Reinvented – An Attosecond Chemist

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Abstract
Attosecond science requires a substantial rethinking of how to make measurements on very short timescales, how to acquire the necessary equipment, technology, and personnel, and how to build a set of laboratories for such experiments. This entails a rejuvenation of the author in many respects, in the laboratory itself, with regard to students and postdocs, and in generating funding for research. It also brings up questions of what it means to do attosecond science, and the discovery of the power of X-ray spectroscopy itself, which complements the short timescales addressed. The lessons learned, expressed in the meanderings of this autobiographical article, may be of benefit to others who try to reinvent themselves.

1. Reinvention

I always seemed to be reinventing my research directions (Fig. 1). The title, immediately embellished by my wife, Mary Gilles, should probably say "Reinvented Again!" Throughout my career, no laboratory seemed to stay constant for more than a generation or two of graduate students. Equipment was dismantled, moved out, and new hardware and instruments erected in their place. A drawback with this approach is that the overall contributions to any single field might not have been plumbed to as much depth, but an advantage is that I stayed interested and highly motivated by inventing and setting up new subjects, like an Assistant Professor reveling in the building of new laboratories much beyond the expected years. Another shortcoming is that one needs to obtain substantial financial resources for changing equipment, far beyond the customary. On the flip side, I continuously embraced the technological state-of-the-art and engaged students who wanted to tackle the newest topics. It might have been easier if I had one technique and area of science and pushed it to the highest level, but by now I would probably have retired due to everything being too familiar. In contrast, I am still trying to invent new scientific directions that employ evolving technologies, requiring the development of impressive laser and technical tools. I am never happier than when a student takes a glimmer of an idea and runs with it, creating something totally new, often in new directions for our laboratory.

1.1 Adaptability

Companies always say the most important characteristic they seek in employees is "adaptability" (1). This is the best advice one can give to all our students. It sometimes used to be called flexibility, but nowadays flexible means working hours and remote locations. From a company standpoint adaptability means a willingness of employees to understand change and to adapt. In my personal life I like things to be relatively constant – I get a new car only after 15-20 years, I put my belongings exactly in the same place every day, and I have my favorite, irreplaceable knife for peeling apples. In my scientific work environment, though, I take chances on new directions to an extent that belies my personal behavior. I never figured out why there is this big difference when I step into the office or the lab, but, gratefully, it led me to investigate many new fields every decade of my career. The subjects spanned from infrared fluorescence kinetics of energy transfer (2), laser isotope separation (Fig. 2) (3), to product-state-resolved ion-molecule chemistry via infrared vibrational fluorescence (4), Fourier transform infrared emission spectroscopy and dynamics (5), alignment-dependent electronic energy transfer (6), surface etching, deposition, and growth, near-field microscopy of photoresists (7-9), femtosecond coherent superpositions and coherent control (10,11), synchrotron beamline investigations of aerosols (12), and low temperature chemistry of Titan (13), among many, many topics in my early years.

1.2 Autobiographies

Many of the subjects noted above are amply described in an autobiography written on the occasion of my 60th birthday (14). Looking back on that article, it is challenging to see how I could improve on that extensive description of my life, important colleagues, and scientific achievements. A different approach, therefore, seemed necessary, for this article in response to the request from the Editors of Annual Review of Physical Chemistry, for an autobiographical piece for Volume 75. Moreover, is it coincidental that the due date for Volume 75 coincides with my own 75th birthday? One has to wonder if the Editors were that cunning. Having been an Associate Editor and Editor of Annual Review of Physical Chemistry myself for a total of 20 years, I truly understand the honor of this task.

My approach in this autobiography is to consider what it is like to be a chemist trying to make scientific contributions as an attosecond scientist, a subject normally dominated by physicists, as well as a number of life's lessons and the value of change. Because of my previous autobiography, I am not going to give the usual location of my birth, how my childhood influenced my career, or name lots of important early colleagues and co-workers. Readers can view the previous autobiography if they want to know those details. Suffice to say, with the seemingly rapid passage of time, a naïve youngster in Colorado (Fig. 3) became a wisened senior in California. Instead what I want to do is share with readers what it is like to reinvent oneself into a major new area of attosecond chemistry and to make some commentaries on science and funding, continuous learning, the long view, teamwork, the importance of students, healthful rejuvenation, and giving back to the community.

2. An Attosecond Chemist

Today one might look back and ask, what would it mean to be an attosecond chemist? Is it just the attosecond time domain that is compelling and interesting, or is there something more to be uncovered with these new spectroscopic tools? The answer to the second question is easy and is a

resounding "Yes" (15-18). Little did any of us know, during the first attempts to make attosecond pulses, that by embracing attosecond technology, it would be the ultrafast X-ray spectroscopic regime (the X-ray spectroscopic revolution (15)) that would become so powerful and compelling and that it would open up new vistas in the field of molecular dynamics. In a field dominated by physicists who want to understand every component of detailed time dynamics and phases of a single electron leaving an atom or surface on attosecond timescales (19-23), Chemists can uniquely contribute through their knowledge of photochemical processes.

In thinking about the first question, an important aspect that remains is how to convince chemists and even some physicists of the value of the somewhat misunderstood attosecond field. We usually say that attosecond science provides electronic dynamics and electronic timescales, a poster child being the timescales for ionization or photoemission. Thus, in my own group, we teased out few hundred attosecond timescales in the strong field ionization of an atom that depend on the final state of the cation that is being formed (24). However, attosecond timescales do not always figure prominently in all investigations, but few-femtosecond timescales do, and the same attosecond extreme ultraviolet and X-ray technology addresses many surprising and important details about chemical dynamics (15,16).

These include curve crossings, intersystem crossing, conical intersections, Jahn-Teller distortion, ring opening, coherent dynamics, and bond breaking, all of which will be documented in more detail below. In the solid state, discoveries include the observation of hole and electron carriers and their thermalization, valley-resolved details, insulator to metal transitions, coherent phonon dynamics, transport of carriers across junctions, and core-exciton dynamics. Even when combined with a somewhat longer optical pulse, the attosecond technology allows abrupt curve crossings to be visualized for the first time in detail (Fig. 4) (25). It is now possible to convince chemists, apart from an occasional reviewer that repeats a mantra: the paper uses the word attosecond, but the work does not have an attosecond timescale. The same could be said for someone who uses femtosecond laser tools and measures features on few-picosecond timescales. Similarly, there are skeptics of the attosecond field who think that there must be some violation of the time-energy uncertainty relationship, not realizing that the time and spectral resolutions are always done separately. This is true for all ultrafast measurements. Thus there is no violation of time-energy uncertainty, as they are not conjugate quantum mechanical variables in the measurements. In fact, time is not even a quantum mechanical observable; it is a parameter that is set by the experimentalist in the lab. Yet, many proposals come back with this incorrect criticism. Even knowing this, there are many, many issues to keep in mind when one approaches the ultimate limits of time, and we are right to be cautious about interpretations.

2.1 Setting the Stage

In 1999, I chaired a DOE Basic Energy Sciences Subpanel on "Novel, Coherent Light Sources" that considered the conceptual proposal and science case being made for building the Linac Coherent Light Source (LCLS) (26). That panel endorsed the principle to build a free electron laser in the United States by taking advantage of the available resources at the Stanford Linear Accelerator Center (SLAC). This was the start of a long journey that led to the building of the LCLS and its substantial upgrades (27). In 2013, I chaired a Department of Energy (DOE) workshop (“Unraveling the Interpretations of Attosecond Measurements," sponsored by the

Council on Chemical and Biochemical Sciences, Office of Science, Office of Basic Energy Sciences) and drafted a Nature Photonics commentary about attosecond science entitled, "What will it take to observe processes in 'real time?' " (28). The article discussed how challenging it is to extract the interpretations of most attosecond measurements without the aid of substantial and comprehensive theory. It eventually led to a clever call for proposals by DOE in the ultrafast X-ray science field linked to the LCLS.

While I am only a minor participant myself in experiments at the LCLS, the credibility that I brought to these panels was a deep knowledge of chemical dynamics and the emerging field of high harmonic generation, which is the laboratory table top method by which attosecond pulses were first achieved in the extreme ultraviolet (29) and now even in the X-ray regime (30). Now the LCLS has also produced attosecond X-ray pulses and the future appears very bright for powerful ultrafast X-ray attosecond spectroscopic measurements that will embrace and reveal much new science.

2.2 Kinetic Timescales and the Pace of Technology

To understand how over a lifetime career I could progress from first measuring energy transfer on the microsecond timescale to eventually delineating chemical dynamics on nanosecond and femtosecond times, and ultimately pursuing attosecond X-ray spectroscopic measurements, it is valuable to consider both technological progress and grant proposals / science funding in the United States. Laser and optical specialists relentlessly pursue the technology to make shorter and shorter pulses and to span more and more wavelengths. Devices and commercial providers followed this natural progression from nanosecond, to picosecond and femtosecond lasers. Pushing this pace, researchers invented new spectroscopic methods that utilize these tools. Shorter timescales are therefore expected when one considers the pace of technology. The coherence of lasers also plays a large role, affording possibilities for coherent multidimensional spectroscopies (31), the equivalent of pulsed NMR in the optical and infrared regimes. To create attosecond pulses, one needs a large state-of-the-art femtosecond laser and some home-built tools based on pulse compression and the process of high harmonic generation (29). The technology to make such short pulses necessarily requires upconverting the photons into the extreme ultraviolet and X-ray regions of the spectrum, for one reason simply to obtain enough electric field cycles to form such a short pulse. My research group, first being knowledgeable about nanosecond lasers and using them for many experiments over decades, took advantage of these short time improvements in technology over several key stages. Before enumerating more about that, let's next consider how the funding works in the U. S.

2.3 Funding Principles

A nicely created proposal for funding has the hallmarks of developing an area of science, identifying the gap in knowledge, logically reasoning why and explaining what will be learned, noting the impact, and then calling up, finally, the technology that is required to do so. It is often anathema to referees to think another way around. Too often, though, in my own career, I found myself wanting to turn this process upside down. I would think: "With this new technology, there will be many novel properties one can measure – we don't know them all yet, but we should try." Some people may think this is an Edisonian approach to science, rather than hypothesis driven. I

don't believe that is quite right. Edison made enormous numbers of trials to achieve a successful light bulb. We do our innovations with excellent theoretical underpinnings, estimates of signal-to-noise ratios, clear decisions about the best approaches, and an understanding of the mitigation of risk, not by enormous numbers of trials. We all know the elated feeling when we develop a detector that increases the count rate beyond our expectations, or a simple modification that improves the signal-to-noise ratio by ten in our experiments, or a new laser with impressive headroom to pursue novel multiple pulse experiments. Pushing technical innovations is a big part of physical chemistry, and we should not have to be embarrassed about it with our peers when we write proposals. However, often to build a complicated new apparatus, it takes much longer than the short lifetime of a typical grant. Moreover, proposals must thread a very narrow path to make big improvements in the technology, especially when the costs are expensive.

In the United States, due to funding mechanisms, corporate goals, and tenure models, we may be losing some of the inventiveness and mechanisms of financial support that provide the long-term investments and innovations in chemical instrumentation and technology. Often technological advances allow the scientifically curious to approach measurements in fundamentally new ways, leading to exciting advances. In some countries, there can be more sustainable funding that invests in laboratories with a longer-term view, sometimes allowing new technology to be pursued in and of itself. The Max Planck Society is one example that seems to permit this long-term view. This is not always the case for the individual chemistry faculty member in the United States, where there is often a three-year time horizon to produce results. There are almost no mechanisms for a ten-year time horizon that may be required to develop a major new technology, such as attosecond chemistry. Sometimes with NIH, it is even said that all the results have to be almost in hand and the aims are written to correlate with those available results. Physical chemistry is one of the areas of chemistry where the technology is very important, and the advances that are made technically by physical chemists benefit scientists across many disciplines. The field could really benefit from a longer time horizon and funding mechanisms for technical development. There are still some ways that this is being accomplished: initial large setup packages of assistant professors, longer-lived Center funding, extremely generous foundation support, and a few five-year types of support.

2.4 Launching New Fields

I can point to several times in the last twenty-five years where it became possible for me launch a major new effort without the need for results to be immediately in hand. However, one had to be a bold risk taker. At NIST, JILA, in Boulder, Colorado, due to the flexibility of the JILA NSF physics group grant, I was able to procure our first femtosecond Ti:sapphire laser to set up an ultrafast time dynamics experiment. This led to many successes in coherent vibrational and rotational dynamics that set the stage for much future expertise in my group (10,11). I came back from a Gordon Conference on nonlinear optics and persuaded my group in Boulder to try to use high harmonic generation to study chemical dynamics. The Air Force Office of Scientific Research was able to provide equipment and grant support to launch our first high harmonic time-resolved photoelectron experiment (32) and the time to do so. That early work on high harmonic generation became the foundation of my research that continues today. Having just moved to Berkeley, there was a Department of Defense MURI call for new instrumentation ideas that could open up revolutionary new fields; our proposal to achieve the first attosecond technology platform in the United States (33,34) was one that was selected. We produced the first extreme ultraviolet isolated

attosecond pulses in the United States and began to use them for scientific investigations. In Berkeley, as a member of an NSF extreme ultraviolet engineering research center through Colorado State University, we were able to demonstrate femtosecond extreme ultraviolet transient absorption for the first time (35,36). This took substantial investments in time and money, and it revolutionized the attosecond field by allowing the first-ever attosecond transient absorption methodology (37).

After these seminal cornerstones provided the foundation for what my group would do in the next several decades, it was still necessary to continue to acquire funding and equipment at a much greater level than individual core grants could provide in order to be competitive in the attosecond field. At Berkeley, catching the rise of interest in attosecond pulses at the Department of Defense and the Keck Foundation, a number of atypical grant possibilities arose, over a span of about 15 years, via the Keck Foundation, NSSEFF fellowship (now Vannevar Bush Faculty Fellowship VBFF), AFOSR and ARO MURIs (Fig. 5), DARPA, and NSF MRI (Major Research Instrumentation). By also successfully proposing new topics for core programs to DOE, AFOSR, and NSF, significant support was obtained for equipment, supplies, and personnel to make major breakthroughs in attosecond and X-ray chemistry – a dream scenario (and a dream team of group members) that rarely occurs.

It is necessary to note again that the typical sizes of individual core grants from federal agencies are insufficient to support such expensive equipment and the technically demanding and costly challenges of a field such as attosecond chemistry. Without the good fortune of additional support for the several million dollar laboratory setups, it would not have been possible to build and maintain a sophisticated set of labs that could push the state-of-the-art and pioneer the attosecond field. I was extremely fortunate to have that chance to do so, given how the funding mechanisms work in the United States. It also would not have been possible without a large number of successful postdoctoral fellowship holders from abroad. With such additional resources, it was possible to continually develop the cutting edge of such challenging and expensive technology that gets at the core of fundamental physical mechanisms of chemical dynamics. The fact that the U. S. does not have a well-funded and highly visible Federal grants program for postdoctoral fellowships is a weakness of our field. Currently, there are significant numbers of postdoctoral fellows across all of chemistry who are now supported by the Beckman Foundation, contributing greatly to a vital postdoc system in the U. S. (full disclosure, I am on the Executive Board for the postdoctoral fellows program at Beckman, so I know this contribution first hand).

3. Attosecond X-rays Uncover Dynamics

A realization I had after a short while in the attosecond subject is that not everything about the attosecond field should be trying to measure time dynamics that are sub-one-femtosecond. Having been around the Advanced Light Source Synchrotron, I learned about core-level spectroscopy and how static X-ray absorption (38) and X-ray photoelectron (39) spectroscopies provide powerful insights into oxidation states, atomic-site-specific chemistry, and even electronic bands in materials. At synchrotrons and free electron lasers, X-ray emission spectroscopy (40) is also prominent. Note, the word used here is "spectroscopic," not diffraction. There are, of course, many powerful ultrafast methods based on diffraction (41), a method that locates the positions and distances between atoms. However, ultrafast core level spectroscopy (42) has the unique ability to

study changes in electronic states and orbitals, to reveal shifting electron / orbital densities in ultrafast dynamics, i.e. to analyze charge states, charge switching, oxidation state changes, passage through conical intersections – where the electronic character of the potentials change, even chiral dynamics and spin states.

Attosecond methodology brings one directly to the subject of inner shell spectroscopies by embracing extreme ultraviolet and X-ray spectral features. The table top method of producing attosecond pulses by the process of high harmonic generation gives "for free" this ultrafast X-ray spectroscopic view. Moreover, it is not just about the highly excited inner shell, core-level states, which are the subject of many investigations (43). Core level absorption transitions start from an inner shell of an atom in a molecule, thus locating a specific atomic site on the molecule, and end in partially occupied valence electronic states where all the chemical action is occurring. A key point is that in X-ray transient absorption spectroscopy the inner shell transition can't reach spatially very far, so the sampling of the valence orbitals is highly spatially localized. Thus in chemical dynamics, a particular atom in a large molecule might uniquely reveal the timescale for the changeover of electronic character from a singlet to triplet state (44,45), or when a radical is formed, the newly created partially occupied radical orbital on one atom becomes the most prominent feature in the X-ray spectrum (46). The excited transition states and severed-bond electronic orbitals that occur when a molecule opens its ring can appear at dramatically new X-ray energies (47,48). Even many electronically excited states normally inaccessible in the optical have unique X-ray signatures (49). Similarly in solid-state materials, the inner shell orbitals can access newly-formed holes in the valence bands and the blocking of transitions when electrons are excited into the conduction band during carrier dynamics (50,51) and valley resolved dynamics (52). Core-level excitons in solids are readily apparent from their sharp spectroscopic features and rapid decoherence times (53,54).

The inner shell orbitals of many different individual atoms in a molecule are contributing to the sensing of the valence electronic orbitals from their unique localized vantage points, which is what chemists want to know when chemical transformations take place. Just to peak one's interest, we can imagine the new kinds of questions that one can answer with ultrafast X-ray spectroscopy if a diradical is formed with single occupied orbitals on two different locations in a molecule or if charge switching or charge migration occurs across a molecule (55), by creating coherent superpositions of electronic states. Many of these features become accessible to X-ray spectroscopic analysis. As one can see from the references above, Leone graduate students, postdocs, and undergraduates have had significant success in this new chemical dynamics domain, sometimes unearthing the participation of unseen electronic states (49), pioneering X-ray spectroscopic features that involve multiple spin splitting effects (56,57), obtaining the direct time-domain observation of Jahn-Teller distortion (Fig. 6) (58,59), and following vibrational coherence X-ray spectroscopy that reveals the slopes of inner-shell potentials along particular coordinates for the first time (60). In some cases the goal involves attosecond pulses for the shortest possible time dynamics and in other cases one is satisfied with few-femtosecond or tens of femtosecond timescales, a small price to pay to be able to visualize new kinds of dynamics and states that are involved for the first time.

4. Teamwork - Young Minds New Approaches

You can sense how thrilled I am with ability to approach chemical dynamics from this new X-ray spectroscopic perspective. However, none of this would have been possible without the young minds who have been most important contributors and collaborators throughout all this venture, especially as the work is so technically challenging. I feel that I am often asking them to do the impossible, and they do it. In this discussion, I am being highly selective (cherry picking) by naming just a few of the students and postdocs who made important contributions to the themes leading up to and following the attosecond and transient X-ray research in our group. I apologize, first of all, to the many students and postdocs who worked on projects other than the transition to attosecond science; looking back, attosecond science has become a central reinvention of the Leone group work, emphasizing the theme of this autobiography. Second, I apologize for not naming every student and postdoc who worked in our attosecond, extreme ultraviolet, and X-ray studies, and who made so many fantastic contributions to the Leone group research in the last decades.

Lora Nugent was a key student who worked throughout our first attempts to make high-order harmonics, who together with Michael Scheer measured dynamics successfully with photoelectron spectra (32). Thomas Pfeifer, Lukas Gallman, and Mark Abel were the very first people who took the challenge to build a setup from scratch to create isolated attosecond pulses (33,34). My long time attosecond collaborator, Prof. Dan Neumark, together with Prof. Jun Ye from Boulder, were central to the success of those first attosecond projects in Berkeley; in Dan's case it has led to many attosecond ventures throughout nearly two decades. Zhi-Heng Loh proposed to me to try to build an apparatus for extreme ultraviolet transient absorption (35,36), while we were struggling with photoelectron measurements that seemed less than satisfactory. It was marvelously successful. Zhi-Heng also proposed, during a visit of Ferenc Krausz to Berkeley, the possibility that we join together to perform the first attosecond transient absorption measurements in Munich, and he went to Munich and helped to transform their attosecond streaking photoelectron apparatus to obtain the first successful attosecond transient absorption measurements (37).

Henry Timmers and Mazyar Sabbar made isolated attosecond pulses routine enough to measure sub-one-femtosecond photoelectron dynamics with tens of attosecond locking (61,62). Birgitta Bernhardt, Adrien Pfeiffer, Hiroki Mashiko, Annelise Beck, Erika Warrick, and Justine Bell made pioneering contributions to understand and interpret attosecond transient absorption through both the decay of the polarization (XUV first, optical second) versus normal attosecond transient measurements (optical first, XUV second) (63-65). As a result of that pioneering work, Wei Cao discovered our first attosecond four-wave mixing process while observing transient absorption signals in atoms. This has blossomed into a whole field of noncollinear phase-matched, attosecond nonlinear four-wave mixing and multidimensional spectroscopic measurements itself, further advanced by Erika Warwick, Hugo Marroux, Ashley Fidler, and others (66-68). Yuki Kobayashi and Kristina Chang pioneered major new attosecond chemical dynamics processes relating to curve crossings, conical intersections, and coherences (18,69-72). The theories set forth by Yuki Kobayashi, together with collaborator Prof. Toby Zeng, are remarkable illustrations of how to interpret attosecond transient absorption chemical dynamics measurements (69,73).

Joshua-Vura Weis and Chang-Ming Jiang succeeded in the first extreme ultraviolet solid-state charge transfer measurements, building a whole new apparatus in the process (74). Andrey Gandman, James Prell, and Lauren Borja took on the task to build two solid-state instruments for

attosecond transient absorption and transient reflectivity. Martin Schulze and Krupa Ramasesha pioneered our first attosecond solid state measurements (75). Lauren Borja, Michael Zürch, and Scott Cushing learned how to analyze for holes in valence bands and electrons in conduction bands with extreme ultraviolet pulses, as well as phonon participation and transport across junctions (50,76,77). Christopher Kaplan and Peter Kraus pioneered transient reflectivity measurements (78), putting this method on a substantial footing as a new direction. Marieke Jager and Christian Ott built a whole new attosecond apparatus for solid-state dynamics and separately studied materials that change phase from an insulator to a metal (79). Hung-Tzu Chang, James Gaynor, and Romain Geneaux pioneered how to measure the rapid decays of core-level exciton states in solids (53,54,80). Coherent phonon dynamics have become a rich new topic for our group (51,81). Ilana Porter pursued some of the first reported nanoparticle dynamics with XUV probing (82).

Andrew Attar accepted the challenge to build our first soft X-ray, carbon K edge transient absorption apparatus, which was wildly successful (47). Andrew Ross and Lou Barreau transformed the carbon K edge X-rays to the attosecond domain with a major new building effort (83). These technologies culminated in many new topics of Jahn-Teller distortion and spin splitting in ions, pioneered by Michael Epshtein, Andrew Ross, Enrico Ridente, and Eric Haugen (56-59). Finally, I have had many super theoretical collaborators, including Martin Head-Gordon, and a specific shout-out to his former student Diptarka Hait, Sonia Coriani, Anna Krylov, Regina de Vivie-Riedle, Bill McCurdy, Robert Lucchese, Tony Dutoi, Eric Neuscamman, and John Stanton, among others. Without their contributions, the interpretations would have been very compromised.

In addition to naming these important individuals, a key take-home lesson from this discussion is that in many, many cases it was the students and postdocs who set the directions and made the discoveries. It would be nice to think that every idea came out of a proposal that I wrote, or that I always gave specific direction to try this or that, but most often that is not the case. Students and postdocs in my group have been telling me their discoveries, creating their own ideas, and triggering new fields since the outset of my career. Early on, I was too critical of suggestions for new ideas. I would not have progressed nearly as far if it were not for learning to listen to the pioneering suggestions and ideas from so many named and unnamed individuals. Each person who has worked with me has truly been a catalyst for new directions. It is the reinvention theme that comes back time and again. Bouncing ideas off of students, listening to what they are thinking, taking interest in their interpretations - this has not only created an engine of innovation and creativity, but it has also led to the great degree of independence and confidence that those individuals have found when they leave for their careers. I have been fortunate to have so many outstanding students and postdocs in my group, and it is teamwork that has led to the many successes in research and the careers of all involved.

4.1 Continuous Learning

Without a doubt, another most important advice I can give, in addition to the adaptability and reinvention topics, is to make continuous learning a life-long goal. Whether my group knows it or not, they are a major vehicle by which I have been chauffeured along in my quest for continuous learning. What my group observes in the laboratory is often the next subject that I set aside to learn. It stimulates me to find a lot of connections to previous subjects, it helps me and the group to generate new ideas, and it provides ways to direct our thinking to more impactful outcomes.

Sometimes proposal pressure is also a great activator to think about how to set forth and solve a challenging problem. I would maintain, though, that all is not black and white when it comes to writing proposals, and ultimately understanding what the realities are in a technologically complicated laboratory often results in a different set of criteria than just posing an interesting topic for a proposal. What students see in the lab matters on so many levels, and how the hundreds of individuals over many decades have presented their findings to me and what they tell me they think their results mean has been so central to my continuous learning. As part of my reinvention story, continuous learning is responsible for changing over to new topics, which I regard as so valuable.

4.2 The Long View

Everyone knows of the mystery movie or show that centers around a character, devious or not, who is planning so far ahead of everyone else that everything falls into place, and the plan is enacted successfully without others even knowing, and it is successful even in light of new attempts to foil the outcome. I am not that character. However, I do like to take a long view and people often say that I have anticipated a new direction or a call for proposals or possible pitfalls, even before it happens. Another way this has been said of me by colleagues is that my skills to preemptively work on something and complete it ahead of time are legendary. Carl Lineberger once said that I would know where every needle and dial should be set in the lab to achieve a desired outcome.

While these personality traits shine through about me to others around me, what I hope this section will provide is some lessons of the long view when it comes to research, both in the laboratory and in proposing new directions. In the laboratory, a lot of people take possible shortcuts when setting up and making experimental measurements, but that can build in inherent weaknesses in the experiments. If it works, it could save time, but if it does not, a whole data set may be bogus. Often a lot patches have been made rather than fixing things correctly, like using temporary glue rather than finding a good optical mount. One can be saddled with so many temporary fixes that progress is disrupted at the most inopportune time when everything deteriorates, or at a minimum it makes big trouble for those who inherit the apparatus. The problems are magnified as the complexity of the technology increases, such as in the attosecond field.

A long view makes careful considerations about how sturdy and reliable each item needs to be, and for how long, weighs the possible choices against costs and lost time, and decides on the appropriate steps based on those facts. The long view is prominent in each of these decisions, and there is no right or wrong. However, the choices that are made affect the success of a laboratory for years. I am probably one of the few group leaders who discusses risk management about the experiments with my students. I find myself to be a middle of the road person. I recommend to do as many things as well as possible within our control and within reasonable cost, but one might have to live within infrastructure constraints to get research done. Often one can make do with poor air conditioning and humidity control and fix things as best as possible on the table with enclosures and other environmental proofing. I would rather make do and get an experiment to work, while others might create a standoff and not do their work for years until a major air conditioning fix is provided by the university. Sadly, the latter is often a loss to science.

Similarly, when thinking about the projects of the group, seeing the relationships between projects, proposals, and setups that might be built, as well as what the scientific landscape might be like in 5 or 10 years down the road – this is a way of planning that I like emphasize. I am always taking the long view as far as what apparatuses might be built, how they might be modified or utilized for a new direction, building in extra capability for a modest cost, taking risks to acquire items that could open new directions, and proposing work that will build conditions for the future of multiple technologies and types of experiments, while lowering the costs in doing so. I think my group is always surprised when I announce a new set of equipment, moving a lab, or a new direction, while they might rather cling to the familiar.

5. Recharging in Summit County, Colorado

My wife, Mary Gilles, and I have had great opportunities to travel and see many interesting places. Many travels are connected to conferences and work for each of us. What is a gift in my relationship with Mary is that she is also a scientist, someone who completely understands the travel and work that I do and appreciates the importance of the science, as well as why I would do anything for each of my group members to help them in their careers. When I showed her a result of the first dynamics on a molecule in the X-ray at the carbon K edge, she totally gets it.

However, with all that potential for travel, we never thought that a simple small condo in Summit County, Colorado, would be something we treasure the most. The amount of value it has given us in terms of our health, lifestyle, and ability to recharge has been remarkable. Summit County, CO, is suggested as one place to live when global warming makes the world unbearable. Simply put, our condo it sitting at 9700 feet of elevation, which is probably going to remain pretty cool even in the worst of times. The number of hiking and biking trails, opportunities for good skiing, and outdoor activities in general has made our little home away from home a treasure.

What we found more than 15 years ago is that with a good internet one can work anywhere. We knew this long before everyone else figured it out with the COVID-19 pandemic. The day we closed on the unit, we were seeking to install high speed internet in our condo. We learned that it was possible to reserve hours a day for hiking or skiing, while still carrying out a huge amount of quality work. I don't know how many proposals I have written and papers I have completed, even this autobiography, while sitting looking out the window at the mountains. Yet, hiking the Colorado Trail in the mountains when huge mushrooms are shooting up everywhere, bicycling up Vail pass, or working our way up Mayflower Gulch when the wildflowers are in full bloom, these are irreplaceable activities that allow us to decompress and share many good moments with family.

6. Giving Back to the Community

There are many ways to give back to the scientific community through service on committees, panels, and reviews, teaching, writing letters of recommendation, evaluations for tenure, and activities in diversity, equity and inclusion. In a very different realm, Mary and I realized the interesting economics of Individual Retirement Account distributions, namely that a person can still take significant tax-free amounts out of an IRA and give them to charities when the person is required to take minimum required distributions. Recognizing this, and talking with Marty Zanni about the recent loss of national awards because of new endowment requirements by the American

Chemical Society, Mary Gilles and I decided to pledge a significant amount from my IRA to help reinstate the Peter Debye Award. The Debye Award was something that made me feel so recognized by my colleagues; that and election to the National Academy of Sciences were key moments in my career, which I hoped many other colleagues far into the future would have a chance to receive.

We made our pledge contingent on whether it would catalyze other donations to make up the rest of the amount to permanently endow the Peter Debye award. I saw this as a way to give back to the community that might often be overlooked and would be very beneficial for the physical chemistry community overall. After contacting previous Debye Award winners, the preliminary donations seemed very promising, and with many additional contacts to other physical chemists, and a GoFundMe site set up by Mary, the Physical Chemistry Division is now about to ratify a contract with the American Chemical Society to reinstate the award in perpetuity starting with the 2025 award year. Mary and I want to thank the many people who donated to reinstate the Debye Award and in particular Marty Zanni, who has been indefatigable in pursuing the fundraising and contracting with the American Chemical Society, based on our initial pledge and the funds that were generated.

7. Final Words

This style of autobiography is new to me. It is as much about life's lessons as a celebration about the successes of my students, postdocs, and undergraduates. Even today I am happy in giving advice to those who are soon about to be going out to their careers, writing new proposals, and tackling the latest equipment problem and how to reinvent that laboratory. After all, it would not be my way to replace what we have without a major reinvention in capability. I am doing all this while looking out the window at the mountains and the skiers below, in a location where I have often done some of my most creative work, Copper Mountain, Colorado.

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 autobiography, with the exception that he is a member of the Beckman Foundation Postdoctoral Fellowship Executive Board, and a comment is made about the benefit of the Beckman fellowships to the chemistry community.

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Fig. 1 Coworkers and logo of the Leone Laboratories (courtesy Marieke Jager – placard, and Teresa Bixby - logo).

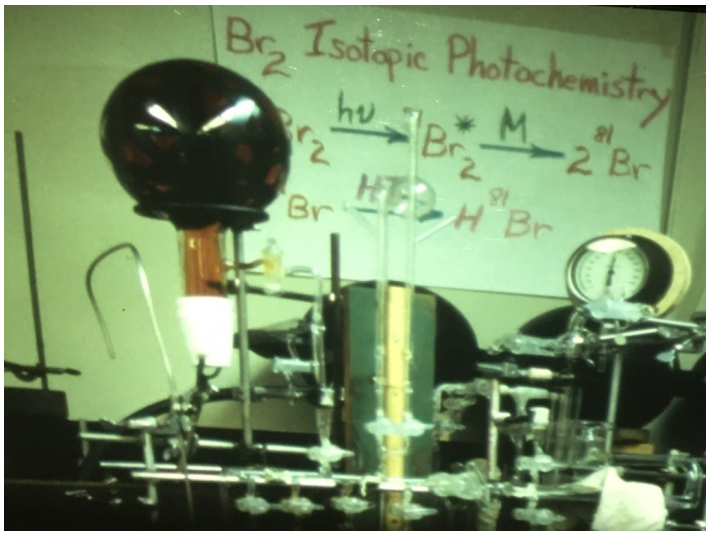

Fig. 2 Steve Leone in the C. B. Moore lab as a graduate student at Berkeley in 1974 , working on laser isotope

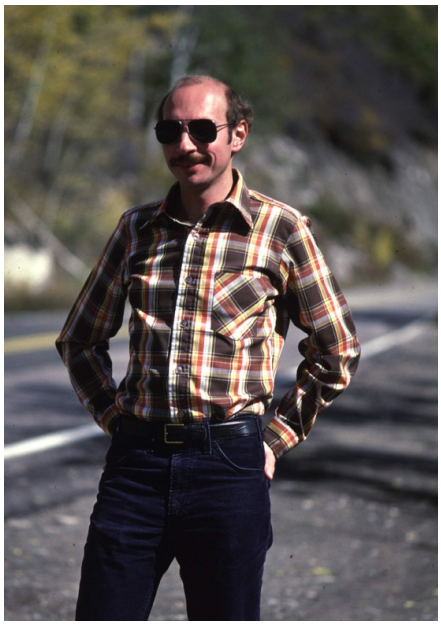

Fig. 3 The 35 year old version of Steve Leone in Colorado.

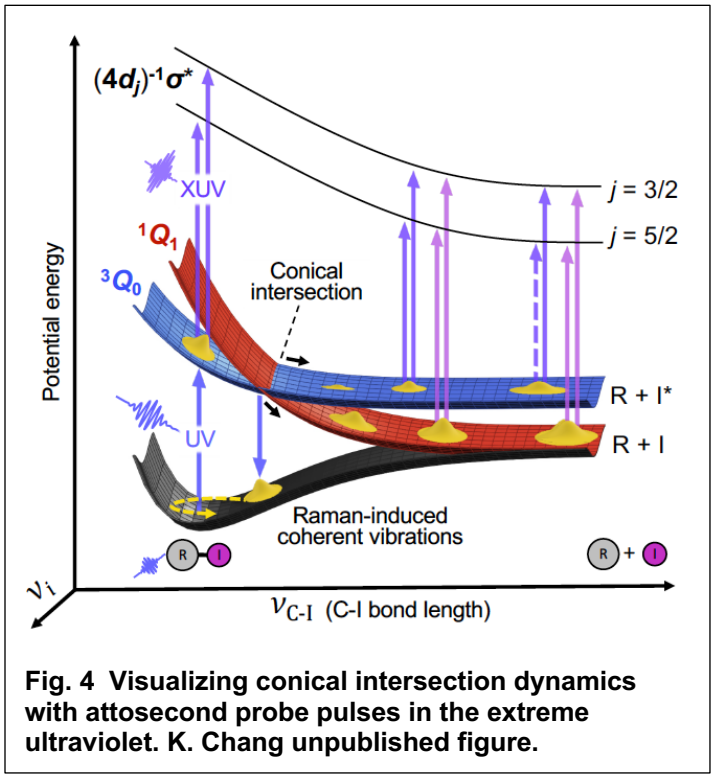

Fig. 4 Visualizing conical intersection dynamics with attosecond probe pulses in the extreme ultraviolet. K. Chang unpublished figure.

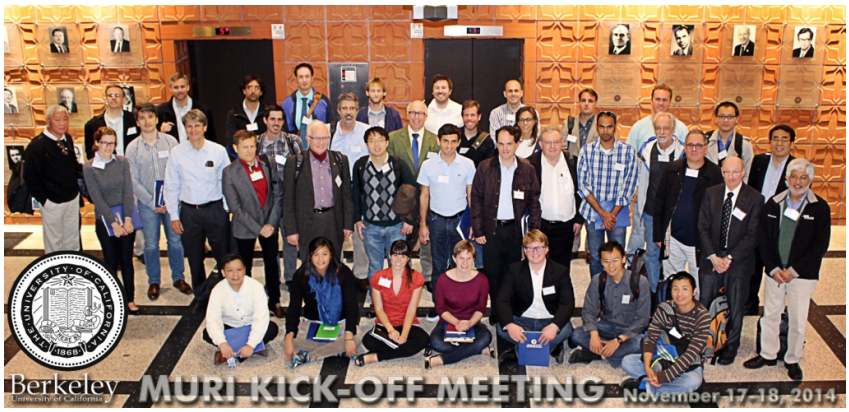

Fig. 5 2014 MURI Attosecond Kickoff meeting for both ARO and AFOSR, with DARPA guests.

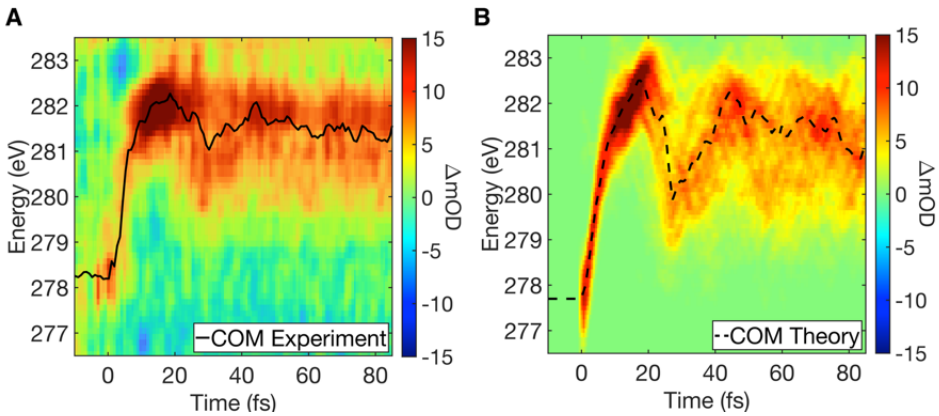

Fig. 6 Experiment (A) and theory (B) showing Jahn-Teller distortion and subsequent scissoring coherent vibrational motion in methane cations by X-ray spectroscopy.

Fig. 7 Mary and Steve decompressing in Summit County, CO.

Fig. 8 Steve and Mary at the 2005 Debye Award festivities.