded the Israel

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Chemical Society Prize for her distinguished pioneering studies in the area of the chemistry of gas phase ions and mass spectrometry and for her long-term activities in advancing science in Israel. She was chairperson of the Chemistry Studies Division (1972−1976) and of The Institute of Chemistry (1994−1997) at The Hebrew University of Jerusalem. Chava served as a member of the Board for Higher Education in Israel and a member at the High Committee for Science and Technology of the Israel Ministry of Education chaired by Prof. Harrari (1991−1992) and acted as the President of the Israel Society for Mass Spectrometry (1991−1994).

Chava Lifshitz was regarded worldwide as a distinguished scientist in the field of gas phase ion chemistry and mass spectrometry. Her research combined experimental and theoretical efforts directed toward the fundamental understanding of structures, chemical reactivity, thermochemistry, and unimolecular reaction dynamics of gas phase ions. Chava's scientific career overlapped with the development of gas phase ion chemistry as a new discipline providing a fundamental background for the field of mass spectrometry. She was actively involved in the development of statistical theories and their application to understanding mass spectra of organic molecules, cluster ions, and, more recently, gas phase biomolecules.

We will not attempt to describe Chava's numerous scientific achievements but will only give a few examples. During her postdoctoral appointment with Frank Long, she found that ionized fluorinated ethylenes, fluoroethane, and fluoropropane undergo direct decomposition from excited isolated electronic states, avoiding internal conversion. These findings were particularly surprising because dissociation of all hydrocarbons reported at that time followed statistical behavior. Chava's conclusion that isolated excited electronic states are involved in dissociation of flurocarbons was based on rather crude experimental methods that were available at the time combined with RRKM calculations. It was found to be correct many years later when more elaborate experimental coincidence methods became available to the research community.

At the cornerstone of statistical theories of unimolecular reactions stands the ergodic hypothesis according to which intramolecular vibrational redistribution (IVR) occurs on a substantially shorter time scale than dissociation of the excited ion. A strong believer of statistical theories, Chava was always interested in understanding and challenging the validity of the ergodic hypothesis. Because IVR normally occurs on the time scale of picoseconds, the experimental examples for statistical behavior are numerous and "non-RRKM" molecules are scarce. Dissociation of the enol ion of acetone is a classical example of apparent non-RRKM behavior in ionic systems. Chava demonstrated that isomerization produces the acetone ion from its enol isomer with two symmetrically placed methyl groups that "remember" the original enol ion structure and dissociate in a manner that is different from the expected 1:1 ratio because of the very short lifetime of the intermediate that circumvents IVR. Since then, nonergodic dissociation of the acetone ion has been extensively studied using a variety of experimental and theoretical approaches.

One of the challenges in studying dissociation of polyatomic molecules is that an ion may have enough energy to dissociate but not enough time to do so on the experimental time scale. The internal energy in excess of the threshold energy required to produce detectable dissociation of a polyatomic ion on the time scale of a mass spectrometer is called the kinetic shift. Chava conducted a number of pioneering studies focused on the determination of kinetic shifts in dissociation of polyatomic molecules and clusters. She realized that the kinetic shift can be partly overcome by ion trapping. Her studies initially utilized trapping assisted by an electron beam. Over the years, her group developed a more elaborate experimental approach, which combined photoionization of ions with VUV light inside a cylindrical ion trap. This technique was used to study time-resolved photoionization and dissociation (TPIMS) of a variety of polyatomic ions. RRKM modeling of the experimental data was used to determine the dissociation threshold and the activation entropy, a measure of the degree of tightness or looseness of the transition state. In many cases, thermochemical data such as bond energies and heats of formation of ions were derived from the modeling. Chava wrote a number of seminal review articles on kinetic shifts in dissociation of polyatomic ions.

Chava's scientific career is marked by a number of fruitful collaborations. She used every opportunity to involve complementary experimental and theoretical approaches in her work through collaborative research. Her pioneering experimental work on dissociation of acetone, toluene, and bromobenzene was followed by in-depth theoretical studies using RRKM calculations on ab initio surfaces. One of her key articles in collaboration with Sason Shaik solved a long-standing problem in organic mass spectrometry concerning the tropylium ion formation from toluene.

Chava conducted a number of studies in collaboration with Rob Dunbar, that combined TPIMS experiments with time-resolved photodissociation (TRPD) experiments developed by Dunbar's group using an FT-ICR mass spectrometer. Simultaneous modeling of TPIMS and TRPD data was performed to improve the precision of the dissociation parameters. Further development of TRPD experiments in Chava's group resulted in design and construction of a novel ion trap/reflectron mass spectrometer specially configured for TRPD studies of peptide radical cations. These experiments utilized laser desorption of peptides followed by photoionization, trapping and collisional relaxation of ions, and photodissociation. In these studies, Chava addressed the following questions: Does IVR precede fragmentation? Does electronic and vibrational energy relaxation take place, or is there site selectivity and charge-directed reactivity of excited gas phase biomolecules? Energy-selected dissociation rate constants for small peptide ions showed a strong dependence on the internal energy and the size of the ion. These experiments unambiguously demonstrated that dissociation of gas phase peptides is statistical and can be described using RRKM/QET. Although Chava used to say that she did not like to "jump into cold water", the construction of this instrument was a very big adventure for her and her group. The TRPD experiments utilized three lasers that were carefully aligned in space and time, a nontrivial task for a group that had never used lasers before the construction of this instrument. Chava's scientific curiosity and persistence allowed her group to carry out truly unique experiments on the unimolecular decomposition of peptide ions.

Studies of unimolecular and bimolecular reactivity of proton bound clusters demonstrated the existence of "magic numbers" in kinetic energy releases (KERs). In general, the average KER increases with cluster size, indicating statistical dissociation of proton bound cluster ions. The marked discontinuity in KERs was observed at closure of the first solvation shell for ammonia clusters. It was demonstrated that gas phase formic acid and acetic acid clusters (e.g., $(RCOOH)_nH^+$) behave in their reactive decay as do the bulk liquid acids. Already for a small size, between $n = 6$ and 7, these clusters evaporate the cyclic neutral dimers. The work on the reactivity of mixed and neat proton bound dimers combined with theoretical calculations by Jan Martin and Victoria Aviyente demonstrated molecular recognition in the ligand switching reactions.

One of the hallmarks of Chava's work was her thorough approach to science, whether it involved her own work or reading papers written by others. After years of misquoting the equation for the entropy of activation by our group (T.B.), it was Chava who sent us a letter in which she gently suggested that we failed to include a term. Her similarly careful reading of a series of difficult papers by Eph Klots on the evaporative ensemble model of cluster ion dissociation led to an edifying chapter on this topic that, for the first time, explained to many of us the origin and utility of this model. It was largely Chava's retelling of this theory that lead to its inclusion in our book on unimolecular reactions (Baer and Hase) as well as to its widespread use by other workers in the field.

In the early 1990s, Chava became interested in unimolecular dissociation of carbon clusters. Unimolecular and bimolecular reactivity of small carbon clusters and fullerenes revealed a number of important discoveries. A periodicity of 4 was observed for the reactivity patterns of small carbon clusters, demonstrating that the rings C_{11}^+, C_{15}^+, and C_{19}^+ are aromatic whereas C_{13}^+ and C_{17}^+ are anti-aromatic. Chava's group combined a number of experimental methods (time-resolved appearance energies, kinetic energy releases, and metastable fractions) with statistical modeling to obtain a definitive value for the C_2 binding energy to the C_{60} fullerene cage. Relative stabilities of fullerenes and endohedral fullerenes containing noble gas and metal atoms were determined from kinetic energy release measurements and the use of the above-mentioned evaporative ensemble theory.

Mass spectrometric observation of the existence of an artificial Ne_2 molecule inside C_{70} was followed by a combined MS and NMR study of He_2 inside C_{70}. A study of the endohedral nitrogen atom in fullerenes revealed the loss of N at the expense of the Rice shrink wrap mechanism by which fullerene cages lose C_2 units. This research involved a large number of collaborative projects with Henry Selig, Helmut Schwarz, Hans-Friedrich Gruetzmacher, Tilmann Märk, Eph Klots, Eleanor Campbell, Adalbert Ding, Martin Saunders, James Cross, and other colleagues.

More recently, Chava's group conducted a number of pioneering studies on the H/D exchange of protonated peptides and multiply hydrogen bonded complexes in a selected ion flow tube (SIFT) using electrospray ionization. The unique ESI/SIFT apparatus constructed in her lab was utilized to study the kinetics of reactions of peptide ions, protein ions, and their clusters at gas pressures of several tenths of a torr. Complementary experiments conducted in collaboration with Alan Marshall's group utilized high-resolution FT-ICR mass spectrometry. Analysis of the H/D exchange data using the probabilistic algorithm developed by Chava's group introduced an additional dimension to these studies providing very detailed structural information.

Chava was not only an outstanding scientist but also an excellent mentor. One of us (J.L.) had the privilege to be Chava's graduate student. She was a patient teacher and a great example for young scientists, sharing her approach to scientific problems, her thoroughness, her knowledge, and her curiosity. A quality that endeared her not only to her students but also to all scientists was her enthusiasm for new ideas, whether developed in her lab or elsewhere. Chava cared for people working with her. She played a very active role in my (J.L.) search for a postdoctoral position, carefully evaluating the various options to ensure that I made a good decision. I have no doubt that many of her students and postdocs received as much career guidance as I did. Chava was particularly active in helping female Israeli scientists establish their scientific careers.

Science was not the only passion in Chava's life. She was a mother of three wonderful children, Ron, Donna, and Orna, and had six grandchildren. Her husband, Assa Lifshitz, is a Professor of Chemistry at the Hebrew University of Jerusalem. Their older son, Ron Lifshitz, is currently a Senior Lecturer in Theoretical Physics at the Tel-Aviv University. Chava always carried pictures of her family and loved sharing stories about her children and grandchildren.

Despite numerous health problems during the past 20 years, Chava always stayed active and extremely productive. It is not surprising that her last proposal got funded just two months before she passed away. Chava never gave up. She worked hard until the last day of her life. Two manuscripts appeared in the *Journal of Physical Chemistry A* in March and November of 2005, and a book chapter on which she was working during the last weeks of her life will be published soon. Many of us were shocked by the announcement of her death because we had extensive communication and continuing scientific discussions with her until her last days. This special issue of the *Journal of Physical Chemistry A* is a tribute to a great person, good friend, and an outstanding scientist.

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