

Terahertz Pioneer: Richard J. Saykally

Water, Water Everywhere...

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GROWING UP as the son of a grocery store owner and school teacher in rural northern Wisconsin, Richard James Saykally¹ boasts that he was the smartest kid in his grade school class because the other guy could never get past long division! When not focusing on his rock band, football, or the most common pursuit of young men in their teens (and perhaps at any age), his college interests shifted from forestry to English and finally back to science where he majored in chemistry. Perhaps it was prescient that he graduated from University of Wisconsin *Eau Claire* and ended up with a stellar academic career focused largely on unraveling the chemical properties of *water*.

In 1970, Saykally entered graduate school at the University of Wisconsin Madison as an analytical chemist. There he connected with assistant professor Claude Woods, who was designing his pioneering experiments to measure microwave spectra of molecular ions. As his first assignment, Woods gave Saykally his personal copy (autographed!) of Townes and Schawlow's, *Microwave Spectroscopy* [1] and Gerhard Herzberg's, *Diatomic Molecules* [2], which he decided to treat like English literature, and read while relaxing at a nearby lakeside retreat. After dozing off to dream about oscillating molecules, he woke up to find Townes's text being torn to shreds by a local quadruped that, for some reason, refused to touch the Herzberg volume. This rather colorful start to his graduate studies in chemistry (one can almost picture the much abused excuse to Woods about the fate of the assignment), was to be par for the course throughout Saykally's career, but it never daunted his *dogged* pursuit of knowledge or his enthusiasm for science.

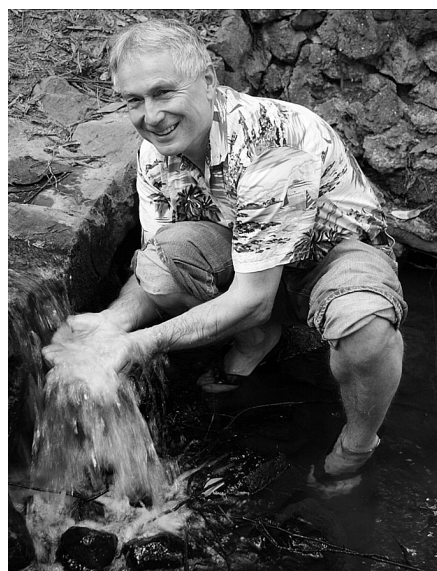
As he freely admits, despite Woods' occasional admonitions about his longevity as an experimental chemist with Saykally in the group (Saykally nearly electrocuted Woods when he forgot to shut down a high voltage power supply as Woods was cleaning out their spectrometer), Saykally was *at the right place at the right time*.

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¹Richard J. Saykally lives with his wife and two teenage daughters in Berkeley, CA, USA. Appropriate for a chemical spectroscopist interested in molecular vibrations, his office and laboratories are located in the solid concrete-walled basement of Hildebrand Hall on the campus of the University of California. Kindly consenting to ignore incoming phone calls, except for one call to check in with his teenage daughter, and sporting his trademark Hawaiian shirt and khaki trousers, we met in his office for this interview on February 25th, 2012.



RICHARD J. SAYKALLY

Near the end of 1971, William Klemperer, noted microwave spectroscopist and astrochemist at Harvard (now retired), came to Madison to give a talk about X-ogen [3]. It was at this time that Dave Buhl and Lew Snyder had just begun millimeter-wave spectroscopy measurements of the interstellar medium using the National Radio Astronomy Observatory 36 foot radio telescope at Kitt Peak². During observations of HCN at 86.3 GHz, a strong unidentified line appeared in the upper sideband at 89.19 GHz that was designated X-ogen (unknown extraterrestrial origin) [4]. Klemperer believed he had an identity: HCO^+ , and a production mechanism for the unidentified species: $\text{H}_2^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}$ [5]. The spectral line had been observed in several regions of interstellar space and, therefore was presumed to be abundant. If Klemperer was correct, this would be the first observation of abundant ions in the interstellar medium, and its importance to astrochemists was wide reaching.

Saykally was extremely excited by Klemperer's lecture and the idea of classifying unidentified chemical signatures in outer space. So was Claude Woods, who had been developing the spectroscopy of electrical discharges in the microwave region (below 50 GHz) using backward wave tubes. In order to reach the X-ogen line frequency, shorter wavelength, narrow band sources were needed. Reflex klystron tubes could reach above 100 GHz, but funding was so tight at this time that Woods had to

²See text and references in the March 2011, Terahertz Pioneer article in this journal.

use his own summer salary to buy a 90 GHz klystron from Oki (Oki Electric, Japan, slightly less expensive than their larger U.S. competitor at the time—Varian). It turned out to be a good investment. The group, with particularly significant contributions from graduate student Tom Dickson (later at Harvard with Klemperer), put together a glow discharge spectrometer with a 10-m path length and detected the first microwave spectrum of an ion (CO^+)! They were later able to form HCO^+ from hydrogen and CO and detect the “X-ogen” line at 89.1885 GHz after cooling the gas to 77 K. Woods proved that the mixture contained the ionic form of HCO by detecting the Doppler shift in the line frequency as the discharge was redirected within the absorption cell (confirming the change in ionic drift velocity). The paper [6] became a classic, having confirmed Klemperer’s theoretical identification of HCO^+ , and proving that glow discharge spectroscopy could work at microwave frequencies (critics believed the noise from the ionized gas would swamp the spectral signal).

The HCO^+ result fed Saykally’s growing interest in ion spectroscopy, and in 1977, upon graduating from Wisconsin, he took up a post-doctoral appointment with Ken Evenson at National Institute of Standards (NIST) in Boulder, CO, USA. Evenson had developed laser magnetic resonance spectroscopy (LMR) [7]–[10], wherein the rotational and fine structure atomic transitions of a wide range of free radicals could be identified by exciting a gas sample with a far infrared laser whose discharge frequency was in close proximity to the transition line under investigation. Evenson was using water vapor lasers, but the field opened up when CO_2 pumped far-IR lasers came on the scene and many more spectral lines became accessible.

When Saykally arrived at NIST he wanted to incorporate his glow discharge techniques into the LMR spectrometers, but found that all of the existing instruments were being used to study free radical reactions of importance in the Earth’s stratosphere. It was the time that Paul Crutzen (1995 Nobel Prize in Chemistry, shared with Rowland and Molina) and Harold Johnston (UC Berkeley) were connecting NO_x emissions from supersonic transports to ozone depletion. As a consequence Saykally built his own instrument and incorporated the concepts he had acquired in the Woods’ lab. Saykally remembers this as a very fruitful and exciting time, perhaps the best in his career. Research funding was flowing freely, there were distinguished visiting scientists passing through NIST all the time, and many experiments that today would never even be allowed due to safety restrictions, were commonplace! In his two years at NIST, Saykally published close to a dozen papers with Evenson and in a continuing collaboration, two highly cited LMR papers on CCH [11] and methylene [12].

Upon finishing his post-doctoral appointment, Saykally looked around for academic positions and was about to accept an offer when his Boulder mentors intervened. They encouraged Saykally to consider Berkeley, where Charles Townes had been working since 1967 and William Gwinn (noted microwave spectroscopist) was still in the lab, although an emeritus professor by this time. Berkeley had not considered Saykally’s application because his thesis at Wisconsin had “taken too long, seven-years” (perhaps they had forgotten the proverb that *haste makes waste*). However, after hearing from supporters at Boulder, Berkeley’s chemistry department agreed

to an interview, and afterwards were impressed enough to make an offer. Saykally moved into a corner of Gwinn’s lab in 1979 and started setting up an LMR instrument to continue his earlier work on ions and radicals.

Gwinn eventually moved out and Saykally moved in. Together with a group of six eager young graduate students (five of whom were women—very unusual at the time), he began to work on identifying molecular transitions for the astrophysics community [13]. He attended Townes’ group meetings and flew with him on the NASA Kuiper Airborne Observatory. He and his students also performed astronomical observations at Hat Creek Radio Observatory, Berkeley’s interferometer array in northern California. His papers on carbon plus (C^+) [14], the hydroxyl ion (OH^+) [15] and the water and other cations and anions [16], [17] are particularly well cited.

This, was again, an exciting time for Saykally, with many of the key astronomical discoveries in the *invisible* far-IR getting a lot of *visibility*. Interested students were plentiful, and Saykally expanded his spectroscopic observations of ions into the mid-IR. He came up with the idea of using velocity modulation to separate ions from their neutral counterparts through an AC discharge technique. Working with post-doctorate Chris Gudeman (now a VP at Innovative Microwave Technology, Santa Barbara, CA, USA), he perfected the technique of velocity modulation laser spectroscopy (VML) just as Gerhard Herzberg (1971 Nobel Prize in Chemistry) came to the Berkeley chemistry department for a six-week visit. Herzberg was so interested in the VML technique that he set up shop in Saykally’s lab while they measured spectra from HCO^+ , H_2N^+ , and H_3O^+ in rapid succession. This technique earned Saykally his tenure, and resulted in many dozens of unique measurements on ionic compounds and just as many well-cited papers throughout the late 1980’s (e.g., [18]–[21]).

At the same time that the VML work was going on, Saykally, along with graduate students Doug Ray (now an associate lab director at Pacific Northwest National Laboratory, Richland, Washington, USA) and Ruth Robinson (now a chemistry professor at St. Cloud State University, Minnesota, USA), pioneered another laser spectroscopy technique—vibration rotation tunneling (VRT) spectroscopy. VRT spectroscopy opened the door to high frequency absorption signatures measurements of Van der Waals interactions via direct measurement of the weak bond vibrations [22]–[25]. The far infrared VRT spectroscopy technique makes use of narrow band THz or far-infrared sources realized by tunable sideband generation of optically pumped (CO_2) gas lasers [26]. Probe signals are sent through a multi-pass resonator cell populated by molecules produced by a pulsed supersonic flow. By sending the appropriate gas mixture through a slit at supersonic speeds, it is possible to produce large numbers of clustered, or weakly bound molecules [27]. Frequency modulation and lock-in detection produces VRT spectra with very high (one part per million) spectral resolution and sensitivity (one part per million) fractional absorption [28]. The same method can also be used to quantify dipole moments [29]. This ability to measure very weak coupling between molecules, especially those forming small clusters, prompted Saykally to start thinking about some fundamental constructs involving intermolecular forces. ArHCl and additional Ar compounds were studied first, but

the work turned to more universal compounds, such as water, very quickly. These ideas were spurred by Klemperer's earlier theoretical and experimental work in the microwave regime on HF dimers, and by Tom Dyke's (University of Oregon, Eugene, USA) work on water clusters.

With a sensitive new tool for probing intermolecular binding in the far IR now in hand (VRT), Saykally and his students, especially post-doc Geoff Blake (currently a Professor at Caltech, Pasadena, CA, USA), began experiments on clustered water. The first of many dozens of papers from Saykally's group on this important molecule came out in 1989 [30] when they measured the water dimer. Foremost on the mind of Professor Saykally, as he began to unravel the dimer coupling structure (intermolecular stretch mode as a direct route to the potential surface), was the beginning of a quest to unravel a "universal first principles model" for the most important molecule on Earth. This quest was to occupy a special niche in his research goals that persists to this day.

The idea of a universal model for water interactions, developed from measurements of molecular clusters, remained a strong theme for Saykally throughout the late 1980's and 1990's. A succession of excellent students and post-docs including Charlie Schmuttenmaer (Yale), Martina Havenith (Ruhr-Universität Bochum), Matt Elrod (Oberlin College), Kun Liu (Oplink Communications), Mac Brown (Los Alamos), Susan Strahan (NASA Goddard), Ron Cohen (Berkeley), Kerry Busarow Cogan (Infineum Inc.), Jenny Loeser (Marin College), Frank Keutsch (University of Wisconsin, Madison), Linda Braly (Lam Research) and many others came through the Saykally lab during this period. They expanded the work on high frequency spectroscopy of molecular clusters, ions and radicals using VML and VRT, and also developed a new spectroscopy technique, infrared cavity ringdown laser absorption spectroscopy, CRLAS [31]–[33].

CRLAS uses a laser to stimulate a gas under test in resonance with a highly reflective cavity. When the laser is turned off the exponentially decaying optical signal is measured, as it leaks out of the resonator. The optical decay constant is highly affected by the presence of the absorbing gas, and therefore gives a very sensitive measurement of the gas absorption properties and dynamics. Although this is not a THz technique, it has been widely used for sensitive measurements of weak molecular coupling.

A lot of theoretical work was required to go from spectra to physical models that could be used to create more accurate computer simulations. Such a model was a personal goal of Saykally's for understanding water as well as other molecular clusters. In 1995, Saykally was fortunate to have received a Churchill Fellowship, which landed him at Cambridge, UK. Here he bumped elbows with David Buckingham, Dave Clary, David Wales and Anthony Stone, amongst others. These were all strong theorists, who helped develop the constructs that led to accurate models for water clusters and many other molecular groupings [34], [35] aided by the spectroscopy data now pouring in from Berkeley. The period from 1986 to 2000 was particularly fruitful, with an average of more than ten major publications per year in top journals. Of particular note are a 1996 review paper on water clusters that made the cover of *Science* [36]; papers on the water dimer, trimer, tetramer, pentamer and

hexamer [37]–[43]; water dipole moment measurements [44]; and carbon [45] and other clusters [46]. This culminated in a highly referenced Proceedings of the National Academy of Sciences paper on water [47], and a featured presentation on clusters at the 2001 Nobel Symposium in Sweden [48].

In 2000, Saykally received the American Chemical Society Langmuir Prize "for the development and application of powerful new techniques in laser spectroscopy that have dramatically enhanced our knowledge of structure and dynamics in ions and clusters." The next year, the Royal Society of Chemistry awarded him their Centenary Medal for "his original contributions to the high resolution spectroscopy of molecules, including his recent determination of the structures of water clusters." Saykally's recognition for elucidating the nature of weak chemical bonds, and especially the detailed energy relationships involved in water clustering, were growing quickly. He was also being lured in several other directions, notably into nanowires, nanolasers and nanochemistry [49]–[55]. However he continued to stay focused on water, and began to work on the chemistry of the water-air interface and the properties of liquid surfaces. These studies brought him into the world of ultrafast laser spectroscopy (new femtosecond and harmonic generation techniques) and back to the detailed chemistry of ions like hydronium (H_3O^+) and hydroxyl (OH^-) that he had studied earlier in relation to the interstellar medium [56], [57].

Teaming up again with former student and present Berkeley Professor Ron Cohen and others, Saykally started examining the physics and chemistry of the water surface (e.g., [58]–[60]). More recently he has turned his attention to the mechanisms of water evaporation and other liquid-air boundary phenomena using X-ray spectroscopy and liquid microjets [61]–[63]. Though these measurements do not involve THz techniques, their importance to problems that have been, and are continuing to be addressed by THz science, is clear. As Saykally clearly attests, our current understanding of both molecular interactions involving liquid water, as well as the simplest surface interface phenomena are extremely *weak*. His recent video lecture, "*What Makes Water Wet? The Latest Word on the Most Important Molecule in the Universe,*" is a *must see* [64].

In concluding my discussions with Professor Saykally, I asked him, after all the incredible breadth and depth of discoveries he had already made in his career in chemical spectroscopy, if there was anything left to keep him excited and to continue to push himself and his students. Without a moment of hesitation he rattled off four major thrust areas that he will focus on for the next several years: understanding the Hofmeister series (selective folding and unfolding of proteins); unravelling the chemistry of liquid surfaces; completing his long sought after first principles' model of water, especially the interactions that occur in bulk water; and, finally, the impact of ions, particularly H_3^+ , on the formation of planets, stars and galaxies. I am certain that these are only a small sample of the problems Professor Saykally will set his sights on in the coming years as he continues to follow the advice he gives to newcomers: "*Be in the right place at the right time, and surround yourself with brilliant people.*" Certainly Professor Saykally is a catalyst for his own success, as well as for the success of so many others.

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