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Once upon Anion: A Tale of Photodetachment

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Abstract

This contribution is very much a personal history of a journey through the wonderful world of anion chemistry, and a tale of how advances in laser technologies, theoretical methods, and computational capabilities continuously enabled advances in our understanding. It is a story of the excitement and joy that come from the opportunity to add to the fabric of science, and to do so by working as a group of excited explorers with common goals. The participants in this journey include me, my students and postdoctoral associates, my collaborators, and our many generous colleagues. It all happened, in the words of the Beatles, “with a little help from my friends.” Actually, it was so much more than a little help!

IN THE BEGINNING

I was born in Hamlet, North Carolina, on December 5, 1939, the only child of Caleb Henry and Evelyn Pelot Cooper Lineberger. My parents were among the earliest members of their families to receive any education beyond high school. Like so many people of their generation, their outlook on life was forever changed by the Great Depression of the 1930s. This wrenching experience, however, convinced them that the only path to a better life for me would be through education. This lesson was implicit in all their actions and undoubtedly guided me for the early portions of my life. These very formative experiences provided the guidance that I only innately sensed but led my path through a PhD in electrical engineering at Georgia Institute of Technology in 1965. This part of the story has been recently chronicled in some detail (1), so here I take up developments beginning near the end of my graduate work at Georgia Tech.

My PhD thesis research at Georgia Tech was carried out under the guidance of Earl McDaniel and John Hooper. It involved an investigation of the cross sections for electron-impact ionization of alkali cations. In retrospect, this work was very much a continuation of my initial childhood interests in electricity, glow discharges, and tinkering. I had the great fortune of being given an empty laboratory for research. I worked with John and Earl to write a research proposal to construct a machine and carry out the proposed measurements. When funded, we could get down to work. The instrument design and measurements of electron-impact ionization of Li^+ , Na^+ , and K^+ constituted my PhD thesis research. Such a complete research experience was wonderful training for a graduate student hoping to establish a career in academia, but, although it has remained my model for how I should train my students, it could not be replicated often.

Toward the end of my graduate work at Georgia Tech, McDaniel told me of a new institute called JILA that was just being formed at the University of Colorado. The scientific objectives of JILA sounded very much like what I wanted to do, and I decided that I should try to obtain a postdoctoral research appointment there. I was lucky enough to get one of two new JILA postdoctoral offers in atomic physics, to begin sometime during 1964–1965. The other recipient was Dick Zare, the author of the other prefatory article in this volume (2)! For reasons that will become clear, our initial meeting at JILA was postponed by just over three years, but we still had a brief, but invaluable (for me at least!), time together at JILA in 1968.

The reason for my delayed arrival at JILA is telling, in that sometimes lemons produce lemonade. While I was an undergraduate at Georgia Tech, it appeared likely that I would be drafted into military service, possibly even before I graduated. As a result, I entered the Advanced Reserve Officer Training Corps program, a step that guaranteed that I would be able to complete my bachelor's degree, but now with an obligation to serve two years in our uniformed military. I was, however, allowed a deferment throughout graduate school. It appeared almost certain that, given the major emphasis then placed on competition with the Soviet Union in the race to space, I would be able to serve my active duty military time at JILA. At the last moment, however, Vietnam intervened, and the final result was that I spent two years with the US Army Ballistic Research Laboratories in Aberdeen, Maryland. Although this career diversion seemed terrible at the time, it quickly became an opportunity in that I was given another empty laboratory, significant funding, and instructions to set up and carry out experiments to better understand the rate of dissociative recombination of electrons with molecular cations, a process of considerable importance in the propagation of electromagnetic radiation through the "disturbed atmosphere" that would follow a nuclear event. I thus had a second chance to build a major apparatus! In fact, four interesting papers resulted from my three years at the Aeronomy Laboratory of the Ballistic Research Laboratories (3–6).

At first, my time in the army seemed to have primarily produced a three-year delay in the initiation of my intended career. It was in fact a true blessing, as I quickly learned when I arrived

at JILA. At JILA, I was surrounded by exceptionally creative and energetic scientists, including Zare. During my three years in the army, Dick had completed his postdoctoral research with Gordon Dunn, spent one year as Assistant Professor of Chemistry at MIT, returned to the University of Colorado for two years as an Assistant Professor of Chemistry and Physics, and received and accepted an offer of a full professorship from Columbia University! To say that the first year at JILA was an eye-opening experience is an enormous understatement. Dick's rapid progression made it apparent to me that the extra time I spent in the army carrying out another research project from scratch was not time wasted. Rather, the time was absolutely critical because it gave me the additional scientific background and experience that I desperately needed if I were to have a chance to be competitive with the kind of peer group I encountered at JILA.

EARLY TIME AT JILA

When I arrived at JILA as a new postdoctoral associate in the fall of 1968, the institute was a hotbed of activity involving newly discovered lasers and laser technology. Zare was extending his new laser-induced fluorescence technique, and Jan Hall was developing methods to stabilize laser frequencies while also working on argon-ion laser development for photoelectron spectroscopy. The first inklings of organic dye lasers were just now appearing in the literature, and physicists at the Environmental Science Services Administration laboratories were developing flash lamp-pumped systems to make dye lasers.

My advisor, Lewis Branscomb, wanted me to work on producing a high-power (1 MW) pulsed-nitrogen laser to photodetach an electron from a slow O^- ion beam, in the process producing a velocity-selected beam comprising either ground-state O^3P atoms or a known mixture of ground and excited O^1D atoms to carry out electronically state-selected ion-pair production reactions. The UV laser was needed to have sufficient photon energy to produce O^1D by photodetachment. A physics graduate student, Ben Woodward, and I succeeded in constructing such a laser with an energy output an order of magnitude higher than that achieved previously. This project was successful because of the collaborative, sharing attitude that characterized Boulder scientists at that time. We eventually published the laser development work (7), but the state-selected experiments were so difficult that they became a lower-priority project when Lewis left JILA to become Director of the National Bureau of Standards in Washington, DC.

At about this time, Peter Sorokin demonstrated the use of a rotatable diffraction grating as a wavelength-selective mirror in a dye laser to produce tunable-laser light! I jumped onto that bandwagon, and JILA's mechanical shop rapidly constructed a flash lamp-pumped Rhodamine 6G dye laser that was tunable in the red portion of the visible spectrum. Using our high-power UV nitrogen laser to pump other dyes, we suddenly had the nearly unique ability to produce intense tunable-laser radiation across the visible spectrum. The potential of these new light sources made us a little bit like kids in a wonderful candy store. Everywhere we looked, there was something new and exciting to sample.

With JILA's expertise in negative-ion studies, coupled with the fact that visible or near-UV radiation could detach an electron from many negative ions, negative-ion photodetachment became my first focus. The first experiment was carried out with Woodward. We employed tunable-laser radiation to observe electron-detachment thresholds and obtain very accurate electron affinities of the corresponding neutral atoms. The first target was S^- threshold photodetachment (8). Why S^- ? It was not for a scientific reason but rather because the photodetachment threshold was expected to lie in the wavelength region covered by Rhodamine 6G! The new light sources made these experiments both far more accurate than previously possible and far simpler to conduct.

Armed with this success, my graduate student, Tom Patterson, and I set out to test the conjecture of Herzberg & Lagerqvist (9) that the 500-nm emission spectrum they had observed in a carbon-rich discharge came from the diatomic carbon anion, C_2^- , and not from either the neutral or cationic form. We carried out the experiment by mass selecting a C_2^- beam from our ion source, crossing the 3-keV ion beam with intense tunable-laser radiation from the flash lamp-pumped dye laser, and looking for the production of energetic neutral molecules as a function of laser wavelength. We knew that one green photon would have insufficient energy to detach an electron from C_2^- , but the absorption of a second green photon would be sufficient for electron ejection. Our expectation was that we would see intense peaks in the production of neutral particles whenever the tunable green laser radiation was resonant with levels of the hoped-for excited state. Indeed, resonant two-photon photodetachment peaks were seen in exactly the locations observed by Herzberg & Lagerqvist, but with our observations, we could state unequivocally that the spectrum they reported was carried by the C_2^- anion (10). The concept of resonance-enhanced multiphoton ionization (REMPI) was certainly not new, but the ability to utilize negative ions with the recent tunable-laser developments enabled these measurements years before it was possible to carry out REMPI on neutral molecules, with their much higher ionization energies. Although the negative-ion REMPI spectra look similar to the bound-bound molecular absorption spectrum, the upper bound state is embedded in photodetachment continua, and the elegant treatment derived by Fano describes the effects of the coupling of a bound state and a continuum (11). Much of our later work concerned these couplings in both atomic and molecular anion photodetachment.

A third new application using our tunable-laser capability became established with my second graduate student, Richard Beyer, who had come from the Ballistic Research Laboratories to work with me at JILA. At that time, an important direction in molecular energy-transfer research involved the determination of energy-flow pathways and the vibrational level dependence of relaxation and intersystem crossing rates. We knew that the intensity and tunability of our nanosecond nitrogen-laser-pumped dye laser would enable us to carry out relatively straightforward studies of single vibronic-level excitation of small molecules and wavelength- and time-resolved observations of the radiative decay of the excited molecule. The initial study centered on a prototype molecule in this field: glyoxal. We observed collision-free and collisional-loss rates of individual glyoxal vibrational levels and were able to make plausible conjectures of energy-flow pathways (12–14). Even though rotational resolution was unavailable at this time, it was possible to implicate $V \rightarrow R$ energy flow as an important contributor to the quenching process.

These and other early experiments presented us with many possibilities for our evolving research program. In the end, however, the primary focus of our research became negative-ion photodetachment. The initial threshold studies expanded to photoelectron spectroscopy, transition-state spectroscopy, homogeneous cluster anions, solvation dynamics, time-resolved cage recombination, and electron transfer. Rather than continuing in this quasi-chronological order, I now allow coherence to prevail and focus on our research in these categories.

ATOMIC ANIONS AND HOMOGENEOUS CLUSTER ANIONS

As the early phase of my career was ending, I was joined by my first postdoctoral associate, Hartmut Hotop, with whom I enjoyed a long and fruitful collaboration. In a short 18-month period, we studied the range of validity of photodetachment threshold laws (15, 16), observed the effect of a permanent electric-dipole moment on threshold photodetachment (17), and devised a sputter ion source for production of metal anions (18). We also found striking examples of very narrow Fano-autodetachment resonances in atomic and molecular photodetachment (15, 19). In addition, through a combination of our brashness and the generosity of Jan Hall, we effectively hijacked Jan's

anion photoelectron spectrometer to pursue both atomic and molecular anion photodetachment. Through many generations of improvement and modification, this device has become one of the workhorse instruments in anion spectroscopy. Hotop twice returned to Boulder to join in writing exhaustive reviews of atomic electron affinities (20, 21), and in 1999 he and others authored a third and final review of the subject (22).

Much of the grist of atomic electron-affinity data leading to the above-mentioned reviews came from the thesis research of Charles Feigerle (23–25), who also rebuilt the anion photoelectron spectrometer to obtain an order-of-magnitude higher resolution (5 meV) and sensitivity. This improved resolution enabled the observation of fine structure levels of many atoms, providing unequivocal identification of the transition that corresponded to the atomic electron affinity. The quest for ever higher resolution in photodetachment spectra, however, would lead inevitably to the use of continuous tunable lasers in threshold or near-threshold photodetachment.

This quest for higher resolution was largely carried out by graduate student Roy Mead, who designed and constructed a coaxial ion-laser beam machine that featured a much larger interaction volume and a potentially significant reduction in the Doppler broadening of threshold spectra. The increased interaction volume made it possible to replace our pulsed laser technology with a continuous tunable-dye laser. To take full advantage of this potentially higher resolution, it was necessary for the tunable-dye laser to be a single-frequency-stabilized laser. In addition, a high-resolution interferometer locked to a single-frequency helium-neon laser as a reference was required to measure laser wavelengths to the accuracy available in the coaxial ion-laser interaction. Once again, much of this technology was enabled through the generous assistance of and advice from Hall. Roy utilized this machine to revisit the earlier C_2^- studies and in the process showed that our molecular ion source readily produced anions with over 1 eV of internal energy (26–28)! This machine also represented the culmination of our quest for ever-more accurate electron affinities. We were able to measure the electron affinity of atomic oxygen to an unprecedented accuracy of $6 \times 10^{-3} \text{ cm}^{-1}$ in work carried out by Dan Neumark and Keith Lykke (29). Subsequent applications of this machine were largely to investigations of state-selected autodetachment of anions involving Keith Lykke, Kazu Yokoyama, and Amy Mullin.

We had evidence that the anions we were producing were extremely hot, especially those produced with our sputter-ion source. Despite our best efforts, the photoelectron spectra of molecular anions produced with this ion source were exceedingly difficult, if not impossible, to analyze with confidence (30). Fortunately, the enhanced sensitivity of our next-generation continuous-anion photoelectron spectrometer came to the rescue. It enabled the replacement of our uncontrolled-discharge ion sources with a flowing-afterglow ion-molecule reactor (31) patterned after one developed in Boulder by Eldon Ferguson and his colleagues. This device allowed us to carry out rational synthetic chemistry with molecular ions, a capability that was essential for later studies.

At this point, however, Doreen Leopold placed a modified version of our sputter-ion source in the 1-Torr flowing-afterglow reactor and was able to produce room-temperature metal cluster anions comprising a dozen or more constituent atoms (32). The photoelectron spectra of these metal-cluster anions showed clearly the first electron shell closing predicted with the free electron model of metals and provided a direct determination of HOMO-LUMO gaps in size-selected clusters (33, 34). These experiments were then carried further by Kent Ervin, Joe Ho, Neumark, and others outside our group.

Whereas the sputter-ion source was invaluable for many purposes, room temperature was not adequate to eliminate vibrational excitation in many of the anions of interest to us. In a quest for additional control over ion formation and ion temperature, Mark Johnson developed a pulsed-supersonic-expansion ion source that enabled our initial investigation of homogeneous molecular cluster anions (35). This development served our group and a number of other groups well,



Figure 1

Lineberger research group in 1983. (Seated) Dan Neumark and Mike Alexander. (Standing) Doreen Leopold, Keith Lykke, Meryl Mantione, Mark Johnson, Ingolf Hertel, and Carl Lineberger.

providing a general methodology to synthesize cold, partially solvated anions and clusters. This was an exciting time in the Lineberger research group, with new things happening in each of the laboratories. **Figure 1** shows the research group in 1983, with JILA Visiting Fellow Ingolf Hertel.

MOLECULAR PHOTOELECTRON SPECTROSCOPY

From the time of the earliest studies of molecular anion photodetachment, we recognized that electron detachment from a radical anion could produce both singlet and triplet forms of the corresponding neutral in a fully allowed process. The possibilities were demonstrated beautifully in the first studies of O_2^- photoelectron spectra obtained by Hall (36), in which both $X^3\Sigma$ and $a^1\Delta$ states of O_2 were prominent features in the photoelectron spectrum. The radiative transition connecting the two neutral states is multiply forbidden, and the radiative lifetime of $a^1\Delta \text{O}_2$ is 45 min. This observation demonstrated the capability of anion photoelectron spectroscopy to characterize different spin states of even transient species, frequently of chemical significance. In fact, the photoelectron spectroscopic observation of the $X^3\Sigma$ and $a^1\Delta$ states of O_2 might have been a new result, except for the fact that $^1\Delta \text{O}_2$ is a significant component of our upper atmosphere. In that environment, the low pressure and the large volume of the “laboratory” allow one to observe the infrared radiation emitted from the $\text{O}_2 a^1\Delta \rightarrow \text{O}_2$ intercombination transition.

It was immediately clear that the relaxed spin-selection rules in anion photodetachment would provide a wonderful opportunity to obtain the energetics of different spin systems for small molecules. Our first effort to exploit this opportunity was a study by Abe Kasdan and Eric Herbst of CH^- (37). In addition to determining the electron affinity of CH and the splitting between the

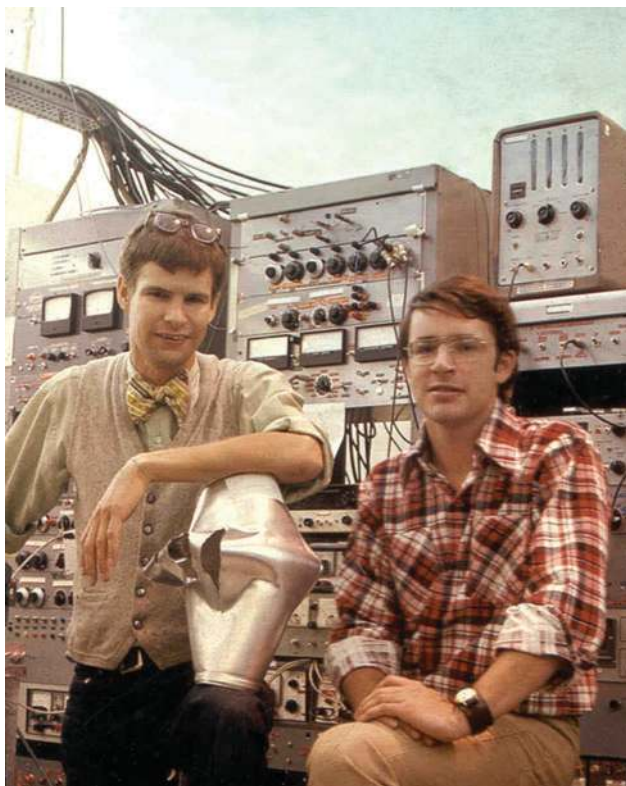


Figure 2

No one was ever injured, and after a couple of detonations that occurred when cooling diazomethane with LN_2 (the aftermath of one is shown here, with Barney Ellison and Paul Zittel), we developed an operational protocol that eliminated the danger.

$X^2\Pi$ and $a^4\Sigma$ states of CH , we could also obtain the singlet-triplet splitting in the anion. This anion excited-state measurement was possible only because our ion source produced a significant component of the excited $a^1\Delta$ state of CH^- . The very hot anions produced by the discharge ion source were quite useful for this small molecular anion because the photoelectron spectrum was still analyzable and now provided both anion and neutral spin-state characterization. We were proud of this experiment and thought that it showed the power of this technique in physical organic chemistry. Moreover, we were quite certain that we were not being fooled by the uncontrolled nature of the ion source and that our answers were correct. To our dismay, however, this work has essentially gone completely unnoticed. However, the next experiment we attempted involved the methylene negative ion (where it turned out that poorly characterized ion-source conditions were a problem), and in this case it seemed that everyone paid attention (38)!

Knowing the importance of the singlet-triplet splitting in methylene, Barney Ellison and Paul Zittel set out to produce the CH_2^- anion. All the obvious available methods using methane as a source gas in our electric discharge ion source failed. A better leaving group was needed, and Barney of course recognized that neat liquid diazomethane would be the ideal reagent for dissociative electron attachment to produce the CH_2^- anion. After several explosive adventures (**Figure 2**), Barney and Paul developed a reliable protocol for handling neat diazomethane in 1-cm^3 quantities and succeeded in generating a relatively intense beam of the CH_2^- anion.

The photoelectron spectrum of the methylene anion (with our early 50-meV resolution) displayed the expected sharp transition to the excited singlet state of methylene, and a very extended, but partially resolved, progression in the ground-state triplet-bending mode. Appropriate spectral shifts were observed following deuteration of the anion, but determination of the origin of the progression, although apparently correct, was not completely unequivocal; the issue was that hot bands resulting from bending vibrational excitation of the anion might be contributing to the spectrum. All of our attempts to change the temperature of the anion beam produced no change in the observed singlet spectrum, and we reported the singlet-triplet splitting of methylene to be $19.6 \text{ kcal mol}^{-1}$. In the publication, it was noted that although hot bands would decrease the splitting, we could find no experimental evidence for their presence (38). At that time, the highest-level electronic-structure calculations indicated a singlet-triplet splitting that was approximately 8 kcal mol^{-1} . Over the next five years, numerous theoretical and experimental papers appeared, all suggesting that there must be a problem with this measurement, but not quite declaring it to be wrong.

Some five years later, Doreen Leopold was able to combine the 6-meV resolution of the new photoelectron spectrometer with the flowing-afterglow ion source constructed by Amy Stevens. With this new ion source, we still could not produce the anion using simple, rational chemistry, but the 1-Torr pressure in the flow tube enabled the cooling of product anions. The desired CH_2^- anion was finally produced by electron impact on ethylene and cooled in the helium flow. The resulting, vastly improved, tenfold-higher-resolution photoelectron spectrum of the cooled CH_2^- anion could be readily analyzed. It showed unequivocally that serious hot-band contamination was present in the earlier photoelectron spectra (31). The new singlet-triplet splitting measurement of $9.00 \pm 0.09 \text{ kcal mol}^{-1}$ was in much better agreement with other new experiments and with high-level quantum calculations (39).

This entire issue arose primarily because, although the highest-level quantum calculations were inconsistent with our early experimental result, it was not possible at that time to state definitively that the calculation simply had to be right, given a molecule of this complexity. With the dramatic growth in computational capability, this no longer is true today for molecules of this size. Both experiment and theory grew from this interaction; an important lesson re-emphasized here is the importance of making measurements that have credible, well-reasoned error assessments. When carried out in this way, even experiments with the wrong result are valuable learning vehicles and impart no loss of trust in the investigators!

Although poorly characterized ion-source conditions were obviously a major problem for methylene, there were occasional cases in which this ion source was the only possible vehicle for the production of interesting anions. For example, there is no reasonable mechanism to deprotonate methane using the flowing-afterglow ion source. However, Ellison and Paul Engelking added ketene to the electrical-discharge ion source, resulting in the appearance of a negative ion at $m/e = 15$. The photoelectron spectrum of this anion was completely inconsistent with the known photoelectron spectra of the other anionic possibilities at this mass, NH^- or CHD^- . However, the observed photoelectron spectrum was consistent with the one expected for the methide anion, which is dominated by an extended progression in the umbrella vibrational mode of the methyl radical (40). Fortunately, analysis of the photoelectron spectrum of such a simple molecule does not require a full understanding of the synthetic procedures leading to its formation! It is our belief that the actual chemistry involves the reaction of one of the ions in the ion source plasma with ketene decomposition products in a surface-catalyzed process; fortunately, the correctness of the photoelectron spectrum analysis does not depend on full knowledge of the anion source chemistry! This early determination of the electron affinity of the methyl radical is one of the most simple molecular electron-affinity measurements ever to

come from our group. It is especially ironic that, in this case, the methide formation mechanism remains elusive; fortunately, the rational synthetic approach afforded with the flowing-afterglow ion-molecule ion source was appropriate for virtually all subsequent studies.

This refined capability to synthesize anions via rational steps was applied to obtain electron affinities and singlet-triplet splittings for a number of key organic-reaction intermediates: substituted methylenes; vinylidene; trimethylene methane; tetramethylene ethylene; allyl, *ortho*-, *para*-, and *meta*-benzynes; and many other small organic radicals (41).

Similarly, the broad view obtained in a photoelectron spectrum has been useful in experimentally analyzing failures of the Born-Oppenheimer approximation, most especially the Jahn-Teller coupling in alkoxy radicals and cyclopentadiene, and multistate vibronic coupling in azoles, triazolyl, propadienylidene, and others (42–48). Most of this latter work involved an absolutely essential collaboration with John Stanton at the University of Texas, with his beyond state-of-the-art calculations to accurately include multistate coupling. Both experiment and theory were essential to obtain credible conclusions and demonstrate the enormous value added from an experimental-theoretical collaboration, in which the demands placed on both components of the collaboration carried the result further than either alone could possibly have accomplished.

Although many other electron affinities of small molecules have been measured using this technique, the principal focus of the direct electron-affinity determinations has been to use these results in thermochemical cycles to provide bond strengths for which credible error analyses could be carried out.

THEMOCHEMISTRY: BOND STRENGTHS

Some of the earliest studies related to bond strengths were a sequence of investigations of methyl carbonyls, where we obtained, for example, electron affinities of $\text{Fe}(\text{CO})_n$, with zero to four carbon-monoxide ligands, using our earliest photoelectron spectrometer and the discharge ion source (49, 50). The electron affinities were accordingly not overly accurate, but when combined with the dissociation energies of the corresponding anions obtained by Bob Compton, a simple thermochemical cycle gave the carbon-monoxide bond strength as a function of the number of carbon-monoxide ligands around the iron atom.

With the dramatically improved photoelectron spectrometer and the flowing-afterglow ion source allowing rational ion syntheses, we embarked on an extensive program of measuring bond dissociation energies of organic molecules. We used a thermochemical cycle that employed the gas-phase acidities of organic molecules determined by colleagues Veronica Bierbaum and Charles DePuy with their flowing-afterglow ion-molecule reactor optimized for studies of chemical kinetics.

In this case, the thermochemical cycle employed involved the electron affinity measured by our group and the gas-phase acidity determined by DePuy and Bierbaum. Again, the great advantage of the measurements was that bond strengths could be determined with credible error analyses, albeit they were not always as small as we desired. Perhaps the best known of these studies involved the systematic deconstruction of ethylene to its atomic constituents, providing the bond strength for each possible distinctive step (51). **Figure 3** illustrates the variation in hydrogen-atom bond dissociation energies as ethylene is systematically dismantled. The error bars arise from believable measurements, and the trends in bond strengths are satisfying at an intuitive level.

One of the intermediates in this molecular destruction derby is vinylidene. This important diradical is in fact the molecule that initiated our foray into reaction-coordinate and transition-state spectroscopies, as described below.

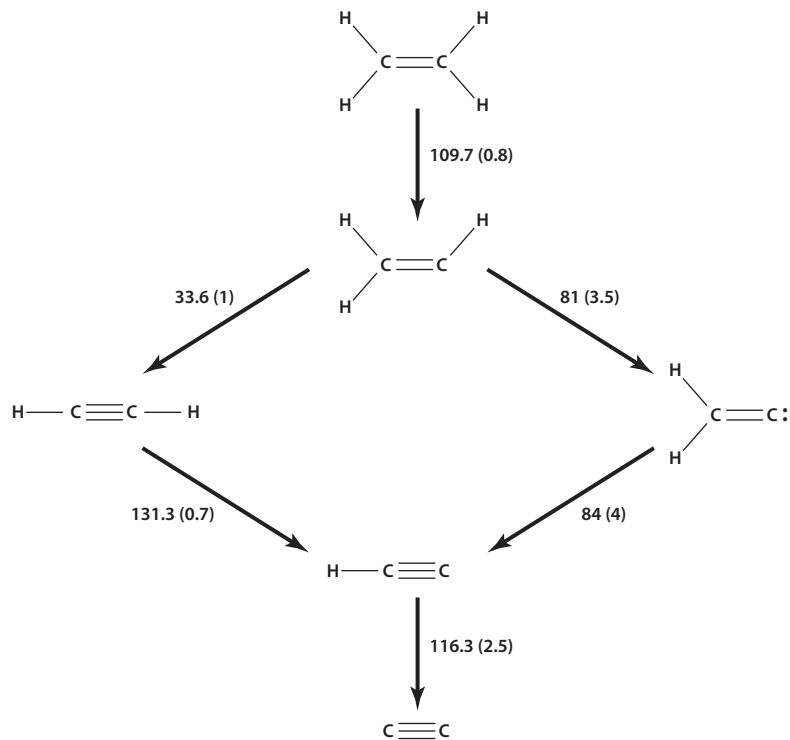


Figure 3

Experimental C-H bond dissociation energies (in kcal mol⁻¹) in the systematic deconstruction of ethylene.

PHOTODETACHMENT PREPARATION OF NONSTATIONARY STATES: TRANSITION-STATE SPECTROSCOPY

One of the great virtues of anion photodetachment is that, if there are no resonant states involved, the electron removal timescale is generally very short compared with that for nuclear motions. The result is that the neutral product formed following photodetachment is created at the geometry of the anion. With luck or by clever choice of anion, it may turn out that the initial configuration of the neutral photodetachment product is near a transition state of a neutral reaction or is one that lies somewhere along a reaction pathway. In any event, the neutral product is definitely not constrained to be in a stationary state. This simple concept forms the basis of negative-ion transition-state spectroscopy.

Our first application of this concept was an investigation of the negative ion of vinylidene, a component of the thermochemical cycle shown in **Figure 3**. In 1983, we had used our discharge negative-ion source to produce an anion whose composition was shown to be C₂H₂⁻. Our chemical intuition made us quite certain that the anion structure had to be the vinylidene structure, H₂CC:⁻. Moreover, the very low-resolution photoelectron spectrum was consistent with this analysis and provided some information on the structure of the vinylidene diradical in the process of undergoing a 1–2 hydrogen shift to form acetylene (52). This experiment began our foray into transition-state spectroscopy and reaction-coordinate spectroscopy, subjects that we continue to investigate to this day. My initial view of this approach was that its applicability was limited to unimolecular rearrangements, but it could definitely provide nonstationary initial states

for time-resolved pump-probe dynamics experiments. Neumark, conversely, recognized that in many circumstances this concept could be applied to transition-state spectroscopy for bimolecular reactions and has beautifully demonstrated the utility of this approach for bimolecular reaction transition-state characterization.

Ervin and I revisited the vinylidene rearrangement to acetylene with the new high-resolution photoelectron spectrometer. Now we could resolve the vibrational mode most closely aligned with the motion leading to the 1–2 hydrogen shift. That vibration was the CH₂ asymmetric rock, which should have been forbidden in C_{2v} symmetry. However, the extreme anharmonicity of this mode (a consequence of its motion being close to the initial reaction coordinate from vinylidene to the very low-lying transition state for the 1–2 hydrogen shift) rendered the overtones observable and confirmed our hypothesis (53).

Later studies, in collaboration with Wes Borden, demonstrated the violation of Hund's rule in cyclooctatetraene, and the anion photoelectron spectrum of C₈H₈[−] exhibited transition-state spectroscopic features that were over six orders of magnitude more intense than the transitions to the vibrational ground state of cyclooctatetraene. This result demonstrated that transition-state features need not be minuscule contributors to a photoelectron spectrum but, in fact, can even be the dominant signature in a photoelectron spectrum (54)! More recently, we have observed the photoelectron spectrum of the oxyallyl anion, a diradical with a ground-state singlet state and the lowest triplet state only 55 meV higher in energy (55, 56). High-level calculations suggest that the singlet state is not a minimum at the anion geometry but that it lies along the reaction pathway for ring closure to cyclopentanone.

All these studies make the point that photodetachment or photodissociation can be utilized to produce nonstationary states of a molecular system, and they open the door to the possibility of carrying out time-resolved dynamics studies utilizing ultrafast pump-probe spectroscopy. This latter activity is the final chapter of this story.

ION-SOLVENT COMPLEXES AND TIME-RESOLVED DYNAMICS

Our dynamical studies of partially solvated ionic complexes took a large step forward with Mark Johnson's development and characterization of an electron-impact ionized, pulsed supersonic expansion. This new ion source took full advantage of the fact that the ion-neutral Langevin collision rate is temperature independent, meaning that the ion-neutral collision rate in a supersonic expansion decreases only at the rate at which the expansion density decreases. In this manner, the aggregation of molecules around an ionic core continues far beyond the "freeze-in" surface associated with the cessation of neutral-neutral reactions in expansions. This class of ion source has become the workhorse of many studies of ion reaction dynamics.

Virtually all the experimental studies using this technique are forms of action spectroscopy, wherein one tracks the appearance of products, rather than the diminution of one of the reactants. The first measurements concerned the ionic photoproducts produced following photodissociation of Br₂[−] in size-selected Br₂[−](CO₂)_n cluster anions. The photoproduct distribution revealed two classes of ionic photoproducts: recombined cluster anions of the form Br₂[−](CO₂)_{m<n} and cage-escaped complexes of the form Br[−](CO₂)_{p<n}. For the recombined product anions, the number of CO₂ solvents attached to Br₂[−] follows the evaporative ensemble model developed by Klots (57–59). The average number of solvent molecules attached to any given product ion is determined by a combination of the energy of the absorbed photon, the internal temperature in the supersonic expansion, and the strength of the ionic chromophore–CO₂ bond. In those cases in which intensity anomalies (magic numbers) in the initial anion mass spectrum were also observed in the ionic photoproduct mass spectra, it was possible to argue convincingly that the magic numbers were

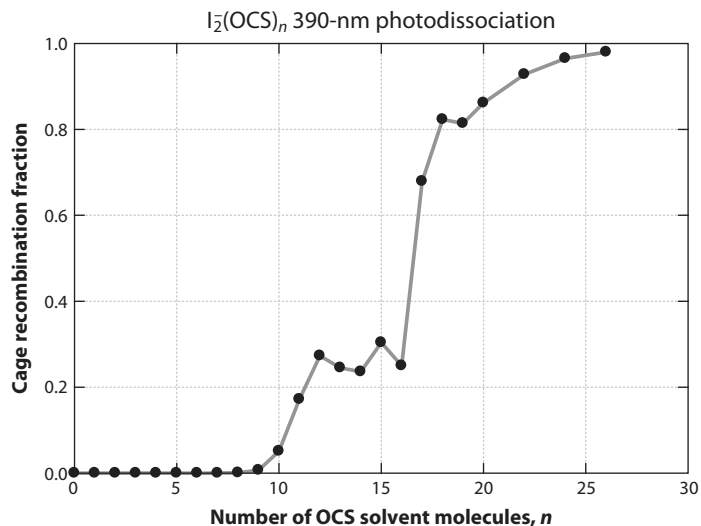


Figure 4

Recombination fraction for $I_2^-(OCS)_n$ excited to the $B^2\Sigma$ state as a function of the number of OCS solvent molecules around the I_2^- chromophore.

associated with particularly stable solvent arrangements. Although one gained a great deal of understanding from the mass spectra and the mass distribution of photoproducts, the spectra did not provide quantitative information concerning the physical arrangement of solvent molecules about the chromophore and provided only minimal understanding concerning how labile the ion-solvent structures might be. Once again, significant advances in this arena resulted from an experimental-theoretical collaboration, in this case with our colleague Robert Parson. Using model ion-solvent potentials and electrostatic solvent-solvent interactions, coupled with Monte Carlo heating and quenching cycles, he obtained a good idea of the structure of the solvent shell and the degree of its rigidity at the temperature corresponding to the expansion (60). Some remarkable structural results were found, giving significantly greater credence to the concept of a local structure around the anionic chromophore. This was perhaps best exemplified in a report by Andrei Sanov and colleagues (61) reporting the cage recombination fraction for $I_2^-(OCS)_n$ when photodissociated with near-UV radiation, as shown in **Figure 4**. The combination of the theoretical solvent-packing configurations and binding energies, coupled with the experimental data, makes it absolutely clear that the addition of the seventeenth OCS solvent molecule completes the first solvation shell around I_2^- . The OCS solvent molecule does so by assuming a previously infrequently occupied position along the I-I internuclear axis, capping one of the iodine atoms. Completely independent of any analysis, the dramatic increase in the cage fraction as the number of OCS solvent molecules is increased from 16 to 17 provides unequivocal evidence that the structure of the first OCS solvation shell around I_2^- is remarkably rigid.

The observed time-resolved recombination dynamics, coupled with theoretical simulations, provide insight into the interactions between a dissociating chromophore and the surrounding, size-selected solvent. The general trend is that the recombination times steadily decrease from ~ 50 ps to a few picoseconds as the solvent shell is expanded from a few solvent molecules to a complete first solvation shell. This behavior is typical of dihalide chromophores excited to the lowest $A^2\Pi$ dissociative state, for a variety of solvents, including CO_2 , N_2O , and OCS. The dynamics and change in recombination times are consistent with theoretical models and simulations. The

surprising behavior was that considerable caging was observed, even with partially filled solvent shells and structures that would appear to be open for cage escape. It was apparent that the simple mechanical model to describe cage recombination was inadequate. The understanding of the observed behavior finally came from theory, which showed that the solvent-solvent attractive forces resulted in asymmetric solvation for partially solvated clusters, with the maximum asymmetry appearing when the first solvation shell was approximately half-filled. This asymmetry produces substantial ($>10^6$ V cm⁻¹) solvent-derived electric fields at the chromophore that significantly modify the electronic structure of the dissociating chromophore. This solvent-field-produced modification of the electronic structure of the dissociating chromophore provides a method to reel in the dissociating chromophore. The electrostatic barrier effectively replaced the missing physical barrier. This behavior was most radically demonstrated in the case of $\text{IBr}^-(\text{CO}_2)_n$, where the $(\text{I-Br})^-$ recombination time increased steadily from 10 to 1,000 ps as the number of solvent molecules was increased from 5 to 10. When the eleventh solvent molecule was added, the recombination time dropped to 8 ps and then stabilized at ~ 3 ps as additional CO_2 solvent molecules were added. Again, theory and simulations were able to reproduce the experimental behavior (62). This particular study provides a special example of the way in which collaborative theory and experiment can provide believable explanations in cases where neither one alone would be convincing.

More recently, this experimental methodology has been expanded to include time-resolved photoelectron spectroscopy as a probe of dissociation dynamics for partially solvated anions. The first example concerned $\text{IBr}^- \text{CO}_2$ excited to the $A^2\Pi$ dissociative state, which correlates with $\text{I}^- + \text{Br}$. With no solvent present, I^- is the only ionic product observed. A single CO_2 solvent molecule, however, opens an electron-transfer channel, producing Br^- at a roughly 3% yield. The observed delayed appearance of the Br^- photoproduct, coupled with knowledge of the shape of the repulsive potential, shows that in this case, the electron transfer must take place over a distance of ~ 7 Å! The nature of the solvent-induced electron transfer and the underlying physical picture were developed through a theory-experiment collaboration with Anne McCoy (63, 64). Once again, the combination of theory and experiment proves to be far more compelling than either separately.

EPILOGUE

If there is a simple message from this article, it concerns the importance of collaborations that bring new or additional insights and tools to address problems of common interest. We are privileged to have the opportunity to explore new frontiers of knowledge. This is indeed a happy story.

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