



*Marilyn E. Jacob*

# On Walking in the Footprints of Giants\*

Marilyn E. Jacox

Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8441; email: jacoxm@nist.gov

Annu. Rev. Phys. Chem. 2010. 61:1–18

First published online as a Review in Advance on October 7, 2009

The *Annual Review of Physical Chemistry* is online at [physchem.annualreviews.org](http://physchem.annualreviews.org)

This article's doi:  
10.1146/annurev.physchem.012809.103439

Copyright © 2010 by Annual Reviews.  
All rights reserved

0066-426X/10/0505-0001\$20.00

\*The U.S. Government has the right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper.

## Key Words

cage recombination, electronic spectrum, free radicals, infrared spectrum, matrix isolation, molecular ions

## Abstract

This article tells of a lifelong fascination with light, a messenger bearing information from realms ranging from the galactic to the submicroscopic. Personal interactions have shaped and informed this life journey. Accounts of some of the most important of these are related. Infrared and electronic spectra have been obtained, often for the first time, for many small free radicals and molecular ions—short-lived reaction intermediates in most chemical processes. The infrared spectrum of a molecule tells how its atoms vibrate with respect to one another and is as characteristic of the molecule as a fingerprint is of a person. Analysis of this spectrum provides sometimes surprising information about the structure and chemical bonding of the molecule in its lowest-energy electronic state. The electronic spectrum provides information on the molecule in more highly excited electronic states, in which its structure or reaction pattern may change or it may decompose.

## BEGINNINGS

I was born in 1929 in Utica, New York. In those days, parents were advised to ignore the fussing of babies, but my mother believed that babies were to be loved. She would take me in her arms, settle herself in a comfortable rocking chair, and sing as she rocked me to sleep. Sometimes she would make up little ditties, including one about the pretty colored lights downtown. From that vantage point, I could look across the Mohawk River flats to the city lights. Mother did not realize what she was doing. The impression was indelible.

One day when I was seven, my father, a baker for a cafeteria chain, had to visit another city to inspect a new oven. He made a quick visit to a nearby store, where he bought me a little book called *Seeing Stars*, a child's introduction to astronomy. Although it was a random choice, I was totally captivated. For years, any visitor who knew anything about the stars became my instant friend. Years later, my high school English teacher assigned the oral presentation topic "What Interests Me Most in the World." By then I was reading all the books I could find on galaxies and the structure of the universe, so my choice of topic was straightforward.

Because office work was one of the few occupations then available for young women, I entered high school as a business major. I learned about common business practices and acquired skill in typewriting and shorthand, which have been quite useful ever since. My family lived in the outer suburbs, and frequently a girl about two years older than I sat with me on the city bus on the way to our center-city high school. She was an excellent student and planned to apply to Cornell University to study chemistry, which she later did. I began to think beyond life in the business world, and soon her ambitions became mine. I switched to college preparatory studies and eagerly soaked up knowledge in a wide variety of subjects. My high school history and social studies teacher, Margaret McClellan, was especially supportive and became my lifelong mentor. Outside school, I took studies of piano and voice seriously.

In our senior year, we were required to read Sinclair Lewis's novel *Arrowsmith*. I was intrigued by the passage in which Martin Arrowsmith's mentor encouraged him to learn as much physical chemistry as he could, because it was so fundamental to research in microbiology. I had already decided to major in chemistry in college, and I thought that anything as basic as physical chemistry would be important to master.

Going away to college would have been financially difficult, and the only college near Utica was a men's school, Hamilton College. In 1946—one year before I was to graduate from high school—Syracuse University established an off-campus college, Utica College of Syracuse University. An interim campus consisting of rooms provided by nearby churches, spacious older homes, a former auto-repair garage, and a decommissioned elementary school building was cobbled together. In the fall of 1947 I began my freshman year there. Many of my classmates were war veterans who had started their families and were eager to take maximum advantage of the G.I. Bill of Rights to improve their prospects in life. The lack of an opportunity to fit into the traditions of one's alma mater could be stacked against the opportunity to build our own new traditions. A year later, Utica College announced plans to become a four-year school, where I completed the requirements for a B.A. degree in chemistry, with a strong minor in mathematics.

Any school is only as good as its faculty. On that count we at Utica College were quite fortunate. The chairman of the Chemistry Department was Dr. John C. Keller, who had received his Ph.D. degree from Cornell and had previously taught for many years at Muhlenberg College, in Allentown, Pennsylvania. Keller had high standards, and brought together a small but excellent chemistry faculty. Once he determined that a student had a serious interest in chemistry, he was strongly supportive. He became my first scientific mentor.

In the spring of 1951, I was overjoyed to be accepted for graduate study at Cornell University, with an offer of a teaching assistantship. I was assigned to help Professor Simon H. Bauer with

a physical chemistry survey course for sophomore civil, mechanical, and electrical engineers. I had a voracious appetite for learning and was eager to add to the normal schedule a special topics course given by Peter Debye, a Nobel laureate, as it had been announced that he would become an emeritus professor at the end of that academic year. I asked a number of graduate students and a few faculty members whether the heavy course load would be too much of a good thing. Because I had done well on my entrance exams and because they believed Debye's course would not be demanding, they agreed that it should work out all right. When I asked that same question to Bauer, I noted that the course reputedly was not demanding. He exclaimed that the decision was really about how many things I could do and do well. He added that it would indeed be possible to get by with participating passively in Debye's course but that the opportunity to learn from him would not come again. I decided that this advice showed far more character than the other replies. I still sometimes take on too much, but that was an important lesson.

As I was selecting my thesis research, my fascination with light came to the fore. No one in the Chemistry Department was then directing research in spectroscopy. The closest match was the research interests of Si Bauer, who had become interested in vibrational-to-translational energy transfer in small molecules such as  $\text{CO}_2$ . He had learned of Russian experimental work using the optic-acoustic effect, which offered the possibility of exciting individual vibrational modes of a molecule with a chopped, filtered infrared beam and monitoring the time delay between photoexcitation and the resulting pressure pulse, measured by a capacitance microphone. I chose that project.

The research was demanding and often discouraging. The setup had to be designed and assembled. The signal was weaker than we had hoped. We obtained results for two vibrational fundamentals and one combination band of  $\text{CO}_2$ , as well as measurements of the same properties when a small concentration of  $\text{H}_2$  or of  $\text{H}_2\text{O}$  was added to the mixture. Later, it developed that the measurement cell suffered from acoustic resonance problems. With the advent of lasers, much stronger signals were achieved. Today, optic-acoustic measurements have important applications.

In May 1956, I finished my research at Cornell and moved on to the laboratory of Professor Oscar K. Rice at the University of North Carolina in Chapel Hill. My studies condensed from the gas phase to the liquid state, with precise measurements of the shape of the two-solution coexistence curve for highly purified mixtures of cyclohexane and aniline. Rice was one of the finest persons I have ever known. Although he was a scientist's scientist and was sought out by eminent scientists in several different fields of physics and chemistry, he was remarkably unassuming. His group regularly attended the joint Duke–University of North Carolina physics seminar, which met alternately on the two campuses. In keeping with the presence of several scientists specializing in low-temperature phenomena in the Duke Physics Department, many of the seminars had a heavy emphasis on cryogenics.

In the fall of 1957, as I was beginning my search for a longer term appointment, the Russians launched Sputnik. The American public awakened from complacency, and soon scientists were highly valued. The only schools out of the 75 I had contacted that were interested in my qualifications were women's colleges, including several of the best of them. One offer was particularly tempting, but the location of the college made suitable housing difficult to find. I broadened my search.

Mellon Institute of Industrial Research, in Pittsburgh, Pennsylvania, had been founded to encourage research in small industries by providing support facilities that could be shared by members of their in-house research teams. The effort had stagnated, and a panel was formed to recommend ways of revitalizing the Institute. This panel recommended the addition of programs in fundamental research to replace the weaker projects. I contacted several of the new project leaders who had come from Cornell. In November 1958 I became a fellow in solid-state spectroscopy at Mellon Institute.

## TRAPPING MOLECULES IN MATRICES

Early in the twentieth century, it had been suggested that free radicals—highly reactive species that have unpaired electrons—are the carriers of most chemical reactions. Indirect means of detecting them supported this hypothesis. However, because of their high reactivity, their concentration in typical reaction systems was too low for them to be detected. In 1950, the flash photolysis technique was introduced in England by Sir George Porter (1). A flow tube containing the precursor was exposed to a short-lived flash, producing a sudden burst of free radicals. After a predetermined time delay, an analysis flash with a continuous radiation background permitted the resulting absorption spectrum to be recorded on a photographic plate. Weak absorptions could be enhanced by cumulative exposures, and reaction rates could be estimated by varying the time delay. Porter successfully applied the technique to a considerable number of moderate-size molecules, while Gerhard Herzberg and his associates at the National Research Council of Canada explored the spectroscopy of small polyatomic molecules of astrophysical interest.

The photographic plate was poorly suited to infrared observations, and other cumulative detectors for the infrared were not available. Early in 1954, George Pimentel and two of his colleagues at the University of California in Berkeley had a brainstorming session during lunch. They speculated that at very low temperatures diffusion of free radicals present in dilute solid solution in an inert, transparent medium might be inhibited, permitting storage of enough free radicals for direct infrared detection. The rare gases and nitrogen are transparent over the very wide spectral region from the far infrared to the vacuum ultraviolet (UV) (2). Pimentel soon assembled a group of enthusiastic graduate students to test the applicability of matrix isolation—as the technique has become known—for isolating free radicals and observing their infrared spectra.

Among these graduate students was Dolphus E. (Dick) Milligan, a talented young black scientist who had already learned a most important lesson from his first mentor, Professor Henry C. McBay, at Morehouse College in Atlanta. McBay, then a young instructor, became one of the finest chemistry educators in the United States. He had no patience with descriptive, memorized answers, but pushed consistently to have his students answer that all-important question, WHY? McBay once told me that Dick had spent the hours on the train from his home in Birmingham to Atlanta memorizing the names, chemical symbols, and common valence states of the 92 elements then known. Although Dick was a diligent student, his grade on the first freshman chemistry exam was a scant 50%. McBay had asked questions that could not be answered by simple memorization but probed more deeply into proofs, derivations, deductions, and relationships between theory and facts. Dick went to him not to plead for a higher grade but simply to say, “I see what you are doing now. This won’t happen again!” And it never did.

At Berkeley, experiments soon established that at 20 K argon and nitrogen were suitably rigid to be good candidates for isolating free radicals. However, early experiments on photolyzing free-radical precursors were disappointing. When Dick completed his thesis project in 1957, he accepted an appointment as a fellow in solid-state spectroscopy at Mellon Institute. He had some ideas about why those first experiments had failed, and was eager to test them.

Although my first work at Mellon focused on phenomena in the infrared spectra of molecular solids, I was intrigued by Dick’s studies, and soon we began to collaborate. Dick reasoned that the importance of cage recombination had been underestimated. Perhaps some free-radical precursors might have a recombination barrier sufficiently high to prevent recombination of the photofragments. This was soon found to be true for chlorine azide. Dick obtained a beautiful infrared absorption spectrum for the NCl free radical. The absorptions of the two chlorine-isotopic species were fully resolved, with the calculated separation and the requisite 3:1 intensity ratio (3). Later, he discovered that methyl azide also photodecomposed irreversibly in an argon or a nitrogen

matrix, but that the initially formed  $\text{CH}_3\text{N}$  free radical rearranged to form  $\text{CH}_2=\text{NH}$  (4). Dick recognized that isotopic substitution was the gold standard for proving the identification. He was a superb synthetic chemist—an art he had learned in McBay's laboratory, which could afford only a meager stock of chemicals—and synthesized a variety of isotopologues of methyl azide for more detailed study. This study became a collaborative effort.

Often we crowded two or three experiments into our work day. While we were conducting an experiment on methyl azide, one day we felt a need for some coffee. A colleague joined us, and the photolysis of our initial sample continued for a considerably longer time than we had intended. When at last we scanned the resulting deposit, the absorptions of  $\text{CH}_2=\text{NH}$  had almost completely disappeared, and several new peaks appeared. These included moderately strong absorptions of HCN and two prominent, unidentified absorptions. Later experiments using an instrument with an extended spectral range located a third new absorption. Isotopic substitution studies determined that the product was the long-sought species HNC, formed, together with HCN, by  $\text{H}_2$  photodetachment from  $\text{CH}_2=\text{NH}$  (5).

Dick's conception of the importance of cage phenomena went beyond simple recombination. He thought that limited atomic diffusion through typical matrix materials might occur and that other free radicals might be stabilized by migration of at least the lighter atoms through the matrix and their reaction with other species trapped in the solid. This we tested by spectroscopic observations on an  $\text{Ar}:\text{O}_2:\text{HI}$  sample. H atoms created by photodecomposition of the HI formed sufficient  $\text{HO}_2$ , an exceptionally important free radical in atmospheric and combustion chemistry, for detection of all three of its vibrational fundamentals (6). Isotopic substitution experiments confirmed its identity and demonstrated that the molecule possesses two nonequivalent O atoms, rather than having the isosceles-triangle configuration obtained in early theoretical calculations.

We had term appointments at Mellon Institute, and in 1962 I accepted a career-conditional appointment in the Surface Chemistry Section at the National Bureau of Standards (NBS) in Washington, DC. During the late 1950s NBS had hosted an active program of free-radical studies, inspired by the possibility that free radicals stored in a solid environment might lead to the development of a new rocket fuel. That program, which had ended shortly before I was hired, revitalized chemistry at NBS. The Surface Chemistry Section was led by Ralph Klein and Milton Scheer, who had studied atomic reactions in solids during the Free Radicals Program and continued to be keenly interested in the topic.

Shortly before I was to leave for Washington, tragedy struck the Milligan family. Their oldest child, Deborah, was a beautiful, bright little girl, but had from infancy suffered from severe asthma. One week after she entered first grade, she was hospitalized with pneumonia, which worsened until she stopped breathing. A tracheotomy was performed—but too late. There was irreversible brain damage, and she died. Dick never fully recovered from this devastating blow.

In April 1963, Dick joined another group at NBS. Less than a year later, he transferred to the Surface Chemistry Section. Our new studies soon began to bear fruit. In 1960, George Pimentel and two of his Berkeley colleagues had produced HCO by photolyzing HI in solid CO and identified the CO-stretching and bending fundamentals of that important combustion reaction intermediate (7). A third, less intense absorption appeared at  $2488\text{ cm}^{-1}$ , well below the accepted range for CH-stretching fundamentals (8). We obtained a sufficiently large sample of CO enriched to 56% in  $^{13}\text{C}$  to obtain the spectrum of  $\text{H}^{13}\text{CO}$ . Spectral analysis strongly supported assignment of the absorption at  $2488\text{ cm}^{-1}$  to the CH-stretching fundamental of HCO. Many other free radicals have since been found to have vibrational fundamentals at atypical frequencies.

Although the position of the ground-state bending fundamental of  $\text{CF}_2$  had long been known, the two stretching fundamentals of that species had never been identified. Dick learned of the synthesis of difluorodiazirine,  $\text{CF}_2\text{N}_2$ , potentially a good source of  $\text{CF}_2$  for matrix-isolation studies.

A sample was obtained, and two very intense CF-stretching absorptions appeared on mercury-arc photolysis of an Ar:CF<sub>2</sub>N<sub>2</sub> deposit. Much weaker absorptions consistently appeared slightly below each of the two prominent peaks. We proposed that these two absorptions were contributed by <sup>13</sup>CF<sub>2</sub> (9), but that assignment was disputed.

Shortly thereafter, we learned of the synthesis of cyanogen azide, N<sub>3</sub>CN, which we then successfully prepared. We obtained the primary photoproduct, NCN, in almost quantitative yield. Its antisymmetric stretching fundamental appeared considerably below the position typical for a C=N stretching vibration (10, 11). Secondary photolysis of NCN also occurred, yielding the previously unknown species CNN (12). Photolysis of N<sub>3</sub>CN in a CO matrix or of an Ar:CO:N<sub>3</sub>CN deposit gave new absorptions that were assigned to CCO (13). Norman Moll and Warren Thompson, of Case Institute of Technology, had also identified CCO in infrared studies of the matrix-isolated products of C<sub>3</sub>O<sub>2</sub> that had been passed through a radiofrequency discharge, and became coauthors of our paper. At Berkeley, Thompson had participated in the first infrared identification of HCO. Since 1988, he has collaborated in most of the experiments conducted in my laboratory. The argon-matrix results suggested that photolysis of NCN initially produced carbon atoms, which could either react with the N<sub>2</sub> molecule at the site of their photoproduction or migrate through the matrix and react with other species. This new avenue to carbon-atom production was then applied to many other systems—among them the reaction of <sup>13</sup>C with F<sub>2</sub>, confirming our earlier assignment of the two stretching fundamentals of <sup>13</sup>CF<sub>2</sub> (14).

Radiation in the vacuum-UV spectral region is required to sever most chemical bonds. We were exceptionally fortunate to have at NBS world leaders in vacuum-UV photochemistry, including Pierre Ausloos, Hideo Okabe, and Jim McNesby. Much of the development of vacuum-UV sources had occurred in their laboratories, and they were quite familiar with lamp-development efforts elsewhere. Especially well adapted to our experiments was the microwave-powered hydrogen discharge lamp designed by Warneck (15), which was an excellent source of 122-nm Lyman- $\alpha$  radiation. We first used this lamp for the photolysis of matrix-isolated NH<sub>3</sub>, for which we observed two vibrational fundamentals, one of them for the first time (16).

Studies of the vacuum-UV photolysis of methane were next on our priority list. A landmark gas-phase flash photolysis study by Herzberg (17) had yielded electronic spectral data for both the CH<sub>2</sub> and CH<sub>3</sub> free radicals, but among the many remaining questions was whether ground-state CH<sub>3</sub> is planar or a trigonal pyramid. Herzberg observed a hot band in the spectrum of CD<sub>3</sub>, implying that its symmetric deformation fundamental lies near 450 cm<sup>-1</sup>. In contrast, Andrews & Pimentel (18, 19) assigned an absorption at 730 cm<sup>-1</sup> to the symmetric deformation of CH<sub>3</sub> produced in an argon matrix by the Li + CH<sub>3</sub>Br or CH<sub>3</sub>I reaction. The lower frequency spectral region was obscured, preventing detection of CD<sub>3</sub>. If this fundamental of CH<sub>3</sub> lies at 730 cm<sup>-1</sup>, its CD<sub>3</sub> counterpart should appear near 550 cm<sup>-1</sup>, 100 cm<sup>-1</sup> above Herzberg's value. Typical magnitudes of free-radical matrix shifts had not yet been established. Gas-phase studies (20, 21) of the 123.6-nm photolysis of deuterium-enriched methanes had indicated that the predominant product was CH<sub>2</sub>, which we expected to observe. Because some CH<sub>3</sub> was also produced in the gas-phase studies, measurements on the CH<sub>3</sub>-*d*<sub>n</sub> species could also be possible. In our experiments on the 123.6- and 122-nm photolysis of Ar:CH<sub>4</sub> samples (22), only the absorption of acetylene appeared near 730 cm<sup>-1</sup>, but a prominent, structured absorption appeared at 619 cm<sup>-1</sup>. A sharper absorption appeared at 611 cm<sup>-1</sup> in the N<sub>2</sub> matrix experiments, with three lower frequency counterparts in studies of CH<sub>3</sub>-*d*<sub>n</sub> samples. This behavior requires that the carrier of the absorption possess three symmetrically equivalent hydrogen atoms. The position of the lowest frequency absorption corresponded well with that reported by Herzberg for  $\nu_2$  of ground-state CD<sub>3</sub>. The isotopic shift on full deuterium substitution is approximately 10 cm<sup>-1</sup> greater than that calculated for the harmonic vibration, requiring dominance of the quartic term in the vibrational potential. This

can happen only for a non-totally symmetric vibration, implying that  $\text{CH}_3$  is planar. Riveros (23) later obtained a very good least-squares fit of the observed  $\text{CH}_3$ - $d_n$  vibrational frequencies to a suitable quartic potential.

Subsequently, Tan & Pimentel (24) refined the earlier measurements on the matrix-isolated  $\text{CH}_3\text{X}$  ( $\text{X} = \text{Br}, \text{I}$ ) + Li reaction products and concluded that the product was not the isolated  $\text{CH}_3$  radical but its complex with the LiX species. Moreover, Tan and coworkers (25) used a rapid-scan infrared spectrometer to observe the out-of-plane deformation fundamentals of the gas-phase  $\text{CH}_3$ - $d_n$  species, produced by flash photolysis of the corresponding isotopologue of  $\text{CH}_3\text{I}$ . The observed vibrational frequencies were only a few  $\text{cm}^{-1}$  from those reported in our studies of the vacuum-UV photolysis of matrix-isolated methane- $d_n$ .  $\text{CH}_2$  was not observed in our experiments, consistent with cage recombination of  $\text{CH}_2 + \text{H}_2$ , also inferred from other experiments by Moll & Thompson (26).

We also studied the vacuum-UV photolysis of matrix-isolated acetylene (27). A band system with origin at 520.6 nm in the argon-matrix observations had been attributed to the Swan bands of triplet  $\text{C}_2$ . Large disparities between both the upper- and lower-state vibrational spacings and those of the Swan bands had been rationalized as a so-called matrix effect. We confirmed that the carrier of these bands was a species of formula  $\text{C}_2$ , but found that in the argon matrix, as in the gas phase (28), the ground state of  $\text{C}_2$  was the singlet molecule. The puzzle remained to be solved.

In 1968, we attended the Gordon Research Conference on Infrared Spectroscopy. Gerhard Herzberg was sitting in the front row when we discussed the Swan band disparity and noted the close correspondence of the vibrational spacings of our argon-matrix bands with those of a new band system that Albin Lagerqvist and he had tentatively attributed to  $\text{C}_2^-$  (29). With his encouragement, we tested their hypothesis by observing the spectrum when a small concentration of cesium atoms, an excellent source of photoelectrons, was added to the deposit. Cesium is notoriously difficult to handle in the lab, but our colleagues Milt Scheer and Joe Fine had developed a clean, relatively trouble-free technique for depositing them (30). Our results strongly supported the  $\text{C}_2^-$  assignment (31). The story of this discovery is related in greater detail elsewhere (32).

Dick and I had both matured in our understanding of the principles and practice of free-radical spectroscopy. Our discoveries during the next few years included the following:

- Identification and assignment of the absorptions corresponding to the hydrocarbon flame bands of HCO (33).
- Study of the reaction of OH with a CO matrix and assignment of the infrared spectrum of the resulting *cis*- and *trans*-HOCO free radicals (34).
- Identification of infrared absorptions of  $\text{ClHCl}^-$  (35) and  $\text{BrHBr}^-$  (36), formed as a result of charge-transfer interaction, and understanding of the role played by charge transfer in their formation (37).
- Detection of  $\text{CCl}_3^+$ , the first cation to be observed in a rare-gas matrix (38). Our colleague Henry Rosenstock had been working on an early edition of tables of ionization energies (39) and shared a preprint with us. The realization that the ionization energy of  $\text{CCl}_3$  was well below the energy of 122-nm radiation led to this identification.
- The reassignment to  $\text{HAr}_n^+$  ( $n = 2, 4, \text{ or } 6$ ) (40) of an absorption initially attributed to H atoms trapped in interstitial sites in the argon lattice (41).

In early 1973, Donald Ramsay, at the National Research Council of Canada in Ottawa, inquired whether we had any recent observations on HNO. He had firm evidence that the NH-stretching and the bending fundamentals of HNO should be reassigned at 2685 and 1500  $\text{cm}^{-1}$ , respectively (42). Such a low NH-stretching frequency would be quite unusual. We decided to codeposit an Ar:NO mixture with an Ar:H<sub>2</sub> mixture that had been passed through a microwave discharge to generate H atoms. A very prominent new absorption appeared at 1563  $\text{cm}^{-1}$ , the undisputed



position of the NO-stretching fundamental of HNO, and less intense absorptions appeared near the positions of the two newly identified gas-phase band centers. Other isotopologues of HNO could readily be prepared and their spectra analyzed to provide a definitive assignment. [Years later, the peaks previously attributed to HNO were reassigned to nitrosomethanol (43, 44), formed by photoisomerization of CH<sub>3</sub>ONO used as the HNO source.] Tragically, just before the galley proofs of our HNO paper (45) arrived, Dick died.

My first experiments after losing my long-time colleague attempted to form the vinyl radical by adding H atoms to acetylene trapped in solid argon. Although a good yield of HCC, first identified in our 122-nm photolysis of Ar:C<sub>2</sub>H<sub>2</sub> samples (27), resulted, the intensity of the single previously identified absorption of vinyl was unchanged. When instead D atoms were generated, no deuterium-enriched product appeared, and when pure argon was discharged, the yield of HCC was just as high (46).

The consistently good yield of HCC from C<sub>2</sub>H<sub>2</sub> interacting with excited argon atoms pointed my research in a unique direction. Application of this modified discharge sampling technique to other small molecules followed. Formation of all the observed products was energetically possible in the 11.5- to 11.8-eV range of the first excited states of argon atoms, clearly demonstrating that backstreaming of molecules into the discharge region—which would result in extensive fragmentation—is minimal.

Another series of modified discharge sampling experiments followed in which the discharge-produced reactant was the F atom. For these studies an alumina discharge tube was used, and a dilute Ar:NF<sub>3</sub> mixture was passed through the microwave discharge. The absorptions of NF and of NF<sub>2</sub> obscured relatively little of the product spectrum. F atoms readily add to some small molecules, including CO (47), O<sub>2</sub> (48), and CF<sub>3</sub>X (X = Cl, Br, I) (49). However, when the reactant molecule contains an H atom, HF is often abstracted. When reaction occurs in the space between the end of the discharge tube and the cryogenic surface, isolated free radicals and HF molecules result. Reaction of F atoms in the solid instead produces the complex of HF with the free radical. In studies of the F + CH<sub>4</sub> reaction, absorptions both of CH<sub>3</sub> and of the CH<sub>3</sub>···HF complex appeared (50). However, when the reactant was CH<sub>3</sub>X, the direction of approach of the F atom in the solid was important, and both CH<sub>3</sub>XF and the F···HCH<sub>2</sub>X complex were formed (51). A detailed survey of the F-atom reaction studies is given in a review paper (52).

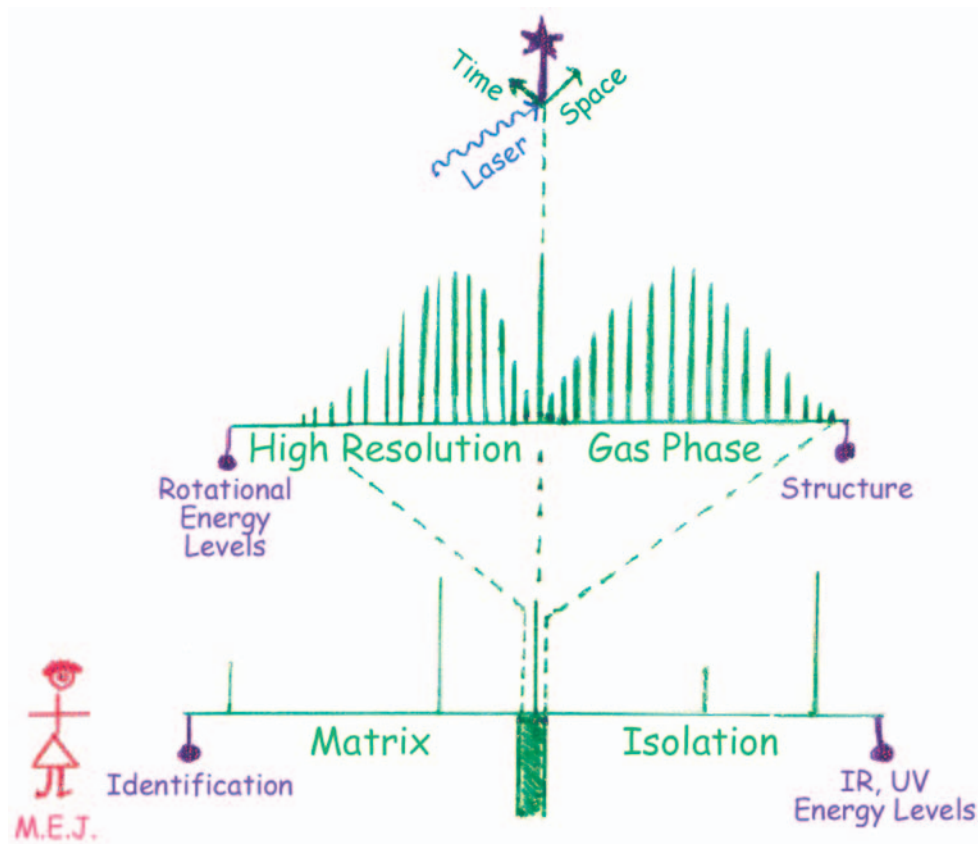
A step-function increase in my infrared capabilities occurred when we acquired a high-resolution Fourier transform infrared spectrometer. Because this instrument included a sample compartment with multiple observation ports, the experimental setups for both my matrix-isolation experiments and the high-resolution gas-phase studies of my colleagues could be permanently stationed. The signal-to-noise ratio and resolution were greatly improved, and the near-infrared spectral region became accessible. Because ground-state infrared bands of HCC with Π symmetry are strongly perturbed by levels of that vibronic symmetry in the low-lying  $\tilde{A}^2\Pi$  electronic state, over 50 absorptions of HCC appeared between 3000 and 8000 cm<sup>-1</sup> (53)!

A second crucial development was the acquisition of a continuous-transfer liquid helium cryostat, which permitted the development of a capability for neon-matrix studies. The measurements for HCC were repeated using a neon matrix, and a detailed assignment was proposed (54). Concurrently, Yen-Chu Hsu and her colleagues in Taipei were conducting laser-excited fluorescence studies of gas-phase HCC (55). Their gas-phase frequencies and proposed assignments agreed well with ours. A few years later, Tarroni & Carter (56) conducted high-level ab initio calculations on HCC and its isotopologues. Their calculated positions and intensities for the near-infrared HCC and DCC absorptions between 2000 and 9000 cm<sup>-1</sup> agreed closely with the neon-matrix observations (57).

## SPECTRA OF MOLECULAR IONS

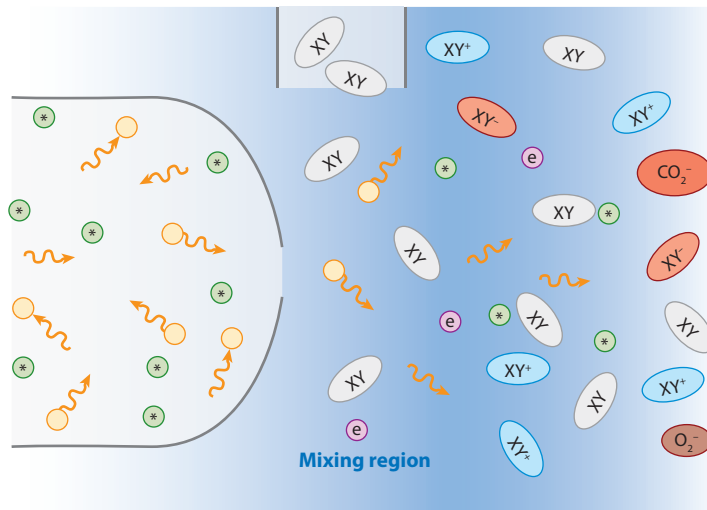
The Mount Everest of my research has long been observing the spectra of small molecular ions. **Figure 1**, sketched to introduce a talk on free radicals, applies equally well to my role in the ion studies. Small molecular ions play important roles in many high-energy processes, including those of astrophysical systems, high-speed flight, and combustion. However, many small molecular ions have a significant probability of reacting on a single collision with another molecule. The corresponding probability for a typical free-radical reaction is smaller by a factor of 100 or 1000. Unlike mass spectrometers, lasers are well suited to remote sensing, but they have a limited range of tunability. If the species is first identified in a neon or argon matrix, the most suitable laser can be selected and tuned to the appropriate spectral region for more detailed gas-phase studies or for remote sensing.

Neon-matrix experiments are key to the study of molecular ions. Many small molecular ions form complexes with argon and the heavier rare gases, resulting in significant shifts in some of their ground-state vibrational fundamentals (58). Although complexation with neon and helium also may occur, usually these complexes are comparatively weakly bound. The first ionization energy of many small molecules is greater than the effective energy limit of 11.8 eV when argon



**Figure 1**

How matrix isolation helps in obtaining ground-state molecular properties for use in studies of chemical reaction systems.



**Figure 2**

Processes that occur in the discharge tube and on the introduction of the molecule XY into the mixing region downstream from the pinhole. The metastable excited rare-gas atoms are shown as green circles with an asterisk in the middle. Rare-gas atoms excited to the two levels with short radiative lifetimes are depicted by gold circles. A sine wave (which designates a photon) is emerging from some of these. Gold circles with an arrow pointing inward represent rare-gas atoms that are absorbing free photons emitted by other rare-gas atoms, a process known as radiation trapping. Electrons generated by the ionization of XY are shown as violet circles with a central “e”. Anions formed by electron capture are colored red, orange, or brown.

atoms are used in the modified discharge configuration. For pure neon, the effective energy limit is raised to 16.84 eV. Virtually all molecules have first ionization energies below that value.

**Figure 2** attempts to envision on a molecular scale the processes that occur in the modified discharge configuration. (Compared to molecular dimensions, the size of the two tubes is vastly out of scale.) The pure rare gas—assumed to be either argon or neon—enters through the tube on the left. Most of its atoms are unexcited and have been omitted from the diagram. A small fraction are in one of the first four excited energy levels of the rare gas. Two of these levels are metastable and have very long lifetimes. The mixture of excited neon atoms and photons emerges through the coarse pinhole in the end of the discharge tube. Another tube, shown at the top, introduces the molecule XY, together with a large excess of unexcited rare-gas atoms (not shown), into the cell outside the discharge region. Studies of many systems have demonstrated that only a small fraction of the XY backstreams into the discharge region, where it would be fragmented into X and Y. In the approximately 2.5-cm path through which the mixture passes before it is frozen onto the cryogenic observation surface, just beyond the right border of the figure, a number of processes may occur. XY is subject to photoionization or Penning ionization, forming  $XY^+$ . Cations and anions are isolated in separate sites in the solid deposit, preserving the overall electrical neutrality of the deposit.

Lon Knight, of Furman University, had already succeeded in using excited neon atoms to produce atoms and small molecular ions for electron spin resonance detection (59, 60), and that technique is much more sensitive than is infrared spectroscopy. Warren Thompson, some of whose earlier related accomplishments are noted above, had moved on to the National Science Foundation, and in early 1988 he began a sabbatical leave in my lab. We decided to test the applicability of the modified discharge configuration for stabilization and infrared studies of molecular ions

trapped in a neon matrix. Our test molecule was  $\text{CO}_2$ , which has a first ionization energy of 13.8 eV. The gas-phase band center for  $\nu_3$  of  $\text{CO}_2^+$  had been measured (61) at  $1423.08\text{ cm}^{-1}$ . We observed its counterpart at  $1421.7\text{ cm}^{-1}$  and the  $\nu_3$  absorption of  $\text{CO}_2^-$  at  $1658.3\text{ cm}^{-1}$  (62). Isotopic substitution studies confirmed both identifications. Our part-time collaboration has continued ever since. Warren has contributed greatly to many other ion studies, including those of *cyc*- and *trans*- $\text{O}_4^+$  (63, 64);  $\text{N}_4^+$  (65);  $\text{CO}^+$ ,  $\text{C}_2\text{O}_2^+$ , and  $\text{C}_2\text{O}_2^-$  (66); and  $\text{CO}_4^-$  (67). Our ion studies are discussed in greater detail in two recent reviews (68, 69).

In 1991, Daniel Forney came to my laboratory from the group of John P. Maier at the University of Basel. The next two years were exceptionally productive. Highlights of the research to which Daniel contributed include studies of the spectra of ions derived from  $\text{C}_2\text{H}_2$  (70), HCN (71),  $\text{SO}_2$  (72), and HCOOH (73). The  $\text{SO}_2$  study included the first experimental identification of the  $\nu_3$  fundamental of ground-state  $\text{SO}_2^+$ , later supported by gas-phase threshold photoelectron measurements (74). The spectrum obtained in the HCOOH experiments included prominent absorptions of  $\text{HCO}_2^-$ , also identified in studies of Ne: $\text{H}_2$ : $\text{CO}_2$  mixtures (75). Recent *ab initio* calculations (76) support this identification.

Later, Catherine Lugez, of the University of Paris, further advanced the frontiers of ion spectroscopy by her studies in my laboratory. Noteworthy were her identification of the ylidion isomers of cations derived from the methyl halides (77) and discovery of infrared absorptions of  $\text{NeHF}^+$  (78).

Since the early 1990s, *ab initio* and density functional calculations have matured sufficiently to be of great value for identifying the spectra of molecular reaction intermediates and predicting their properties. Collaborations with Karl Irikura and Russ Johnson, of NIST, have been helpful in interpreting our spectra and in my learning about this new field.

Recent studies of  $\text{NO}_3$  led me to revisit the realm of uncharged free radicals. Eizi Hirota and his colleagues (79–81) thoroughly characterized the gas-phase spectrum of ground-state  $\text{NO}_3$  and definitively ascertained it to possess  $D_{3h}$  symmetry. Because of strong interaction of the ground state with two low-lying excited electronic states, the spectrum includes several prominent combination bands that are still incompletely assigned. In 2007, Stanton (82) applied the multimode coupling model developed by Köppel and coworkers (83) to the infrared spectrum of  $\text{NO}_3$ . The results suggest that the prominent  $\text{NO}_3$  absorption at  $1492\text{ cm}^{-1}$ , long assigned to the  $\nu_3$  fundamental, is instead contributed by a combination band and that  $\nu_3$  should have an extremely weak absorption near  $1000\text{ cm}^{-1}$ . We discovered that a good yield of  $\text{NO}_3$  trapped in solid neon could be obtained by photoexcitation of a Ne: $\text{O}_2$ :NO deposit, making possible the measurement of the infrared spectra for eight isotopologues of  $\text{NO}_3$  (84). Although  $\text{NO}_3^-$  has isotopic shifts characteristic of moderate vibrational interactions (85), the interaction constants derived for  $\text{NO}_3$  are extremely large. Concurrently, Stanton (86) was performing the adiabatic counterpart of his earlier calculations, including determination of the magnitudes of isotopic shifts. Real-time comparison between the results of our experiments and his new calculations was exciting, and the agreement was remarkably good. Using the new synthetic procedure, Helmut Beckers and Helge Willner, of the University of Wuppertal, measured the far-infrared  $\nu_4$  absorption for five isotopologues of  $\text{NO}_3$  trapped in solid neon (87). The position and isotopic shifts agree closely with those predicted by Stanton.

## THE VEEL PROJECT

For some years, typical magnitudes of matrix shifts in infrared absorption maxima from the corresponding gas-phase band centers were unknown. At a high-resolution infrared spectroscopy meeting held at NBS in the summer of 1980, J.W.C. Johns and A.R.W. McKellar, of the National

Research Council of Canada, presented a poster comparing their measured gas-phase infrared band centers with the positions of approximately 20 fundamentals of free radicals trapped in matrices. The agreement was remarkably good. I was excited by this validation of the work Dick and I had conducted over almost 20 years, and resolved to continue comparing gas-phase and matrix frequencies for small free radicals.

The project soon broadened into a detailed compilation of the ground-state spectroscopic properties of small transient molecules. In a year or two, the tables formed an impressive stack, and I took several copies to the International Symposium on Molecular Spectroscopy in Columbus, Ohio, to give to individual researchers who were also concerned with free-radical spectroscopy. Shortly thereafter, I published evaluated gas-phase and inert solid matrix data for the ground-state vibrational fundamentals of approximately 480 covalently bonded transient molecules with from 3 to 16 atoms in the *Journal of Physical and Chemical Reference Data* (88). Comparisons with the positions of the gas-phase band centers were possible for 69 vibrational fundamentals of species trapped in solid neon, 109 in solid argon, and 32 in solid nitrogen.

Morris (“Mo”) Krauss, of NBS, had been conducting ab initio calculations on the uranium oxides. One day, he stopped me in the hall to ask how large I would expect the matrix shift to be for these and other small inorganic molecules. I did not know, but resolved to try to find out. This took shape as a systematic comparison of observed matrix shifts for the ground-state vibrational energy levels of diatomic molecules (89). There followed a review of matrix shifts for the electronic band origins of the low-lying valence states of diatomic molecules (90). In 1994, a third paper reported the magnitudes of ground-state fundamental frequency shifts for diatomic and small polyatomic transient molecules trapped in neon and argon matrices, including a discussion of possible relationships between type of vibration (e.g., stretch, bend) and the magnitude and direction of shift (91).

The 1984 paper (88) attracted the attention of the NBS Office of Standard Reference Data, which was conducting a competition for new data-evaluation proposals. I was encouraged to apply. Although I was initially reluctant, I decided to fit time into a busy schedule to evaluate and compile electronic energy-level data for species with from three to six atoms. The project was originally envisioned to include only relatively high-resolution gas-phase data, but during the proposal review process I was contacted by Mel Robin, of Bell Laboratories, who conditioned his support on the inclusion of low-resolution data such as those obtained from photoelectron spectroscopic studies. I took a deep breath and promised to comply. In later years, I became one of the principal users of such data. The initial electronic energy-level compilation, which included data for approximately 500 molecules, was published in 1988 (92). New data were rapidly accumulating, and the six-atom cutoff omitted much important data for somewhat larger molecules. A supplement published in 1990 (93) included selective extension to molecules that include heavier atoms and to the electronic spectra of species with more than six atoms.

In 1994, Monograph Number 3, *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*, in the series sponsored by the *Journal of Physical and Chemical Reference Data* was published (94). Evaluated data for more than 1550 small polyatomic transient molecules with from 3 to 16 atoms were included. Two supplements have since appeared (95, 96).

The energy-level data from the Monograph provided material for a new database that was initially designed as one of a series for personal computer searching, to be distributed by the NIST Standard Reference Data Office. Because *Vibrational and Electronic Energy Levels of Small Polyatomic Transient Molecules* was a rather ungainly title, some of the younger members of the Standard Reference Data staff, in a playful mood, proposed the name “VEEL.” (Where’s the beef?) It stuck.

In a few years, the Internet took hold, and the floppy-disk versions of the database were phased out in favor of online searches. VEEL became a part of the NIST Chemistry WebBook,

still supported and available online (<http://webbook.nist.gov/chemistry/>). By early 2009, the database included over 4000 molecules.

Periodically, I continue to update the compilation of matrix shifts in ground-state vibrational fundamentals. The least perturbing matrix materials are neon and argon. At the beginning of 2007, 244 comparisons were possible for uncharged and charged species trapped in solid neon. The average deviation of the neon-matrix frequency from the gas-phase one was 0.0%, and the vast majority of the deviations were smaller than 1%. Some 529 comparisons were available for species trapped in an argon matrix. The maximum in the distribution appeared at a deviation (gas – argon) of +0.3%, and its full width at half-maximum spanned approximately 1.2%.

## THE ROAD AHEAD

New information on the vibrational and electronic spectra of small polyatomic transient molecules continues to accumulate rapidly. Despite this progress, our knowledge of the vibrational and electronic energy levels of these species is far from being complete. Even many triatomic molecules may have more than one structure (e.g., HCN, HNC), and for larger molecules the number rapidly escalates. These different structures have different reactivities. Matrix isolation offers a first step to characterizing molecular structures and chemical bonding properties. The vast majority of chemical reactions involve short-lived reaction intermediates. Understanding their properties enhances the possibility of controlling their reactions.

During the past two decades, there has been enormous progress in our ability to predict molecular structures and energy levels using *ab initio* and density functional calculations. Package programs are widely available, and their application often yields results that agree quite well with measured values. Nevertheless, the temptation to replace measurements by computational solutions must be resisted. Gas-phase measurements remain the ultimate standard, but where argon- or neon-matrix data are available, they generally agree considerably more closely with the gas-phase band centers than do values obtained with these package programs (68). Even more sophisticated calculations may have difficulty reproducing experimental results because of such computational problems as inadequate consideration of static and dynamic electron correlation, the occurrence of symmetry breaking, and appreciable interaction with low-lying excited electronic states. The development of computational tools remains a work in progress, best supported by collaborations between the experimental and theoretical communities.

### SUMMARY POINTS

1. Cage recombination is important in determining the products of photolysis or photoionization when molecules are trapped in cryogenic solids. Although molecules are isolated, small atoms may undergo at least limited diffusion and subsequent reaction.
2. When molecules are introduced into the system downstream from the region of a discharge excited in pure argon or neon, ions are formed in sufficient concentration for infrared detection in the solid formed by rapidly freezing the products. Uncharged species also often are formed.
3. Approximate charge neutrality of the solid is necessary to avoid repulsion of ions from the cryogenic surface.

4. Product formation in such a discharge-flow system is governed by the processes that can occur at energies below the first excited states of the argon (11.5 to 11.8 eV) or neon (16.6 to 16.84 eV) atoms excited in the discharge. Extensive fragmentation of the molecule is minimal.
5. Because of the very high reactivity of many small molecular ions, products of binary ion-molecule reactions often contribute prominent absorptions to the spectrum.
6. Comparison of the positions of the ground-state vibrational fundamentals of a large number of small free radicals trapped in a neon or an argon matrix with the positions of the gas-phase band centers yields a distribution for the neon matrix that is sharply peaked at 0.0% deviation. The distribution for an argon matrix is somewhat broader, but most fundamentals lie within 1% of the corresponding gas-phase band centers.

## 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.

## LITERATURE CITED

1. Porter G. 1950. Flash photolysis and spectroscopy: a new method for the study of free radical reactions. *Proc. R. Soc. Lond. A* 200:284–300
2. Whittle E, Dows DA, Pimentel GC. 1954. Matrix isolation method for the experimental study of unstable species. *J. Chem. Phys.* 22:1943
3. Milligan DE. 1961. Infrared spectroscopic study of the photolysis of chlorine azide in solid argon at 4.2 K. *J. Chem. Phys.* 35:372–73
4. Milligan DE. 1961. Infrared spectroscopic study of the photolysis of methyl azide and methyl- $d_3$  azide in solid argon and carbon dioxide. *J. Chem. Phys.* 35:1491–97
5. Milligan DE, Jacox ME. 1963. Infrared spectroscopic evidence for the species HNC. *J. Chem. Phys.* 39:712–15
6. **Milligan DE, Jacox ME. 1963. Infrared spectroscopic evidence for the species HO<sub>2</sub>. *J. Chem. Phys.* 38:2627–31**
7. Ewing GE, Thompson WE, Pimentel GC. 1960. Infrared detection of the formyl radical HCO. *J. Chem. Phys.* 32:927–32
8. Bellamy LJ. 1957. *The Infra-Red Spectra of Complex Molecules*. New York: Wiley
9. Milligan DE, Mann DE, Jacox ME, Mitsch RA. 1964. Infrared spectrum of CF<sub>2</sub>. *J. Chem. Phys.* 41:1199–203
10. Milligan DE, Jacox ME, Comeford JJ, Mann DE. 1965. Infrared spectrum of the free radical NCN. *J. Chem. Phys.* 43:756–57
11. Milligan DE, Jacox ME, Bass AM. 1965. Matrix isolation study of the photolysis of cyanogen azide. The infrared and ultraviolet spectra of the free radical NCN. *J. Chem. Phys.* 43:3149–60
12. Milligan DE, Jacox ME. 1966. Matrix isolation study of the infrared and ultraviolet spectra of the free radical CNN. *J. Chem. Phys.* 44:2850–56
13. Jacox ME, Milligan DE, Moll NG, Thompson WE. 1965. Matrix isolation infrared spectrum of the free radical CCO. *J. Chem. Phys.* 43:3734–46
14. Milligan DE, Jacox ME. 1968. Matrix-isolation study of the reaction of atomic and molecular fluorine with carbon atoms. The infrared spectra of normal and <sup>13</sup>C-substituted CF<sub>2</sub> and CF<sub>3</sub>. *J. Chem. Phys.* 48:2265–71
15. Warneck P. 1974. Heat of formation of HCO radical. *Z. Naturforsch.* 29A:350–51

---

6. Presents evidence for H-atom diffusion through solid argon, forming the first triatomic molecule to be stabilized in a rare-gas matrix.

---

16. Milligan DE, Jacox ME. 1965. Matrix isolation infrared spectrum of the free radical  $\text{NH}_2$ . *J. Chem. Phys.* 43:4487-93
17. Herzberg G. 1961. Spectra and structures of free methyl and free methylene. *Proc. R. Soc. Lond. A* 262:291-317
18. Andrews WLS, Pimentel GC. 1966. Infrared detection of methyl radical in solid argon. *J. Chem. Phys.* 44:2527-28
19. Andrews L, Pimentel GC. 1967. Infrared spectrum of the methyl radical in solid argon. *J. Chem. Phys.* 47:3637-44
20. Mahan BH, Mandal R. 1962. Vacuum ultraviolet photolysis of methane. *J. Chem. Phys.* 37:207-11
21. Ausloos PJ, Gorden R Jr, Lias SG. 1964. Effect of pressure in the radiolysis and photolysis of methane. *J. Chem. Phys.* 40:1854-60
22. **Milligan DE, Jacox ME. 1967. Infrared and ultraviolet spectroscopic study of the products of the vacuum ultraviolet photolysis of methane in Ar and  $\text{N}_2$  matrices. The infrared spectrum of the free radical  $\text{CH}_3$ . *J. Chem. Phys.* 47:5146-56**
23. Riveros JM. 1969. Anharmonicity of the out-of-plane vibration of the methyl radical. *J. Chem. Phys.* 51:1269-70
24. Tan LY, Pimentel GC. 1968. Methyl alkali halides: a new molecular type; infrared spectra by the matrix isolation technique. *J. Chem. Phys.* 48:5202-4
25. Tan LY, Winer AM, Pimentel GC. 1972. Infrared spectrum of gaseous methyl radical by rapid scan spectroscopy. *J. Chem. Phys.* 57:4028-37
26. Moll NG, Thompson WE. 1966. Reactions of carbon atoms with  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{D}_2$  at 4.2°K. *J. Chem. Phys.* 44:2684-86
27. Milligan DE, Jacox ME, Abouaf-Marguin L. 1967. Vacuum ultraviolet photolysis of acetylene in inert matrices. Spectroscopic study of the species  $\text{C}_2^-$ . *J. Chem. Phys.* 46:4562-70
28. Ballik EA, Ramsay DA. 1963. The  $A' \ ^3\Sigma_g^- - X' \ ^3\Pi_u$  band system of the  $\text{C}_2$  molecule. *Astrophys. J.* 137:61-83
29. Herzberg G, Lagerqvist A. 1968. A new spectrum associated with diatomic carbon. *Can. J. Phys.* 46:2363-73
30. Scheer MD, Fine J. 1962. Kinetics of  $\text{Cs}^+$  desorption from tungsten. *J. Chem. Phys.* 37:107-13
31. **Milligan DE, Jacox ME. 1969. Studies of the photoproduction of electrons in inert solid matrices. The electronic spectrum of the species  $\text{C}_2^-$ . *J. Chem. Phys.* 51:1952-55**
32. Jacox ME. 2004. Vibrational and electronic spectra of neutral and ionic combustion reaction intermediates trapped in rare-gas matrices. *Acc. Chem. Res.* 37:727-34
33. **Milligan DE, Jacox ME. 1969. Matrix-isolation study of the infrared and ultraviolet spectra of the free radical HCO. The hydrocarbon flame bands. *J. Chem. Phys.* 51:277-88**
34. Milligan DE, Jacox ME. 1971. Infrared spectrum and structure of intermediates in the reaction of OH with CO. *J. Chem. Phys.* 54:927-42
35. Milligan DE, Jacox ME. 1970. The infrared spectrum of the  $\text{ClHCl}^-$  ion isolated in an argon matrix. *J. Chem. Phys.* 53:2034-40
36. Milligan DE, Jacox ME. 1971. Infrared spectrum of the  $\text{BrHBr}^-$  ion isolated in an argon matrix. *J. Chem. Phys.* 55:2550-60
37. **Jacox ME. 1978. The stabilization and spectra of free radicals and molecular ions in rare-gas matrices. *Rev. Chem. Intermed.* 2:1-36**
38. **Jacox ME, Milligan DE. 1971. Matrix-isolation study of the vacuum-ultraviolet photolysis of chloroform. Infrared spectra of the  $\text{CCl}_3^+$ ,  $\text{HCCl}_2^+$ , and  $\text{HCCl}_2^-$  molecular ions. *J. Chem. Phys.* 54:3935-50**
39. Franklin JL, Dillard JG, Rosenstock HM, Herron JT, Draxl K, et al. 1969. *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions*. Washington, DC: Natl. Bur. Stand. U.S.
40. Milligan DE, Jacox ME. 1973. Infrared spectroscopic evidence for the stabilization of  $\text{HAr}_n^+$  in solid argon at 14 K. *J. Mol. Spectrosc.* 46:460-69
41. Bondybey VE, Pimentel GC. 1972. Infrared absorptions of interstitial hydrogen atoms in solid argon and krypton. *J. Chem. Phys.* 56:3832-36

---

22. Demonstrates the planarity of ground-state  $\text{CH}_3$ .

---



---

31. Presents support for identification of first gas-phase diatomic anion; develops method for stabilizing anions in rare-gas matrices.

---



---

33. Uses ground- and excited-state matrix data for assignment of a complicated gas-phase UV band system.

---



---

37. Demonstrates the role of charge transfer in cation production; discussion of interactions of excited argon atoms can be extended to neon atoms.

---



---

38. Presents first use of photoionization for cation production in rare-gas matrices.

---



---

**51. Demonstrates product dependency on direction of attack of an F atom on a molecule trapped in solid argon.**

---



---

**62. Demonstrates the stabilization of CO<sub>2</sub><sup>+</sup> and CO<sub>2</sub><sup>-</sup> in solid neon following interaction with excited neon atoms and their resonance radiation.**

---



---

**63. Illustrates the prevalence of ion-molecule reactions in neon-matrix experiments.**

---

42. Clough PN, Thrush BA, Ramsay DA, Stamper JG. 1973. Vibrational frequencies of HNO. *Chem. Phys. Lett.* 23:155–56
43. Müller RP, Huber JR. 1983. Reversible, light-induced isomerization of matrix-isolated molecules—nitrosomethanol. *J. Phys. Chem.* 87:2460–62
44. Müller RP, Huber JR, Hollenstein H. 1984. Photochemical preparation of nitrosomethanol: vibrational frequencies, force field, and normal coordinate analysis of the *cis* and *trans* isomers. *J. Mol. Spectrosc.* 104:209–25
45. Jacox ME, Milligan DE. 1973. Matrix isolation study of the reaction of H atoms with NO. The infrared spectrum of HNO. *J. Mol. Spectrosc.* 48:536–59
46. Jacox ME. 1975. Matrix isolation study of the vibrational spectrum and structure of HC<sub>2</sub>. *Chem. Phys.* 7:424–32
47. Jacox ME. 1980. The reaction of F atoms with CO in an argon matrix. Vibrational and electronic spectra of FCO. *J. Mol. Spectrosc.* 80:257–71
48. Jacox ME. 1980. The reaction of F atoms with O<sub>2</sub> in an argon matrix. Vibrational spectra and photochemistry of FO<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>. *J. Mol. Spectrosc.* 84:74–88
49. Jacox ME. 1980. Matrix isolation study of the reaction of fluorine atoms with the trifluoromethyl halides. Infrared spectroscopic evidence for the CF<sub>3</sub>X<sup>•</sup> free radicals. *Chem. Phys.* 51:69–76
50. Jacox ME. 1979. The reaction of F atoms with methane in an argon matrix. *Chem. Phys.* 42:133–48
- 51. Jacox ME. 1985. Reaction of F atoms with the methyl halides. Vibrational spectra of CH<sub>3</sub>X<sup>•</sup> and of H<sub>2</sub>CX<sup>•</sup>-HF trapped in solid argon. *J. Chem. Phys.* 83:3255–67**
52. Jacox ME. 1985. Spectroscopy and photochemistry of free radicals formed by the reaction of F atoms with small molecules. *Rev. Chem. Intermed.* 6:77–120
53. Jacox ME, Olson WB. 1987. The  $\tilde{A}^2\Pi - \tilde{X}^2\Sigma^+$  transition of HC<sub>2</sub> isolated in solid argon. *J. Chem. Phys.* 86:3134–42
54. Forney D, Jacox ME, Thompson WE. 1995. The infrared and near infrared spectra of HCC and DCC trapped in solid neon. *J. Mol. Spectrosc.* 170:178–214
55. Hsu Y-C, Shiu Y-J, Lin C-M. 1995. Laser-induced fluorescence spectroscopy of CCH ( $\tilde{X}^2\Sigma^+$ ) in vibrationally excited levels up to 4500 cm<sup>-1</sup>. *J. Chem. Phys.* 103:5919–30
56. Tarroni R, Carter S. 2003. Theoretical calculation of vibronic levels of C<sub>2</sub>H and C<sub>2</sub>D to 10 000 cm<sup>-1</sup>. *J. Chem. Phys.* 119:12878–89
57. Tarroni R, Carter S. 2004. Theoretical calculation of absorption intensities of C<sub>2</sub>H and C<sub>2</sub>D. *Mol. Phys.* 102:2167–79
58. Bieske EJ, Dopfer O. 2000. High-resolution spectroscopy of cluster ions. *Chem. Rev.* 100:3963–98
59. Knight LB Jr, Steadman J. 1982. An experimental procedure for ESR studies of rare gas matrix isolated molecular cation radicals: <sup>12</sup>CO<sup>+</sup>, <sup>13</sup>CO<sup>+</sup>, <sup>14</sup>NH<sub>3</sub><sup>+</sup>, and <sup>15</sup>NH<sub>3</sub><sup>+</sup>. *J. Chem. Phys.* 77:1750–56
60. Knight LB Jr. 1986. ESR investigations of molecular cation radicals in neon matrices at 4 K: generation, trapping, and ion-neutral reactions. *Acc. Chem. Res.* 19:313–21
61. Kawaguchi K, Yamada C, Hirota E. 1985. Diode laser spectroscopy of the CO<sub>2</sub><sup>+</sup> n<sub>3</sub> band using magnetic field modulation of the discharge plasma. *J. Chem. Phys.* 82:1174–77
- 62. Jacox ME, Thompson WE. 1989. The vibrational spectra of molecular ions isolated in solid neon. I. CO<sub>2</sub><sup>+</sup> and CO<sub>2</sub><sup>-</sup>. *J. Chem. Phys.* 91:1410–16**
- 63. Thompson WE, Jacox ME. 1989. The vibrational spectra of molecular ions isolated in solid neon. II. O<sub>4</sub><sup>+</sup> and O<sub>4</sub><sup>-</sup>. *J. Chem. Phys.* 91:3826–37**
64. Jacox ME, Thompson WE. 1994. Evidence for the stabilization of rectangular O<sub>4</sub><sup>+</sup> in solid neon. *J. Chem. Phys.* 100:750–51
65. Thompson WE, Jacox ME. 1990. The vibrational spectra of molecular ions isolated in solid neon. III. N<sub>4</sub><sup>+</sup>. *J. Chem. Phys.* 93:3856–62
66. Thompson WE, Jacox ME. 1991. The vibrational spectra of molecular ions isolated in solid neon. VII. CO<sup>+</sup>, C<sub>2</sub>O<sub>2</sub><sup>+</sup>, and C<sub>2</sub>O<sub>2</sub><sup>-</sup>. *J. Chem. Phys.* 95:735–45
67. Jacox ME, Thompson WE. 1991. The vibrational spectra of molecular ions isolated in solid neon. VI. CO<sub>4</sub><sup>-</sup>. *J. Phys. Chem.* 95:2781–87
68. Jacox ME. 2002. The spectroscopy of molecular reaction intermediates trapped in the solid rare gases. *Chem. Soc. Rev.* 31:108–15

69. Jacox ME. 2007. The infrared spectroscopy of the products of ion-molecule reactions trapped in the solid rare gases. *Int. J. Mass Spectrom.* 267:268–76
70. Forney D, Jacox ME, Thompson WE. 1992. The vibrational spectra of molecular ions isolated in solid neon. VIII. HCCH<sup>+</sup> and HCC<sup>-</sup>. *J. Mol. Spectrosc.* 153:680–91
71. Forney D, Thompson WE, Jacox ME. 1992. The vibrational spectra of molecular ions isolated in solid neon. IX. HCN<sup>+</sup>, HNC<sup>+</sup>, and CN<sup>-</sup>. *J. Chem. Phys.* 97:1664–74
72. Forney D, Kellogg CB, Thompson WE, Jacox ME. 2000. The vibrational spectra of molecular ions isolated in solid neon. XVI. SO<sub>2</sub><sup>+</sup>, SO<sub>2</sub><sup>-</sup>, and (SO<sub>2</sub>)<sub>2</sub><sup>-</sup>. *J. Chem. Phys.* 113:86–97
73. Forney D, Jacox ME, Thompson WE. 2003. The infrared spectra of *t*-HOCO, HCOOH<sup>+</sup>, and HCO<sub>2</sub><sup>-</sup> trapped in solid neon. *J. Chem. Phys.* 119:10814–23
74. Mo Y, Yang J, Chen G. 2004. Zero kinetic energy photoelectron study of SO<sub>2</sub><sup>+</sup> ( $\tilde{X}^2A_1$ ) using coherent extreme ultraviolet radiation. *J. Chem. Phys.* 120:1263–70
75. Jacox ME, Thompson WE. 2003. Infrared spectra of HOCO<sup>+</sup> and of the complex of H<sub>2</sub> with CO<sub>2</sub><sup>-</sup> trapped in solid neon. *J. Chem. Phys.* 119:10824–31
76. Krekeler C, Mladenovic M, Botschwina P. 2005. A theoretical investigation of the vibrational states of HCO<sub>2</sub><sup>-</sup> and its isotopomers. *Phys. Chem. Chem. Phys.* 7:882–87
77. Lugez CL, Forney D, Jacox ME, Irikura KK. 1997. The vibrational spectra of molecular ions isolated in solid neon. XIV. CH<sub>3</sub>F<sup>+</sup>, CH<sub>3</sub>Cl<sup>+</sup>, CH<sub>3</sub>Br<sup>+</sup>, and their ylidion isomers. *J. Chem. Phys.* 106:489–503
78. Lugez CL, Jacox ME, Johnson RD III. 1999. The vibrational spectra of molecular ions isolated in solid neon. XV. Infrared spectroscopic evidence for NeHF<sup>+</sup> and HFFH<sup>+</sup>. *J. Chem. Phys.* 110:5037–46
79. Ishiwata T, Tanaka I, Kawaguchi K, Hirota E. 1985. Infrared diode laser spectroscopy of the NO<sub>3</sub>  $\nu_3$  band. *J. Chem. Phys.* 82:2196–205
80. Hirota E, Kawaguchi K, Ishiwata T, Tanaka I. 1991. Vibronic interactions in the NO<sub>3</sub> radical. *J. Chem. Phys.* 95:771–75
81. Kawaguchi K, Ishiwata T, Hirota E, Tanaka I. 1998. Infrared spectroscopy of the NO<sub>3</sub> radical. *Chem. Phys.* 231:193–98
82. Stanton JF. 2007. On the vibronic level structure in the NO<sub>3</sub> radical. I. The ground electronic state. *J. Chem. Phys.* 126:134309
83. Köppel H, Domcke W, Cederbaum LS. 1984. Multimode molecular dynamics beyond the Born-Oppenheimer approximation. *Adv. Chem. Phys.* 57:59–246
84. Jacox ME, Thompson WE. 2008. The infrared spectroscopy and photochemistry of NO<sub>3</sub> trapped in solid neon. *J. Chem. Phys.* 129:204306
85. Forney D, Thompson WE, Jacox ME. 1993. The vibrational spectra of molecular ions isolated in solid neon. XI. NO<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>. *J. Chem. Phys.* 99:7393–403
86. Stanton JF. 2009. On the vibronic level structure in the NO<sub>3</sub> radical: II. Adiabatic calculation of the infrared spectrum. *Mol. Phys.* 107:1059–75
87. Beckers H, Willner H, Jacox ME. 2009. Conflicting observations resolved by a far IR and UV/Vis study of the NO<sub>3</sub> radical and of O<sub>2</sub> complexes with NO isolated in Ne matrices. *ChemPhysChem* 10:706–10
88. Jacox ME. 1984. Ground-state vibrational energy levels of polyatomic transient molecules. *J. Phys. Chem. Ref. Data* 13:945–1068
- 89. Jacox ME. 1985. Comparison of the ground state vibrational fundamentals of diatomic molecules in the gas phase and in inert solid matrices. *J. Mol. Spectrosc.* 113:286–301**
90. Jacox ME. 1987. Comparison of the electronic energy levels of diatomic molecules in the gas phase and in inert solid matrices. *J. Mol. Struct.* 157:43–59
91. Jacox ME. 1994. The vibrational energy levels of small transient molecules isolated in neon and argon matrices. *Chem. Phys.* 189:149–70
92. Jacox ME. 1988. Electronic energy levels of small polyatomic transient molecules. *J. Phys. Chem. Ref. Data* 17:269–511
93. Jacox ME. 1990. Vibrational and electronic energy levels of polyatomic transient molecules. Supplement 1. *J. Phys. Chem. Ref. Data* 19:1387–546

---

89. Evaluates frequency shifts of ground-state fundamentals of inorganic diatomics trapped in various inert matrices.

---

94. Jacox ME. 1994. *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*. J. Phys. Chem. Ref. Data Monogr. 3. Washington, DC: Am. Chem. Soc./Am. Inst. Phys./Natl. Inst. Standards Technol. 461 pp.
95. Jacox ME. 1998. Vibrational and electronic energy levels of polyatomic transient molecules. Supplement A. *J. Phys. Chem. Ref. Data* 27:115–393
96. Jacox ME. 2003. Vibrational and electronic energy levels of polyatomic transient molecules. Supplement B. *J. Phys. Chem. Ref. Data* 32:1–441



# Contents

On Walking in the Footprints of Giants <i>Marilyn E. Jacox</i> .....	1
Novel Computational Methods for Nanostructure Electronic Structure Calculations <i>Lin-Wang Wang</i> .....	19
Hyper-Raman Scattering by Molecular Vibrations <i>Anne Myers Kelley</i> .....	41
Chemistry of Hofmeister Anions and Osmolytes <i>Yanjie Zhang and Paul S. Cremer</i> .....	63
Tuned Range-Separated Hybrids in Density Functional Theory <i>Roi Baer, Ester Livshits, and Ulrike Salzner</i> .....	85
Subcellular Dynamics and Protein Conformation Fluctuations Measured by Fourier Imaging Correlation Spectroscopy <i>Eric N. Senning and Andrew H. Marcus</i> .....	111
Oxide Surface Science <i>Ulrike Diebold, Shao-Chun Li, and Michael Schmid</i> .....	129
The Diabatic Picture of Electron Transfer, Reaction Barriers, and Molecular Dynamics <i>Troy Van Voorhis, Tim Kowalczyk, Benjamin Kaduk, Lee-Ping Wang, Chiao-Lun Cheng, and Qin Wu</i> .....	149
Electrostatics of Strongly Charged Biological Polymers: Ion-Mediated Interactions and Self-Organization in Nucleic Acids and Proteins <i>Gerard C.L. Wong and Lois Pollack</i> .....	171
Dynamics on the Way to Forming Glass: Bubbles in Space-Time <i>David Chandler and Juan P. Garrahan</i> .....	191
Functional Motifs in Biochemical Reaction Networks <i>John J. Tyson and Béla Novák</i> .....	219

Electronic Properties of Nonideal Nanotube Materials: Helical Symmetry Breaking in DNA Hybrids <i>Slava V. Rotkin</i> .....	241
Molecular Structural Dynamics Probed by Ultrafast X-Ray Absorption Spectroscopy <i>Christian Bressler and Majed Chergui</i> .....	263
Statistical Mechanical Concepts in Immunology <i>Arup K. Chakraborty and Andrej Košmrlj</i> .....	283
Biological Cluster Mass Spectrometry <i>Nicholas Winograd and Barbara J. Garrison</i> .....	305
Bio-Enabled Synthesis of Metamaterials <i>Christopher C. DuFort and Bogdan Dragnea</i> .....	323
Superresolution Imaging using Single-Molecule Localization <i>George Patterson, Michael Davidson, Suliana Manley, and Jennifer Lippincott-Schwartz</i> .....	345
From Artificial Atoms to Nanocrystal Molecules: Preparation and Properties of More Complex Nanostructures <i>Charina L. Choi and A. Paul Alivisatos</i> .....	369
Transition-Path Theory and Path-Finding Algorithms for the Study of Rare Events <i>Weinan E and Eric Vanden-Eijnden</i> .....	391
Complex Fluids: Probing Mechanical Properties of Biological Systems with Optical Tweezers <i>H. Daniel Ou-Yang and Ming-Tzo Wei</i> .....	421
Enhanced Sampling of Nonequilibrium Steady States <i>Alex Dickson and Aaron R. Dinner</i> .....	441
Fluctuations in Biological and Bioinspired Electron-Transfer Reactions <i>Spiros S. Skourtis, David H. Waldeck, and David N. Beratan</i> .....	461

## Indexes

Cumulative Index of Contributing Authors, Volumes 57–61 .....	487
Cumulative Index of Chapter Titles, Volumes 57–61 .....	490

## Errata

An online log of corrections to *Annual Review of Physical Chemistry* articles may be found at <http://physchem.annualreviews.org/errata.shtml>