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My Trajectory in Molecular Reaction Dynamics and Spectroscopy

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Abstract

This is the story of a career in theoretical chemistry during a time of dramatic changes in the field due to phenomenal growth in the availability of computational power. It is likewise the story of the highly gifted graduate students and postdoctoral fellows that I was fortunate to mentor throughout my career. It includes reminiscences of the great mentors that I had and of the exciting collaborations with both experimentalists and theorists on which I built much of my research.

This is an account of the developments of exciting scientific disciplines in which I was involved: vibrational spectroscopy, molecular reaction mechanisms and dynamics, e.g., in atmospheric chemistry, and the prediction of new, exotic molecules, in particular noble gas molecules.

From my very first project to my current work, my career in science has brought me the excitement and fascination of research. What a wonderful pursuit!

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1. INTRODUCTION

In this scientific autobiography I describe my career in theoretical physical chemistry, in the context of which I highlight topics, research challenges, and methodologies. I began research many years ago when I was 21; I am writing these lines at 75 years of age. The landscape of theoretical chemistry has changed dramatically during this period. I attempt to point out how the rapid, major developments in the field have influenced my research, as was presumably the case for many of my colleagues in theoretical physical chemistry.

I did not make my journey in science by myself. From the early stages of my career until now, I have been fortunate to have a group of graduate students and postdoctoral fellows (postdocs) I have mentored but also learned enormously from. Working together, sharing ideas and results, and watching the growth and development of gifted young scientists were certainly some of the best parts of my journey in science. Thus, my group members, their contributions, and their interactions with me are all a key part of my story.

Important also in my formative years as a scientist were the roles of my doctoral and postdoctoral advisors. To my great fortune I was mentored by two giants who hugely influenced the development of theoretical chemistry. My personal comments on their research approaches and philosophies may therefore be of interest. Another aspect that has greatly influenced my career is cooperation with colleagues, experimentalists, and theorists. I was fortunate to have stimulating collaborators, the interactions with whom were enlightening. This is rightly a major element of my autobiography as well.

2. GETTING MOTIVATED FOR CHEMISTRY: EDUCATION

I became fascinated by science in the early years of high school. My chemistry and physics teachers were both charismatic and inspiring and knew how to convey the magic of science. Inspiring teachers are certainly a major factor behind many careers in science. I was beginning to vaguely entertain a future in science at those early stages. My parents, who were extremely supportive in general, encouraged me strongly in this direction. They both grew up in very hard times and never had a chance to attend high school or beyond. However, admiration for scholarship was part of their culture.

With this background, I enrolled in the fall of 1962 as a chemistry student at the Hebrew University of Jerusalem in Israel (HUJI). The curriculum was intensive and kept us students very busy. There were many lectures to attend each week and many laboratory classes. However, we had no courses on quantum chemistry. I found myself spending significant time reading on valence bond theory. I performed well in the official courses but found that I most enjoyed what I read on quantum theory and chemical bonding, superficial as my understanding certainly was at that time. Of the courses I took, one of the most stimulating was taught by Saul Patai, a distinguished physical organic chemist. His lectures on the mechanisms of organic reactions, following the approaches of Christopher K. Ingold, Edwin S. Gould, and others, were thought provoking. Many insights were obtained from qualitative, chemically intuitive electronic structure considerations! I discussed with Patai some ideas on the possible relevance of quantum chemistry to the material he presented, which he seemed to appreciate. I was stunned when he suggested that I should pursue a doctorate with one of the leading quantum chemists in the world, Charles A. (C.A.) Coulson at the University of Oxford, of whom I had already heard. Patai got support from other HUJI professors, recommended me to Coulson (whom he knew), and worked to get me a scholarship to Oxford. By the summer of 1965, I graduated as a B.Sc. with Distinction from the HUJI and was on my way to the University of Oxford to pursue a doctorate under Coulson. This was incredible

luck and an absolutely thrilling challenge. I was excited about it but was worried whether I could meet the standards of a great scientist and his research group.

3. GRADUATE STUDENT OF CHARLES A. COULSON AT OXFORD

When I came to Oxford, Coulson was already widely recognized as one of the leaders of quantum chemistry. I found that people who knew him admired him greatly. An applied mathematician by background, his scope of knowledge and interests were astonishing, covering broad areas of mathematics, physics, and chemistry.

In his approach to quantum chemistry, Coulson emphasized concepts and models more than large-scale calculations. His celebrated work on the electronic structure of conjugated molecules is an example of the power of his approach. Coulson successfully aimed at simplicity of interpretation, realizing that this can bring very helpful insights. At the same time, his work was also characterized by elegance and rigor. Coulson's insights into molecular orbital theory contributed greatly to the success of the method. He expressed the view that concepts and models as well as computational techniques would play major roles in the future of quantum chemistry. He could not foresee at the time the rapid, almost explosive growth of computational power that made it such a dominant force in the evolution of the field (Coulson died in January 1974).

As a research advisor, Coulson was unsurpassable, and his personal kindness was legendary. He was supportive, always open to hearing my ideas, and responded from a positive point of view. As extremely busy as Coulson was, he always replied quickly to any question I had. Coulson's influence inspired my desire to start research as soon as possible.

Coulson had a large group with a strong international presence. There were quite a few gifted students and postdoctoral visitors. Most group members pursued research on quantum-chemical topics, but some were involved in other areas of quantum theory. Furthermore, the group was part of the Mathematical Institute, where most of the faculty and students were from various mathematical disciplines, and most of the research done was not related to chemistry. In this environment I learned a lot of mathematics that was new to me. This knowledge in both quantum theory and methods of mathematical physics benefited me greatly, and I liked it. At the same time, this kept me away from thinking of mainstream chemistry. I was not the only one to have such an experience. Tony Joseph was a brilliant student of Coulson's with a chemistry background. During his Doctorate of Philosophy (DPhil) program he began to drift toward mathematics, and today he is a world-class pure mathematician.

As the research topic for my doctorate I chose molecular scattering theory, which seemed a hot topic then. I had some ideas on the properties of elastic molecular scattering, did some algebraic derivation, and being all excited about it I wrote up a manuscript and showed it to Coulson. He strongly praised the paper and urged me to submit it but refused to be a coauthor because he did not contribute to it. The paper was accepted, and I was elated. I felt that I had joined the research community, even though I realized that my contribution was a modest one. This first, early success added momentum to my research. I published four papers in my 3 years working toward the DPhil, all on the properties of elastic molecular scattering. Coulson called this a "burst of creativity." On the strength of this, I was elected as Graham Senior Scholar at Pembroke College, a status that carries some prestige in Oxford. Before I got my DPhil, I was awarded the Senior Mathematical Prize (second prize) for my research.

In summary, I felt that I was very successful in my Oxford years. I got to work with a great scientist (and a most wonderful person) and got his appreciation; I found that I could be productive in research, having published my first papers; and I learned a lot of exciting science (especially quantum theory) and loved it greatly.

I realize now that my research contributions were only of modest weight, with little impact on the field. It was more than enough, though, for me to continue in the world of research.

4. POSTDOCTORAL FELLOW WITH MARTIN KARPLUS AT HARVARD

Toward the end of my DPhil I applied for postdoctoral positions with several distinguished theoretical chemists in the United States and received some attractive offers. I decided to work with Martin Karplus at Harvard University; I had followed his work, and it caught my enthusiasm. His work on classical trajectory studies of chemical reactions, in addition to being extremely interesting, was related to the topic of scattering, in which I had already published. The famous relation that Karplus established, which linked the dihedral angle of a class of molecules to nuclear magnetic resonance (NMR) data, was a great example of creative model development.

Thus, in August 1968 I arrived at Harvard as a postdoc of Karplus. As I was to find out, the time was a so-called Golden Age for chemical physics and especially for chemical dynamics at Harvard. The molecular beam experiments of the Hershbach group and the classical trajectory calculations by the Karplus group provided constant excitement. William H. (Bill) Miller, then a Junior Fellow at Harvard, had highly creative and deep theoretical ideas, and I quickly developed an admiration for him. Luckily for me, Miller was very willing to discuss his ideas and vision and was very clear in explaining them. I shall always be grateful for what I learned from him. William P. (Bill) Reinhardt was then an assistant professor; he not only was a brilliant scientist but was also very kind and approachable. The postdocs and graduate students were also impressive in their research ability. Barry Honig was the first postdoc of Karplus that took on a biomolecular subject, a direction that was to grow hugely in the following years. David Chandler impressed me greatly with his insights into statistical mechanics. In brief, many of the leaders of theoretical chemical physics were there, and I loved being in that environment.

However, a problem arose when I had to decide on my research topic. I very much liked the physical understanding that the classical trajectory calculations of molecular reactions could provide, but I had no experience with computing and did not know how to write code (at Oxford an electronic calculator was all that I had used). The biomolecular field was clearly very promising, but I had no knowledge in biology. I decided to fall back on quantum scattering theory, my field at Oxford. I thought of a problem that looked very interesting to me. The basic measurable quantity in elastic scattering is the differential cross section, $\sigma(\theta)$, as a function of the scattering angle θ . Solving the Schrödinger equation for the scattering process results in a complex-valued scattering amplitude $f(\theta)$, which is related to the cross section by $\sigma(\theta) = |f(\theta)|^2$. So, is the information on the phase of the scattering amplitude lost in the experiment, or can it somehow be recovered? Using the important quantum-mechanical property of unitarity of the scattering amplitude, I was able to show that the phase of the scattering amplitude can be obtained from the measurable cross section through a certain integral equation. Furthermore, I found mathematical procedures that could lead to numerical determination of the phase. Karplus encouraged me and provided insights on the implications of my results. The paper we published on this was very well reviewed (1). There was a previous paper on the topic by a leading scattering theorist (2), but our results went further. I was delighted with the paper, even proud to some extent, as it gave me confidence in my ability to do significant research. To date, depending on the criteria used, I still consider it one of my best papers. But my success with this paper also left me with some worries in evaluating my postdoc at Harvard. The phase-determination paper is essentially in mathematical physics; it did not have any impact on chemistry. I was not able to contribute to Karplus' research directions, which truly changed mainstream chemistry. Was Karplus himself disappointed with my work as postdoc? Two experiences indicate to me that he appreciated my work all the same. First, he

supported me strongly in my search for a position to go back to Israel. With the influence and support of Karplus, I rather quickly obtained a position as senior scientist (equivalent to assistant professor in the United States) at the Weizmann Institute of Science. Second, many years later, when I was inducted into the American Academy of Arts and Sciences, Karplus gave me a very great honor by coming to the ceremony. He kindly invited me to dinner, and the conversation showed that he did appreciate me as his former disciple.

In fact, my stay in the Karplus group had a profound effect on my future science career. It became obvious to me that to do useful work in chemistry, I also needed to learn some of the skills of a computational scientist. This took a long time, but by then I had already decided that I wanted to remain in chemistry and not pursue mathematical physics. More specifically, I was very influenced by the insights that can be gained from classical trajectory studies of molecular reactions. Years later, for other systems and problems, I followed such an approach.

5. AT THE WEIZMANN INSTITUTE OF SCIENCE

After a year as a postdoc and a total of 4 years abroad, I returned to Israel. I needed it personally. I greatly enjoyed my time at both Oxford and Harvard, but I was missing home: my aging parents, my friends, and the places and atmosphere that I was used to. I felt fortunate to have a tenure-track faculty position at the young age of 25. In retrospect, however, I was not scientifically mature enough for the move, and problems began to surface. The Weizmann Institute was then, as it is now, an outstanding research establishment. However, the Department of Chemical Physics had at that time only a handful of faculty members, and the number of students and postdocs was also extremely small. Worse still, they were all in research fields very far removed from mine. For the first 2–3 years, I hardly had anybody to talk about science with, and I needed it. The result was that I felt isolated. However, there was a very positive element in that situation: Shneior Lifson, the head of the department, who I came to recognize as a great scientist, and whom I liked very much. Lifson, with a background in statistical mechanics, was pursuing the development of valid, accurate, and practical force fields to describe the properties of biological molecules. He was a deep thinker, with sharp, cutting logic and with a great ability to present ideas. I enjoyed every moment I could discuss science with him. Unfortunately, in my first 2 years at the Weizmann, Lifson was rarely there. He was promoting the Open University in Israel and was largely absorbed by this.

Working in isolation, I was not able to choose a new, good research direction. I returned to my old topic of scattering theory from a mathematical perspective and with little connection to chemistry. I published several papers in these years, e.g., on analytically solvable models of scattering. These papers are totally useless, and there is no point in mentioning the results. My first 3 years at the Weizmann were thus a professional failure.

However, in my personal life, this period was one of great happiness. I met H  l  ne Grigoriu and fell in love with her. H  l  ne lived in France but visited Israel and was thinking of settling there. After a courtship of 2 years, we married in 1972. Our marriage was an extremely happy one. The love and care of H  l  ne and her wisdom and advice were my greatest support in life. My world darkened greatly when she passed away in October 2015.

The Weizmann Institute was known then for a tough policy on tenure. Realizing that my achievements were disappointing, I got quite worried. Things improved after the third year or so, partly because I made changes to my research, and partly because I lucked out. I detail the main developments here.

1. I began to write programs, learned about computational methods, and started to use computers. This enabled me to pursue applications, not just analytic work.

2. New faculty members joined the department. A wonderful addition for me was Moshe Shapiro. A theorist of both analytic skills and physical insights, Shapiro's research interests overlapped with mine. We discussed science extensively and began to collaborate. Our topic of cooperation was the inversion problem of scattering, a topic that was of considerable conceptual interest (3) but also of chemical relevance (4). The aim of the inversion topic in scattering is to determine the potential (e.g., atom-atom interaction) from scattering data. Shapiro and I developed quantum-mechanical algorithms for the inversion problem in elastic scattering that were efficient and realistically applicable enough to be of interest. The papers on this did not appear until 1976 but were well received (5, 6).
3. I began to recruit graduate students. As I found, good students contribute enormously to research. I also learned a lot from my discussions and interactions with them. A first outstanding student was Max Berkowitz. I enjoyed his physical insights and his analytic skills. After getting his PhD, Berkowitz developed a very successful academic career. For many years now he has been a professor at the University of North Carolina in Chapel Hill. Since then, mentoring students and postdocs has been a pivot of my work. Berkowitz joined me at the Weizmann, but we did most of our research when I was already at the HUJI.

A positive development that taught me about highly interesting research by others was the much increased presence of Lifson and his group in the department from about 1972. His then-student Arie Warshel and his postdoc Michael Levitt were developing Lifson's idea of constructing realistic, reliable force fields to describe the properties of proteins. Lifson explained to me the vision of the approach, and the enthusiasm and obvious brilliance of Warshel and Levitt gave me the feeling that very important research was being accomplished. Warshel and Levitt shared the 2013 Nobel Prize with Karplus, and I am glad that I witnessed the development of an important discipline of computational chemistry.

Just as the process of deciding on my tenure had begun, a surprising development completely changed my professional situation. The HUJI decided to recruit additional theorists. It was suggested that I apply, and to my delight I was offered the position of associate professor. Two main considerations influenced my decision to accept: First, I was very doubtful about my prospects of obtaining tenure at the Weizmann Institute, and second, I was very disappointed with my research in the first 3 years there. I felt a strong urge to have a fresh start in a new place.

6. A TRANSITION TO JERUSALEM WITH MANY CHANGES

I was hoping that my move to the HUJI would facilitate change for the better in my approach to research, and this did indeed happen. The move invigorated me. I changed research topics, became eager to cooperate in research, and searched eagerly for students to recruit.

Being at the university, I had to teach, and in my first semester I was assigned to teach an undergraduate course in physical chemistry. I invested a lot in the preparation and discovered that I love teaching. The contact with young students is invigorating. Also, I found that by preparing and teaching a class my perspective on the topic becomes broader. Over the years, the students who took my classes liked the lectures. I got several prizes for excellence in teaching. Teaching also induced some students to join my research group.

Two excellent students, Victoria Buch and Tamar Yinnon, joined my group soon after I came to the HUJI. A third superb student, Ron Elber, joined a little later. I already had Berkowitz, who was registered at the Weizmann. Berkowitz, Buch, and Elber continued on to academic careers that have had substantial impacts on their fields. I was very fortunate to have such a team.

Soon after I came to Jerusalem, I obtained several very useful results, as I detail below.

6.1. Intermolecular Potentials Obtained by the Inversion of Scattering Data

I have mentioned the methods that I developed with Shapiro for the inversion of the differential elastic cross sections. The major new step was the adaptation and application of these methods to measured cross sections, including the determination of very accurate interaction potentials. This resulted from collaboration with Udo Buck of the Max Planck Institute (MPI) of Göttingen, a superb, high-powered experimentalist. This marked a new type of research activity for me: joint theoretical-experimental projects. It was all inspired by a visit I had to Göttingen. The MPI there was the top place in the world for research with molecular beams. I was very impressed to learn of the deep, sophisticated physics behind the design. I enjoyed collaborative projects with Buck for many years.

The key paper of this project, on the determination of a very accurate $He - Ne$ potential by inversion, was published in *Physical Review Letters* (7), my second paper in this very reputable journal. The paper produced a nice echo in the field. A couple of years later, we made another important step forward in the field: Working with Buch, we developed an inversion method for anisotropic, orientation-dependent atom-molecule potentials. The method requires rotationally inelastic cross sectional data as well as elastic data (8). Buck was impressively successful in carrying out the measurement for $Ne + D_2$. The determination of an orientation-dependent atom-molecule potential by inversion of rotationally inelastic data, using a new theoretical method and a novel experiment, was also published in *Physical Review Letters* (9) and was highly reviewed.

I should note that despite these successes, we stopped pursuing the inversion method in the following years: Ab initio calculations of intermolecular potentials became accurate enough, and the effort involved is much less than that required for inversion. Thus, the success we had was of historic interest only. That is how things are and should be: If a new, better scientific approach emerges, old approaches should be abandoned.

6.2. Theory of Vibrational Relaxation of Molecules in Solid Matrices

I was reading extensively at that time on topics beyond my projects, in search of interesting new challenges from experimental data.

A topic that caught my attention due to puzzling experimental results was the relaxation of hydride molecules, e.g., HCl and NH_3 , in noble gas matrices. The surprising finding was that HX molecules relax vibrationally much faster than do the isotopomers DX , although the $v = 1 \rightarrow v = 0$ energy gap for HX is much larger (10, 11). The experimentalists guessed correctly that the rotational mode may be involved, but a quantitative, systematic model was not available. Working with Berkowitz, we were able to develop a very successful model based on simple physical considerations (12–14). The model assumes that nearly all of the vibrational energy released from HX or DX is transferred to localized modes of the guest molecule in the cage. These are the molecular rotation and translation in the cage (a localized phonon). There may be a small amount of excess energy that goes to one or two bulk phonons. The rotational energy spacing of HX is much larger than is that of DX , which explains the isotope effect. The energy disposal according to the model is shown in **Figure 1**.

This has remained the generally accepted model for the process. One of our papers was published in *Physical Review Letters* (13). François Legay, one of the leading experimentalists on this, hosted me in his laboratory at the University of Paris in Orsay and very kindly tutored me from his deep knowledge.

My experience in the field led me to pursue other, very different processes in noble gas solids, yielding groundbreaking results that are mentioned later.

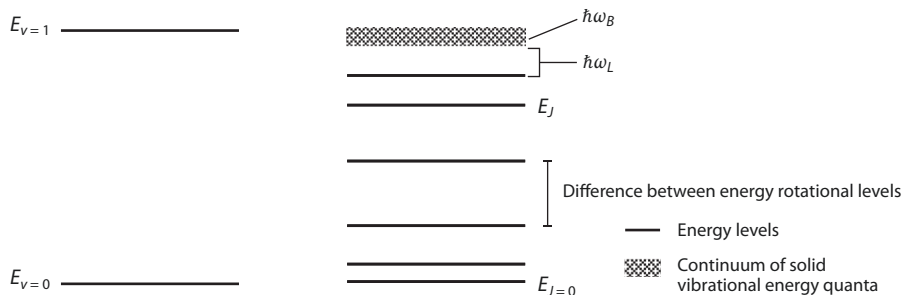


Figure 1

Energy scheme for vibrational relaxation in solids. E_v denotes vibrational levels, E_J shows rotational levels, ω_L is a local phonon frequency, and ω_B is a bulk phonon frequency. Figure is based on the results of Reference 14.

6.3. The Vibrational Self-Consistent Field Method: First Step

I met Mark Ratner of Northwestern University on his visit to the HUJI in 1976. From the outset, I greatly enjoyed talking with him. His mind was always open and willing to entertain new ideas. The need to efficiently treat anharmonic coupling had become of great interest then, motivated by progress in spectroscopy. We thought of and implemented an approximation that greatly simplified the calculation of the energy levels of coupled vibrational states. It is based on treating each vibrational mode as moving in the mean field of all of the other modes. This was the vibrational self-consistent field (VSCF) approximation, which we first applied for simplistic model systems (15). I did not recognize at the time the potential of this method for extensions and improvements and the promise of extensive applications. VSCF, combined with major extensions, improvements, and applications, is certainly one of my main contributions to physical chemistry. While we did this work independently, we were preceded by a similar paper by Joel Bowman (16). Both I (often in cooperation with Ratner and later others) and Bowman kept developing VSCF throughout our careers. This was not a competition, for, as it turned out, each of the groups developed the theory in different directions. For example, Bowman focused on very accurate extensions for systems of moderate size, while my group aimed at variants for larger systems, as is described later. I view later stages in the development of VSCF as more important than my first paper. All the same, as the attention to the method grew, this first article has also grown in number of citations. The work in cooperation with Ratner was great, and we continued to collaborate for many years.

The research results that my group obtained during that period were of significance to several areas of physical chemistry. Recognition of the contributions was reflected in a good number of conference invitations, citations of our papers, etc. Two years after my appointment as an associate professor at the HUJI I was granted tenure. After two more years, I was promoted to full professor. The group was very active and additional members joined. It was a wonderful phase.

7. SCATTERING FROM SURFACES AND QUANTUM MOLECULAR DYNAMICS

Promotions have the merit of reducing pressure and energizing and encouraging ventures into new problems and research subjects. Around 1980, our group began to very actively pursue two topics that were new to us: molecular scattering from surfaces and time-dependent quantum molecular dynamics (MD). Both led to very fruitful results.

7.1. Molecular Scattering from Surfaces

This period was one of great activity in experimental molecular beam scattering from crystalline surfaces. Our first contribution on this subject was the development of an approximate quantum-mechanical method (the sudden approximation) for the diffraction of atoms from crystalline surfaces (17). Methods for that purpose were then in short supply. Coauthors on the paper are Yinon, a previously mentioned graduate student, and John Murrell, a well-known theorist from the University of Sussex who visited us then. We also derived useful approximations for rotationally inelastic and vibrationally inelastic molecule-surface scattering (18–20). These projects were done in cooperation with Donald J. Kouri of the University of Houston, a good friend and a collaborator of many years.

Elber and I cooperated with Aviv Amirav (at Tel Aviv University) and his then-student Eli Kolodney on molecular dissociation in impulsive molecular-surface collisions, e.g., I_2 in impact on solid MgO (21–25). The topic is of considerable chemical interest. The molecular beam experiment by Amirav and his students was innovative. Elber and I used classical MD to treat the process, given the high energies. This work led to determination of the dissociation mechanism and demonstrated that substantial energy is delivered from the I_2 upon impact on the surface in the form of a shock wave. The work met with considerable interest at the time. The outstanding students Elber and Kolodney continued on to very successful academic careers. Elber holds a chair at the University of Texas, Austin, and Kolodney is professor at the Technion, Israel.

I continue to study molecular reactions at surfaces at present, focusing on liquid water surfaces.

7.2. Approximate Quantum Dynamics for Coupled Vibrational Modes: The Time-Dependent Self-Consistent Method

I spent the academic year of 1981–1982 on sabbatical in the United States, most of it at Northwestern University. It led to a fruitful cooperation and exchange of ideas and the launching of new projects with Ratner and George Schatz. The main step was an attempt to develop a useful approximation for quantum dynamics for systems of many degrees of freedom. The method that we called the time-dependent self-consistent field (TDSCF) approximation treats each vibrational mode as being governed by the time-dependent mean field of all the other modes (26). Mathematically, the method is not new but goes back to the early stages of quantum theory. The new aspect was to adapt it for molecular vibrations (26). Buch implemented it for van der Waals clusters in a model framework (26), and in cooperation with Schatz additional applications to larger models of this type were explored, providing useful insights (27). Later tests established the validity of TDSCF for certain types of processes (28). Progress in experimental time-domain spectroscopy motivated a demand for such methods.

The original TDSCF paper ranks as one of my most cited papers and one that still continues to be cited. Unlike so-called static VSCE, TDSCF was rarely used in attempts to quantitatively compute properties of realistic systems. Instead it was employed as a basis for deriving extensions, a very elegant example being the study of Makri & Miller (29) of TDSCF applied to a molecular reaction in the environment of a harmonic bath. A simplified, semiclassical TDSCF was proposed by our group (30). The generalization of the method by Meyer et al. (31) and Manthe et al. (32) proved very successful and was later pursued by many other groups (33). This method, multiconfiguration time-dependent Hartree (MCTDH), leads to accurate results for realistic systems of moderate size. However, the method is far more computationally demanding than is TDSCF.

8. ATOM SCATTERING FROM DISORDERED SOLID SURFACES

The Fritz Haber (FH) Research Center for Molecular Dynamics at the Chemistry Department of the HUJI was founded in 1982 with support from the German Ministry of Science. Raphy

Levine was the founding director. Early members included Ronnie Kosloff, Avi Ben-Shaul, Noam Agmon, and myself. It has been a professional home to me within the HUJI since then. From its early stages, the FH Center gained a strong international reputation in the dynamics of molecular processes and also in other disciplines of theoretical chemistry. Following the establishment of the center, there was an influx of graduate students, postdocs, and international visitors.

One of the main topics of our research group in the first years of the FH Center was atom scattering from disordered solid surfaces. The characterization of disordered surfaces is very challenging. A major motivation from experimental results was the brilliant work of George Comsa and coworkers of KFA, Jülich in Germany. We established cooperation with the Comsa group on the structural properties of isolated defects on crystalline surfaces and other types of disordered surfaces. Useful connections were established between characteristics of the disorder and the angular distribution of the scattering. This work was done in cooperation with Herschel Rabitz of Princeton University and with Joel Gersten of the City University of New York (34, 35). A step forward was made when we introduced wave-packet calculations to the scattering using the algorithm of Kosloff, with his cooperation (36, 37). Most important is the joint theoretical-experimental study of our group and the Comsa group on He scattering from isolated vacancies and CO adsorbates on Pt(111) (38). That has provided detailed insights on the properties of these isolated defects.

9. ELECTRONIC EXCITATION IN ATOM-METAL COLLISIONS AND H ATOM DIFFUSION ON METAL SURFACES

In the early 1980s we pursued two interesting processes related to the interactions of atoms with metal surfaces. One of these topics involved the probability of electron-hole pair excitation in the impact of an atom or molecule on a metallic surface. The model we applied to this process was developed by Zvi Kirson, a postdoc, in cooperation with Abe Nitzan, with whom I had several rewarding collaborations, and Ratner (39–41). Our findings suggest that for a closed-shell collider, the probability of electron-hole pair excitation is negligible. For an H atom collider, the results suggest significant excitation probabilities. The problem remains open due to the drastic simplifications made in the model, but the study was a step forward on this challenging topic.

K. Birgitta Whaley was an exceptionally gifted postdoc working jointly with me and with Nitzan (then at Tel Aviv University) in the years 1984–1986. We pursued another very challenging problem, that of hydrogen diffusion on metal surfaces. An interesting prediction of the simple quantum model we developed is that the H atom is delocalized at very low temperatures over more than a single unit cell (42). Whaley continued after her postdoc to a faculty position at the University of California, Berkeley (UC Berkeley) and to an impressively successful academic career.

10. PHOTOCHEMISTRY IN SOLID MATRICES AND IN CLUSTERS

This research topic was one of the main research directions of our group for a long time. We have been involved in this broad subject since 1988 and still currently pursue important problems in the field.

A motivation for pursuing photochemistry in matrices and in clusters comes from their general relevance to photochemistry in condensed phases. Noble gas matrices are useful as models because of the simple nature of the medium, while clusters are useful due to their finite sizes.

10.1. Photochemistry in Matrices

During my sabbatical at Northwestern University in 1981–1982, I met V. Ara Apkarian, an outstanding student of Eric Weitz. Apkarian was working on vibrational energy relaxation in matrices, a field that I previously pursued. When he was appointed assistant professor at the University of California, Irvine (UC Irvine), we began a joint experimental and theoretical project to explore photochemical reactions in noble gas matrices. Our main target was to study the cage effect, a fundamental concept in condensed phase reactions, to determine the mechanisms of, timescales for, and probabilities of cage exit. Roger Alimi was then a graduate student; he went on to produce results of major importance for the field.

The approach we employed was to carry out classical MD simulations for the excited state using empirical potentials. There is, of course, a concern about the role of quantum effects, which were neglected at the cryogenic temperature of the matrices. Our hope was that due to the high kinetic energies of the photofragments, the quantum effects would not be large. Some evidence supports this assumption. Early simulations were for HI in Xe, F₂ in Ar, and Cl₂ in Xe, for all of which cage exit was predicted depending on the excitation energy (43–45).

Experiments on cage exit probabilities were carried out by Apkarian for F₂ in Kr (46) and by Nikolaus Schwentner and coworkers for Cl₂ in Ar (47). In both cases good agreement was found between theory and experiment. The referenced theoretical–experimental papers were published in *Physical Review Letters* and were well reviewed (46, 47). The MD calculations also predict the effects of temperature and pressure. High pressure was shown to significantly affect cage exit in the case of Cl₂ in Xe (48). The high pressure limits the molecular orientation in the cage. This is supported at least semiquantitatively by experimental results (48).

Calculations at a similar level were done for ICN in Ar (49). In an effort to estimate quantum effects, MD simulations were carried out for HI in Xe, in which the H atom was treated by quantum wave packets and all other atoms classically. A significant quantum effect was found for the energy relaxation of the H atom in the cage (50).

However, evidence mounted that the classical MD approach with a single empirical excited state had problems. Experimental spectroscopy and theoretical arguments indicated that more than a single excited state is involved in the systems studied. To treat the excited states of molecules in noble gas media, an approach based on diatomics in molecules (DIM) (51) was adopted. This is a semi-empirical electronic structure method that models the interaction between the noble gas atom and outer-shell orbitals of the atoms of the guest molecule. The method leads to 12 relevant potential energy surfaces for HCl in the noble gas environment. Including the effect of spin-orbital coupling in the potential surfaces of the systems is important. Even for a single halogen atom in the matrix, six relevant potential surfaces arise and are required to treat the dynamics (52). The different potential energy surfaces can have intersections, and these may lead to nonadiabatic transitions. We treated such transitions by the celebrated surface-hopping method of John Tully (53). Anna I. Krylov, then an excellent graduate student in our group, developed an impressive algorithm for treating the photochemistry of hydrogen halides, HX, using MD with surface hopping, employed for DIM potentials. The method can describe recombination of the photofragments as well as the photodissociation step (54). The algorithm was later extended by Masha Niv, another very capable student, for XY molecules (X, Y = halogens) (55). Applications for HCl in Ar (54) and F₂ in Ar (55) showed that cage exit as well as recombination involves both spin-flip and spin-conserving nonadiabatic interactions.

In 1998 I entered into a new collaborative project that enhanced our research on photochemistry in matrices. This multi-investigator project called SFB 450 and centered at the Free University of Berlin (FU Berlin) was established by the German Ministry of Science. The general subject

of this large project was the analysis and control of ultrafast photoinduced reactions. Thanks to the requests and efforts of my friend and collaborator Jörn Manz of FU Berlin, I became part of this project. Three principal investigators (PIs), Manz, Schwentner (then an experimentalist in the Physics Department of FU Berlin), and myself, had as our goal the study of ultrafast photoinduced reactions in noble gas matrices. The project was highly rewarding to me. It provided uninterrupted funding for a duration of 12 years—I believe that such long projects offer depth and perspective to the science done. The interactions among our group were very positive, and the cooperation worked very well, with Schwentner carrying out challenging experiments, and Manz, myself, and our groups pursuing the interpretations. A very interesting result was the demonstration of an ultrafast spin-flip transition in the photodynamic of ICl in Ar. The normal expectation was for much larger timescales than those that were observed, in view of the relatively weak spin-orbit coupling of the Cl atom. The nonadiabatic simulations provided insights into this effect. Joint papers of significance to the field were published (56, 57).

I note that Krylov is now a distinguished professor at the University of Southern California (USC). Niv is an associate professor in the Department of Agriculture at the HUJI.

10.2. Photochemistry in Clusters

Clusters, with their typically floppy structures, make it possible to explore aspects of photochemistry that are not often revealed for rigid solids. Also, clusters of different sizes can be used to study different cages. How large should a cluster be to exhibit a cage effect in photochemistry? Curt Wittig of USC, an inspiring collaborator, showed in an elegant experiment that a single-atom cage effect takes place in the photolysis of HBr in Ar $\cdots$ HBr (58). My postdoc Alberto García Vela carried out calculations to interpret the findings. García Vela was also able to unravel interesting quantum effects in the photolysis of HCl in Ar — HCl (59–61). He used a mixed quantum-classical method in these calculations. Hybrid quantum-classical calculations were also carried out for the much larger cluster HI(Xe)₁₂, in which the H atom was treated by a wave packet and the other atoms by classical trajectories (62). Pronounced quantum effects were found (62).

For clusters Rg_n(HX) with a large enough *n*, geometries corresponding to HX adsorbed on the so-called surface of (Rg)_n are possible. Niv and Krylov studied the photochemistry of (Ar)_nHCl for the surface-adsorbed geometry using DIM potentials and nonadiabatic MD (63). A surprisingly strong cage effect was found, probably due to the encapsulation of the H atom in the initial (Ar)₁₂HCl structure. Experiments by Buck and his coworkers were carried out for very large (Ar)_nHBr clusters. The experiments provide evidence for a surface-adsorbed HBr (64).

The photochemistry of molecules in an environment other than noble gas atoms is often rich and interesting but is very hard to treat due to the complexity of the interactions (65). I mention two studies from that time by Anne McCoy, then an exceptional postdoc in our group. McCoy explored the photochemistry of the (HCl)₂ dimer as a model for hydrogen-bonded clusters in such processes. She carried out classical trajectory calculations sampled from the initial quantum mechanical ground state (66). The results showed several dynamic processes: an internal reaction involving exchange of one hydrogen with the other, a reaction leading to formation of H₂, and resonances when an H atom oscillates between Cl and HCl (66). The processes strongly depend on the initial configurations, which are governed by the ground state wave function.

McCoy also studied the dynamics following electron photodetachment from ClHCl[−] (67). ClHCl[−] is a symmetric molecule at equilibrium, and upon photodetachment lands on the transition state for the Cl + HCl' and Cl' + HCl reactions. The calculations determined the quantum dynamics of Cl $\cdots$ H $\cdots$ Cl'. The TDSCF approximation was used. Transition-state resonances were found in accord with experimental results. McCoy continued on to a very successful academic career and is now a professor at the University of Washington in Seattle.

The final example I mention is from a recent research result (68). Laura McCaslin, until recently a postdoc at the HUJI, carried out very sophisticated classical dynamics calculations for the process of two electron photodetachment from the $F^-(H_2O)$ cluster. This was done in collaboration with pioneering experiments by Daniel Strasser and coworkers, also from the HUJI. Shahi et al. (68) used intense femtosecond laser pulses to double detach the cluster and observe products by coincidence imaging. The double ionization eventually produces $[F \cdot H_2O]^+$, which undergoes multiple processes. The $[F \cdot H_2O]^+$ species is open shell with strong electron correlations.

McCaslin adopted the equation of motion-coupled cluster method to treat the potentials in MD simulations. Insights were obtained, including the formation of $(H_2O)^+ + F$, which is the main channel. This is a step forward on a novel and very challenging type of process. McCaslin's research achievements led to her very recent appointment to Sandia Livermore National Laboratory, where she is building her own group.

I believe that our group made substantial contributions over the years to this field. The topic is related to photochemistry in atmospheric aerosols, which is central to research now.

11. DUAL POSITIONS AT THE UNIVERSITY OF CALIFORNIA, IRVINE, AND AT THE HEBREW UNIVERSITY OF JERUSALEM: A SECOND PROFESSIONAL HOME

In 1988 I was approached by several leading universities in the United States and also the Weizmann Institute in Israel with offers to move there. I decided not to move. However, I accepted another, more unusual offer: to become a part-time professor at UC Irvine and spend 3 months of the year there while also remaining affiliated with the HUJI. The arrangement took effect in 1990. This turned out to be one of the best things that happened to me in my professional life. Since then I have had two professional homes that I am very happy with. At first, I had some doubts about how it would work, but it has in fact worked well. Hélène, our son David, and I went to Irvine for 2–3 months in the summer or the beginning of the fall each year and stayed at on-campus accommodations within walking distance from my office. David was born in 1982 and thus grew up partly in Jerusalem and partly in Irvine. I taught courses in the summer or in the fall. Some members of my Jerusalem-based group traveled with me and pursued their research at UC Irvine. Most important is that chemistry developed between my colleagues and me at UC Irvine. In particular, many collaborations developed. I coauthored joint papers with more than 10 of my UC Irvine colleagues.

I was fortunate enough to get grants from US funding sources and to recruit graduate students and postdocs based at UC Irvine. I am now professor emeritus both at UC Irvine and at the HUJI but continue to have small research groups at both universities. I also continue to spend time each year at UC Irvine. There is no doubt that the availability of e-mail, Zoom, and phone communication is a great help for such long-range appointments. To me, this has been very rewarding.

12. EXTENSIONS AND IMPROVED ALGORITHMS FOR VIBRATIONAL SELF-CONSISTENT FIELD METHODS

As of 1986, our group began to develop major improvements and extensions to VSCF methodology. The improvements came in stages, and the process was rather slow. All aspects of VSCF were treated, from conceptual ones, to better and faster algorithms, to variants of higher accuracy. By the year 2000, a completely transformed and far more powerful VSCF methodology was at hand. The general thrust of our effort was to build a method capable of treating large molecules, e.g., biological molecules such as peptides, at a level adequate for the quantitative interpretation

of experiments. I believe this was accomplished to a large extent, and I consider it a highlight of my research.

12.1. Good Coordinates for Vibrational Self-Consistent Fields

For very floppy clusters or molecules, normal modes are inadequate to describe the vibrations of the system (69). VSCF may give excellent results for such systems if adequate coordinates can be found. However, in all realistic cases we investigated, such coordinates, if found, are curvilinear, and we were only able to find these by physical intuition. With such insight Zlatko Bačić, then a postdoc, was able to find elegant coordinates that work well for VSCF in the case of the HCN $\leftrightarrow$ HNC molecule (70). (Bačić continued to do well at later stages and is now a professor at New York University.) Tom Horn, also a postdoc then, found good curvilinear coordinates for the very floppy clusters XeHe₂ and I₂He (71). Interestingly, even for the more rigid Ar₃, hyperspherical coordinates do better in VSCF than in normal modes (72). Clearly, good curvilinear coordinates are not a generally practical way for improving VSCF.

12.2. Vibrational Self-Consistent Fields in Normal Modes and the Pairwise Mode-Mode Coupling Approximation

Joon O. Jung was a graduate student of mine at UC Irvine. He made remarkable contributions to VSCF methodology. Realizing that normal coordinates are the most practical choice for most systems, he constructed a very efficient algorithm for VSCF based on grid calculations in normal modes. To simplify the multidimensional potential, Jung introduced the approximation of including only pairwise couplings between different normal modes (72–74).

12.3. Correlation-Corrected Vibrational Self-Consistent Fields with Second-Order Perturbation Theory

In 1996 Jung and I published a method that corrected for the separability correction of basic VSCF by including correlation effects between different normal modes. This was done by applying second-order perturbation theory (PT2) to go beyond basic VSCF. This results in VSCF-PT2 (74). The important merits of this correction were its simplicity and its favorable scaling with the number of vibrational modes. The first application provided was to water clusters up to $n = 5$. However, it was clear from the algorithm that the method could be applicable to much larger systems. The method has become a major workhorse of anharmonic vibrational spectroscopy: it is still in extensive current use. The resulting paper (74) has so far been cited several hundred times. In the early phase of VSCF theory, Ratner, Buch, and I attempted to go beyond separability in VSCF by using a configuration interaction (CI) approach (75), but that proved to be computationally inefficient and poor in scaling behavior. Very accurate CI-type algorithms were developed by Bowman & Christoffel (76). These seem directed for small- or moderate-sized systems. Ove Christiansen (77, 78) introduced the very elegant vibrational coupled cluster theory. This one also seemed to be directed toward accurate calculations of relatively small systems. Finally, Norris et al. (79) considered the effects of higher-order perturbation theoretic terms beyond VSCF-PT2. Generally, these do not make substantial contributions.

12.4. Ab Initio Calculations of Anharmonic Vibrations: Electronic Structure Combined with Vibrational Self-Consistent Fields

Accurate empirical potential surfaces for large polyatomic systems are not usually available. The fitting of ab initio potentials is an option, and important progress in fitting algorithms has recently

been made. However, the fitting of multidimensional potentials at a high level of accuracy is still a major challenge. Therefore, direct *ab initio* calculations of anharmonic vibrations are a desirable goal. Galina Chaban joined my group as a postdoc in 1998. She did her PhD with Mark Gordon at Iowa State University and came endowed with a great deal of knowledge about electronic structure theory. She joined forces with Jung, and together they developed a very effective, powerful code for *ab initio* calculations of anharmonic spectroscopy (80). In this algorithm, an electronic structure code is selected, the equilibrium structure and normal mode coordinates are computed, and then the VSCF equations are solved and the vibrational energies and wave functions are obtained. The code made possible a large number of VSCF and VSCF-PT2 applications in a short time (80–83). Types of systems for which many applications of VSCF-PT2 were made include biological molecules and hydrogen-bonded complexes.

Ab initio VSCF is used extensively. We were helped on this method by Gordon. We implemented the VSCF code in GAMESS, the important suite of programs developed by Gordon and his team. Gordon and his group also made important contributions to VSCF theory (84). I had fruitful research collaborations with Gordon, which I enjoyed.

Following her excellent postdoc work, Chaban was appointed to a research staff position at NASA's Ames Research Center. Jung is a senior member of the research team at Merck Boston.

12.5. *Ab Initio* Anharmonic Calculations for Degenerate Vibrational States

VSCF-PT2 may break down (although this does not necessarily happen) for vibrational degenerate states. This is due to a well-known problem of perturbation theory. Basic VSCF, which is a nonperturbative theory, is not subject to this problem, so one may use it in such cases. Nikita Matsunaga of Long Island University spent time with me at UC Irvine, and we proposed a remedy (85). It involves diagonalizing the subspace of VSCF degenerate states and then correcting by perturbation theory (85). Although the method was successfully tested for several small systems (85), it has still not been applied for large systems, which is the main strength of our other VSCF variants.

13. ANHARMONIC EFFECTS IN VIBRATIONAL SPECTROSCOPY OF BIOLOGICAL MOLECULES

The spectroscopy of biological molecules has been a major direction in the application of VSCF methodology by our group. The motivation for the pursuit of this topic is the hope that spectroscopy can be useful in learning about biomolecular structure. There are many systems for which the leading methods for biomolecular structure determination, X-ray crystallography and NMR, cannot be used. This motivation is strengthened by the progress in recent years in the experimental spectroscopy of biomolecules. By the available evidence, the role of anharmonic contributions to the spectra is very significant. Localized vibrations such as stretching modes of O – H, N – H, and C – H can have anharmonic frequency shifts of 10% or so. Modes such as torsions often involve very large anharmonic effects. For spectroscopy, including anharmonic effects is essential. In this section, I outline the main applications of our methods to biomolecular spectroscopy.

13.1. The All-Mode Wave Functions and Fundamental Excitation Energies of a Protein: Vibrational Self-Consistent Field Calculations for a Model of BPTI

The objective of this project was to demonstrate the feasibility of VSCF for proteins, specifically bovine pancreatic trypsin inhibitor (BPTI) (86). Adrian Roitberg, the lead author of the paper, was

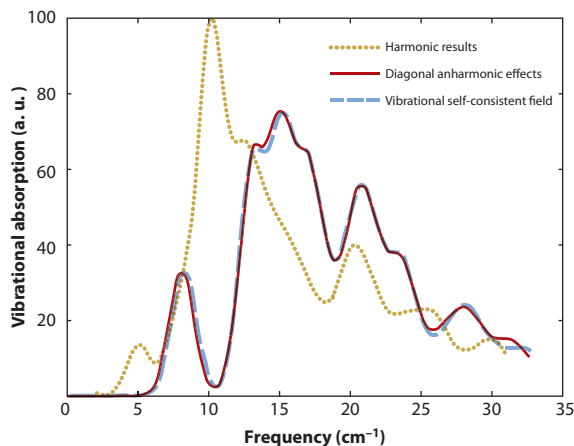


Figure 2

Anharmonic and harmonic frequencies of bovine pancreatic trypsin inhibitor (BPTI) computed by vibrational self-consistent field (VSCF). The thin, dotted yellow line represents the harmonic results; the solid, red thick line shows diagonal anharmonic effects; and the blue dashed line shows the VSCF results. Figure adapted from Reference 86.

a postdoc working with me and with Ratner. Elber, another coauthor, was at that time a professor at the HUJI. Our calculations used the biomolecular force field MOIL that was developed by Elber's group. It provides reasonable structures and very likely reasonable normal modes. However, a major flaw of the MOIL force field (and most force fields) is that the local stretching vibrations are modeled as harmonic. The anharmonic effects in this model are due to the other types of vibrations. Basic VSCF was used. Roitberg employed a quartic approximation for the force field. The initial vibrational state was the ground state. The main result, as shown in **Figure 2**, was that anharmonicity strongly influences the absorption spectrum (86). This conclusion is expected to also hold for real systems, and recent findings for peptides using ab initio potentials support this. The main problem that prevented much more quantitative spectroscopic prediction is the inadequacy of the potential surfaces. The current evidence from peptide spectroscopy is that ab initio potentials have sufficient accuracy, but these are not obtainable for proteins.

Despite its limitations, the study was a breakthrough both for insights into the power of the method and for the qualitative prediction of the spectrum. I am very glad that it was published in *Science* (86). Roitberg continued on to a very successful academic career; he is currently a professor at the University of Florida.

13.2. Biological Building Blocks and Their Hydrogen-Bonded Complexes

Accurate anharmonic spectroscopy calculations may seem a demanding task even for glycine. The advent of ab initio VSCF-PT2 has greatly simplified such calculations. We obtained results for glycine (several isomers) (87), the glycine–water complex (several structures) (88), N-methylacetamide (83), and several other systems of similar sizes soon after the development of the method. Jung and postdocs Chaban and Susan Gregurick did the calculations. In all of these applications, excellent agreement was found between calculations and experimental results. In all cases there were strong anharmonic effects. By the test of spectroscopy, MP2 was found to give better results than the density functional theory (DFT) BLYP and B3LYP variants. These calculations added much to our knowledge of the potentials of biological building blocks and their

interactions with water. A challenging theoretical–experimental system involving important anharmonic effects is the G...C nucleobase pair (89). This project was done in collaboration with Mattanah S. de Vries at the University of California, Santa Barbara, who carried out very elegant experiments on this system. The calculations were very ably done by Brina Brauer, a postdoc, and we benefitted also from cooperation with Pavel Hobza at the Institute of Organic Chemistry and Biochemistry in Prague. As shown in **Figure 3**, good agreement was found between calculations and experimental results. The results contributed to our knowledge on the interactions in the G...C pair (89).

Strong anharmonic interactions in hydrogen-bonded complexes are, of course, not at all unique to biomolecules. Ab initio VSCF-PT2 was also applied to numerous hydrogen-bonded complexes between inorganic molecules. These can be very challenging even for small systems due to strong anharmonicity, e.g., $F^-(H_2O)_n$ (90). VSCF-PT2 also proved to be successful in these cases.

13.3. Anharmonic Vibrational Spectroscopy Calculations for Peptides and Peptide–Water Complexes

To obtain good agreement with spectroscopic experiments for peptides, the inclusion of anharmonic effects is essential. VSCF-PT2 calculations using empirical force fields of analytical form are very efficient (91). The improved algorithms are due to Liat Pele, then a graduate student (91). Unfortunately, such force fields have poor accuracy for spectroscopic calculations. Potentials from electronic structure methods are, of course, much more computationally demanding. With improvements in the VSCF codes for large systems, such calculations have, however, become increasingly feasible (92). The person who should mostly be credited for this progress is Tapta Roy, who was a postdoc in my group and is at present assistant professor at the University of Central Jammu in India. We continue to cooperate closely. Roy's calculations have contributed much to the understanding of peptide spectroscopy (93–95). In the collaboration we had with the groups of Oleg Boyarkin and of Tom Rizzo at École Polytechnique Fédérale de Lausanne (EPFL) (93, 94), the calculations that were pursued helped to determine complex structures. Thus, we were able to validate conformational structures of Gramicidin S, a cyclic decapeptide (93). From a theoretical–experimental study, we determined the structure of Gramicidin S with hydration by two water molecules, including the geometry of the waters at the peptides (94). Most recently, we validated the structure of a linear pentapeptide (95). Results for other peptides were also good (96).

Another approach by which important contributions to peptide spectroscopy were made is the use of classical MD simulations using DFT potentials on the fly. This method is being extensively applied by Marie-Pierre Gageot and colleagues (97, 98). The classical method and the quantum VSCF-PT2 are to an extent complementary in their optimal domains of applications: VSCF-PT2 works best for the higher frequency transitions and treats systems as being initially in the ground state. Classical MD is best applied at ambient temperatures for low-frequency modes.

13.4. Spectroscopy of Sugars and of Sugar–Water Complexes

It has been a great privilege for me to cooperate on saccharide spectroscopy with John P. Simons of Oxford University, the pioneer and maestro of this field (99). Simons brought excitement to the field with his experiments on high-resolution vibrational spectroscopy on saccharides in mass spectrometric conditions. This project is relatively recent and is still being pursued.

Several important lessons were learned from these experiments. The hydration of monosaccharides and disaccharides was studied by both experiments and calculations of the sugar clusters with one and two water molecules (100, 101). This led to determination of the preferred hydration

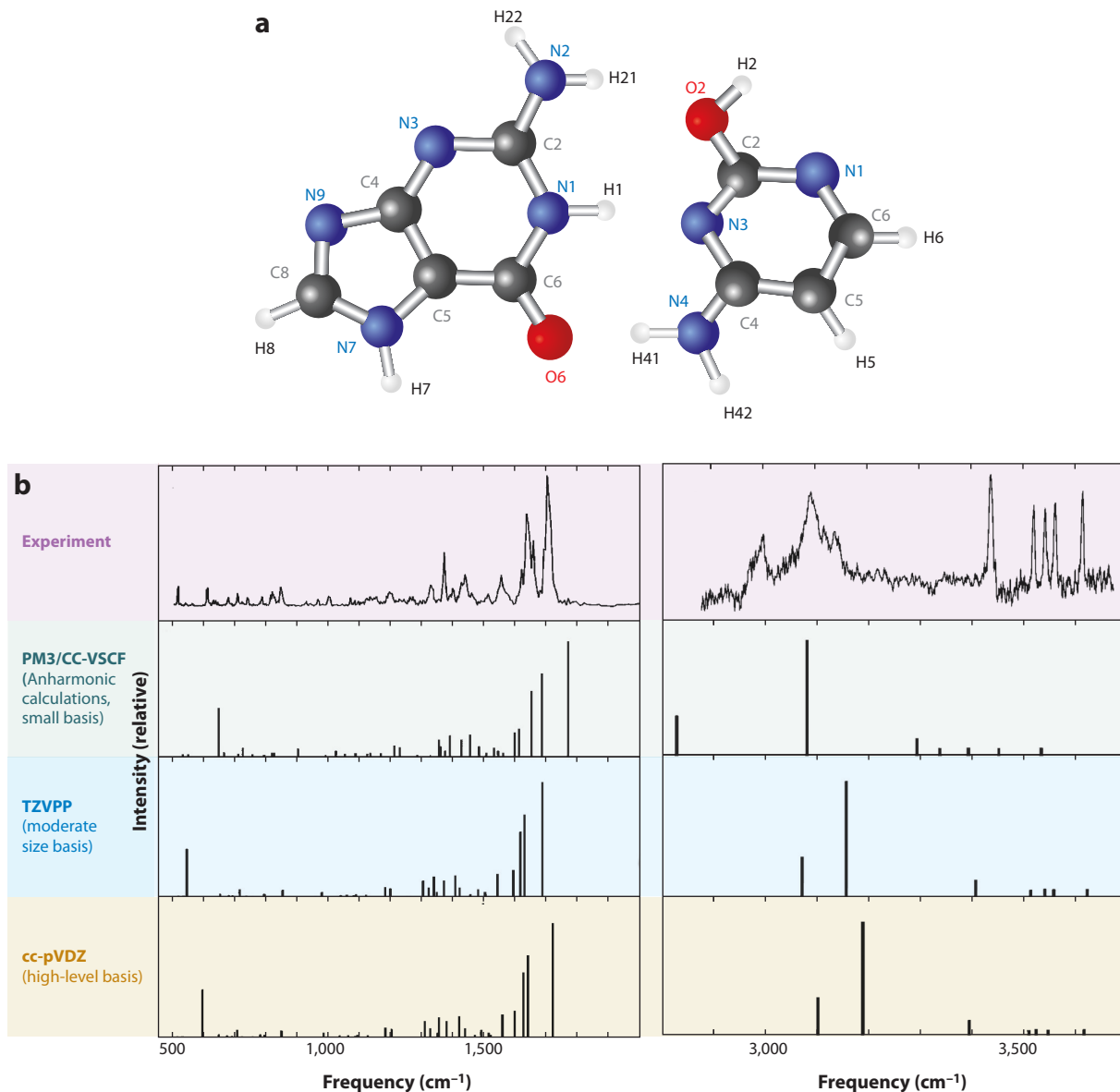


Figure 3

(a) The structure of the G...C complex. (b) Frequencies of the G...C complex, showing calculated versus experimental results. Abbreviations: cc-pVDZ, correlation-consistent polarized valence double zeta; CC-VSCF, correlation-consistent vibrational self-contained field; PM3, Parametric Method 3; TZVPP, valence triple zeta with two sets of polarization functions. Figure adapted with permission from Reference 89.

sites, with conclusions on sugar–water interactions. For cellobiose, a fundamental building block in nature, structural rigidity of both the sugar conformation and its hydrates was found. That rigidity was found to persist up to room temperature. The calculations on sugar hydration were done by postdocs Madeleine Pincu, Lin Jin, and Brauer. Another study focused on anharmonic effects in the spectra of α -glucose, β -glucose, and sucrose in both the gas and solid phases (102).

Ilana Bar of Ben-Gurion University, a collaborator in this, did experiments for the solid phase. A third direction of our project on sugars dealt with protonated saccharides and related species. First, Svemir Rudić and Simons found evidence for an intramolecular proton-bound dimer of a saccharide species that was formed in photoionization of a complex in a molecular beam. This was supported by the *ab initio* MD simulations of Hong-Bin Xie, then a postdoc in my group (103). In a computational study of protonated β -D-galactose and its singly hydrated complex, we explored intermediate structures, proton transfer dynamics, and the spectroscopy of species formed (104). Xie is presently a professor at Dalian University in China, and Jin, another postdoc who worked on this, is on the faculty of Northwestern Polytechnical University, also in China.

Most recently, very interesting results were obtained on the oxocarbenium ion and on protonated anhydrogalactose and protonated methyl galactopyranoside (105). The research involved *ab initio* MD (AIMD) simulations and VSCF calculations carried out by Michelle Dvores, a graduate student in my group, in collaboration with infrared multiple photon dissociation (IRMPD) spectroscopic experiments and interpretation by our collaborators Philippe Maître and Pierre Çarçabal, of the University of Paris at Orsay, and Simons. One important finding is the very likely identification of the reactive intermediate oxocarbenium ion in the processes studied. This species is postulated to play a major role in many sugar reactions. Another important result is that structures of the species studied can have a wide range of lifetimes, from extremely short ones to essential stability. These are perhaps the first results on the lifetimes of protonated sugar species.

We have a long way to go on the topic of sugars. However, it seems to me that the results obtained are quite promising.

14. FINLAND DISTINGUISHED PROFESSOR AT THE UNIVERSITY OF HELSINKI

I received a very appealing offer from friends in Finland in 2010: to be nominated for the position of Finland distinguished professor (Fi Di Pro) at the University of Helsinki (UH). This was a 5-year, part-time position. It required spending some part of the year in Helsinki but could be held in addition to my tenured positions at the HUJI and at UC Irvine. With the position came funding for four coworkers, postdocs, or students at the UH. I had special affection for the scientific community in Finland. In 1993, I was invited for a very nice visit there, during which I was awarded the Medal of the University of Helsinki. In 2007, I was elected Foreign Member of the Finnish Academy of Science and Letters, obviously a great honor for me. I had wonderful projects in cooperation with Markku Räsänen of the UH on new noble gas molecules that I was excited about. I knew Lauri Halonen, also from the UH, and thought very highly of his work. I therefore knew that the scientific collaboration would be very good, and I accepted the nomination. The department and the individuals in it were very welcoming to me. I found the working conditions excellent, and life in Helsinki during my visits was convenient. I recruited Jaroslaw Kalinowski of Poland as a PhD student. He turned out to be very good, and he did a fine doctorate. His real priority, however, was computer science. He is currently in computer science at Aarhus University in Denmark. I also recruited two very capable postdocs, Sampsa Riikonen of Finland and Garold Murdachaew of the United States. Murdachaew is still in Helsinki as a research fellow at Aalto University.

I developed new collaborative projects with Räsänen and with Halonen. The Halonen group carries out both theoretical and experimental research. In our joint work, Halonen did theory. Our cooperation addressed a single central topic of major importance: the dissociation of acids in water media into ions. We explored the mechanism of acid ionization in several types of water environments, mostly at interfaces. AIMD simulations were our prime tool of investigation. A

number of very interesting results were obtained. Riikonen was the leading coauthor on a paper that showed that there is no ionization of HNO_3 at a crystalline ice surface but that ionization at vacancies on ice surfaces is very efficient and occurs on a picosecond timescale (106). Murdachaew found that the dissociation of HCl into ions in a water layer adsorbed on α -quartz also takes place on an ultrafast timescale (107). In both cases experimental evidence supported the theoretical findings. The topic needs much further study, but the results obtained so far throw light on one of the most basic chemical processes in water.

My collaboration with Räsänen during the Fi Di Pro dealt with three subjects. The first of these subjects was new molecules of the noble gases. Most of the work we did on this was carried out prior to the Fi Di Pro period, so I discuss this topic in Section 15. The second subject was vibrational spectroscopy of molecules in matrices, while the third was reactions of Criegee intermediates, on which Räsänen was planning matrix experiments. The work on all of these subjects was productive.

Vibrational spectroscopy was always the prime probe of processes in matrices. The low temperatures and high resolution make *ab initio* VSCF, which is fully quantum mechanical, an ideal tool for interpretation. Experiments by Räsänen and Leonid Khriachtchev gave surprising results on the relative magnitudes of frequencies of HKrCl and HXeCl in different noble gas matrices. Kalinowski carried out calculations that innovated theoretical matrix spectroscopy. Using a single-layer Ng cage (where Ng is a noble gas atom) around each of the molecules, employing a high-level (MP4) electronic structure method in anharmonic VSCF calculations, produced results in agreement with those of experiments and provided an interpretation. I consider this to be a major achievement in theoretical matrix spectroscopy (108). This highlights the power of VSCF methodology to provide quantitative understanding of spectroscopic experiments.

To guide Räsänen, who was planning novel experiments on Criegee intermediates, Kalinowski and I carried out predictive calculations in the reaction dynamics of these poorly understood species. Calculations were carried out for the smallest Criegee intermediate CH_2OO starting from the local minimum structure and pursuing classical trajectories at room temperature. The important innovation was the use of an *ab initio* multireference second-order perturbation (MR-PT2) method for the potential. The time evolution of the species showed a sequence of processes involving isomerizations and finally decomposition into $\text{CO} + \text{H}_2\text{O}$ (109). Interesting dynamic behavior was found: The electronic configurations of the wave function changed dramatically with the nuclear position in time (108). Snapshots of the dynamics, also indicating the leading electronic configuration at each snapshot, are shown in **Figure 4**.

I very much appreciated my time as Fi Di Pro in Helsinki; I enjoyed the collaborations, and I think my productivity was good. I strongly recommend increased contacts with Finland in light of the excellent scientific community there.

15. A NEW CHEMISTRY OF THE NOBLE GASES

The noble gas elements are the most challenging to harness into chemical bonding, hence the conceptual importance of noble gas compounds. The first noble gas molecule, xenon hexafluoroplatinate, was synthesized by Neil Bartlett in 1962 (110). Fluorides of xenon were prepared soon after that. Use of the highly reactive element fluorine was the main approach for the preparation of noble gas compounds. In 1995, Räsänen and coworkers discovered a large new family of noble gas compounds and thereby greatly enriched the field. These new gases were of the type HNgY , where Y is an electronegative group (111). I was fascinated by these compounds. The first contribution by my group to the field was to apply our VSCF code to the spectroscopy of the compounds (82, 112). The HNgY species are very anharmonic, and spectroscopy is essential for identification of the species. VSCF proved a perfect tool for the purpose. Successful calculations were carried out

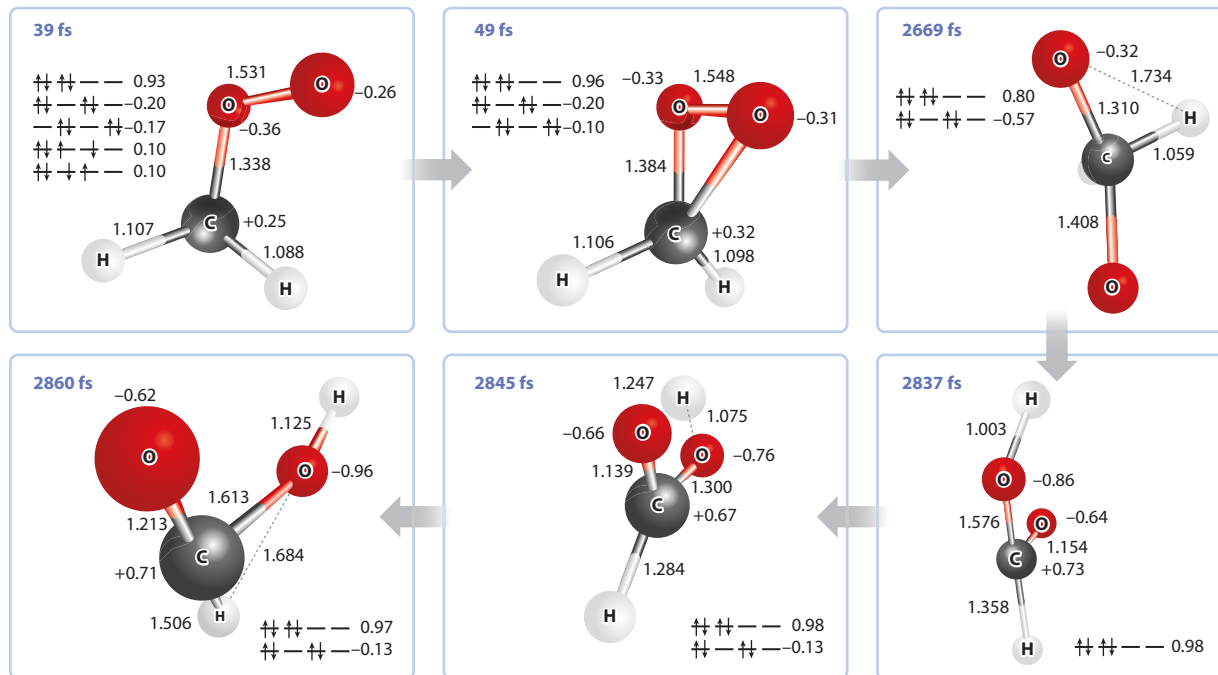


Figure 4

Snapshots from the dynamics of CH_2OO at room temperature. The leading electronic configuration for each snapshot is indicated. These configurations are taken from ab initio molecular dynamics calculations using the multireference second-order perturbation method. Figure adapted with permission from Reference 109.

by Jan Lundell and by Chaban (82, 112). We extended the spectroscopic calculations to include the effects of the matrix site, which provided insights into the formation mechanism of HNgY and helped in the interpretation of the experiments (113–115). This work was led by Zsolt Bihary, then a graduate student in my group at UC Irvine. He is presently professor of applied mathematics at Corvinus University in Budapest.

My favorite contribution to noble gas chemistry is the prediction of noble gas hydrocarbon compounds. In 2002, the idea occurred to me that an insertion compound of Xe into acetylene should be stable. This was based on the high electron affinity of the acetylenic group. An intuitive guess convinced me that a covalent $(\text{H-Xe})^+$ bond combined with ionic interaction with $(\text{CCH})^-$ should suffice for the local stability of HXeCCH . Lundell and Arik Cohen, a graduate student in my group, carried out ab initio calculations to test this, and the results supported the intuitive prediction. In addition, the existence of HXeCCXeH was predicted. I was excited by the results. However, the reviewer at the *Journal of the American Chemical Society* (*JACS*) suspected them and rejected our manuscript. Fortunately, the *Journal of Physical Chemistry A* accepted it for publication (115). Luckily for me, Räsänen of Helsinki and Vladimir Feldman of Moscow trusted the predictions, independently carried out the experiments, and both succeeded in preparing HXeCCH in matrices (116, 117)! In experimental–theoretical cooperation with the Räsänen group, HKrCCH was made, and its spectroscopic properties, structure, and energetic stability computed (118). Several related organic compounds of Xe were later prepared by Räsänen and by Feldman. To my knowledge, the acetylenic-based molecules are now the largest class of noble gas compounds.

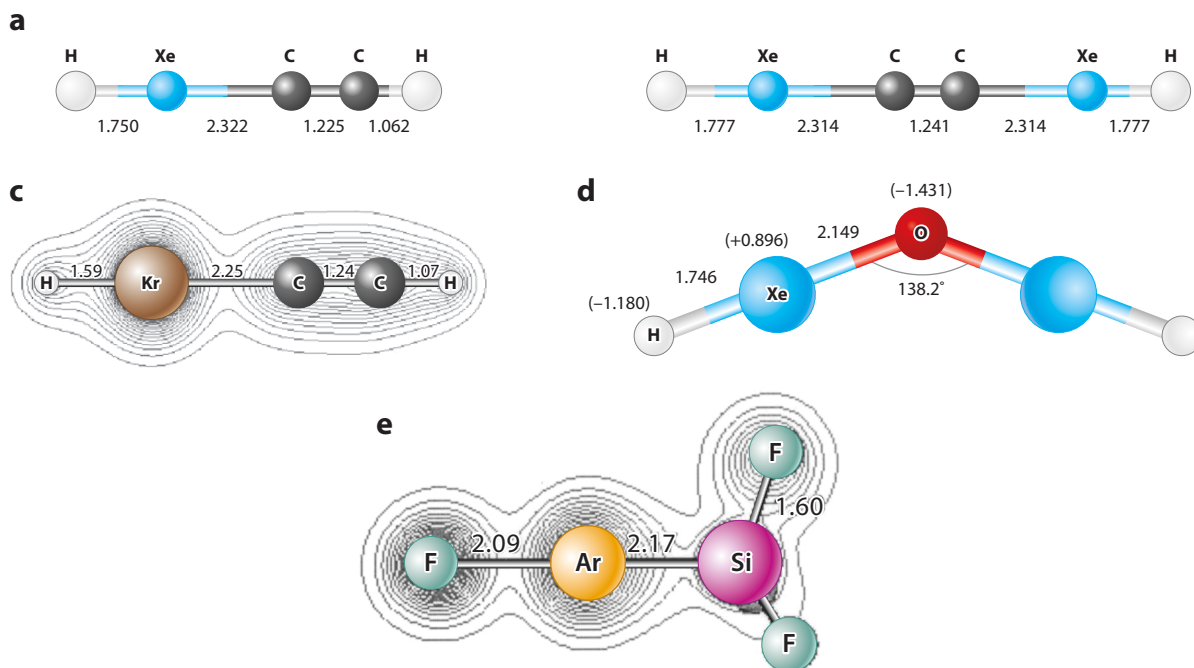


Figure 5

New noble gas molecules either (*a, b, e*) predicted theoretically or (*c, d*) computed in a joint experimental–theoretical project. The molecules shown are (*a*) HXeCCH (115), (*b*) HXeCCXeH (115), (*c*) HKrCCH (118), (*d*) HXeOXeH (119), and (*e*) FArSiF₃ (120). Panels *c* and *e* also show electron density contours. Panel *a* and *b* adapted with permission from Reference 6, panel *c* adapted with permission from Reference 119, panel *d* adapted with permission from Reference 120, and panel *e* adapted with permission from Reference 121.

Other notable contributions by my group are: In experimental–theoretical cooperation with the Räsänen group, HXeOXeH was prepared in the matrix, and its spectroscopic and structural properties were determined (119); the existence of compounds with argon–carbon and argon–silicon chemical bonds was predicted (120); the decomposition pathways and lifetimes of HXeOH and HXeOXeH as a function of temperature were computed (121); and the stability of HXeCCH in acetylene was determined (122). The latter two contributions are the work of Ehud Tsvion, a graduate student in the group. Finally, a very recent study of interest, led by Cohen of our group and in cooperation with Räsänen, Khriachtchev, and postdoc Masashi Tsuge, is on HXeBr in a CO₂ matrix (123). This topic is important for the study of noble gas compounds in environments of higher temperatures than matrices and in molecular media. It may be relevant to future applications.

I believe that our research has greatly advanced noble gas chemistry. **Figure 5** shows some of the systems we discovered or studied.

16. MICROSCOPIC UNDERSTANDING OF ATMOSPHERIC REACTION MECHANISMS

The theory of atmospheric chemistry is currently my main field of research. I came to this field not very long ago with essentially zero background. Soon after Barbara Finlayson-Pitts joined the Department of Chemistry at UC Irvine, I came to talk to her about her research. I was well aware of

her reputation but knew very little of her work. I got a fascinating description ranging from motivation to exciting research problems. A cooperative research plan quickly developed. Finlayson-Pitts was pursuing experiments on the reaction of OH radicals with salty water aerosols. The results could not be understood by considering only bulk reactions. It seemed that surface reactions must play a major role. To understand why, Pavel Jungwirth, then visiting from the Czech Academy of Sciences in Prague, Doug Tobias, a high-powered computational chemist at UC Irvine, and I joined forces. MD simulations of salty waters were carried out. The results showed substantial availability of Cl^- ions for reaction at the surface. With the experiment, kinetics modeling, and the MD results, the story came together nicely: Ions at the surface can greatly enhance reactions of gas-phase species with aerosols! The paper was accepted for publication in *Science* (124) and has had a major impact. This was an experimentally led paper, but the theory also stirred a lot of interest in the location of ions at the water–air interface. Excited by this work, I have continued to pursue atmospheric chemistry as a major research direction.

I mention at this point two research centers of which I was fortunate to become a member and that helped me greatly in my research.

16.1. AirUCI

AirUCI (Atmospheric Integrated Research at UC Irvine) is a research team in the environmental sciences in which several PIs from UC Irvine are involved. It was established by Finlayson-Pitts almost 20 years ago. It aims to provide researchers pursuing atmospheric chemistry with a framework to interact. To my good fortune, I was among the first to join. The atmosphere is stimulating and collaboration is encouraged. Many of my papers on atmospheric chemistry are AirUCI collaborations. AirUCI has grown a lot in membership since it was formed. It is now codirected by Finlayson-Pitts and Sergey Nizkorodov.

16.2. CAICE

CAICE (Center for Aerosol Impacts on Chemistry and the Environment) is a National Science Foundation Center for Chemical Innovation. It pursues understanding of aerosol particles and their impact on the environment and climate. CAICE is led by Kimberly Prather at the University of California, San Diego (UC San Diego), with PIs from about 10 universities across the United States as participants. With students and postdocs, CAICE numbers about 100 people in total. CAICE is a highly interactive research environment and collaboration between PIs is strongly encouraged. Because PIs from several universities are involved, many of the interactions, meetings, and seminars take place by Zoom, and these are held very frequently. The projects we have pursued so far in CAICE are on atmospheric reactions at surfaces and on photochemistry in aerosols. We have cooperated both with experimentalists and theorists.

Yifat Miller was a very prolific and creative graduate student in my group in Jerusalem and had already published on other topics when she got interested in atmospheric chemistry. Her work led to a very nice cooperation with Finlayson-Pitts. When Finlayson-Pitts and her coworkers spectroscopically studied the hydrolysis of NO_2 in thin films, a topic of major atmospheric interest, Miller carried out VSCF calculations to identify the species and help in providing an interpretation (125). A related study pursued by AIMD simulates the cleavage of N_2O_4 , the dimer of NO_2 , into NO^+ and NO_3^- in water clusters. The results were published in a strongly reviewed *JACS* paper (126). Another important topic was pursued in cooperation between Miller, Gordon, Tobias, and Finlayson-Pitts (127). The results showed that only for very large water clusters does NO_3^- prefer an internal location (127). Miller was also involved in a cooperative project with Veronica Vaida

of the University of Colorado, Boulder. Vaida suggested the possibility of photodissociation of certain molecules in the atmosphere by overtone excitation. Miller's AIMD calculations showed the process is expected to occur for sulfuric acid (128). After an impressive thesis, Miller continued on to a very successful postdoc at the National Institutes of Health. She is now professor at Ben-Gurion University in Israel.

The research done within the CAICE framework has so far produced several results of considerable importance.

16.3. Acid–Base Particle Formation and Growth

The formation and growth of particles is a topic of physical depth that is extremely challenging both theoretically and experimentally and is of major atmospheric importance. Finlayson-Pitts pursued a very successful project in this field, exploring the formation of particles made of methanesulfonic acid (MSA) and organic amines in the presence of water and of ammonia; she worked with a group of coworkers that included Veronique Perraud, Matt Dawson, and Haihan Chen. This collaboration obtained very interesting results. I was eager to contribute to the interpretation of experiments by computational studies. Two good postdocs of mine pursued the project: Mychel Varner, who joined us in 2011, and then Jing Xu, who came to us in 2015. Varner and Xu's strategy was to develop small cluster models of the particles and try to predict the properties of large particles by extrapolation. They used quantum chemical calculations and AIMD. The skilled analysis of Varner and Xu led to success in the interpretation of the experiments and to some predictions of new effects. Highlighted results of the project include: a simplified mechanism for new particle formation from MSA, amines, and water (129); reactions of MSA with amines and ammonia in the formation of new particles (130); proton transfer in mixed clusters of MSA, methyl amine, and oxalic acid (131); and particle formation and growth from oxalic acid, MSA, trimethylamine, and water (132). Varner is now assistant professor at Iona College in New York. Xu is assistant professor at Zhejiang A & F University in China.

16.4. The Photochemistry of Pesticides

Experiments by the Finlayson-Pitts group on the irradiation of a thin film of the pesticide imidacloprid (IMD) in the visible spectrum surprisingly observed nitrous oxide (N_2O) in the gas phase as one of the products of the photochemistry. Intuitive chemical considerations suggested that NO_2 should be formed as a gas-phase product. Simulations by Dorit Shemesh, a research associate in my group, determined a likely reaction pathway and provided a photochemical reaction mechanism that seems compatible with all of the experimental findings (133). In modeling the reaction path, Shemesh used state-of-the-art semi-empirical ground- and excited-state potential energy surfaces for IMD. MD excited-state simulations using the semi-empirical potentials seem a powerful tool for the field.

16.5. The Photochemistry of Aldehyde Clusters

Aldehyde photochemistry is known to be of atmospheric importance. Shemesh and I have cooperated with Nizkorodov and his then-student Sandra Blair on the photochemical reactions of aliphatic aldehydes in aerosols. Experiments were done in condensed phase. The computational model used was an $n = 5$ cluster of pentanal. Shemesh used a semi-empirical quantum-chemical potential surface for the excited states in MD simulations for the photochemical process. An important result is that cross-molecular hydrogen transfer reactions play a larger role than do unimolecular reactions (134).

16.6. Mechanism and Competition of Halide Substitution and Hydrolysis in Reactions of N_2O_5 with Seawater

The reactions of N_2O_5 with seawater are of unique importance in heterogeneous atmospheric chemistry. For this reason, understanding the reactions of N_2O_5 was set as one of the prime goals of CAICE. The group of PIs pursuing this topic within the CAICE framework includes Gil Nathanson [University of Wisconsin at Madison (UW Madison)], Tim Bertram (UW Madison), Mark Johnson (Yale University), David Limmer (UC Berkeley), and Andy Götz (UC San Diego). Nathanson and Bertram pursue experiments on N_2O_5 interactions in macroscopic systems (water surfaces and aerosols). Johnson is pursuing reactions in clusters. Limmer and Götz pursue theory and computations. The fact that the CAICE experiments include both macroscopic and microscopic systems offers an enormous advantage of depth and perspective. To my good fortune, we had fruitful, exciting collaboration with Johnson, Nathanson, and Bertram as well as with theorist Götz. N_2O_5 is known to have two major reactions with seawater: One is hydrolysis, which formally corresponds to $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$; the other is substitution by Cl^- , formally presented as $\text{Cl}^- + \text{N}_2\text{O}_5 \rightarrow \text{ClNO}_2 + \text{NO}_3^-$. Previous to our work, the microscopic mechanism of the reactions and the nature of the competition between them was unknown. The real system is very complex to simulate computationally. McCaslin, then a postdoc with me, did outstanding work by developing a simple but very successful model for the processes (135). The model is based on the three-component cluster $(\text{N}_2\text{O}_5)(\text{Cl}^-)(\text{H}_2\text{O})$, for which McCaslin computed the reaction pathways and AIMD simulations at a high-level DFT. The results provided good insight and were directly relevant to small clusters (Johnson experiments) but also more qualitatively to macroscopic systems. The paper was published in *Science Advances* (135). Another important accomplishment related to this topic is due to the work of Estefanía Rossich Molina, a recent postdoc in our group. Molina investigated the hydrolysis of N_2O_5 on a large pure water cluster. Her results show that the process can indeed take place at the surface of the droplet. Previously the process was widely assumed to take place in bulk (136).

16.7. The Reactions of N_2O_5 with Anions in Water: Theoretical Model Calculations and Experiments

Experiments by the Bertram and Nathanson groups showed that the presence of sulfates and carboxylate ions in seawater suppresses the formation of ClNO_2 , which is produced by a substitution reaction of Cl^- with N_2O_5 . Model calculations by Natalia Karimova, a postdoc with me at UC Irvine, provided understanding of the experimental findings and in addition provided important insights and new predictions for the reactions of N_2O_5 with ions in water media (137). The model that Karimova developed has N_2O_5 initially at the surface of the hydrated ion, the latter consisting of 12 water molecules. A prereaction complex is formed in all cases and is substantially distorted in structure compared with that of the nonhydrated ion (**Figure 6**). Transition state calculations and AIMD simulations were pursued (137). We expect the results and the model to also be relevant to the reactions of ions in water.

16.8. Optical Properties and Photochemistry of Atmospheric Chromophores

This is a new direction for our group in CAICE, but there is considerable momentum in our work on this. We are pursuing cooperation with Vicki Grassian (at UC San Diego) who is doing condensed-phase experiments. Most calculations so far are on the absorption spectra of organic chromophores dissolved in water with treatment of the effects of pH and of salt.

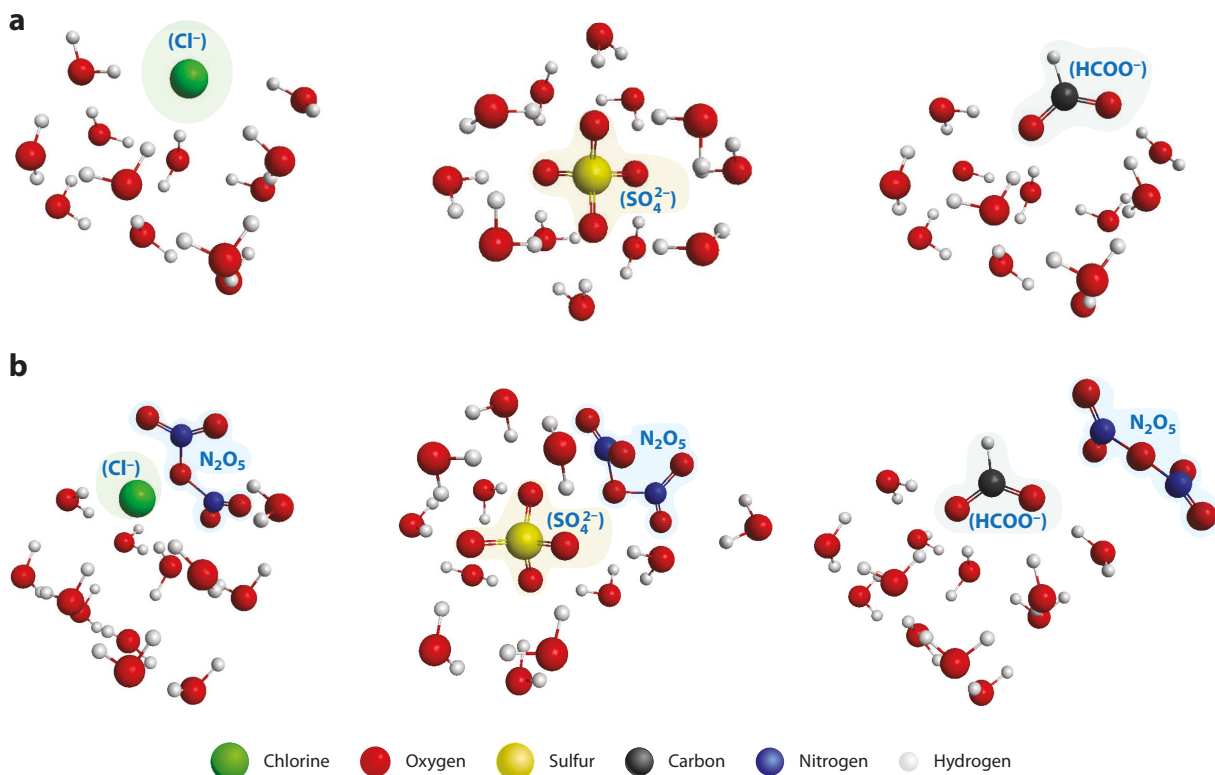


Figure 6

Structures of hydrated anions (*a*) not in contact with N_2O_5 and (*b*) in complexes with N_2O_5 . Results shown are for chloride, sulfate, and formic anions. Figure adapted with permission from Reference 138.

Our first CAICE photochemistry paper also deserves a mention. It deals with the photochemical dynamics of acrylic acid, a model for a family of organic chromophores. The calculations by Shemesh were carried out both by using AIMD, with a high-level ab initio excited state potential, and by a recent semi-empirical excited-state potential. The various photochemical reaction channels and the corresponding products were computed and are in good accord with the experimental results (138). This is encouraging for future work on other systems.

17. OTHER CURRENT RESEARCH TOPICS

In this section I mention two other research topics that we are actively pursuing.

17.1. Polynitrogen Compounds and Materials

The term polynitrogen applies to compounds or materials made only of nitrogen atoms. I study such materials mainly because of the exotic chemistry involved. Several years ago, in calculations by Barak Hirshberg, then a graduate student, and in cooperation with Krylov of USC, we predicted the existence of a crystal made of N_8 molecules (Figure 7) (139).

According to the calculations, this material should be stable at ambient pressures. Calculations of dynamic properties including thermal reactions are being pursued. Most exciting is the fact

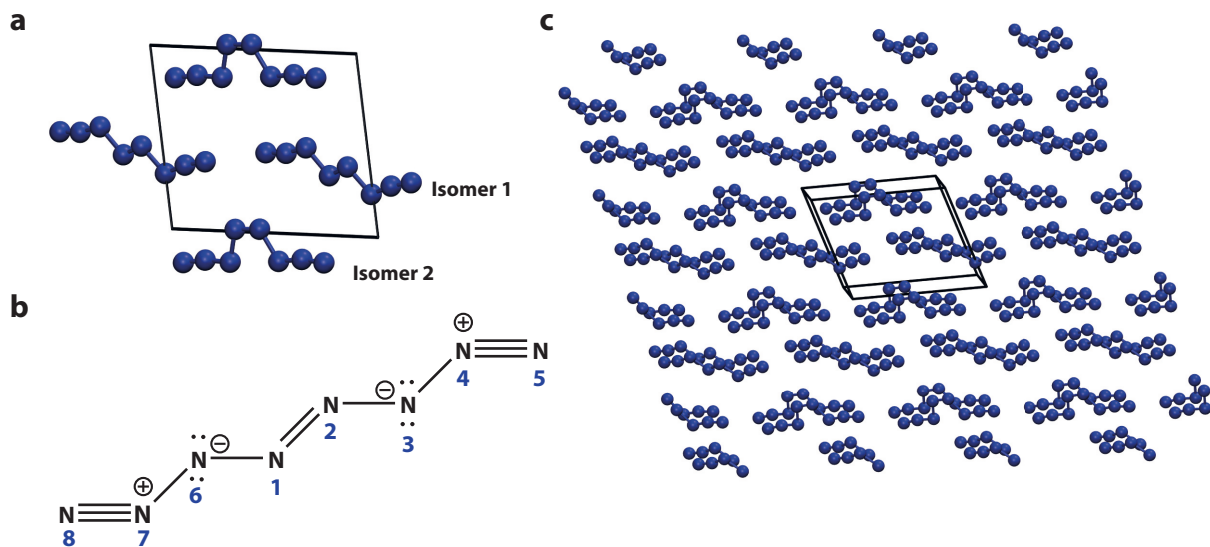


Figure 7

Crystal structures of the predicted N₈ solid. (a) Unit cell of the crystalline solid N₈ showing two isomers, EEE and EZE. (b) Lewis structure of N₈ as computed. (c) Crystalline lattice of the N₈ solid. Figure adapted with permission from Reference 140.

that the existence of this solid was very recently confirmed experimentally (140)! The paper on the prediction of the N₈ solid, published in *Nature Chemistry* (139), stirred a good deal of interest in the research community and seems to have stimulated related work by other groups. This also ranks with my favorite contributions. Hirshberg, the outstanding former student who did this work and who is now a postdoc with Michele Parrinello at ETH Zürich, has just been appointed assistant professor at Tel Aviv University.

About a year ago, my student Itai Zakai obtained very interesting results on the nitrogen-rich material (so not a perfect polynitrogen) N₅⁺[B(N₃)₄][−] (141). A solid corresponding to this formula was made by Karl O. Christe at USC. Zakai explored the building block of the solid and also of the dimer. He obtained the atomistic structure, the charge distribution, and the reaction dynamics upon temperature jump and mechanical impact. An interesting mechanism was found that involves ultrafast release of several N₂ molecules (141). Polynitrogens and nitrogen-rich materials seem to hold the promise of an interesting new chemistry of nitrogen atoms.

17.2. New Approximate Method for Time-Dependent Vibrational Quantum Dynamics of Large Systems

Our study from 1982 introduced the TDSCF approximation (also referred to as TDH) for dynamics in time of polyatomic vibrations. That method still requires major computational effort for large systems due to the need to compute many integrals at each time point. In 1995, Jungwirth was a postdoc working with me in Jerusalem, and we introduced an approximation that was computationally much simpler than TDSCF but that had almost the same accuracy (142). This is the classical separable potential (CSP) approximation, which like TDSCF involves mean-field effective potentials that are computed classically in CSP. Recently, working with Hirshberg and Lior Sagiv, presently a PhD student, we adapted the method for vibrational spectroscopy calculations (143). In calculating vibrational frequencies, the method yielded results of good accuracy.

We are currently using the method for time-dependent vibrational spectroscopy. It is expected to be applicable for systems as large as proteins.

18. WORK AS PROFESSOR EMERITUS

I am now professor emeritus at both the HUJI and UC Irvine. I have small (but good!) research groups in both places. I also have some extramural funds to support my group members. I very much enjoy the research I am doing. Thus, the system treats me well, and I am very grateful for it.

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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Errata

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