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*footnotes to a program

The molecular laser isotope separation program at Los Alamos was the first major program in applied photochemistry. Like every technology involving fundamentally new phenomena, this effort had disconcerting surprises as well as satisfying discoveries. Participants in the early years of the program gave us this glimpse of basic research at work.

The molecular laser isotope separation program was formally established at Los Alamos in 1972, but early discussions and preliminary work began the year before. Throughout the summer of 1971 Reed Jensen of J Division and his graduate student John Lyman were doing CO_2 laser induced chemical reactions with SF_6 and N_2F_4. In October that year Roy Greiner, a spectroscopist in GMX-2, sent a memo about the possibilities for uranium laser isotope separation to Keith Boyer, who was to be leader of a new laser division. During the fall an informal uranium task force collected information and read the literature. On the first of February 1972, L Division became operational, and Keith Boyer asked Paul Robinson to assemble the task force on a more formal basis. From various areas of the Laboratory came a core group: Ted Cotter, Roy Feeber, Roy Greiner, Burt Lewis, Reed Jensen, and Paul Robinson. Along with other interested chemists and physicists, they met each week for hours of discussion.

It appeared that monochromatic high-intensity radiation from lasers would make isotope enrichment possible, since in previous attempts the inadequacies of conventional discharge lamps had been the major handicap. The group's first major decision was to work with uranium-bearing molecules rather than with uranium atoms. For one thing, Avco Corporation was already working with atomic uranium. For another, producing uranium atoms requires very high temperatures. Those in the group who had worked on the rocket reactor for the Rover project were well aware of all the difficulties in dealing with uranium at very high temperatures. Also, some of the chemists had experience with uranium hexafluoride (UF_6) gas and thought the molecular approach offered more latent technical possibilities.

The goal of the project was to induce photodissociation of UF_6 molecules containing uranium-235. There seemed to be a variety of possible approaches, but the one that caught everybody's imagination, because it was conceptually so straightforward and so credible, was the idea of using infrared laser radiation to excite the vibrations of the UF_6 molecules containing uranium-235 without affecting any of the molecules containing uranium-238. It seemed quite likely this first step would increase the susceptibility of the [235]U-bearing molecules to dissociation by means of ultraviolet radiation. Two steps had already appeared in a French patent for selective ionization, but the French method had not been attempted and did not even mention photodissociation.

Every new concept is contingent upon what is not known. Just how possible was dissociation with lasers? In a book titled *The Chemistry of Uranium* by Katz and Rabinowitch was a tantalizing hint. The text reported that an attempt to measure the UF_6 Raman spectrum with ultraviolet light had failed because a fluffy white solid kept forming. It was possible that the solid was the product of dissociation. In the experiment the UF_6 had been dissolved in Fombic's fluid. Would dissociation also occur in a gas? A sort of bible for the group was an Oak Ridge report, written by R, L. Farrar, Jr. and D. F. Smith, that summed up all that was then known about uranium isotope separation; among other things it clearly indicated that at room temperature UF_6 infrared bands were about 30 times wider than the frequency difference between the peaks of the absorption bands for the two isotopic species. The Los Alamos spectroscopists had to agree

that the amount of enrichment possible at room temperature would be very small.

Cooling the gas seemed a possible solution but had its own problems. During April Roy Greiner did calculations that showed how at very low temperature the infrared absorption bands of UF_6 would become much narrower and the absorption features sharper. However, simple static cooling was out of the question because it would only freeze the gas to an unusable solid. Ted Cotter, who had experience in gas dynamic cooling, suggested that the low temperature could be obtained, for a brief moment, by mixing UF_6 with a light carrier gas and making a supersonic expansion through a nozzle. Because lasers are capable of pulses as short as 100 nanoseconds, the rapidly flowing gas would, relatively speaking, just be sitting there letting things happen to it. It seemed likely that the vapor pressure of the cold UF_6 would be very low, but Reed Jensen pointed out that a slit nozzle could extend the optical path length of the irradiation zone to as much as a meter.

By the first of May the group had at least a conceptual solution to the problems of cooling. There remained the question of how much energy would be required to break apart the strongly bonded UF_6 molecule. Working from a number of chemical papers, Burt Lewis did an "absolutely monumental" calculation that suggested UF_6 would dissociate with 76 kilocalories per mole, which corresponded to light just short of 4000 angstroms. It was energy that lasers could provide.

The pieces of the puzzle had come together, and early in July 1972 patent application was tiled for the mainline process. Experiments began. In the attic of the CMR building, a dank place filled with pipes, Paul Robinson, Burt Lewis, and Al Zeltmann of CNC-2 constructed a commercial nitrogen laser and a l-meter-long cell to hold UF_6. In September they were successful: when the laser was turned on, gas pressure gradually dropped, gas molecules disappeared, a white solid formed. Photodissociation had occurred. Furthermore, the experiment was reversible with the introduction of fluorine gas.

Meanwhile an attempt at spectroscopy was started. Jack Aldridge arrived "just" for the summer, but stayed on as a permanent member of the group. At a firing site on Two-Mile Mesa, a slit nozzle from earlier laser experiments was fitted into a 55 gallon drum patched with teflon putty and pumped out to create a vacuum, Some gas dynamics data were collected, but spectroscopy was impossible without a bigger blowdown system. The group's fluid dynamics engineer was Al Sullivan, who now built at TA-46 a structure declared worthy of pharaohs. An old Rover reactor aluminum pressure vessel, as a feed vessel, was coupled through a nozzle with an irradiation region to a huge space simulation chamber previously used to test arc-jet thrusters. With this enormous contraption the team had 20 seconds of gas flow before the chamber was filled. Al Sullivan, Jack Aldridge, and David Fradkin, who had come along with the space chamber, did experiments of SF_6 in N_2 gas and by late summer of '72 had proved that spectral simplification could be done in a supersonic gas stream, The Department of Military Applications was impressed by the summer's work and granted half a million dollars toward equipment for cooling UF_6.

The basic ideas and physical principles for the mainline process were quite correct from the beginning; however, experimental progress altered many of the quantitative details and required advances in many disciplines. To start in a lighter vein, the classified project was having trouble getting supplies. Early in 1973, to expedite matters, the project received the title JUMP, a term chosen as a suggestion rather than an acronym. (This was later modified to JUMPer to comply with code book

regulations.) The project was again expedited in the fall of '73 by what was informally called the "Harold Resonance." Harold Agnew, Director of the Laboratory, made available to the project both personnel from other divisions and moneys from his discretionary fund.

When the group began to cool UF_6, they discovered they could not nearly reach the estimated concentrations of supercooled gas. Since then Bud Lockett has made substantial improvements in the theory that describes the kinetics of condensation. However, at that time they simply had to accept an unexpected homogeneous condensation. had to live with lower concentrations, and had somehow to provide proportionally more optical path length in the gas.

There was to be a similar experience with the estimations for possible selectivity. The group had a model that gave a surprisingly good interpretation of the observed onset of ultraviolet absorption by UF_6 in the 400 nanometer region at room temperature. In the model the ultraviolet absorption spectrum of each vibrationally excited molecule was exactly a step function of frequency, and the position of the step shifted in frequency in exact proportion to changes in vibrational energy. According to the model very high selectivity would be possible at a sufficiently low temperature, After a while the group was to discover that nature uses a gentle ramp rather than a step function.

But before the group could make significant discoveries about spectra and isotopic selectivity, they had to have the right lasers. In the beginning there were no lasers at suitable wavelengths. They went to Ken Nills, a researcher in diode lasers at Lincoln Laboratory, and asked him to develop what they needed. Ken Nills designed a semiconductor diode laser, flew with it to Los Alamos, and ran spectroscopy with the group. By early summer of '74 the group had observed and confirmed to five figures the frequency required for isotopic selectivity.

The 16-micron absorption band was easily the strongest absorption feature of UF_6. Los Alamos had no laser at 16 microns. There were also possibly usable bands near 12 microns and 8 microns, but there were no lasers available at those wavelengths, either. The Los Alamos scientists found themselves in the position of having to design lasers to a priori specifications-something that had never been done. Steve Rockwood was placed in charge of a laser development group. The first usable laser at 16 microns, and the workhorse of the early experiments, was the hydrogen fluoride, optical parametric oscillator (HF OPO) laser, a unique, tunable laser developed by George Arnold and Bob Wenzel. Later the group obtained 16 micron laser light by shifting the output of the CO_2 lasers with the hydrogen Raman cell.

Other problems were solved and other advances made as the project matured. DeForrest Smith, one author of the Oak Ridge report, agreed to come part time to Los Alamos. His advanced calculations remarkably predicted the fine structure that would result from rotational energy changes in a vibrational peak, and he became a decision-making member of the team.

One persistent problem was the large amount of gas that flowed through the irradiation region during the 20-second run. Early in 1974 Keith Boyer suggested a pulsed valve that could provide a millisecond flow of gas coordinated with the laser pulses. The pulse valve was integrated into a recirculating loop, a system which has been steadily improved.

Problems were sometimes solved with outside help. The program sponsored research at other national laboratories, universities. and industries. For example, the AEC eased classification restrictions to allow a team from the Gaseous Diffusion Plant at Oak Ridge to instruct the Los Alamos group in systems for handling UF_6, using gaseous diffusion technology. Later, Sandia Laboratories developed a rare-gas halide laser to be used in the ultraviolet region. The Sandia team then joined the Los Alamos project.

A sad comedy of errors that developed in the U.S. Patent Office provided diversion from purely scientific problems. The first series of patent applications were tiled early in July 1972 and became the concern of the Special Laws Administration. The AEC Division of Classification held the original research application of July 3, 1971, as Restricted Data until the material could be examined. In September the application was placed under Secrecy Order and was upgraded to Secret Restricted Data in February 1973. In August 1973, when an application for an improved mainline process was tiled, the Laboratory received indications that the U.S. government was becoming less interested in classification and more interested in the possibilities of patents. From then until 1978 the applications went through a bewildering series of indecisions connected with weapons proliferation. Meanwhile an unclassified German application for much the same material was filed with another section of the Patent Office in 1975, was accepted without a complete interference search, and issued into the literature in 1977. In fact, a comprehensive patent for the Los Alamos mainline process is yet to be issued to the Laboratory.

The difficult problems in the research into laser isotope separation have led to important advances in basic science. The development of narrow linewidth tunable lasers has brought about a revolution in molecular theory. Advances in infrared molecular spectroscopy have yielded precise and detailed knowledge of complex polyatomic molecules, not just as static objects but also as dynamic ones. Scientists can now label most of the myriad spectral features as transitions between identified states and can evaluate the information to determine the structure of the molecule, its shape, and its resistance to deformation.

The interaction of experimental and theoretical work on the project has resulted in new understanding of electronic spectra. Electronic structure, which involves the motion of electrons in the molecule, is qualitatively different from molecular structure, which deals with the arrangements, the rotations, and the vibrations of atoms within the molecule. Excitation of electronic states in the two-step method of laser isotope separation involves frequencies in the ultraviolet region. It was the scant knowledge of electronic structure that caused poor predictions of the absorption edges in the ultraviolet region of UF_6 when the project began. Now scientists know where the electronic energy states are and how the overlapping of a number of transitions contributes to the observed spectrum of the cold gas.

As for the old problem of supercooling the gas, that has become a matter of engineering mastery. One now needs only a simple piece of apparatus that occupies no more floor space than a desk. Flick a switch and, 10 and behold, there is one's chosen very cold gas to look at.

Perhaps the most extraordinary discovery of the whole project has been multiple-photon excitation. That polyatomic molecules can absorb many single-frequency infrared photons was not even suspected at the beginning. Between 1971 and 1973 the first hints of the phenomenon appeared in the work being done. Between 1973 and 1974 both Los Alamos and the Institute of Spectroscopy in the Soviet Union demonstrated multiple-photon excitation leading to isotonically selective dissociation in sulfur hexafluoride (SF_6). Multiple-photon excitation is now known to occur in all polyatomic molecules at both high and low laser intensities and is an essential part of the infrared step of the Laboratory's uranium enrichment process. The details of this complicated phenomenon are still being studied, but clearly multiple-photon excitation will play a major role in laser isotope separation and other areas of applied photochemistry.

Molecular laser isotope separation is still a program in progress, a technology not yet technically complete, but already its research has provided entirely new fields of knowledge. ■