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(photo from NIST archives)

Marilyn E. Jacox

A Brief Scientific Biography[†]

Marilyn Esther Jacox was born April 26, 1929, in Utica, New York, the daughter of Grant Burlingame and Mary Elizabeth (Dunn) Jacox. After her graduation from the Utica Free Academy in 1947, she attended Utica College of Syracuse University, an off-campus branch of Syracuse University that had been established to respond to the educational needs of local young people and of veterans returning from World War II. She was fortunate in having as her mentor Dr. John C. Keller, the Chairman of the Chemistry Department. Dr. Keller, who had received his Ph.D. degree in physical chemistry from Cornell University, set exceptionally high standards for the new Chemistry Department that he had just established in Utica. It was soon announced that Utica College would offer a full four-year program, which Marilyn Jacox completed on the Utica campus. In June 1951, she received the Bachelor of Arts degree in chemistry, *summa cum laude*, from Syracuse University. In September 1951, she began graduate studies in physical chemistry at Cornell University. Her thesis research, directed by Professor Simon H. Bauer, was concerned with the application of the optic-acoustic effect to studies of energy transfer from selected vibrational modes of carbon dioxide to its translational degrees of freedom. In September 1956, she obtained her Ph.D. degree in physical chemistry from Cornell University. Until October 1958, she pursued postdoctoral research under the direction of Professor Oscar K. Rice, of the Chemistry Department at the University of North Carolina in Chapel Hill. This research was concerned with the shape of the coexistence curve in the two-phase cyclohexane−aniline system.

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Dr. Jacox's concern with the spectroscopy of free radicals and other reaction intermediates trapped in inert solid matrixes began soon after she became a Fellow in Solid State Spectroscopy at the Mellon Institute (now a part of Carnegie-Mellon University) in Pittsburgh, PA. There she met Dr. Dolphus E. Milligan, who in 1957 had completed his doctoral research in Berkeley under the direction of Professor George C. Pimentel. In 1954, Pimentel, together with Eric Whittle and David Dows, had suggested that, if their solids were sufficiently rigid to prevent molecular diffusion, the rare gases and nitrogen might be suitable media for trapping and storing concentrations of free radicals great enough for direct spectroscopic identification. Because these inert matrix materials are completely transparent from the far-infrared to well into the vacuum ultraviolet, they were expected to be exceptionally versatile solvents for such studies. Infrared studies were especially appealing, since at the time no detection systems were available for obtaining the infrared spectra of free radicals. Dolphus Milligan had joined a group of very enthusiastic graduate students in pursuing these studies at Berkeley. However, although it was soon established that the rare gases and nitrogen did form appropriately rigid solids at cryogenic temperatures, attempts to obtain the spectra of free radicals proved to be difficult. At Mellon Institute, Dr. Milligan was able to test his ideas regarding the implications of the cage effect for free radical stabilization in solids. Dr. Jacox soon joined in these studies. There followed an exceptionally productive 15 year collaboration—first at Mellon Institute and then, starting in 1963, at the National Bureau of Standards in Washington, DC— which was terminated by Dr. Milligan's untimely death in 1973.

Dr. Milligan had envisioned that, if atoms could diffuse through the solid rare gases, it might be possible to stabilize free radicals by atom–molecule reactions in the matrix. The test system used by Drs. Milligan and Jacox for this study was the reaction of H atoms, produced by the mercury-arc photolysis of HI, with O_2 trapped in an argon matrix. All three vibrational fundamentals of HO_2, an exceptionally important species in studies of atmospheric and combustion chemistry, were observed for the first time in the resulting infrared spectrum. Isotopic substitution was found to be essential to positive spectroscopic identifications. In the HO_2 study, the identification was confirmed by both deuterium- and ^{18}O-substitution experiments.

The second condition under which Dr. Milligan had envisioned that free radicals might be stabilized in rare gas or nitrogen matrixes was photodecomposition of a precursor molecule into fragments for which there was a significant barrier to reverse recombination. This proved to be true for a number of azides. However, Dr. Milligan soon realized that when methyl azide was photolyzed in an argon or a nitrogen matrix the initially formed CH_3N rearranged into $CH_2{=}NH$. Dr. Jacox began to work with Dr. Milligan on analyzing the isotopic data for this system. Soon, they discovered that on prolonged mercury-arc irradiation $CH_2{=}NH$ also photodecomposed and prominent infrared absorptions of HNC resulted. This species had previously been proposed to result from the rearrangement of HCN at high temperatures but had not been observed. Subsequent radioastronomy studies demonstrated that HNC is an important interstellar molecule, and years later it was observed in the gas phase when HCN was heated to a sufficiently high temperature.

Somewhat later, Drs. Milligan and Jacox studied the photodecomposition of cyanogen azide, N_3CN, in argon and nitrogen matrixes. They completely characterized the infrared spectrum of the expected product, NCN, and observed both the previously reported electronic transition and a new band system at higher energies. However, the surprising result was that NCN in turn underwent photodecomposition at 254 nm, producing N_2 and C atoms. It then became possible to produce a number of new free radicals, including CNN, CCO, HCCl, and CCl_2, by reactions of these C atoms in the matrix environment.

Interaction with photochemists and radiation chemists at the National Bureau of Standards was exceptionally important in the search for suitable vacuum-ultraviolet photolysis sources. A microwave-powered discharge through a H_2/He mixture which was flowing through a tube separated from the cryogenic cell by a LiF or a MgF_2 window proved to be an extremely useful source of 122-nm radiation, which was highly effective for stripping H atoms from simple molecules. In their first study with this source, Drs. Milligan and Jacox succeeded in obtaining the infrared spectrum of the NH_2 free radical, produced by the photolyis of NH_3. There soon followed the identification of the very prominent ν_2 absorption of CH_3. The isotopic shifts observed for this fundamental showed a "negative anharmonicity", requiring the quartic term in the potential function to predominate and the molecule to be planar. Many other simple free radicals were formed using this photolysis source. Noteworthy was a study of HCN, in which the previous infrared identification of HNC was confirmed. The formation of HO_2 by the $H + O_2$ reaction became a diagnostic for the presence of a small leak in the system.

Ultraviolet spectra taken as a part of the CH_3 identification project showed a very complicated absorption pattern between 200 and 260 nm which Drs. Jacox and Milligan were able to assign to the absorption counterpart of the so-called hydrocarbon flame bands, which had resisted many previous efforts at assignment but which were believed to be contributed by the very important combustion intermediate HCO. (A small oxygen impurity in the sample accounted for the production of HCO in the CH_3 study.) Because earlier matrix isolation studies in Berkeley and by Drs. Jacox and Milligan had yielded a complete ground-state vibrational assignment for HCO, it was possible to propose an almost complete assignment of the hydrocarbon flame bands. More recent gas-phase studies in other laboratories are consistent with this assignment.

Working with Mlle. Luce Marguin (now Dr. Luce Abouaf-Marguin), a summer guest worker from Paris, France, Drs. Milligan and Jacox studied the 122-nm photolysis of C_2H_2 in various inert matrixes. The infrared spectroscopic identification of the CC-stretching fundamental of the exceptionally important HCC free radical resulted. Dr. Jacox has published several more recent papers on this species, culminating in the proposal of detailed assignments for the very complicated near-infrared absorption spectra of HCC and DCC. Shortly after that paper was published, gas-phase laser fluorescence studies performed by an outstanding research group in Taiwan provided strong support for the proposed assignments and detailed spectroscopic data for several of the bands.

Anomalous results in the study of the 122-nm photolysis of C_2H_2 led to the discovery that ions could be stabilized in matrixes. Studies in other laboratories had resulted in the assignment of a band system with origin near 520 nm to the Swan bands of triplet C_2. However, the upper-state vibrational spacings were some 200 cm^{-1} greater than the gas-phase values for the Swan bands, and the lower-state vibrational spacings were about 150 cm^{-1} larger than those for the gas-phase Swan bands. It had been supposed that there might be anomalously large matrix shifts for small molecules such as C_2. However, in the early 1960s, it had been discovered that the Swan bands of triplet C_2 did not arise from the ground-state of that molecule, for which a singlet state lies approximately 600 cm^{-1} lower in energy. Drs. Abouaf-Marguin, Milligan, and Jacox established that the carrier of the “Swan bands” in the matrix experiments did indeed possess two carbon atoms and no hydrogen atoms. However, there also appeared a very prominent absorption contributed by the Mulliken band of singlet C_2 at 238 nm, as well as the Phillips bands of singlet C_2 in the near-infrared spectral region. In 1968, Drs. Jacox and Milligan reported this anomaly at a Gordon Research Conference. Professor Gerhard Herzberg, of the National Research Council of Canada, noted that the vibrational spacings attributed to the Swan bands corresponded closely with those for a gas-phase band system that he and Professor Albin Lagerqvist, of the University of Stockholm, had tentatively assigned to C_2^-. This was the first molecular anion for which a gas-phase spectroscopic identification had been proposed. Professor Herzberg urged the continuation of the matrix experiments and subsequently proposed a magnetic deflection experiment that did not prove to be feasible. However, colleagues at the National Bureau of Standards had been using an atomic beam of cesium for studies in surface science, and Drs. Milligan and Jacox decided to try photolysis experiments on $Ar.C_2H_2.Cs$ deposits. In the first such experiment, they observed a 30-fold enhancement in the 520-nm “Swan band” absorption relative to the Mulliken band of singlet C_2. This enhancement could be explained by the capture of photoelectrons produced from cesium by C_2, known to have an exceptionally large electron affinity. Not only did this result strongly support the spectroscopic identification of C_2^- by Herzberg and Lagerqvist but also it paved the way for the spectroscopic identification of a number of other anions, including NO_2^-, SO_2^-, $ClHCl^-$, and NNO_2^-, in rare gas matrixes.

Before very long, Drs. Jacox and Milligan also discovered that 122-nm radiation from their H-discharge lamp led to the stabilization of molecular cations in their experiments. The first infrared absorption of a molecular cation to be identified was the 1037-cm^{-1} ν_3 fundamental of CCl_3^+, formed on 122-nm photolysis of $HCCl_3$ in an argon matrix. When a 107-nm argon resonance lamp was substituted, the predominant cation formed from $HCCl_3$ was instead $HCCl_2^+$. It was also noted that in 122- and 107-nm photolysis experiments on argon-matrix samples in which anions were formed from species which contained H (or D) atoms a new absorption at 903 cm^{-1} (644 cm^{-1} in D-containing systems) appeared. The formation of HAr_2^+ at comparable energies in earlier gas-phase studies with mass spectrometric detection led Drs. Jacox and Milligan to propose that HAr_2^+ might also be produced in the argon-matrix experiments and that HAr_2^+ and DAr_2^+ might contribute the new infrared absorptions. Several more recent studies in various laboratories have confirmed this identification.

Shortly after Dr. Milligan’s death in 1973, Dr. Jacox began a new series of experiments in which a beam of argon atoms passing through a discharge tube with a coarse pinhole in the end was excited by a microwave discharge. Outside the discharge tube, this beam was allowed to interact with a mixture of the molecule of interest in a large excess of argon carrier gas, and the products were rapidly frozen on the cryogenic observation surface. When the molecule was C_2H_2, consistently high yields of both C_2^- and the HCC free radical were observed. In other systems, the H-atom stripping was found to be much less extensive than had been observed when the 122-nm hydrogen-discharge lamp was used. As an example, when the starting molecule was CH_3OH, the predominant infrared absorptions produced were those of CH_2OH, and much less H_2CO, HCO, and CO were produced.

A variation on these experiments in which an Ar/NF_3 mixture was passed through an alumina discharge tube was found to provide an excellent source of F atoms for matrix isolation studies. Both the addition of F atoms to small molecules and H-atom abstraction from small H-containing species were extensively studied.

In 1988, with Dr. Warren E. Thompson, on sabbatical leave from the National Science Foundation, Dr. Jacox returned to studies of the interaction between excited rare gas atoms and small molecules, using excited neon atoms instead of excited argon atoms. These experiments required the use of a neon matrix, maintained at approximately 5 K by a continuous-flow liquid helium cryostat. In the first experiments, they found that Penning ionization and photoionization of CO_2 by the excited neon atoms and their resonance radiation led to stabilization of sufficient CO_2^+ for detection of its ν_3 infrared absorption very close to the previously reported gas-phase band center. A prominent absorption of CO_2^-, produced when electrons resulting from the photoionization of CO_2 were captured by other CO_2 molecules, was also present. Because the first excited states of neon atoms, between 16.6 and 16.85 eV, are sufficiently high in energy to provide an almost universal photoionization source (excepting only neon and helium atoms), this system has been useful for studying many other molecular ions. The ions are formed outside the discharge tube; the observed cation products are those which have appearance potentials below 16.85 eV, and extensive fragmentation of the starting molecule and isotopic “scrambling” do not occur.

Molecular ions are much more highly reactive than are most free radicals. Because the probability of reaction of a small molecular ion with the parent species or another molecule on a single collision often exceeds 10%, spectral data for dimer ions such as O_4^+, O_4^-, N_4^+, and $(CO)_2^-$ and ion−molecule complexes such as $O_2C\cdots O_2^-$ have been accessible in these experiments. Recently, the $(NO)_3^-$ species has also been observed, and, with the aid of both experimental and ab initio studies of its various isotopomers, its structure has been determined. A number of the molecular ions studied in these experiments have been observed to photoisomerize into other structures. Reversible photoisomerization of HCN^+ into the more stable HNC^+ has been studied, and infrared absorptions of both CH_3Br^+ and the slightly more stable H_2CBrH^+ ylidion have been identified. Because CH_3Br^+ has a ^2E ground state, it is subject to Jahn-Teller distortion, leading to the appearance of nine distinct vibrational fundamentals, all of which were observed. Infrared absorptions were identified for cations and anions derived from a number of first- and second-row fluorides. The vibrational fundamentals of HCl^+, HBr^+, and HI^+ all appeared within 1% of the gas-phase band centers, and absorptions of the corresponding dimer cations, as well as of $HFFH^+$, were identified for the first time. However, the infrared absorption of HF^+ did not appear; because of the unusually low proton affinity of the F atom, proton sharing between it and the neon matrix occurred, resulting in the stabilization and spectroscopic identification of the $NeHF^+$ complex.

For approximately 15 years, Dr. Jacox has been comparing and critically evaluating vibrational and electronic spectral data for small transient molecules, including free radicals, molecular ions, and other highly reactive species, in the gas phase and trapped in inert solid matrixes. An important aspect of this work has been the publication of a paper comparing the ground-state vibrational fundamentals of diatomic molecules in the gas phase with the corresponding fundamental absorptions observed in neon, argon, krypton, xenon, and nitrogen matrixes. Neon was found to be the least perturbing of these matrix materials, with argon almost as satisfactory. Except for the alkali metal and group IIIa halides, most of the fundamental absorptions of diatomic molecules observed in these two matrixes appeared within 1% of the corresponding gas-phase band centers. In a companion paper, similar conclusions were reached for the comparison of valence transition origins in the electronic spectra of diatomic molecules.

The publication of a series of critical evaluations of vibrational and electronic spectral data for small polyatomic transient molecules observed in the gas phase and in inert solid matrixes was followed by the preparation of *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*, which appeared in 1994 as *Journal of Physical and Chemical Reference Data,* Monograph No. 3. Dr. Jacox has continued to support this effort both by the publication of supplements and by the preparation of computer-searchable versions of the database and of a section of the NIST Chemistry WebBook (http://webbook.nist.gov/chemistry).

Dr. Jacox has served as a research chemist at the National Bureau of Standards, now the National Institute of Standards and Technology, since November 1962. She was Chief of the Photochemistry Section from October 1973 to November 1974 and of the Environmental Chemical Processes Section from November 1974 to April 1978. She was a NBS (NIST) Fellow from June 1986 to December 1995 and has been a Scientist Emeritus from January 1996 to the present.

Dr. Jacox is active in the scientific community. She was elected a Fellow of the American Physical Society, the American Association for the Advancement of Science, and the Washington Academy of Sciences. She is also a long-standing member of the American Chemical Society. She served as President of the NBS/NIST Chapter of Sigma Xi in 1988–89. She also served on the Executive Committee of the Inter-American Photochemical Society in 1978–79 and as Chairman of the Election Committee of that organization in 1980. She served on the Editorial Boards of *Reviews of Chemical Intermediates* from 1984 to 1989 and of the *Journal of Chemical Physics* from 1989 to 1991. She was Secretary of Executive Women in Government in 1981 and Vice Chairman of that organization in 1982. She has served on several National Science Foundation and Army Research Office panels and was a member of the U. S. Air Force High Energy Density Materials Panel from 1986 to 1993.

Dr. Jacox has received several awards. The first of these was the Utica College Outstanding Alumnus Award, conferred in 1963. At 1987 ceremonies marking the 40th anniversary of Utica College, she was named a member of their 40 Alumni of Achievement. She received the 1968 Washington Academy of Sciences Award in Physical Sciences. In 1970, she was presented with the U. S. Department of Commerce Gold Medal Award for Distinguished Service. She was among the six recipients of the 1973 Federal Woman's Award. That same year, she received the Samuel Wesley Stratton Award of the National Bureau of Standards. In 1989, she received the Ellis R. Lippincott Award in Vibrational Spectroscopy, followed in 1990 by the Hillebrand Prize of the Chemical Society of Washington and in 1991 by the WISE Lifetime Achievement Award of the Interagency Committee for Women in Science and Engineering. In 1993, the Sc.D. degree, *honoris causa*, was conferred on her by Syracuse University.

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