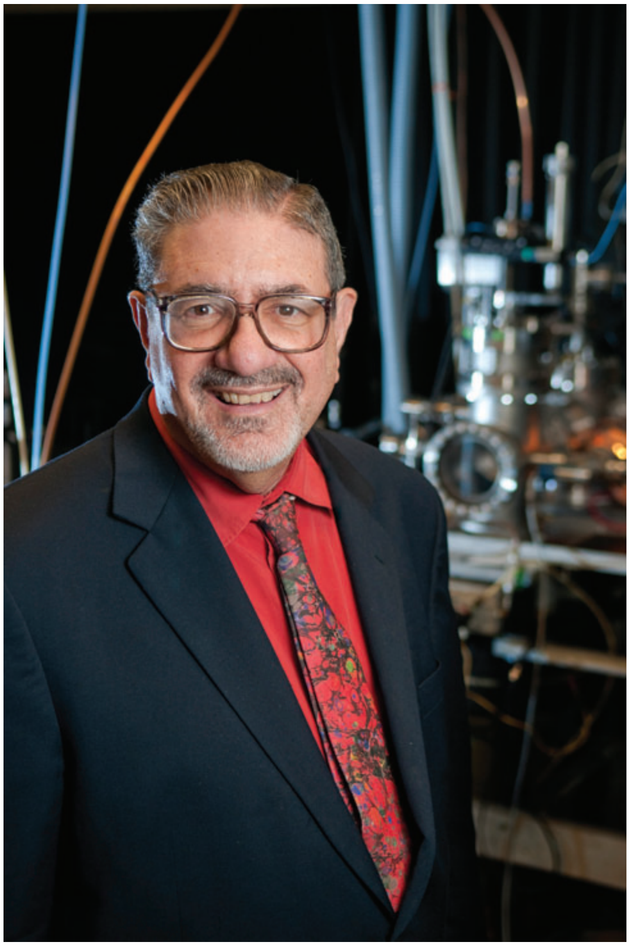

Richard N. Zare

The Hydrogen Games and Other Adventures in Chemistry

Richard N. Zare

Department of Chemistry, Stanford University, Stanford, California 94305-5080;
email: zare@stanford.edu

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Abstract

I seem to have started off on the wrong foot in life, but I am extremely fortunate that I soon found my footing in the company of physical chemists. I consider myself to be very lucky to be doing something that constantly brings me in contact with bright minds, stimulating conversations, and exciting experiments. My work has allowed me to learn astounding facts about the molecules and atoms that make up our surroundings and ourselves. For this article, I focus on one aspect of my research, understanding the fundamental principles of the simple reaction between a hydrogen atom and a hydrogen molecule. Although my group and others have been studying this seemingly simple reaction for well over 30 years, it continues to provoke questions about the properties of matter.

INTRODUCTION[1]

Life has never been simple for me. In fact, I tend to make things more difficult than they need to be. As I look back on my life, I marvel at how I have been transformed from a maladjusted individual to a person who enjoys working with people and rejoicing in their success and accomplishments.

For this, I have to thank the global community of chemists, a tight-knit and exceedingly helpful group. I use a small anecdote to illustrate my point: My oldest daughter, Bethany, was ready for college in 1982. Like a normal teenager, she considered her father to be a negative quantity and sought to put some distance between us. During her first week at the University of Southern California, someone broke into her dorm room and stole her wallet. It contained all her money and identification.

She called me collect, "Daddy, I need you to wire me money."

I told her that it was very hard to wire money to someone without identification, so I asked her to find the USC chemistry department, mention my name, and see if anyone would be willing to help her.

Bethany retorted, "Daddy, this is ridiculous. Don't you understand? One of the reasons why I came to USC is because no one knows you here."

I told her I was not going to argue with her during a collect call and ordered her to march over to the chemistry department. Well, being a new freshman, Bethany could not find the chemistry department and instead went to a place called the Loker Hydrocarbon Institute. The first man she bumped into was future Nobel laureate George Olah who, on hearing her name and plight, asked if she was my daughter and gave her $100 on the spot. Bethany called me again (still collect, even though she now had money) and exclaimed, "Daddy, guess what? You're famous!"

But I knew the truth: It was not fame that helped Bethany. Chemists help each other in tight spots because they are generous and kind. For this reason, I am honored and humbled to be part of this community and find it especially astounding in contemplating my early years that the passage of time has been kind enough for me to be in a position to be asked to write this prefatory article.

ALMOST FAILING KINDERGARTEN AND OTHER EARLY ADVENTURES

I was born in Cleveland, Ohio, and at an early age moved with my family to a nearly all-Jewish community called Cleveland Heights. I was the first of three children born to Dorothy and Milton Zare in 1939 (**Figures 1** and **2**). I still feel bad about how I treated my younger brother, Michael, when we were children. I was jealous of any love my parents showed him. My sister, Nancy, and I were sufficiently far apart in age that there was less interaction, but I do remember using Nancy as a human projectile against Michael, often with devastating success.

I was truly an obnoxious child. I remember at about age 3 or 4 urinating into my father's aquarium to avenge a spanking from him. I did not know that it would kill all his tropical fish, but I regard this episode as one of my earliest chemistry experiments. I also dabbled in culinary chemistry by cooking breakfasts for Michael and seeing what he would eat. "Here, Mikey," I would say, "try these scrambled eggs with sugar, salt, and mustard." Poor Michael was always willing to sample my food because the alternative was to go hungry.

I had a rebellious personality, which did not bode well for kindergarten. There was only one requirement to pass kindergarten: You had to be able to tie your shoelaces. I discovered that if I did not tie my laces, eventually someone would do it for me. Hence, I did not find a reason to learn

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[1] Some of this material has appeared previously in an autobiography I wrote (1).

Figure 1

Age 3, posing with my favorite stuffed animal and my favorite toy, a Holgate wooden block wagon.

Figure 2

Picture of my father, Milton, and my mother, Dorothy.

this skill. I had many quarrels with my parents over this decision. However, on the day before the kindergarten year ended, I learned to tie my shoelaces. I graduated from kindergarten—barely.

In first grade, I failed reading. The class used a reader featuring the activities of two middle-class white children, Alice and Jerry, and their dog, Spot. The book was repetitious with excellent picture cues. I memorized the text by listening to it. When I was called on by the teacher to read, I simply recited the story from memory while holding up the book. This got me quite far until my teacher realized that I was not actually reading.

All this behavior got me sent to the school counselor, who said that I should go to a professional family psychologist. My family was relatively poor. My father failed out of graduate school at Ohio State University while studying chemistry. He worked at a clerical position in the American Gas Association. The psychologist visits were a financial hardship and were discontinued after two visits. The psychologist had met alone with my parents and said my father should show more love to me—a statement that my mother would repeatedly use against him in arguments. It was not a happy family.

My maternal grandmother, Grandma Amdur, was a big influence on me. She was part of the Amdur clan from which came Professor Isador (Izzy) Amdur at the Massachusetts Institute of Technology's Department of Chemistry; he was famous for his pioneering studies with atomic and molecular beams. Grandma Amdur taught me to treasure learning. She told me that my Jewish heritage carried responsibilities. I vividly recall the horror of discovering that all the members of my father's family who had remained in Poland did not survive World War II. Grandma Amdur laid a heavy burden on me at an early age when she told me that for the betterment of Jewish people everywhere, I must do something significant with my life. Later in life, I generalized this call to action to include people from all walks of life.

MORE FORAYS INTO CHEMISTRY

In November 1947, we moved to Lyndhurst, Ohio, which was almost like a farming community. At school, I was able to score well enough on some tests to advance from the second grade to the third grade. It came as a terrible shock to me to find that all my classmates were singing Christmas carols. This was not done back in Cleveland Heights and I did not know the words. When my third-grade teacher noticed I was not singing, she disciplined me. She made me stand in the corner of the classroom wearing a dunce cap. Being the individual I was, not only did I say that I did not know the words, but I also announced to my teacher and classmates that I believed they were "full of lies." I did not think Jesus was the son of God. My classmates beat me up after school. I became very lonely. I began to show off by learning lots of science and mathematics. My classmates began to tease me by calling me "the little professor."

When I was 10, I discovered chemistry books at home, leftovers from my father's time at Ohio State University. Both my parents told me to leave the books alone because they only led to unhappiness. I read them at night under the covers of my bed with a flashlight.

My father would not buy me a chemistry set, but I was determined to find a way to play with chemicals. I made friends with a local pharmacist. At that time, the pharmacist could provide you with carbon black, sulfur, and potassium nitrate, all the necessary ingredients for gunpowder. I had so much fun. The pharmacist knew what I was doing and urged me to be careful. I first started with explosions but later got interested in dissolving various metals in vinegar, crystallizing the solution, and looking at the colors of the metal salts. I also remember making a vacuum tube radio and an electric motor.

However, a low point came in seventh grade when I was about 12 years old. My science teacher, Mr. Hart, belonged to that special class of educators who feel they must provide answers to all questions and never admit any fault. I, unfortunately, was very interested in pursuing some questions in science and felt the noblest thing to do was to seek the truth. Soon we were locked in conflict, with me pointing out to Mr. Hart that there were some questions to which he did not know the answer because no one knew the answer. Moreover, some of the things he was saying were wrong or incomplete. I would travel on weekends by bus to the Cleveland Public Library and find references that questioned or contradicted what Mr. Hart was claiming. I would check out books and then read from them out loud in class to attack whatever Mr. Hart was claiming to teach us. Often, I was sent to the principal's office for this behavior, but I was undeterred. In one of the parent-teacher conferences, Mr. Hart confessed to my parents, "I hate his guts." Soon the school principal told my parents that I was disruptive and needed to go to a private school.

This was impossible for my parents because they had so little money. Fortunately, I won a scholarship to attend a private school in Shaker Heights, Ohio, called University School for Boys. I did not realize at the time that my winning of the scholarship helped them satisfy their Jewish quota. Transferring to University School for the tenth grade was really good for me. It helped me to grow up and I did well there, although the same-sex environment did little to promote my socialization with the opposite sex.

When I applied to colleges in my last year of high school, I had to get a scholarship because of my family's financial difficulties. I was turned down by Swarthmore, whose officials told my headmaster that I was socially inept. But I was accepted into Harvard University, Caltech, MIT, and the University of Chicago. I decided to go to Harvard because they offered me a full scholarship.

One of my high school teachers, Mr. Chilton Thomson, was independently wealthy and taught English for the love of the language and the pleasure of interacting with young people. He decided that I needed to be appropriately outfitted and had his personal tailor fly into Cleveland to take my measurements. Mr. Thomson provided me, at his expense, with clothing for a gentleman. I remember feeling overwhelmed by this generosity. I asked him, "How can I ever repay you?" He told me I could not, which was certainly literally true. He said, however, that later in life when I could help someone in need, he wanted me to do so. I have never forgotten this request.

In my last year of high school, I made a computer out of relays (my grandchildren laugh at this now). On my own, I rediscovered how to manipulate binary numbers (Boolean algebra). With relay switches, I made a primitive computer that would add, subtract, multiply, and divide. But at its best, the computer could only do 3 times 9 and only get the correct answer if the relays did not stick. The computer won me first prize in the Northeastern Ohio Science Fair. I was sent with my high school science teacher to Los Angeles to the National Science Fair. It was a great experience and gave me a chance to meet a person who has been influential in my life, my second cousin, Abe Zarem.

When I called Cousin Abe, he told me that he had heard that I had built a binary computer and would be pleased to see me. He told me to come to "binary nine Green Street" in Pasadena, California. He had taken a second mortgage on his house and started a company called Electro-Optical Systems, a name he would later change to EOS, before selling it at a huge profit to Xerox Corporation. I was surprised by the address and asked if I heard it correctly. My cousin told me that if I had built a binary computer, I could find the location of his company. I went to 1001 Green Street and met this memorable individual, who promptly gave me a test to determine whether I had the right stuff to go on in science. He asked a number of questions that bewildered me, and I felt I did very poorly. I did not discover the answers to some of these questions until about the end of my undergraduate studies, but he certainly inspired me to try to solve problems such as "What would be the probability of a die (one half of a pair of dice) coming up different ways if you shaved slightly one of its faces?"

HARVARD

I had aspirations to be a computer scientist. At the beginning of my first year at Harvard, I talked my way into the most advanced class in mathematics, even though I had never studied calculus. I did miserably and received a C+ for which I had to promise the mathematics instructor, Professor Andrew Gleason, that I would abandon any thoughts of majoring in mathematics.

I had some inspiring teachers. My undergraduate adviser was Professor William Klemperer, and he was also my teacher for an introductory course on quantitative analysis. We were asked to determine the amount of calcium in a limestone sample using wet chemistry. I remember Professor Klemperer confiding to the class that we were wasting our time because the proper way to do it was to use atomic absorption spectroscopy. I said to him after class that I had never heard of atomic spectroscopy, so he told me to read a little book by Gerhard Herzberg called *Atomic Spectra and Atomic Structure*. I found it fascinating. The summer between my freshman and sophomore year I built my own atomic spectrometer in Cleveland, using a carbon arc as the light source into which I introduced different metal salts. I captured the spectra with a camera behind a glass prism.

During my last undergraduate year, I asked Professor Klemperer for advice about which graduate schools to attend. I really wanted to work with him, but he did not have tenure. Harvard had a reputation of seldom keeping its untenured faculty, and I felt I could not take that risk. I asked him who else was doing exciting chemistry. He mentioned a young man who had been a Harvard Junior Fellow the year before by the name of Dudley Herschbach who was trying to study chemical reactions in a fundamentally new way with crossed molecular beams. I went to Professors E.B. Wilson and William Lipscomb and asked them the same question. Each man mentioned Herschbach's name. I wrote to Herschbach, who was starting as an assistant professor in the department of chemistry at University of California, Berkeley, to ask if I could join his research group. Herschbach wrote back a wonderful letter telling me how the university was an experimenter's paradise, but I needed to apply to the department for admission to their graduate program. Little did I know then that my polling of the Harvard chemistry department faculty would result in me returning to Harvard in two years when Herschbach accepted their offer to become a full professor in physical chemistry!

GRADUATE SCHOOL: DUDLEY HERSCHBACH AND SUSAN

Professor Herschbach is my lifelong hero and my biggest scientific influence (**Figure 3**). He was developing the field of crossed molecular beams for studying chemical reactions, one collision at a time. I think I disappointed him as a graduate student by never doing a crossed-beam experiment. I decided that the project he suggested was too hard. It was the analysis of the decomposition of molecules by radiation to find the angular distribution of the photofragments using a molecular beam so that the photodissociation process could be studied molecule by molecule. This was in the age before lasers, and my pessimistic conclusion was a correct one. Instead, I plunged into working out the theory of photodissociation dynamics, which led naturally to a deep interest in angular momentum theory. My decision to avoid doing experiments with molecular beams may have been the reason why I graduated with a PhD degree in just three years!

I met my wife, Susan, on a blind double date arranged by my roommate while at Berkeley. Susan had graduated that year from Pomona College with a major in mathematics and had come to UC Berkeley to work there. My roommate fell in love with anyone within sight wearing a skirt. He met Susan's roommate in our apartment complex and immediately invited her out. She did not trust him and proposed a double date. When I came home that evening, I found I was going to a viola concert with someone I did not know. After that evening, Susan and I each confided in our respective roommates that we hoped never to see each other again.

Figure 3

My joy upon receiving the 2007 Dudley R. Herschbach Award for "Excellence in Research in the Field of Collision Dynamics" at the Dynamics of Molecular Collisions Conference in Santa Fe, New Mexico.

But my roommate then switched his affections to Susan, so she and I ended up running into each other repeatedly. I had purchased a motorcycle, and one day I took Susan on it into the beautiful Berkeley hills to show off my motorcycle skills. I took a great spill going down a hill. Susan was thrown off the bike but was unhurt. I was less fortunate, with the bike falling on top of me and the hot tailpipe burning my leg so severely that I had to spend several days in the hospital. During that time, Susan brought me sandwiches with Italian Genoa salami, my favorite. I was deeply moved by this kind act. Susan and I have now been married for 49 years (**Figures 4** and **5**). I am so thankful to her for the support that has made whatever I have achieved possible. She raised our family of three girls, and I am so proud of all of them.

NO ONE LEAVES MIT

One day, Professor Herschbach asked me if I would like to stay in the area. I said yes, hoping he meant Harvard. In front of me, he picked up the telephone and called Professor Arthur C. Cope, then the head of the chemistry department at MIT. After he hung up, he told me that I would be invited to MIT to give a lecture, and, unless I did something horribly wrong, I would get a job there as an assistant professor. In those days, that is how faculty appointments were made in the United States.

I was offered the MIT position in 1963 but deferred accepting it for a year so that I could take a postdoctoral position at the Joint Institute for Laboratory Astrophysics (JILA) at the University of Colorado in Boulder. I was officially a postdoctoral research associate with Professor Ed Condon but worked mostly with Professor Gordon Dunn, trying to learn how to do experimental work but often creating more problems than solving them. JILA was a research institute jointly administered by the US National Bureau of Standards, which later became the National Institute for Standards and Technology, and the University of Colorado, primarily the department of physics and astrophysics. This wonderful experiment was mostly the brainchild of Dr. Lewis M. Branscomb, who would later become Director of the National Bureau of Standards before joining IBM as their chief scientist.

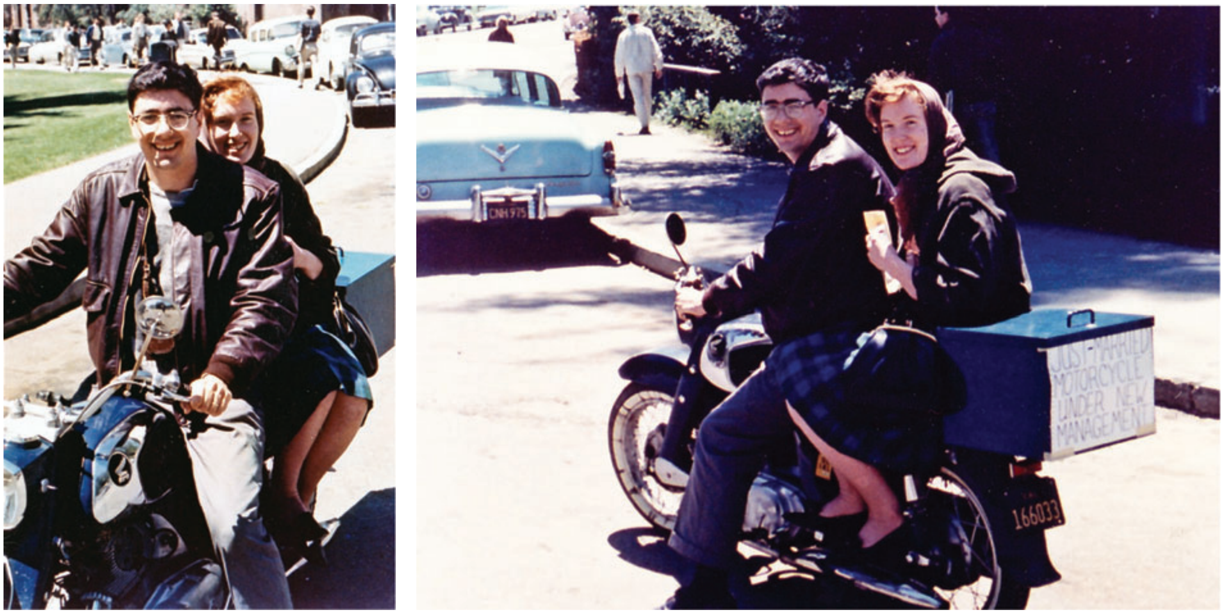

Figure 4

Photographs taken near the chemistry department of the UC Berkeley campus shortly after Susan and I were married (1962). The sign on the back of the box reads

JUST MARRIED
MOTORCYCLE
UNDER NEW
MANAGEMENT.

Figure 5

Photograph of my wife and me taken on April 23, 2011, by Dee Rogers.

At JILA, I tried to determine the cross section for dissociative recombination when an electron collided with a molecular hydrogen ion (H_2^+) and neutralized it. I tried to contact members of the department of chemistry at the University of Colorado, which was being led by a superb organic chemist, Professor Stanley Cristol. But he was quite dismissive, claiming whatever it was I was attempting to do did not qualify as chemistry.

On the other hand, the chair of the department of physics and astrophysics, Professor Wesley Brittain, was eager to grow his department and thought I was a promising young person. He suggested that I consider staying on at the University of Colorado as a member of his department. I told him that I was already committed to going to MIT, so I could not accept this flattering offer.

When I arrived at MIT a year later in 1964, I found that Cope was no longer the head of the department, and no preparations had been made for my arrival. I was without a laboratory but was told I could use the chemistry department's machine shop to build equipment for my proposed molecular beam experiments. The department had broken into warring factions without Cope's leadership, and it was very hard to know whom to turn to for help. My cousin Izzy Amdur was a physical chemist in the department. I wanted to ask him for advice and help, but he was on sabbatical in Japan, so I was very much on my own.

When I went to the chemistry department machine shop to construct vacuum chambers out of stainless steel, I was informed that this machine shop would work only with aluminum, brass, or plastic. From my experience at JILA, I felt that stainless steel was imperative, so I tried to go to the physics department machine shop. To my great dismay, I was told by other chemists, particularly Carl Garland, that the physics department machine shop was already receiving too many work orders from the chemistry department; Garland had told them not to accept work orders from me because mine would jeopardized his own projects.

What was I to do? Not knowing much about university administration, I looked through the MIT telephone book and made an appointment to see the provost when, of course, the proper course would have been to see the dean. I also wrote a letter of despair to Izzy but would not receive a return letter from Japan for a month. By then, matters were already on a different course. The provost I was supposed to see was Charles Townes, but he had been recently replaced by a young electrical engineer by the name of Jerry Wiesner, who would later become president of MIT before becoming President John F. Kennedy's science advisor.

Wiesner asked me how things were going in the chemistry department. I explained my need to machine stainless steel and the lack of support. He advised me to practice patience. I told him that I had not come to MIT to learn patience but to get research done. I could see that this comment fell on deaf ears, so I blurted out, "Do you know I have an offer to leave MIT?" He looked through his notes and found no mention of the offer. He told me that this information was very important, and I should have told him right away. He asked about the offer, so I told him about JILA. Wiesner looked me straight in the face and said, "But that is not a credible offer."

Surprised, I asked what he meant. He replied, "No one leaves MIT to go to the University of Colorado."

I left his office devastated. There was no way I could do my research at MIT. I called Condon, who flew to Boston and met with me about two weeks later. He carried with him an offer to join JILA and the University of Colorado physics and astrophysics department. I put a letter of resignation on Wiesner's desk, saying I would serve out my nine-month teaching contract. Immediately, Wiesner asked me to reconsider and gave me access to the machine shop at the Research Lab of Electronics, which would cut stainless steel. But my decision had been made. Later on, I would meet Wiesner again when we both served on IBM's Scientific Advisory Committee, and we would both laugh about our first encounter.

JILA was a researcher's delight. It was there that I became deeply involved in experimental work with lasers. I had discovered early on during my time with Dunn that my ability to perform experiments ranged between disappointing to disastrous. But I had a special knack for coming up with new ideas. It was at JILA that I took the first laser-induced fluorescence spectra of molecules (2). My small research group also started experiments to probe highly exothermic reactions that produced electronically excited products, in which we analyzed the product's chemiluminescence.

Three short years later, I received an offer from Columbia University in New York City. After agonizing what to do, I accepted it, and at age 29, I became one of the youngest full professors in the university's history. At Columbia, we used laser-induced fluorescence to study the quantum state distribution of products of bimolecular reactions. I loved New York City, but with three young daughters, it was not possible at that time to live in Manhattan, send them to public schools, and not worry about their safety. Susan and I did not consider private schools for our girls because of my salary and our parenting philosophies. So we lived in New Jersey, and I crossed the George Washington Bridge into and out of New York City at least twice a day.

I made wonderful friends in the Columbia chemistry department faculty, but Susan found life more trying. We received an offer to move to Yale University, which we turned down. Then came an offer from the California Institute of Technology, which greatly interested Susan because California was her home state, but it did not interest me as much. More offers came. After much soul searching, we decided on Stanford University in 1977.

Stanford is an unusual university. The campus hosts schools for humanities and sciences, to which I belong, as well as engineering, medicine, law, business, Earth sciences, and education, all in easy walking distance from each other. The strong connections between departments, schools, and intelligent people who follow a "work-hard, play-hard" ethic are the real joys of Stanford.

"NOTHING IS HAPPENING!"

I have enjoyed many professional successes for which I owe so much to my graduate students and postdoctoral research associates who really made them happen.[2] Let me concentrate here on a single topic from our body of work—understanding the fundamental principles of chemical reactions, collision by collision. It is a passion that was kindled during my graduate days in the Herschbach group. I have been particularly fascinated by chemical transformations of the elementary sort. For example, I am very proud that we have continued to study the chemical reaction of a hydrogen atom coming to a hydrogen molecule and exchanging hydrogen atoms to form a new hydrogen molecule plus a hydrogen atom. When I first showed this reaction, $H + H_2$ goes to $H_2 + H$, to my mother in the late 1970s, she exclaimed, "Richie, look at this! Nothing is happening!"

Well, you have to make something happen. We either use the heavy isotope of hydrogen, deuterium, and make $H + D_2$ go to $HD + D$, or we do other tricks, such as use *ortho* and *para* hydrogen and resolve the final rotational states of the products. Either approach is a challenge to explain to your mother!

Much has been written about this reaction system, and I point those interested in it to two reviews (3, 4). Of all the elementary chemical reactions to study, the $H + H_2$ bimolecular exchange reaction is certainly among the most important ones. Its significance is not as an industrial process, but as a system that guides theory and experiment. It is considered to be the simplest neutral bimolecular reaction because the H_3 (the total of H and H_2) reaction system has only three electrons, which makes the calculation of its potential energy surface amenable to the most advanced methods.

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[2] For a full description, please consult my website (**http://www.stanford.edu/group/Zarelab**). Herein readers will find a complete list of publications as well as information on all Zarelab coworkers, past and present.

But what is simple for the theorist is not necessarily simple for the experimentalist. Indeed, the H + H_2 reaction is devilishly difficult to study because the hydrogen atom must be produced in situ, and the hydrogen molecule cannot be easily detected by spectroscopy because it lacks a dipole moment. Without a dipole moment, there are not any strong infrared transitions, and the first electronic excited state lies deep in the vacuum UV region of the electromagnetic spectrum. As a result, many experiments in the past have relied on mass spectrometric detection, but this approach is not sensitive to the internal vibrational-rotational states of the molecular product.

I was very pleased to be part of the team that was the first to directly determine the internal excitation of the H_2 product using resonance-enhanced multiphoton ionization (REMPI) (5) in 1977. In the REMPI process, the molecule is made to gulp down more than one photon, causing it to transition from the ground state to excited state and then to the ionization continuum. It was natural to extend REMPI in 1982 to determine the relative populations of the vibrational-rotational (v, J) states of H_2 and its isotopologues, HD and D_2 (6, 7). The following year, we succeeded in measuring the internal state distribution of the $H + D_2 \rightarrow HD + D$ reaction (8–12). In a typical experiment, we expanded a gaseous mixture of D_2 and HBr through a pulsed nozzle and into a vacuum. The HBr was photolyzed at a known controlled wavelength to create H atoms that had a fixed speed relative to the D_2 molecules. The HD(v', j') products from the reaction were detected in a state-specific manner by (2+1) REMPI. In this method (**Figure 6**), the HD

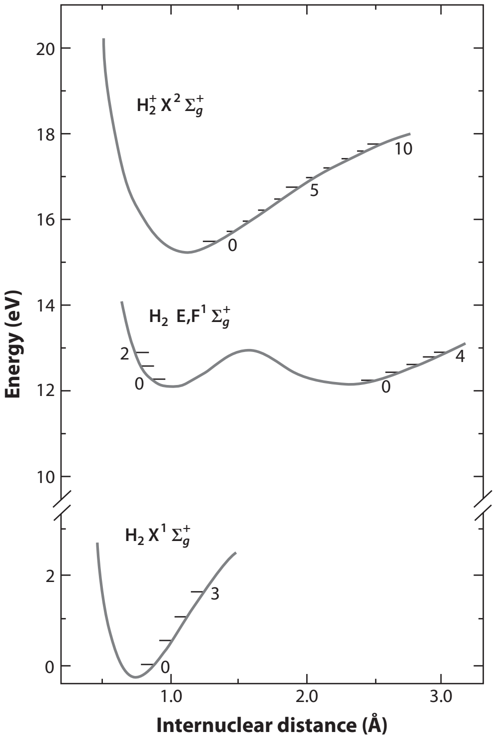

Figure 6

Potential energy diagram for the relevant levels in the (2+1) REMPI detection of molecular hydrogen. Two photons cause a transition from a specific vibrational-rotational level of the H_2 X state to a specific vibrational-rotational level of the H_2 E,F state, which is followed by one-photon absorption to create the H_2^+ molecular ion. The same scheme is also employed for the (2+1) REMPI detection of HD and D_2, but the locations of the vibrational-rotational levels change. Figure taken from Reference 12.

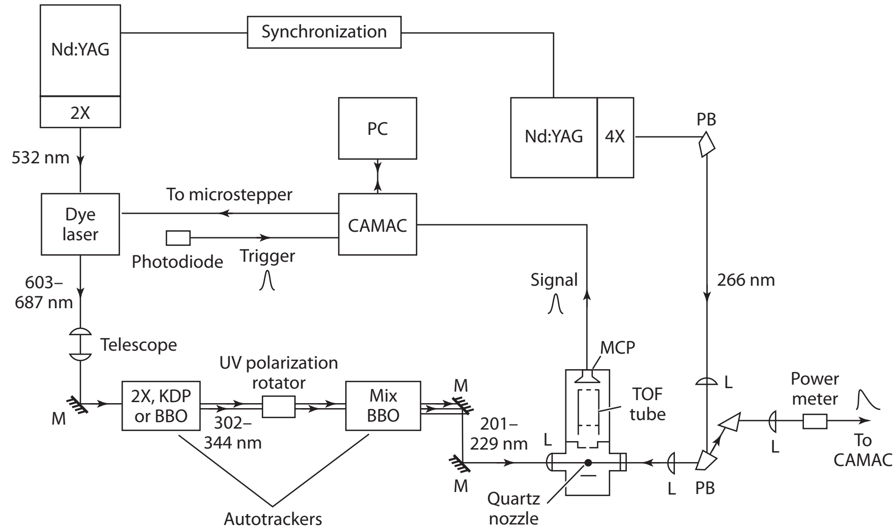

Figure 7

Schematic diagram of the experimental configuration for the initial REMPI experiments. Figure taken from Reference 12. Abbreviations: BBO, beta barium borate crystal; CAMAC, computer automated and management control (modular data-handling system); KDP, potassium dihydrogen phosphate crystal; L, lens; M, dichroic mirror; MCP, multichannel plate; PB, Pelin-Broca prism; PC, personal computer; TOF, time of flight.

molecule is pumped from the ground state, denoted by X, to a bound excited electronic state having a double-well potential, denoted by E,F by means of a two-photon transition. Another photon ionizes molecules in the E,F state to form HD^+, a charged particle that can be readily detected. The determination of the relative populations in the different internal states of HD depended on a careful analysis and calibration of the two-photon line strengths of the E,F-X transition of molecular hydrogen (13–16).

Many experiments in my laboratory followed that recorded different internal state distributions at various collision energies. The observations were compared to quasiclassical trajectory calculations and ultimately to a full quantum mechanical scattering treatment (17–21).

These REMPI experiments used two lasers (**Figure 7**). One photolyzed a hydrogen halide precursor, such as HBr, DBr, HI, or DI, to produce fast hydrogen atoms. The other detected the reaction product. Getting these two lasers to work at the same time often proved to be a challenge with a reaction system with such a small cross section (on the order of one square angstrom). But we soon progressed to using two more laser sources to prepare the H_2 reagent in a known vibrational-rotational level by stimulated Raman pumping. We reacted it with fast D atoms to achieve the first measurements of rovibrational to rovibrational integral cross sections (22, 23).

The next advance, which I regard as a significant one, was to determine state-resolved differential cross sections of the reaction products by the "photoloc technique" (24, 25). Photoloc stands for photoinitiated bimolecular reactions analyzed by the law of cosines. Prior to this work, differential cross sections had been determined using crossed molecular beams in which the detector was rotated. The photoloc technique uses a single molecular beam and has many advantages. One advantage is being able to detect reaction products with cross sections as tiny as 0.0001 square angstroms, which is perhaps a thousand times more sensitive than the crossed-beam technique.

Let me briefly describe in general terms how the photoloc technique works. A mixture of a diatomic photolytic precursor AX and a diatomic reagent BC is supersonically expanded into a vacuum, causing both AX and BC to be cooled and to travel together at the same speed. Let m_A, m_{BC}, μ, m_C, and μ' be the masses and reduced masses of the reactants and products; the total mass of the reaction system can be defined as $M = m_A + m_{BC} = m_{AB} + m_C$, and the difference between the potential energy of the products and reactants is ΔE. Upon photolysis of the AX precursor at frequency ν of the laser, the speed of the AB product in the center-of-mass frame, u_{AB}, is given by

$$u_{AB} = (m_A/M)[2(E_A\mu - \Delta E)/\mu']^{\frac{1}{2}}, \tag{1}$$

where

$$E_A = (m_X/m_{AX})[h\nu - D_o(AX)] \tag{2}$$

is the translational energy of the A photofragment. In Equation 2, $D_o(AX)$ is the energy required to break the AX bond to produce photofragments A and X of masses m_A and m_X from precursor AX with mass m_{AX}; h is Planck's constant. Because the BC molecule is standing still relative to the motion of the photofragment A, the speed of the center of mass of the reaction system, u, is

$$u = m_A v_A/M = (m_A/M)(2E_A/m_A)^{\frac{1}{2}}. \tag{3}$$

Thus, both the speed of the center of mass and the speed of the AB product in the center of mass are known. The experimental measurement is the speed of the AB product in the laboratory frame, v_{AB} (**Figure 8**), which is accomplished by means of time of flight. As seen in **Figure 8**, the laboratory velocity of AB, $\boldsymbol{v_{AB}}$, is the vector sum of $\boldsymbol{u}$ and $\boldsymbol{u_{AB}}$. The direction of the velocity vector $\boldsymbol{u_{AB}}$ is not known, but it must lie somewhere on a sphere of radius u_{AB}. The measurement of v_{AB} provides the lengths of the three sides of the triangle shown in **Figure 8**. We apply the law of cosines to determine the center of mass scattering angle θ, i.e.,

$$\cos\theta = \left(v_{AB}^2 - u^2 - u_{AB}^2\right)/(2uu_{AB}). \tag{4}$$

The laboratory speed profile of the AB product can be directly mapped into the scattering angle distribution, that is, the differential cross section. Note that we do not need to know the angular distribution of the photofragment A because the photoloc technique is based on measuring speeds, not velocities. In this sense, instead of having one crossed molecular beam, we have "millions and

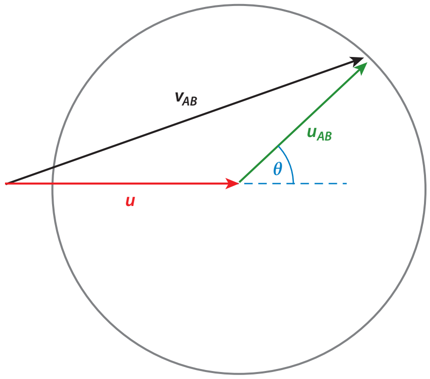

Figure 8

The photoloc technique. By measuring the speed distribution of the state-resolved AB product in the laboratory, we obtain the distribution of scattering angles θ by knowing the center of mass speed and the speed of the AB product in the center of mass.

millions" (to paraphrase Carl Sagan) of different crossed molecular beams for which each reactive scattering event provides the scattering angle.

By the photoloc technique, we obtained differential cross sections for a number of product states of the hydrogen atom–hydrogen molecule bimolecular exchange reaction (26–40). Further significant improvements involved the use of a position-sensitive detector (41). All these efforts show the power of ion imaging (42), which was applied to this reaction system early on (43).

Several intriguing results emerged from these studies. The $H + H_2$ reaction system has a preferred collinear geometry for the reaction and a barrier of approximately 0.5 eV. The expectation is that products in low rotational levels are back-scattered, whereas those in higher rotational levels are side-scattered. It was a great surprise to find that at certain collision energies, there was a pronounced forward-scattered peaking in the differential cross section for the $HD(v' = 3, j' = 0)$ product of the $H + D_2$ reaction at a center of mass collision energy of 1.64 eV (30–33). This feature was reproduced by full quantum calculations and attributed to a time-delayed scattering mechanism. But its origin was not immediately obvious (33). From an operational viewpoint, this feature represented a rapid change in the form of the differential cross section, and we referred to it as some form of a resonance (4).

Exactly the same behavior was also observed for $HD(v' = 2, j' = 0)$ but at a different collision energy (1.25 eV) (40). This behavior has been explained as being a result of the opening of an adiabatic barrier threshold (also referred to as a "quantum bottleneck state"). The system slows down as it passes over this threshold, which allows the temporarily associated atoms to rotate round before scattering the products into the forward direction (44). This phenomenon seems completely general and should be observed in many other reaction systems. Recently, a semiclassical interpretation has been given, and the phenomenon is described as an example of reactive glory scattering (45).

Another surprise to me was our study of $H + D_2$ inelastic scattering. You may think that to produce vibrationally excited D_2 products, it would be necessary to strike the D_2 molecule close to head-on, which would result in back-scattered products. Instead, we found appreciable forward scattering in some cases (46). Comparison with quasiclassical trajectory calculations led to the conclusion that instead of the D-D bond being compressed during the collision, it was extended by attractive interaction with the incoming H atom, allowing some trajectories to be forward scattered (47). Thus, this inelastic scattering event is really the result of a frustrated chemical reaction in which the incoming H atom grabs onto the nearest D atom of D_2 and pulls on it, but releases it because it is traveling too fast to capture it and form the HD product. The abandoned D atom then snaps back to its D atom partner, causing the D_2 to become vibrationally excited. Again, this conclusion is expected to hold for other reaction systems in which there are strong chemical forces between the collision partners.

Along the way, it was only natural for us to examine the related reactions, $H + HX \rightarrow H_2 + X$ and $D + DX \rightarrow D_2 + X$, where X is the halogen atom Br or I. Although these reaction systems no longer allow a detailed comparison with theory, they proved to be quite remarkable in several respects (48–53). We were able to observe the strong influence of indistinguishable nuclei on the vibrational-rotational product state distribution in a chemical reaction (48, 49), achieved the first application of ion imaging to a bimolecular reaction (50, 52), and found strong experimental and theoretical evidence for reactions occurring far from the minimum energy path (53).

For $H + HBr$, we identified two distinct reaction mechanisms. The first one is a direct reaction mechanism in which the incoming H atom collides with the HBr molecule and forms an H_2 product that recoils away immediately. The second, an indirect reaction mechanism, has the H atom undergoing several collisions with HBr before the H_2 product is formed. A search for the

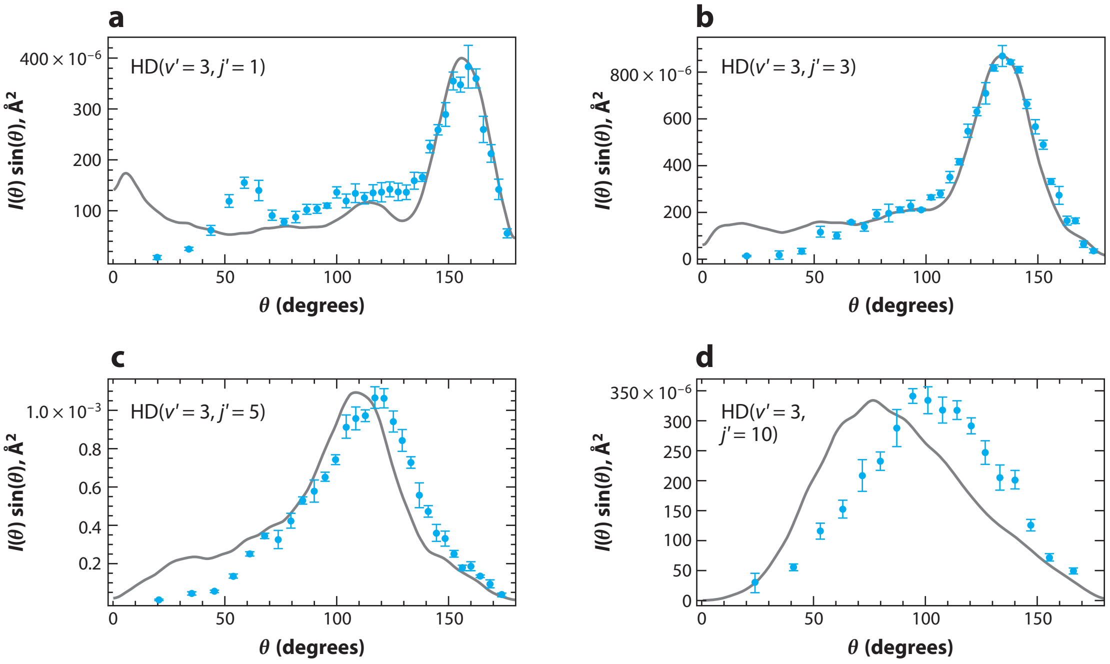

Figure 9

Differential cross sections for the $H + D_2 \rightarrow HD + D$ reaction at 1.97-eV collision energy for (*a*) HD($v' = 3$, $j' = 1$), (*b*) HD($v' = 3$, $j' = 3$), (*c*) HD($v' = 3$, $j' = 5$), and (*d*) HD($v' = 3$, $j' = 10$). The error bars represent one standard deviation of three to four replicate measurements. Figure taken from Reference 55.

nonadiabatic production of spin-orbit-excited Br in the D + DBr reaction showed that this channel contributes 1% or less for the conditions studied (54).

The agreement between experiment and theory for the $H + D_2$ reaction is very good, although not yet perfect (34, 35, 38–40). **Figure 9** shows a comparison between experiment and theory for the HD($v' = 3$, $j' = 1, 3, 5$, and 10) products at a collision energy of 1.97 eV (55). As can be seen in the figure, intermediate j' values agree most closely, but the forward-scattering features for low j' values are less well reproduced. The high j' theoretical values predict more sideways-scattered products than were observed.

This is not the place to go into detail about this benchmark three-atom system, but it is clear that theory and experiment have nearly matched each other. The close agreement is truly gratifying, but the remaining small discrepancies give hope that we can refine our experiments or discover what is needed to improve our theoretical understanding (or both).

From a logical standpoint, it might seem that no further low-energy experiments need to be performed on the $H + H_2$ reaction system. But experiments have continued to reveal features that were present in the calculations but whose significance was not appreciated. In this regard, it is interesting to speculate about two types of truth. The "truth for the physicist" is how well theory and experiment agree with one another. With regard to the "truth for the chemist," what matters most is what general principles can be learned from these detailed studies and how they might be roughly applied to more complicated chemical reactions that cannot presently be modeled well by computation.

With these thoughts in mind, I hope to continue to look at this reaction system in ever-increasing detail. There is still much to learn, especially as higher–collision energy experiments introduce nonadiabatic effects in which both the ground state and the first excited state potential energy surfaces of the H_3 system must be simultaneously considered to correctly describe the reaction dynamics.

PHILOSOPHY ABOUT SCIENCE

As an undergraduate, I did a double major in chemistry and physics. My PhD was in chemical physics. However, my interests are increasingly moving toward biological problems. All these research projects, of course, depend on mathematics to back them up with quantitative measurements, and many of the payoffs require engineering. All these activities—chemistry, physics, biology, mathematics, and engineering—take place together. Important problems do not come with the names of departments or disciplines on them!

I am a strong believer in interdisciplinary work, but I believe that interdisciplinary work only succeeds when it is first firmly grounded in disciplines. You must learn a discipline very well to succeed, but this is not enough. You must believe that you can teach yourself whatever you need to know to solve some interesting problems. And part of teaching yourself is the willingness to work with other people and ask questions.

Experimental work in my laboratory is more like a comedy of errors than a straight, logical narrative. One crazy thing happens after another. Persistence pays off, and a high frustration threshold is necessary. You must have confidence that there are rational explanations for what is being observed, and you must regard one failure after another as the guide to making something finally work. Many people think that a great discovery happens when the researcher shouts “Eureka!” My experience is that the sign of a breakthrough is when the researcher remarks, “Oh, look at that. It looks really funny!”

There are people who chase prizes. I think it is vanity. A scientific career is not about prizes. Yes, they are meaningful, and they serve the important purpose of signaling to the next generation what is valued. But the satisfaction and fulfillment I cherish in my life come from the work that I am doing and how that work has affected other people.

I am so lucky, so fortunate, that I am doing something that I love. I certainly did not know what would become of me when I graduated from college. I did not foresee where I would rise, and in some sense, I really have done quite well. I certainly have exceeded my own expectations.

Many people start out on one path and surprise themselves by ending up on another path. Changing career paths can lead to growth. If you do not love your job, you should think about leaving it for something you do love. Of course, every job has its drudgery, frustrations, and politics. What is important is to be able to pass through the negative and dwell in the land of the positive. Blessed are those who achieve equanimity in this age of angst, stress, and false gods. It is easier if you love the work itself. You must try again, be willing to take risks, and see what happens. There is no guarantee of what life will provide, no matter which career direction you choose. But you cannot do better than to try your best. To ask for more than that from yourself is folly.

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