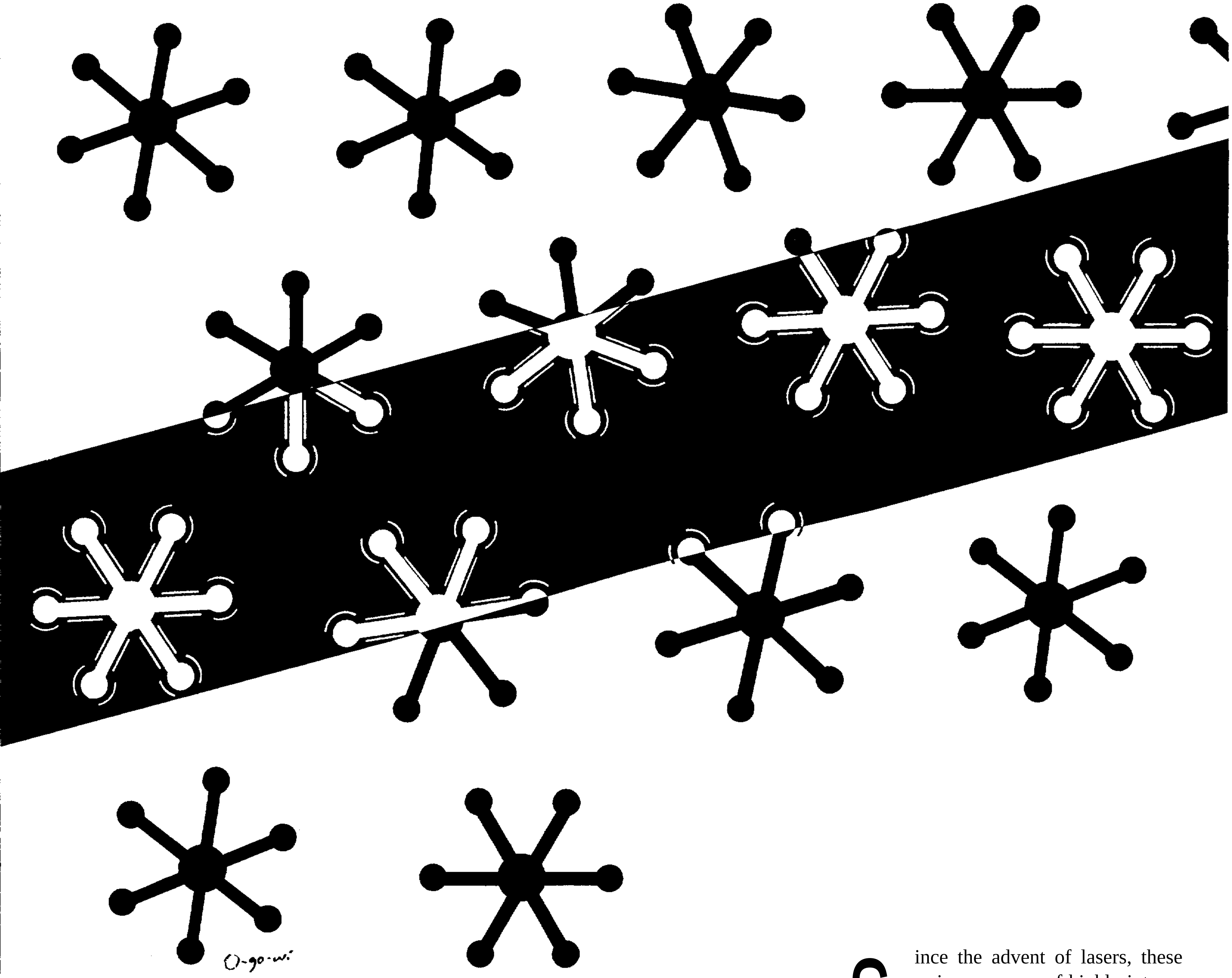


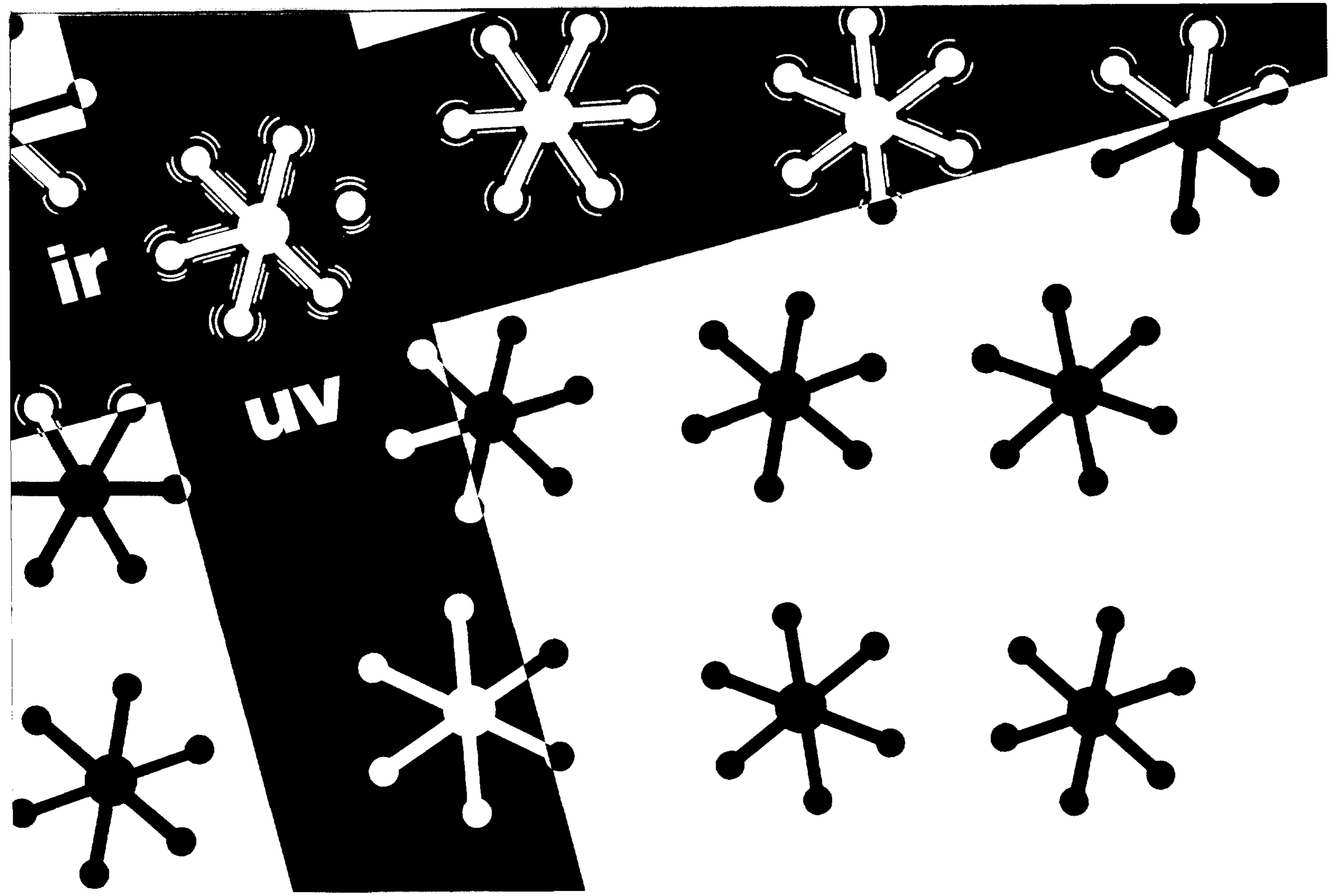
Based on recent discoveries in science and advances in engineering, the Los Alamos molecular laser isotope separation process appears to be an economical method for uranium enrichment.

by Reed J. Jensen, O'Dean P. Judd, and J. Allan Sullivan

Since the advent of lasers, these unique sources of highly intense and nearly monochromatic radiation have been proposed as tools to induce or catalyze chemical reactions. Of all the reactions investigated, laser isotope separation has received the most attention worldwide and may be the first major commercial application of lasers to chemistry.

Laser isotope separation was first demonstrated nearly a decade ago for boron and to date has been applied on a laboratory scale to many elements throughout the periodic table. But the goal is to find laser processes that are more economical than conventional separation techniques. Los Alamos researchers have developed a practical process for separating sulfur isotopes based on laser irradiation of sulfur hexafluoride molecules, and the Soviets have developed commercially applicable laser processes for separating both sulfur and carbon isotopes.

However, the primary motivation behind the generous funding of this field is the



Separating Isotopes With Lasers

promise of an economical method for producing bulk quantities of enriched uranium, the fuel of nuclear reactors. Here, success has been much harder to achieve. But the difficulties encountered have been beneficial in the larger perspective, having stimulated fundamental scientific advances that are strongly influencing the broad field of laser chemistry. Among them are the discovery of multiple-photon processes, a revolution in infrared spectroscopy of heavy molecules, an increased understanding of molecular electronic structure and of condensation processes in cooled gases, the development of new, high-intensity, tunable laser systems, and practical methods for producing gas flows at low temperatures. These advances have also contributed to major progress in the Laboratory's molecular laser isotope separation process for uranium.

Natural uranium is a mixture of isotopes and contains 99.3 per cent uranium-238 and only 0.7 per cent of the fissile isotope uranium-235. To increase the concentration of uranium-235 to that required of reactor fuel, the two isotopes must be sorted according to some difference in their chemical or physical properties. But the electronic and therefore the chemical properties of the two isotopes are so nearly identical that chemical processing is difficult and inefficient. Conventional methods for separating isotopes of uranium, as well as those of other elements, rely instead on physical processes that are affected by the small differences in the masses of the different isotopes.

The gaseous diffusion method which currently produces most of the enriched uranium for nuclear reactors, consists of passing gaseous uranium hexafluoride molecules (UF_6) through a series of chambers separated by porous barriers. The lighter molecules, those containing uranium-235, diffuse through the barriers slightly faster. So in each successive chamber the concentration of uranium-235 relative to that of uranium-238 increases slightly. More than a thousand chambers are needed to increase the concentration of uranium-235 to the fuel assay of 3.2 per cent required for light-water reactors. Gaseous diffusion thus requires a very large and expensive facility and, moreover, consumes large amounts of electrical energy.

Other separation techniques based on mass differences include the gas centrifuge, multiple distillation, and electromagnetic separation. Of these, the gas centrifuge is being explored as an alternative to gaseous diffusion (see sidebar "Economic Perspective for Uranium Enrichment").

What may prove to be more economical is a separation process driven by lasers. The idea is quite simple. Since atoms or molecules containing different isotopes have slightly different energy levels, they have slightly different absorption spectra-that is, they absorb radiation with different frequencies (Fig. 1). Consequently, radiation of a particular frequency can selectively excite an

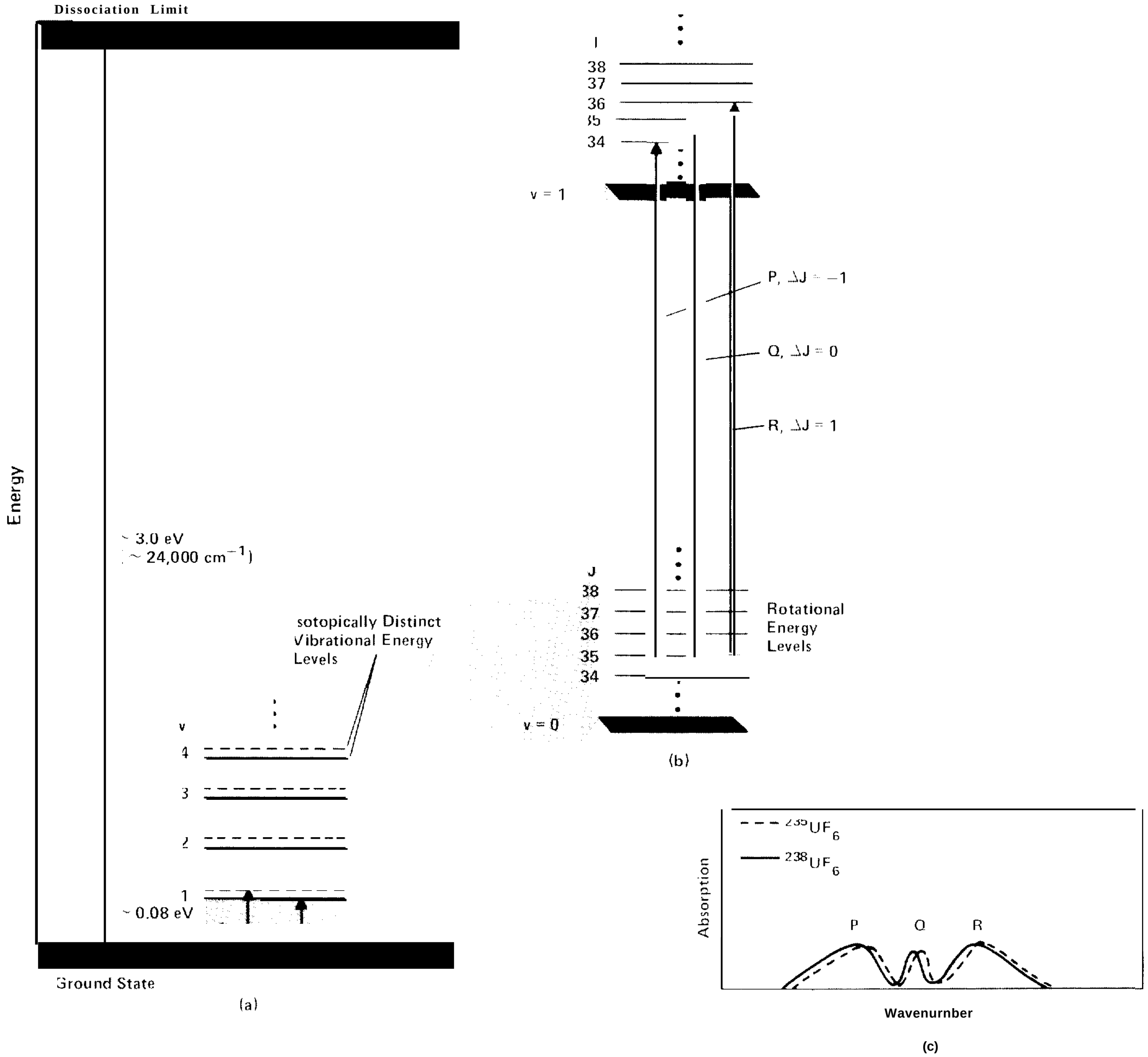


Fig. 1. The shift in vibrational energy levels of one molecular isotopic species relative to another shown in (a) is reflected in (c) as a shift in the infrared absorption spectra. (a) Within the ground electronic state of a molecule are many vibrational states resulting from oscillatory motion of the nuclei about their equilibrium positions. Shown here schematically are the energy levels for a vibrational mode of UF_h known as the v_l mode. The energy levels are labeled by v, the number of vibrational energy quanta of the state. The arrows represent absorption of infrared photons that raise a molecule from the ground state to the first vibrational state. The different lengths of the arrows for the two isotopic species represent the different photon energies, or frequencies, needed to excite the two isotopic species. The difference, although small (less than 1.25 X 10^{-4} electron volt, or 1 reciprocal centimeter, for UF_6, allows selective excitation by nearly monochromatic laser light. (b) One of the vibrational transitions indicated in (a) is shown in more detail. Each vibrational state is split into many rotational states labeled by J, the number of rotational angular momentum quanta of the state. A t room temperature molecules typically populate rotational states with high J values. During a transition between vibrational states, the change in J, ΔJ, *is restricted to —1, O, or +1. Such allowed transitions are denoted as* P-,Q-, *and R-branch transitions, respectively. (c) The infrared absorption bands of $^{235}UF_b$ and $^{238}UF_e$ from 620 to 630 reciprocal centimeters include transitions from the ground state to the first excited state of the v, vibrational mode. Absorption that excite the V_B mode occur over a broad band of frequencies because molecules in the ground state occupy many rotational states and the molecules in each rotational state can undergo* P-, Q-, *or R-branch transitions to the first excited vibrational state. The absorption band of $^{235}UF_6$, is shifted slightly to higher frequencies relative to that of $^{238}UF_6$.*

atom or molecule containing one isotope to a higher energy level and leave other isotopic species undisturbed. Then, depending on the type of excitation, the selectively excited species can be separated from the others by conventional physical or chemical methods.

For selective excitation to be practical as a separation technique, it must produce a large change in some chemical or physical property of the excited species. One possibility is to excite a molecule to such a high energy level that its chemical reactivity increases substantially. The molecule can then react with another chemical species, and the product containing the desired isotope can be separated from the mixture by conventional techniques. This type of bimolecular process has many applications in selective photochemistry.

However, the more widely studied laser isotope separation techniques involve only photons and a single atomic or molecular species. For example, the atomic vapor process under development at Lawrence Livermore National Laboratory uses selective photoionization to separate uranium isotopes. Through a multistep excitation process laser photons selectively ionize atoms of uranium-235. The ions are then separated from the neutral uranium-238 atoms by an electric field.

The separation technique being studied at Los Alamos uses selective photodissociation of molecules into stable fragments. As discussed below in more detail, a molecule can be excited to the point of dissociation in several ways. A two-step process is the basis of our technique. An infrared laser selectively excites vibrations of gaseous UF_6 molecules containing uranium-235 ($^{235}UF_6$. These vibrationally excited molecules are then dissociated by an ultraviolet laser into uranium pentafluoride ($^{235}UF_5$) plus a fluorine atom. The $^{235}UF_5$ molecules coalesce to form particulate that are easily separated from the remaining gas.

The various techniques for isotope separation have been investigated vigorously at Los Alamos and at many other research centers around the world since the early 1970s when high-intensity tunable lasers became available. However, isotope separation based on selective photoexcitation of atoms and molecules is not a new idea. In fact, photochemical separation was attempted with conventional radiation sources long before the invention of lasers. In 1922 efforts were made to separate the two naturally occurring chlorine isotopes by irradiating them with white light that had been filtered through a cell containing only the more abundant chlorine isotope. These experiments were unsuccessful. About ten years later Stanislaw Mrozowski suggested that mercury isotopes might be separated by selective excitation with the 253.7-nanometer resonance line of a mercury arc lamp and subsequent reaction with oxygen. This separation was achieved experimentally by Kurt Zuber in 1935. In the early ’40s Harold Urey proposed a photochemical method for separating uranium isotopes, but his proposal lost in competition with the gaseous diffusion technique. After the war, an enlarged effort to separate mercury isotopes by photochemical techniques succeeded in producing small amounts of product. Carbon and oxygen isotopes were also separated by using a strong spectral line of an iodine lamp to excite carbon monoxide molecules.

These pre-laser experiments involved a one-step process in which absorbed photons with frequencies in the visible or ultraviolet spectral region selectively excite electronic states of one isotopic species. Although this technique works in a few isolated cases, it is not generally applicable in molecules. Most molecules have very broad, structureless electronic absorption bands, and selective excitation is not possible.

These early efforts were also limited by the radiation sources then available. Photochemical isotope separation requires highly monochromatic, highly intense radiation. The few reasonably monochromatic discharge lamps were not very intense and covered only a small number of wavelengths. Monochromatic sources at other wavelengths were created from conventional white light sources (for example, with filters or gratings), but their intensity was even lower.

High-intensity tunable lasers have removed many of the limitations of the early experiments. Lasers can be tuned to match any absorption feature that shows a distinct isotope shift. In particular, high-intensity infrared lasers can selectively excite the isotonically distinct vibrational levels of molecules. Because of its high monochromaticity, laser light can excite a desired species with reasonable selectivity even when absorption features of other isotopic species partially overlap those of the desired isotopic species. Thus, both the tunability and high monochromaticity of the laser are crucial for selective excitation.

Other properties of laser light contribute to the efficiency of selective excitation. First, since laser light has a high degree of spatial and temporal coherence, a laser beam can propagate over long distances and interact efficiently with large volumes of process material. Second, a high-intensity laser beam can saturate the absorbing material. In other words, the beam contains so many photons that almost all the molecules that can be excited will be excited. Finally, the laser pulses are short compared with the average time for the selectively excited molecules to lose their energy either through collisions with unexcited molecules or through other loss channels. Short pulses are essential if the excitation process is to be isotonically selective and efficient in its use of laser photons.

Laser photons are quite expensive and represent the major cost in any laser chemistry process, including laser isotope separation. To illustrate, a mole (6×10^{23}) of photons costs about 1 to 3 dollars, whereas chemical reagents typically cost about 10 to 20 cents per mole. Efficient use of laser photons is therefore a primary factor determining the economy of a laser isotope

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SIDEBAR 1:

Economic Perspective for Uranium Enrichment

The future demand for enriched uranium to fuel nuclear power plants is uncertain, Estimates of this demand depend on assumptions concerning projections of total electric power demand, financial considerations, and government policies. The U.S. Department of Energy recently estimated that between now and the end of this century the generation of nuclear power, and hence the need for enriched uranium, will increase by a factor of 2 to 3 both here and abroad. Sale of enriched uranium to satisfy this increased demand can represent an important source of revenue for the United States, Through fiscal year 1980 our cumulative revenues from such sales amounted to over 7 billion dollars, and until recently foreign sales accounted for a major portion of this revenue. The sole source of enriched uranium until 1974, the United States now supplies only about 30 per cent of foreign demand, New enrichment capacity planned in this country should include means of reducing enrichment costs to permit capturing a larger share of the foreign trade in this commodity. Laser isotope separation shows promise of accomplishing this goal.

Currently, gaseous diffusion is the process by which uranium is enriched at the large-scale production facilities in the United States. Three such facilities exist (at Oak Ridge, Tennessee; Paducah, Kentucky; and Portsmouth, Ohio) whose total enrichment capacity will soon reach 27.3 million separative work units per year.

Separative work units (abbreviated SWU) are the customary measure of the effort required to produce, from a feed material with a fried concentration of the desired isotope, a specified amount of product enriched to a specified concentration and tails, or wastes, depleted to a specified concentration. For example, from feed material with a uranium-235 concentration of 0.7 per cent (the naturally occurring concentration), production of a kilogram of uranium enriched to about 3 per cent (the concentration suitable for light-water reactor fuel) with tails depleted to 0.2 per cent requires about 4.3 SWU.

Gaseous diffusion is based on the greater rate of diffusion through a porous barrier of the lighter component of a compressed gaseous mixture. For uranium enrichment the gaseous mixture consists of uranium hexafluoride molecules containing uranium-235 ($^{23\$}UF_6$) or uranium-238 ($^{238}UF_6$). The enrichment attainable per diffusion unit is quite low, being limited theoretically to less than the square root of the $^{238}UF_6$ to $^{235}UF_6$ mass ratio, or about 1.004. Therefore, the slightly enriched product from one diffusion unit, consisting of a compressor and a diffusion chamber, is passed through a second unit whose product in turn is passed through a third unit, and so on. (The theory of separative work and optimal arrangement of separation units was pioneered by R. E. Peierls and P. A. M. Dirac.) To enrich uranium from 0.7 per cent uranium-235 to about 3 per cent requires approximately 1250 units, Gaseous diffusion plants are therefore very large and expensive.

They have, however, proved very reliable. The main disadvantage of the process is the great amount of electric power required to operate the many compressors. A standard gaseous diffusion plant operating at full capacity demands about 3000 megawatts electric. For comparison, a typical large electric power plant produces 1000 megawatts electric. As the cost of electric power increases, its consumption becomes an increasingly important factor in the cost of enriched uranium. (In fiscal year 1980 about 75 per cent of the production costs at gaseous diffusion plants was for electricity.)

With the expectation of reducing power consumption, attention is now focused on the gas centrifuge, another method for enriching uranium. The Gas Centrifuge Enrichment Plant now being constructed at Portsmouth, Ohio will contribute 8.75 million SWU per year to the national enrichment capacity by 1994. In a gas centrifuge $^{235}UF_6$ and $^{238}UF_6$ are separated by the centrifugal force imposed on UF_6 by a rapidly rotating container. For this process a considerably smaller number of centrifuge units (less than 10) are required to reach the desired enrichment. However, the throughput per centrifuge unit is very small compared to that of a diffusion unit-so small, in fact, that it is not compensated by the higher enrichment per unit. To produce the same amount of reactor-grade fuel requires a considerably larger number (approximately 50,000 to 500,000] of centrifuge units than diffusion units. This disadvantage, however, is outweighed by the considerably lower (by a factor of 20) energy consumption per SWU for the gas centrifuge.

Compared to diffusion and the centrifuge, laser isotope separation offers the potential for much greater enrichment and throughput per separation unit. Therefore, a laser isotope separation facility would be much smaller, including only about ten separation units. In addition, the process would consume an equal or lesser amount of energy per SWU than the gas centrifuge. These advantages lead directly to reduced capital and operating costs.

For a laser isotope separation process involving selective excitation of $^{235}UF_6$ molecules with infrared lasers and their dissociation with an ultraviolet laser, a facility with the standard capacity of 8.75 millions SWU per year is estimated to cost about 1 billion dollars. (Laser casts account for approximately half of the direct capital costs.) This is considerably lower than the estimated cost of a new gaseous diffusion plant (about 5 billion dollars) or that of a gas centrifuge plant (about 6 billion dollars). The annual operating cost for a laser isotope separation facility is estimated to be about 100 million dollars, in contrast to about 500 million for a gaseous diffusion plant and 100 to 200 million for a gas centrifuge plant. Our estimates of capital and operating costs for a laser isotope separation facility indicate a cost per SWU of about $30; the current commercial cost for enriched uranium is $110 per SWU.

The considerably lower cost per SWU for laser isotope separation opens the possibility of turning the large stockpile of wastes from gaseous diffusion plants into a valuable uranium resource. These wastes contain about a third of the $^{235}UF_6$ originally present in the feed material and are estimated to amount to more than 500,000 metric tons by the end of 1990—an amount containing enough uranium-235 for 1800 reactor-years of operation.

These advantages imply that laser isotope separation should be thoroughly investigated as a potentially economical process for large-scale production of enriched uranium. ■

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separation process.

We said earlier that a fairly large amount of energy must be deposited in a molecule to make a substantial change in its physical or chemical properties. In the pre-laser experiments this energy was deposited through a one-step, or single-photon, process. When high-intensity infrared lasers became available, new multistep excitation processes became possible. Unlike the single-photon process, these multistep methods can achieve isotopic selectivity on virtually all atoms or molecules.

In the sections that follow, we will describe these excitation methods and their application to isotopes of medium and heavy elements. Great success has been achieved in separating medium-weight isotopes with infrared photons through what is known as multiple-photon excitation and dissociation. Progress has also been made on the more difficult problem of separating isotopes of heavy elements such as uranium. Laboratory-scale experiments based on the infrared-plus-ultraviolet dissociation of UF_6 have been very successful. The lasers and gas flow systems necessary to scale up the process have been built, and designs for a full-scale plant have been studied. But challenges still remain in both the science and engineering needed to optimize the process and its economics on a large scale. The physics of the molecular excitation is not sufficiently defined to choose process parameters that optimize selectivity, and some problems associated with irradiating large volumes of material have yet to be solved. But we are rapidly drawing nearer to our goal.

Molecular Laser Isotope Separation Methods

Three methods of molecular photodissociation have been used successfully to separate isotopes: a single-photon process, in which a

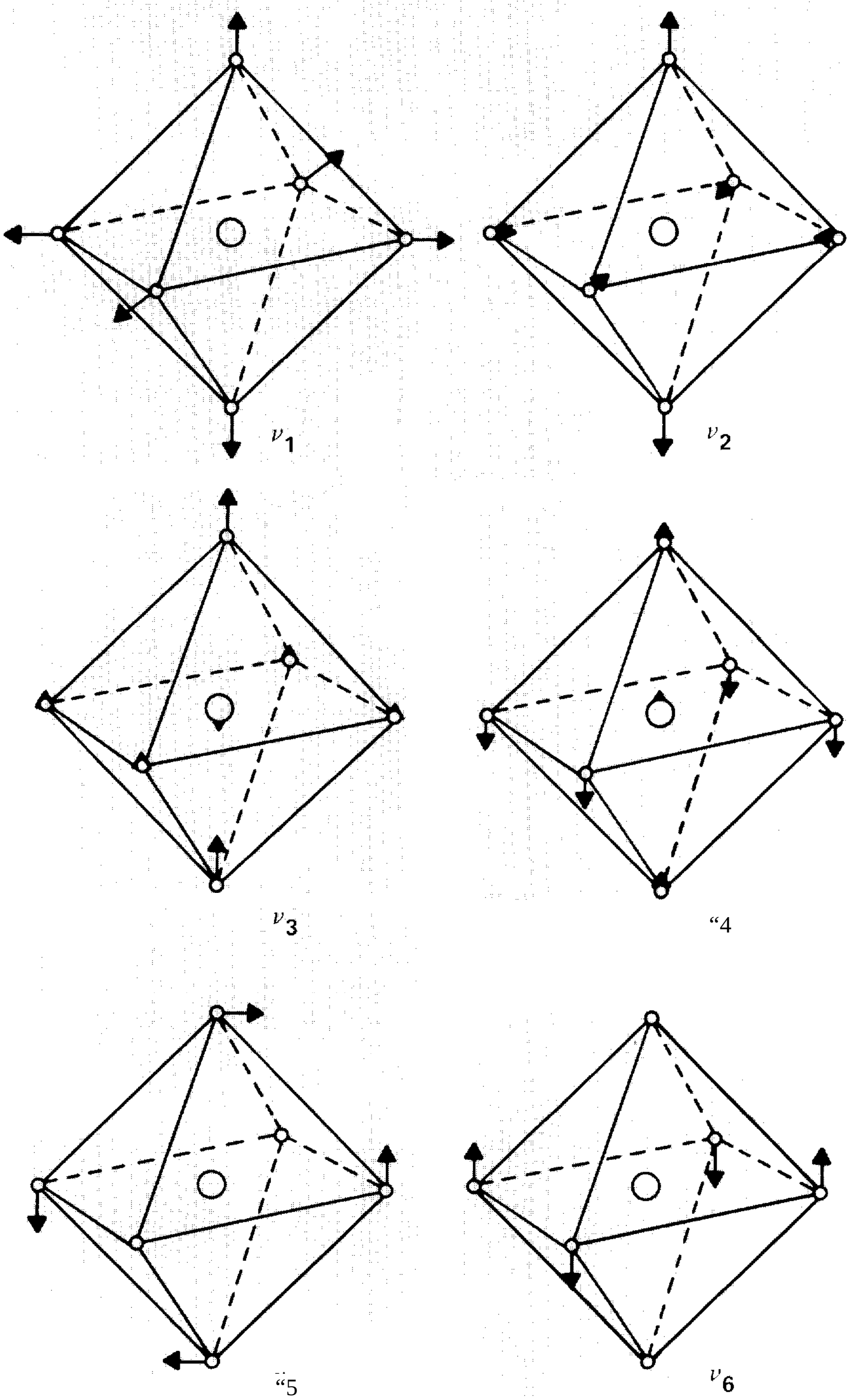

***Fig.** 2. In the ground-state configuration the fluorine nuclei in a sulfur hexafluoride (SF_6) molecule occupy the vertices of a regular octahedron about the central sulfur nucleus. Shown here are the six fundamental vibrational modes that, singly or in combination, describe the complex motion of SF_6 and other octahedral molecules, such as UF_6. Only the v_3 and v_4 modes can be excited by absorption of infrared photons, and, since only these modes involve motion of the sulfur nucleus, any shifts due to sulfur isotopes are confined to these particular modes. The v_3 mode stretches one S-F bond and compresses a second S-F bond that is colinear with the first. The v_4 mode bends the four coplanar S-F bonds.*

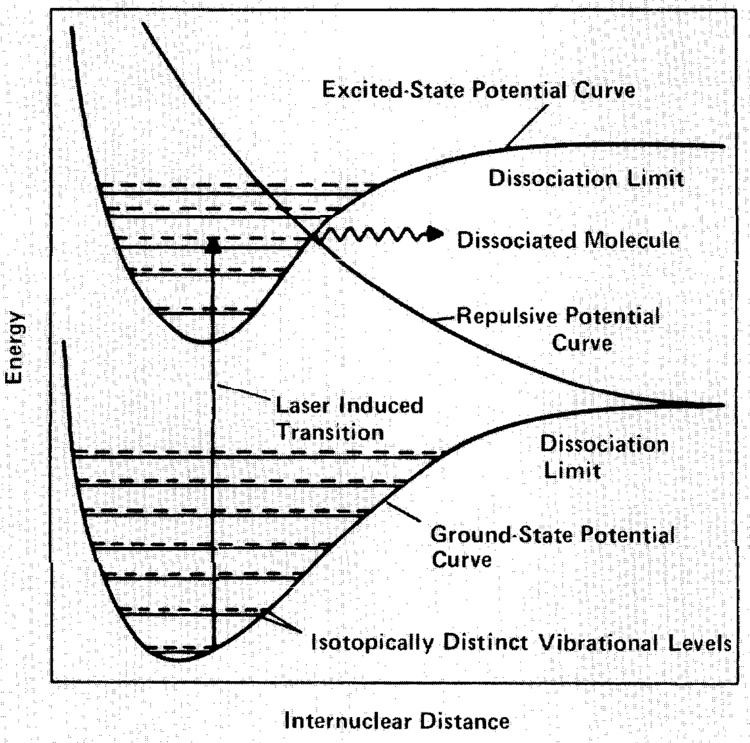

Fig. 3. Predissociation. The three potential energy curves depict the molecular binding energy as a function of internuclear distance. The curves for the ground electronic state and the bound excited electronic state exhibit energy minima and thus represent stable molecular configurations. The curve for the repulsive electronic state represents an unstable configuration in which the molecule dissociates because the forces are always repulsive. The usual photodissociation process involves a transition directly to a repulsive electronic state. The arrow represents a photon-induced transition of one isotopic species to a vibrational state within the bound excited electronic state. This transition can result in predissociation in which the molecule tunnels from the bound excited electronic state to the repulsive electronic state and then dissociates.

visible or an ultraviolet photon excites a molecule to a "predissociative" state; a two-step process, in which an infrared photon excites a vibrational state of a molecule and an ultraviolet photon dissociates the excited molecule; and a multistep infrared process, in which infrared photons excite successively higher and higher vibrational states of a molecule until its dissociation limit is reached.

In all these processes, including predissociation, selectivity is based on the isotonically distinct energies of the molecule's vibrational states. In a vibrational state the nuclei of a molecule undergo oscillatory motion about the ground-state configuration (Fig. 2) at some frequency. This frequency depends on the masses of the nuclei. In particular, molecules containing lighter isotopes vibrate at higher frequencies. Consequently, vibrational excitation of a molecule containing a lighter isotope requires absorption of a photon at a higher frequency. This mass-dependent shift in the absorption spectrum has been exploited to dissociate molecules of one isotopic species selectively and thus achieve isotope separation.

PREDISSOCIATION. The usual photodissociation process involves a photon-induced transition from a bound ground electronic state to an electronic state for which the internuclear forces are always repulsive. The lifetime of such a repulsive electronic state is so short that dissociation follows the transition with nearly unity probability. Predissociation (Fig. 3) involves a photon-induced transition not directly to a repulsive electronic state but to a predissociative state—a vibrational state within a bound excited electronic state that is energetically coupled to the repulsive electronic state. That is. the bound excited and repulsive electronic states have the same energy (the curve-crossing energy) at some internuclear distance greater than the equilibrium internuclear distance for the ground electronic state. Then, if the bound excited and repulsive electronic states have certain symmetry relations and if the energy of the vibrational state is near the curve-crossing energy, dissociation occurs by tunneling from the bound excited electronic state to the repulsive electronic state. This dissociation by tunneling is called predissociation because it requires a photon energy less than that required for dissociation directly from the repulsive electronic state. By tuning a laser to the frequency matching the transition energy of the isotopic species of interest, that species can be selectively excited and dissociated.

A requirement for isotopic selectivity of predissociation is that the shift of the vibrational energy levels for the different isotopic species be greater than their energy widths. The energy width of a state is determined in part by its lifetime, and longer-lived states have narrower energy widths. Predissociative states in some molecules are relatively long-lived, and selective predissociation not only works but also has a high quantum yield. That is, if the molecule absorbs a photon of the right frequency to raise it to a predissociative state, it will almost always dissociate rather than decay to lower-energy states through emission of photons.

One successful application of this process is the predissociation of formaldehyde (H,CO) to produce carbon monoxide enriched in carbon-13. Laser photons with a wavelength of 334 nanometers excite $H_2{}^{13}C0$ molecules to a vibrational level of an excited electronic state that predissociates into hydrogen and carbon monoxide molecules. Some of the $H_a{}^{12}C0$ molecules also dissociate, but early experiments produced carbon monoxide with a concentration of carbon-13 greater by a factor of 3 or 4 than its initial natural isotopic abundance.

Predissociation of formaldehyde with a laser of different wavelength has also been studied as a practical way to separate hydrogen and deuterium. From an equal mixture of H_2CO and D_2C0, products have been obtained with deuterium-to-hydrogen ratios of 9, in contrast to the original ratio of 1. Although these results seem impressive, the natural abundance of deuterium is so small (about 0.015 per cent) that the enrichment must be increased significantly for any practical application.

This process is being actively investigated by the Canadians at Ontario Hydro for production of the heavy water needed in their CANDU (Canadian deuterium uranium) power reactors. A CANDU reactor requires about 800 kilograms of heavy water per megawatt of capacity, and at the present cost of $250 per kilogram, the heavy-water inventory represents about 15 to 20 per cent of the total capital cost of the reactor. Recent predissociation experiments at Ontario Hydro show enrichments on the order of 1000. and experiments based on multiple-photon dissociation have also demonstrated high enrichments. These results indicate that laser isotope separation may be a potentially promising technology for low-cost production of heavy water.

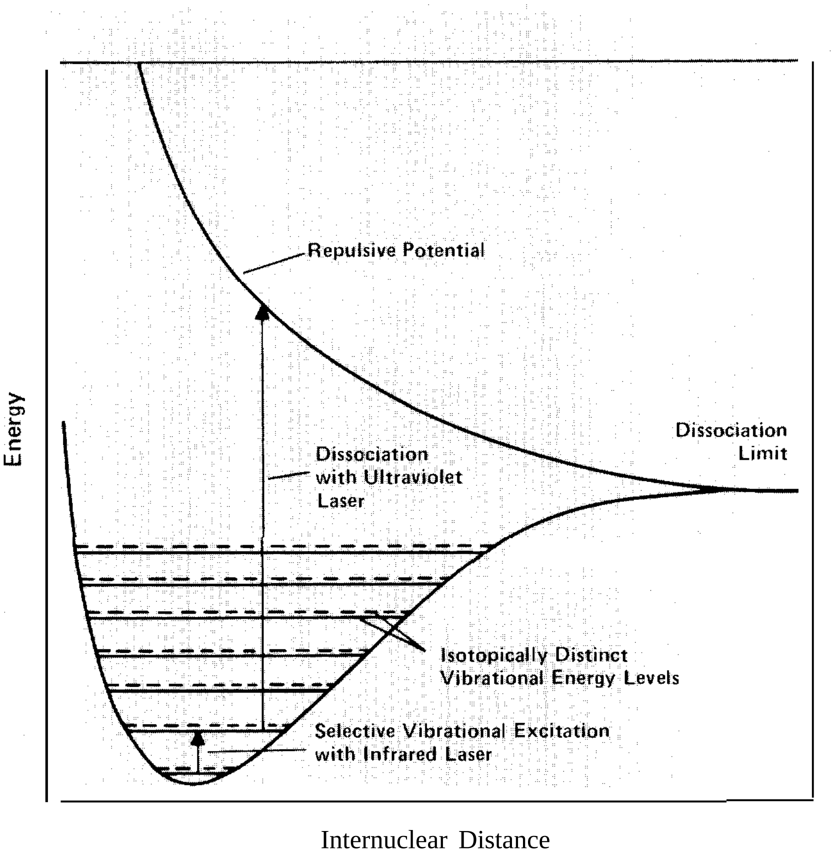

Fig. 4. ***In two-step photodissociation, an infrared laser selectively excites a vibrational level of one isotopic species and thereby raises molecules of that species closer to the dissociation limit. An ultraviolet laxer then raises the excited molecules to an unstable electronic configuration represented by the repulsive potential. The molecule then dissociates into stable chemical fragments. (Predissociation can also occur in the ultraviolet step.)***

TWO-STEP PHOTODISSOCIATION. In predissociation a single laser provides both the isotopic selectivity and the dissociation. The quantum yield for this process is quite high, but selectivity is limited to a few molecules with distinct features in their electronic absorption spectra. However, we can make photodissociation selective in a very wide range of molecules by breaking the process into two steps, the first providing high selectivity and the second efficient dissociation (Fig. 4).

In the first step infrared lasers selectively

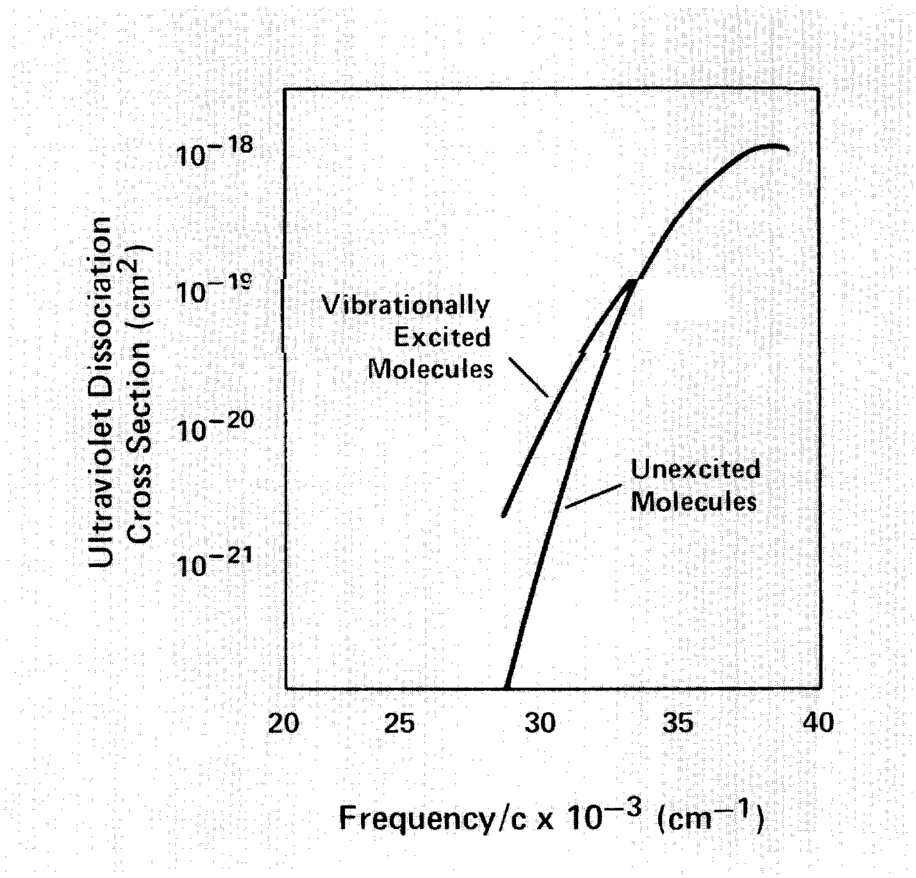

Fig. 5. The effect of vibrational excitation induced by an infrared laser on the ultraviolet dissociation cross-section spectrum of CF_3I. Vibrational excitation increases the dissociation cross section at a given ultraviolet frequency and shifts the spectrum to lower frequencies. At about 29,000 cm^{-1} the dissociation cross section for the selectively excited molecules is about 10 times larger than that for the unexcited molecules. Data from "Laser Isotope Separation of Carbon by Multiple IR Photon and Subsequent UV Excitation of CF_3I Molecules, " I. N. Knyazev, Yu. A. Kudriavtzev, N. P. Kuzmina, V. S. Letokhov, and A.A. Sarkisian, Applied Physics* 17, *427-429 (1978).

excite the vibrational states of one isotopic species and not the others. To date most experiments involving selective vibrational excitation have dealt with molecules whose vibrational transition frequencies overlap the output frequencies of the carbon dioxide ($C0_2$) laser. This laser operates at several wavelengths centered around 10 micrometers with a pulsed optical output that can be varied over a wide power range.

The second step is dissociation of the selectively excited moleucles with an ultraviolet laser. Figure 4 shows that dissociation from a vibrationally excited state requires an ultraviolet photon with an energy, and hence frequency, lower than that required for dissociation from the ground state. In an ideal situation the lower-frequency ultraviolet photons will not dissociate the unexcited molecules, and the selectivity of the first step will be preserved.

In this two-step process the excitation and the dissociation must occur on a time scale that is short compared to the lifetime of the intermediate vibrational state. Otherwise, the excited molecules can lose their vibrational energy through collisions to other isotopic species or to lower-energy vibrational states not accessible to dissociation. Since the $C0_2$ laser is normally operated with a pulse length of 50 to 100 nanoseconds, which is shorter than the lifetime of the vibrational state. most vibrationally excited molecules will not lose their energy before being dissociated by the ultraviolet laser pulse if the pressure of the absorbing molecular gas is sufficiently low. For 100-nanosecond pulses the gas pressure must be a few torr or less to avoid the effects of collisions.

Two-step photodissociation has been applied successfully to the separation of carbon isotopes in trifluoroiodomethane (CF_3I). This molecule has a strong vibrational absorption at a frequency covered by the $C0_2$ laser. Among the parameters influencing the dissociation are the frequency of the ultraviolet laser and the fluence of the infrared laser. (The fluence, or time-integrated intensity, of a laser beam is a measure of its energy per unit beam area.)

Figure 5 shows the ultraviolet dissociation cross section, or dissociation probability, as a function of ultraviolet photon frequency. Before infrared excitation the dissociation cross-section spectra for different isotopic species are nearly the same. The cross section is zero at low frequencies and then rises steeply to a nearly constant value. Infrared excitation increases the photodissociation cross section at a given frequency and shifts the threshold for dissociation to lower frequencies (to the red). This shift allows one to choose an ultraviolet laser frequency at which the dissociation cross section is large for excited molecules (the selected isotopic species) and small for unexcited molecules. If the infrared excitation were perfectly selective, the ratio of the dissociation cross section for the excited molecules to that for the unexcited molecules at a given ultraviolet frequency would be a direct measure of the highest enrichment attainable.

Figure 6 shows that the dissociation cross section increases with the fluence of the infrared laser. Therefore, one might expect better selectivity at higher fluences. But because the selectivity of the infrared excitation is finite, some molecules of the unwanted isotopic species are vibrationally excited. Higher infrared fluence increases the dissociation cross section of these molecules also. Consequently, higher fluence increases the concentration of the unwanted isotopic species in the product and thus degrades the overall selectivity. A similar situation holds in the case of heavy elements.

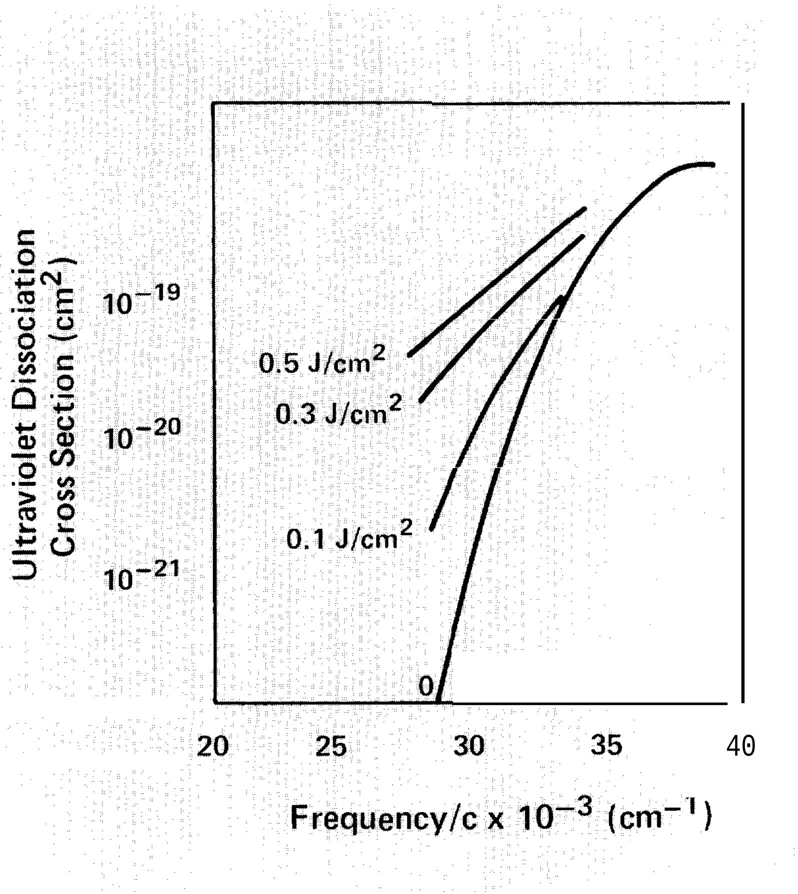

Fig. 6. The low-frequency edge of the ultraviolet dissociation cross section spectrum for CF_3I. Each curve is labeled by the fluence of the infrared laser pulses that provided vibrational excitation of the molecules. As the infrared fluence increases, the cross section at a particular ultraviolet frequency increases and the threshold frequency for dissociation shifts more and more to the red, that is, to lower frequencies. This red shift indicates that higher infrared fluences raise the molecules to higher vibrational states. Data from source cited in Fig. 5.

MULTIPLE-PHOTON DISSOCIATION. Figure 6 also shows that the threshold frequency for ultraviolet dissociation shifts more and more to the red as the infrared laser fluence increases. These relatively large shifts clearly indicate that the $C0_2$ laser is exciting the molecules to very high vibrational states. Thus, many photons of equal energy are being absorbed by a single molecule, a very surprising result! If molecular vibrations were governed by forces that increased linearly with displacement, as they are in a harmonic oscillator, the energy difference between vibrational states would be constant and photons with this constant energy could "resonantly" induce transitions to higher and higher vibrational states (Fig. 7a). But most molecular vibrations are enharmonic, that is, they involve nonlinear forces. The anharmonicity results in progressively smaller energy differences between vibrational states. Thus, as a molecule's vibrational energy increases, it should absorb infrared photons of lower energy and its interaction with constant-energy photons should quickly become nonresonant and ineffective.

The discussion above suggests that a molecule should absorb only one photon at the frequency corresponding to the energy of the transition from the ground state to the first vibrational state. In fact. this type of resonant absorption is observed in diatomic and many triatomic molecules. Experiments have shown, however, that polyatomic molecules can absorb many single-frequency infrared photons, and these photons can excite the molecule to high vibrational states and even to the dissociation limit (Fig. 7b). Even more intriguing is the fact that this multiple-photon process can be isotonically selective and can therefore be used for isotope separation.

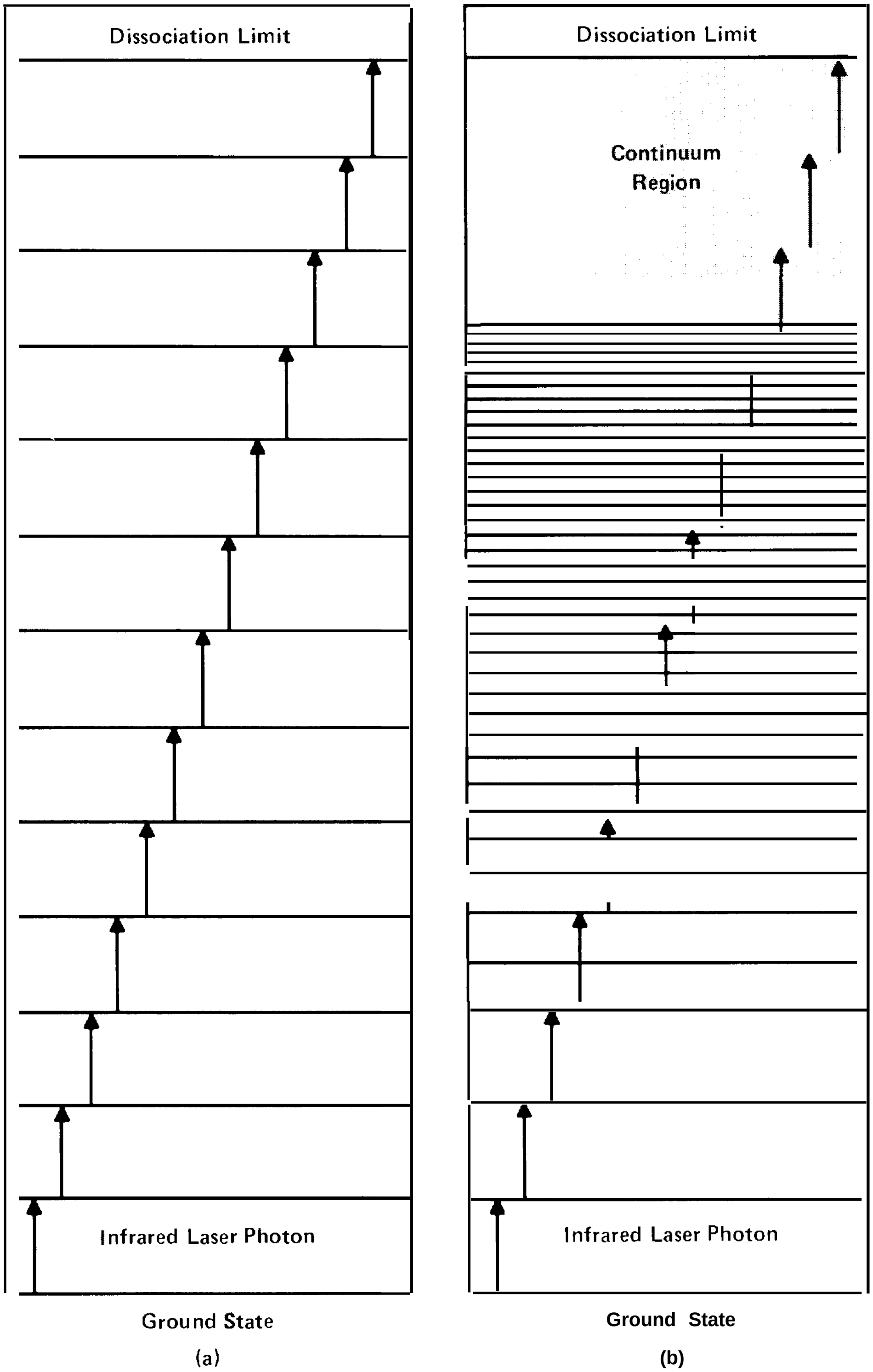

Fig. 7. In multiple-photon excitation a molecule absorbs many infrared photons of the same energy. If the molecule's vibrational energy levels were equally spaced as in (a), multiple-photon excitation could be understood as a resonant excitation at each step of the vibrational ladder. The absorbed photons are represented by arrows whose lengths exactly match the constant energy spacing between levels in (a). But, as shown in (b), the vibrational ladder for any physical molecule is enharmonic. That is, the spacing between vibrational levels decreases with vibrational energy. Therefore, the energy of the absorbed photons becomes increasingly mismatched with the energy spacing. Theoretical modeling is aimed at explaining why absorption can occur in the presence of this mismatch.

Between 1971 and 1973 a number of Los Alamos researchers, with the encouragement of Keith Boyer, pioneered experiments leading to the discovery of multiple-photon excitation phenomena. In the course of work with tetrafluorohydrazine (N_2F_4), John Lyman and Reed Jensen published experimental results showing that dissociation occurs in response to infrared-laser-induced vibrational excitation and that the distribution of vibrational energy in the molecules is far from thermal equilibrium. To our knowledge the first correct explanation of multiple-photon excitation and dissociation and the first suggestion of their application to isotope separation were summarized in a Laboratory memorandum by C. Paul Robinson in 1973. Then in 1975 experiments at the Institute of Spectroscopy in the Soviet Union and at Los Alamos were reported that demonstrated these amazing phenomena for sulfur hexafluoride (SF_6). The results were clear: under collisionless conditions, a polyatomic molecule could absorb 45 photons, a 0.1-electron volt photon source could break a 4-electron volt chemical bond, and multiple-photon dissociation could exhibit isotopic selectivity.

Since 1975 there has been an explosion of theoretical and experimental studies of this phenomenon throughout the scientific centers of the world. It now appears that multiple-photon excitation occurs in all polyatomic molecules. The process occurs most readily at high radiation intensities but is also clearly manifest at low intensities. Also, it occurs over a broad range of the frequencies within a given absorption feature of a molecule. Theory and experiment have provided a qualitative description of the excitation mechanism, which is primarily a multi step process rather than a multiphoton process involving virtual states. (The latter may, however, be important at some excitation frequencies.)

For some molecules the experimental results can be understood in terms of quantitative theoretical models. But these models are not unique: conceptually different models can be made to fit the experimental data. Moreover, collisional effects have not been modeled nor is their inclusion straightforward. Additional work will be required to provide a satisfactory and detailed understanding of the complex interaction between the molecules and the radiation field (see "Multiple-Photon Excitation" in this issue). There still exist two basic questions. How is the absorbed energy distributed among the various vibrational modes of a molecule at different degrees of vibrational excitation ? And how does absorption of one photon affect the absorption probability for the next?

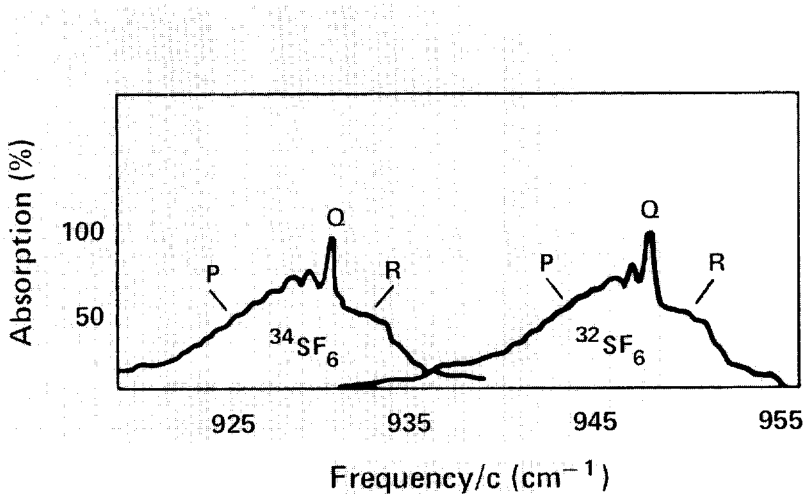

Fig. 8. The low-intensity v_3 absorption bands of $^{34}SF_6$ and $^{32}SF_6$. The absorption band for the heavier isotopic species is shifted to the red by 17 cm^{-1}. The Q-branch peaks correspond to transitions in which* J *does not change. The* P *and* R *branches correspond to transitions in which $\Delta J =$ 1 and +1, respectively (see Fig. I).

Despite these uncertainties we know that multiple-photon excitation plays a key role in all molecular isotope separation processes that include vibrational excitation. And the process provides an efficient means of separating isotopes in medium-weight molecules using infrared lasers alone.

The three photodissociation techniques described above can be used to separate isotopes of most elements. Table I lists some of the elements whose isotopes have been separated at Los Alamos. This list could be extended substantially by including published results from other research institutions.

Laser Isotope Separation in SF_6

A more detailed look at the work done on separating sulfur isotopes will illustrate specific features of selective multiple-photon excitation, as well as generic considerations involved in the development of a practical molecular isotope separation process.

The four naturally occurring isotopes of sulfur and their abundances are sulfur-32 (95.0 per cent), sulfur-33 (0.76 per cent), sulfur-34 (4.22 per cent), and sulfur-36 (0.02 per cent). The odd-nucleon isotope sulfur-33 is of value as a tracer because its presence can be detected by nuclear magnetic resonance techniques. Its applications include agricultural studies and structural studies of proteins,

The Los Alamos process for separating sulfur isotopes is based on SF_6, an octahedrally symmetric molecule like UF_6. Some researchers refer to SF_6 as the hydrogen atom of multiple-photon excitation because it is the molecule most studied in the attempts to understand the phenomenon. Here we will discuss only those results relevant to isotope separation.

Portions of the low-intensity infrared absorption spectra of $^{32}SF_6$ and $^{34}SF_6$ at room temperature are shown in Fig. 8. Absorption at these frequencies induces excitation of the v_3 vibrational mode of the molecule's ground electronic state (see Fig. 2). There are many absorbing transitions corresponding to different initial and final rotational states of the v_3 vibrational mode. The highest peak for each isotope, labeled Q in Fig. 8, results primarily from transitions in which *J*, the quantum number for the molecule's rotational angular momentum, does not change. The other portions of the v_3 absorption band. called *P* and *R* branches, correspond to v_3 transitions in which *J* decreases and increases, respectively, by unity. Note the 17-reciprocal centimeter (cm^{-1}) isotope shift of the Q-branch peak from 931 cm-l for $^{34}SF_6$ to 948 cm^{-1} for $^{32}SF_6$.

In early investigations of SF_6, we could not even resolve the smaller peaks near the Q-branch peaks nor could we identify the specific transitions that give rise to the Q-branch peaks. Thanks to the revolution that has occurred over the past seven years in high-resolution molecular spectroscopy, we now know what transitions are being excited in the Q branch as well as the origin of the subsidiary peaks. Called hot bands, the subsidiary peaks are due to v_3 vibrational transitions from low-energy vibrational states rather than the molecule's ground state (see "The Modern Revolution in In-

TABLE I

MOLECULAR LASER ISOTOPE SEPARATION SUCCESSES AT LOS ALAMOS

Molecule	Isotopes	Laser System	Dissociation Mechanism
H_2CO (in liquid Xe)	**$^{1,2}H$**	**Frequency-doubled dye laser (319 nm) and HeCd laser (325 nm)**	**Predissociation**
BCl_3	**$^{10,11}B$**	**CO_2 laser (10 μm) plus ultraviolet flashlamp**	Two-step photodissociation
BCl_3	**$^{10,11}B$, $^{35,37}Cl$**	**CO_2 laser (10 μm)**	Multiple-photon dissociation
CF_2Cl_2	**$^{12,13}C$**	**$C0_2$ laser (10 nm)**	Multiple-photon dissociation
CS_2	**$^{12,13}C$, $^{32,34}S$**	**ArF laser (193 nm)**	Predissociation
CS_2 (in liquid N_2, Ar, or Kr)	**$^{12,13}C$**	**Iodine resonance lamp (206 nm)**	Predissociation
0 *	**$^{16\text{-}18}O$**	**ArF laser (193 nm)**	Predissociation
$U0_2F_2$(in liquid CH_30H)	**$^{16,18}O$**	**Dye laser (448 and 455 nm)**	Predissociation
SiF_4	**$^{28\text{-}30}Si$**	**CO_2 laser (9 μm)**	Multiple-photon dissociation
SF_6, SF_5C1, S_2F_{10}, SF_5NF_2	**$^{32\text{-}34}S$**	**CO_2laser (10 μm)**	Multiple-photon dissociation
MoF_6	92,94-98, 100MO	**CO_2 laser (9 μm)**	Multiple-photon dissociation
UF_6	^{233,238} u	Raman-shifted $C0_2$ laser (16 μm) plus ultraviolet laser	Two-step photodissociation

frared Spectroscopy" in this issue). This detailed spectroscopic data has provided the basis for quantitative theoretical models of the excitation process.

Pulses from a $C0_2$ laser tuned near either of the isotonically distinct Q-branch peaks of the v_3 vibrational mode of SF_6 will selectively dissociate that isotopic species if the laser intensity is sufficiently great. The dissociated molecules, namely SF_5, then undergo further dissociation to SF_d, which is then converted to SOF_2 for separation from the other chemical species by fractional distillation.

The selectivity of this process depends on both the laser frequency and its fluence. Figure 9 shows the probability for dissociation of SF_6 as a function of laser fluence at a laser frequency of 944 cm-l. We see that at low fluences only the $^{32}SF_6$ molecules are dissociated, but at higher fluences the other isotopic species may also dissociate. This decrease in selectivity is predominantly due to a broadening of the vibrational states' energy widths in the presence of intense radiation fields.

At high laser intensity we can achieve the best selectivity for $^{32}SF_6$ by tuning the laser to the red of its 948-cm^{-1} peak in the low-intensity spectrum, or closer to the excitation frequency of the unwanted isotopic species. We can see this quantitatively in Fig. 10, where the dissociation spectrum at high laser intensity is superimposed on the low-intensity absorption spectrum. Why this laser tuning is optimum for $^{32}SF_6$ seems puzzling until we realize that the laser is pumping molecules up the entire ladder of vibrational states, all the way to dissociation. Since the energy difference between vibrational states decreases as the molecules reach higher states, those molecules some distance up the ladder will more readily absorb radiation at frequencies lower than the frequency required to reach the first vibrational state. Thus, the frequency for selective vibrational excitation at high intensity is red-shifted from that at low intensity.

One measure of the efficiency of an

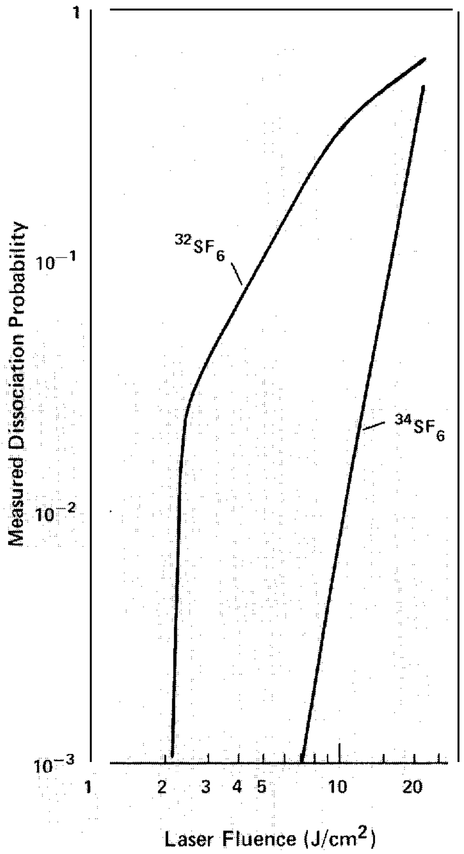

Fig. 9. Probability of dissociation for $^{32}SF_6$ and $^{34}SF_6$ *as a function of* $C0_2$ *laser fluence. The laser is tuned to 944 cm*$^{-1}$*, slightly to the red of the Q-branch peak of* $^{32}SF_6$ *and far to the blue of the Q-branch peak of* $^{34}SF_6$ *(see Fig. 8). The dissociation probability increases sharply with laser fluence. At low fluences only* $^{32}SF_6$ *dissociates, but at high fluences* $^{34}SF_6$ *also dissociates. With the laser tuned to 944 cm*$^{-1}$*, the best compromise between selectivity and the amount of* $^{32}SF_4$ *produced is achieved with fluences in the range of 2 to 8 J/cm*^{2}*. Data from "Energy and Pressure Dependence of the* $C0_2$ *Laser Induced Dissociation of Sulfur Hexafluoride, " W. Fuss and T. P. Cotter, Applied Physics 12,265-276 (1977).*

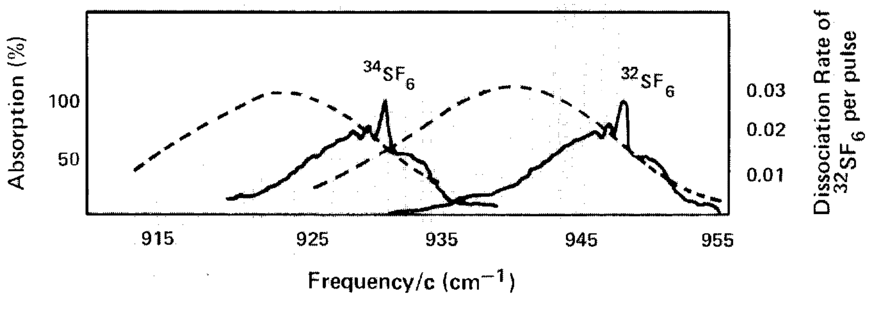

Fig. IO. Comparison of the high-intensity multiple-photon dissociation probability spectra (dashed) and the low-intensity absorption spectra for $^{34}SF_6$ *and* $^{32}SF_b$ *show's that the best selectivity for multiple-photon dissociation of* $^{32}SF_6$ *occurs with the high-intensity laser tuned to the red of its !ow-intensity absorption peak. This red shift is caused by the anharmonicity of the molecule's vibrational energy ladder. Dissociation probability data from "Explanation of the selective dissociation of the* SF_6 *molecule in a strong IR laser field, " R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puretskii, JETP Letters 23,22 (1976).*

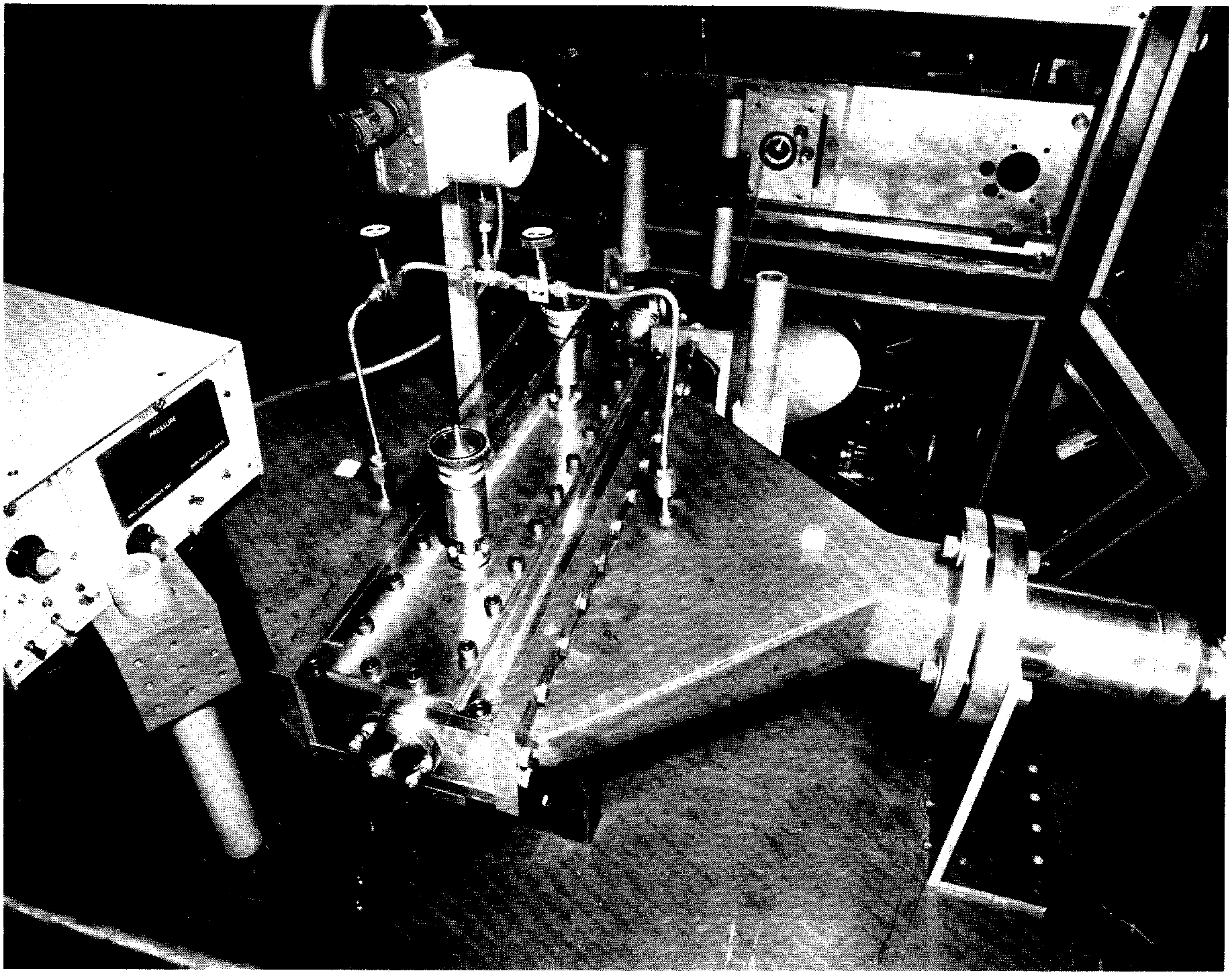

Fig. 11. Photograph of plant prototype constructed at Los Alamos for production of sulfur-33 and sulfur-34 by multipie-photon dissociation of SF_6. Shown are the gas expansion area leading into the photolysis chamber (center front) and the high-repetition-rate pulsed $C0_2$ laser (center rear).

isotope separation process is the enrichment parameter β. In the case of the sulfur isotopes, 13 for, say, sulfur-34 is defined as

$$\beta_{34} = \frac{(^{34}N/^{32}N)_{\text{product}}}{(^{34}N/^{32}N)_{\text{feed}}} ,$$

where ^{34}N and ^{32}N are the number densities of sulfur-34 and sulfur-32, respectively. The laboratory experiments based on multiple-photon dissociation of SF, with single-frequency infrared radiation have produced values of β_{34} as high as 1000.

To see how well the process would work on a larger scale, Los Alamos scientists have constructed and operated a small plant prototype for production of sulfur-33 and sulfur-34 by multiple-photon dissociation. The prototype (Fig. 11) consists of a gas recirculation system that provides a continuous flow of SF_6 gas through an irradiation zone and a $C0_2$ laser with an output energy of 0.5 joule per pulse that irradiates the gas at a repetition rate of 200 hertz. Dimensions of the irradiation zone in centimeters are 50 by 0.3 by 0.3. The laser, tuned to the $^{32}SF_6$ high-intensity absorption peak, selectively dissociates the molecules by multiple-photon excitation and produces $^{32}SF_4$ plus fluorine atoms. Back reaction of the fluorine atoms with $^{32}SF_4$ is prevented by adding hydrogen and a small amount of water vapor to the system. A fast chemical reaction occurs that converts SF_4 to SOF_2, which is chemically inert and can be separated from the other chemical species.

After a fixed period of operation, the gas is pumped from the system, and the various chemical species are separated in a distillation column. In 6 hours this system produces about 1 gram of SF_6 with a β_{34} of about 2.2

and a β_{33} of about 2.0. More than 99 per cent of the sulfur atoms in the SOF_2 distillate are the sulfur-32 species.

Multiple-Photon Excitation of Heavy Elements

In SF_6 multiple-photon dissociation was achieved by tuning high-intensity CO_2 lasers to the red of the absorption peak of the lighter isotopic species. Both the frequency shift and the high intensity were necessary for efficient dissociation of the lighter molecules. But these conditions can also compromise the selectivity. Since the laser is tuned closer to the unwanted isotopic species' absorption peak and since this absorption feature is broadened by the strong electromagnetic field, the probability of exciting and dissociating both isotopic species is increased and the selectivity is reduced.

For SF_6 the isotope shift is large enough that the red shift and the power broadening of the absorption peak at high intensities do not destroy the selectivity. But for heavy elements, whose isotope shifts may be smaller by a factor of 10 or more, these effects can reduce the selectivity drastically. In fact, the red shift in the absorption peak of the excited species can be much larger than the isotope shift between species.

These problems can be circumvented to a large degree by using two infrared lasers with different frequencies and intensities (Fig. 12). A low-intensity laser is tuned near the resonant frequency of the ground-to-first-vibrational-state transition of the lighter molecule. This laser selectively excites the lower vibrational states of the molecule. A second high-intensity laser is tuned to the red-shifted absorption peak of the excited molecules. This laser interacts predominantly with those molecules tagged by the first laser and excites them to higher vibrational states and, at sufficiently great intensities, to dissociation.

In principle, one could replace the second high-intensity laser with additional infrared lasers of lower intensity to provide a more nearly resonant excitation up the entire vibrational ladder to dissociation. Another alternative is to use two-frequency infrared excitation followed by dissociation with an ultraviolet laser. As discussed below, this latter scheme has been chosen for separation of uranium isotopes. Optimization of any laser isotope separation process with respect to the excitation method and the exact laser tunings depends on the individual molecule. In evaluating the tradeoffs, the economics of the process plays an important role.

The advantages of two-frequency infrared excitation for the heavier elements has been

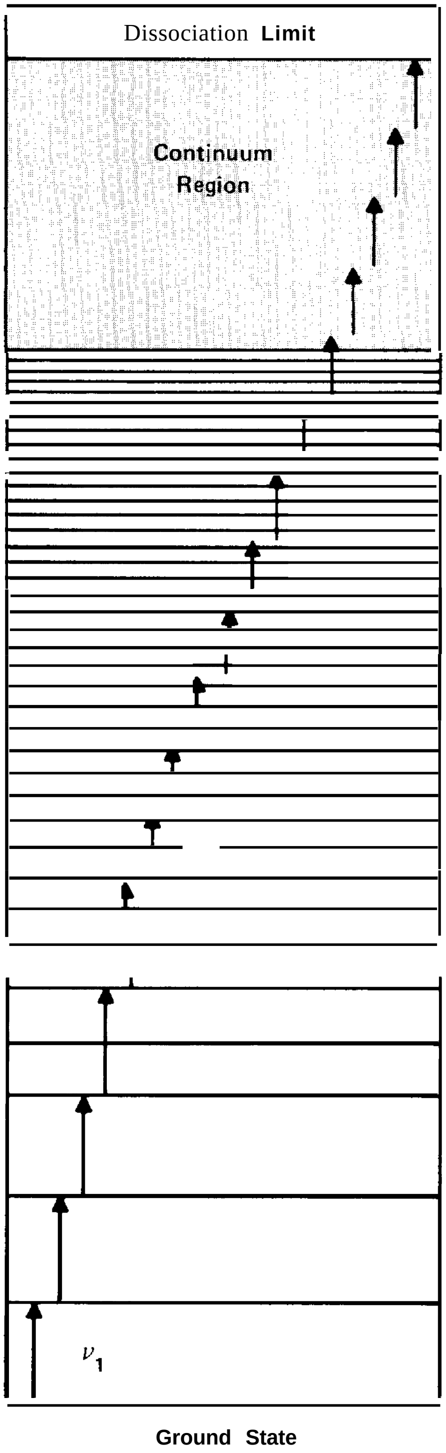

Fig. 12. Isotopic selectivity of multiple-photon excitation in heavy elements can be enhanced by using two infrared lasers. A first low-intensity infrared laser selectively excites molecules of one isotopic species to the first few low vibrational levels. A second infrared laser, lower in frequency and higher in intensity than the first, interacts predominantly with those molecules excited by the first laser and excites them to high vibrational levels. These molecules can then be dissociated with either an ultraviolet laser or with the second infrared laser at sufficient intensities. Note that the distribution of vibrational levels becomes a quasi-continuum at high energies. Rotational and Coriolis splitting of the high-energy levels makes the distribution even more continuous. The near continuum of levels leads to an almost resonant excitation by the second laser.

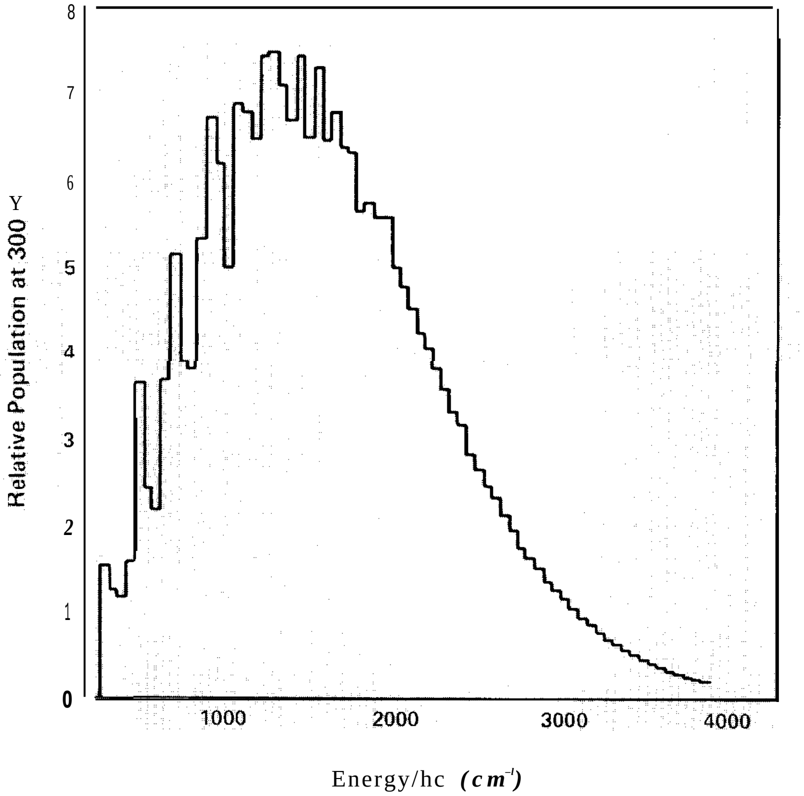

Fig. 13. At room temperature only a very small fraction (about four-thousandth) of the molecules in a sample of UF$_6$ at room temperature occupies the ground state. Most of the molecules are distributed as shown here among many vibrational states. (The lowest vibrational state is at 143 cm-l and the lowest state of the v_3 vibrational mode is at 628 cm–’. At 300 kelvin the thermal energy is 210 cm^{-1}.) Therefore, at room temperature only a small fraction of the molecular population can be excited with a narrow’ bandwidth laser.

demonstrated for osmium by Soviet researchers. They separated osmium- 187 (1.6 per cent) and osmium-192 (41 per cent) by selective dissociation of osmium tetroxide (0s0_4) with a pulsed CO, laser. The isotope shift in the absorption spectrum of this molecule is 1.3 cm^{-1}. Single-frequency excitation produced a β_{187} of only 1.15. With two-frequency excitation β_{187} was increased to 1.5. Since the fractional increase of the enriched product varies as $\beta - 1$, the two-frequency excitation increased this quantity by a factor of 3.

The Uranium Enrichment Process

The primary motivation behind laser isotope separation studies at Los Alamos has been the development of an efficient, economical process for enriching uranium. Our early decision to focus on a molecular rather than an atomic process was based in part on the fact that a molecular process offered more possibilities. For several reasons the molecule selected was UF$_6$. One reason was that the techniques for handling this gas were well known from its use in gaseous diffusion plants, We chose a two-step (infrared-plus-ultraviolet) photodissociation process, several years before the discovery of multiple-photon dissociation.

The idea was to selectively excite the v_3 vibrational mode of ^{235}UF$_6$ (analogous to the v_3 mode of SF$_6$ shown in Fig. 2) and then dissociate the excited molecules with an ultraviolet laser into fluorine atom, s and ^{235}UF$_5$. The UF$_5$ molecules condense into particulate that are easily separated from the process material.

The first step in this process, selective excitation by infrared lasers, is the most critical and has been much more difficult to achieve in UF$_6$ than in SF$_6$. The reasons are twofold. First, although the CO$_2$ laser conveniently covered the 10-micrometer region corresponding to the frequencies of the SF$_6$ v_3 vibrational mode, no lasers were available at the frequencies of the UF$_6$ vibrational transitions. The strongest absorption in UF$_6$ corresponds to V$_3$ transitions around 16 micrometers; consequently, we had to design new high-intensity pulsed lasers at these frequencies. Our success represented a first-usually a laser is developed before its applications are known. However, development of the appropriate laser systems at the required frequency and intensity specifications took some time and was a pacing item during the early years of the program (see sidebar “Lasers for Uranium Enrichment”).

The second set of problems arises from the fact that uranium is a heavy element, much heavier than sulfur. The isotope shift of the v_3 vibrational mode of UF$_6$ is less than 1 cm^{-1} compared to 17 cm^{-1} for SF$_6$. The power broadening mentioned in the previous section therefore becomes much more serious. Moreover, because the fundamental vibration modes of UF$_6$ are much lower in energy than those of SF$_6$, at room temperature most of the UF$_6$ molecules are not in the ground vibrational state but are distributed among thousands of vibrational states (Fig. 13). Even high-energy vibrational states of UF$_6$ (those with energies much greater than thermal energy) are populated at room temperature because of their large degeneracies. Hence only a small fraction of the molecular population can be accessed with a narrow bandwidth laser. In addition, the v, absorption band of UF$_6$ is significantly broadened and red-shifted at room temperature, and any spectral features with an isotope shift are obscured within the room-temperature bandwidth of about 30

continued on page 22

SIDEBAR 2:

Lasers for Uranium Enrichment

Like radar and sonar, the acronym laser (light amplification by stimulated emission of radiation) has achieved the status of a familiar word. But the principles upon which lasers operate may not be so familiar. Atoms or molecules can exist only in certain definite energy levels. In the presence of a photon with an energy equal to the difference between the energies of two such levels, atoms or molecules can undergo either of two processes, absorption or stimulated emission. In absorption, the more familiar process, an atom or molecule in the lower energy level absorbs the photon and makes a transition to the upper energy level. In stimulated emission an atom or molecule in the upper level makes a transition to the lower level and emits a photon, The emitted photon and the stimulating photon are spatially and temporally coherent (that is, they have the same phase and energy) and travel in the same direction. If the upper energy level has a greater population of atoms or molecules than the lower level (a condition known as population inversion), an intense field of coherent radiation can be produced as the emitted photon in turn stimulates another atom or molecule in the upper level to emit a photon, and so on. The atoms or molecules are then said to be lasing.

Developing a working laser is not as simple as explaining its operating principle. The first requirement is a collection of atoms or molecules among whose energy levels are suitable upper and lower levels between which lasing can occur. (Suitable here refers to the ease of producing and maintaining a population inversion. That is, the upper level must be easily populated, and the lower level, as it is populated by lasing, must be easily depopulated.) Then, this active medium must be "pumped" to achieve a population inversion. Electron bombardment or exposure to an intense light source are common methods of pumping. And usually the active medium must be contained within a suitable optical cavity, such as a pair of highly reflecting mirrors. The cavity provides the feedback for lasing. To extract energy from the cavity, one of the mirrors is partially transmitting. The output of the cavity is an intense, highly monochromatic beam of light.

Compared to light from other sources, laser light can be much more intense, monochromatic, and directional. Lasers producing such light with wavelengths ranging from the ultraviolet to the far infrared are now available. In fact, some lasers can be tuned to cover a wide range of wavelengths. The many applications of laser light take advantage of one or more of its unusual properties.

Normally, a laser is developed ***before*** its applications are conceived. But our program for enriching uranium presented the reverse situation—the application was at hand, but lasers with the required properties did not exist.

The properties demanded of an infrared laser for the first step in our enrichment scheme, selective vibrational excitation of $^{235}UF_6$ molecules, were a wavelength near 16 micrometers, narrow frequency bandwidth, high energy per pulse (greater than 0.1 joule), and short pulse length (on the order of 0.1 microsecond). Another highly desirable, if not mandatory, property was tunability, either continuous or in discrete steps. Our search for such a laser began about eight years ago with suggestions from within and without the Laboratory. Among the suggestions were the following: a 16-micrometer CO_2 laser based on different vibrational levels of the molecule than is the 10.6-micrometer $C0_2$ laser; an optical parametric oscillator based on the nonlinear crystal cadmium selenide (CdSe); nonlinear frequency mixing of carbon monoxide (CO) and CO_2 lasers in the semiconductor cadmium germanium arsenide ($CdGeAs_2$), a material referred to at the time as unobtainium; optically pumped carbon tetrafluoride (CF_4 or ammonia (NH_3) lasers; and frequency shifting of the output of the 10.6-micrometer CO_2 laser by Raman scattering.

Because of early success with the optical parametric oscillator and the frequency-mixed CO-CO_2 laser, these two lasers were the main tools for our early experiments. Later, the optically pumped CF_4 and NH_3 lasers were demonstrated experimentally and were developed as high-energy lasers. These are still used in some of our experiments. The 16-micrometer CO_2 laser was successfully demonstrated but proved to have the wrong frequency for the process,

The most powerful laser system at 16 micrometers results from Raman scattering of the 10,6-micrometer CO_2 laser's output by the second rotational energy level in parahydrogen. (Raman scattering refers to an interaction of photons with a molecule in which the scattered photons undergo a frequency change determined by the molecule's rotational or vibrational energy levels.) Suggested early in the program, this concept is covered by a patent issued to its Los Alamos originators. We did not pursue its development until it was experimentally demonstrated about three years ago at Stanford University and at Exxon Nuclear Co., Inc. A system based on this concept is now the major 16-micrometer laser under development for the program, Its energy per pulse is greater than 1 joule, its pulse length is typically 50 nanoseconds, and its frequency is variable over a sufficient range. In addition, the system is efficient, converting as much as 40 per cent of the 10.6-micrometer input energy into 16-micrometer laser light.

The second step of our enrichment scheme, dissociation of the vibrationally excited $^{235}UF_6$ molecules into $^{235}UF_5$, required a laser with a wavelength in the ultraviolet and, like the infrared laser, with high energy per pulse, short pulse length, and tunability. The rare-gas halide lasers, which were developed in 1975, satisfied these requirements. The rare-gas halides belong to a class of diatomic molecules, referred to as excimers, that have a stable excited electronic state and an unstable ground state. This situation is ideal for a laser because a population inversion is easily produced and maintained.

The first rare-gas halide lasers yielded only millijoules of energy and were cumbersome to operate, The technology grew rapidly, however, and today these devices are relatively compact, easy to operate, and produce energies in excess of several joules at repetition rates of one to several hundred hertz.

The rare-gas halide lasers that we have used for isotope separation experiments (and their wavelengths in nanometers) are ArF (190), KrF (254), XeBr (282), XeCl (308), and XeF (354). The wavelengths of these lasers can be increased or decreased by Raman scattering involving vibrational levels of hydrogen, deuterium, or methane. These additional wavelengths provide the opportunity to study the enrichment process as a function of ultraviolet laser frequency over a very broad range.

Much of the technology of rare-gas halide lasers and their Raman shifting was pioneered at Los Alamos. In terms of intensities and repetition rates, the rare-gas halide lasers available today are suitable for use in a production plant prototype. The goals of current development include the increased reliability and longer operational life required for a full-scale plant. ■

continued from page 19

cm–’. The only way to increase the ground-state population and narrow the absorption features is to cool the gas.

Figure 14 shows the collapse of the UF_6 population into the ground state and a few low-energy vibrational states as the temperature is decreased. This collapse simplifies the v_3 absorption band, as shown in Fig. 15. At room temperature and relatively high density the band has very broad features that obscure the Q-branch peaks of both isotopes. But at low temperature a medium-resolution spectrum shows sharp. well-separated Q-branch peaks for the two isotopic species.

More detailed low-temperature spectra have been obtained by scanning across the v_3 absorption band with a tunable semiconductor diode laser. A significant effort has gone into determining the exact value of the isotope shift and identifying the specific rotational-vibrational transitions that can be excited in this frequency interval. Figure 16 shows a high-resolution scan near the $^{235}UF_6$ Q-branch peak. In the Los Alamos uranium enrichment process the infrared laser is tuned to a frequency in this region. A spectrum at even higher resolution would show many additional rotational subcomponents within the structure of Fig. 16. As discussed in “The Modern Revolution in Infrared Spectroscopy,” these subcomponents are due to Coriolis forces and octahedrally invariant tensor forces. The choice of a particular frequency for the selective infrared excitation is based on this detailed knowledge of the low-intensity absorption spectrum.

EXPANSION SUPERCOOLING OF UF_6. Knowing that any uranium enrichment process would require cooling the UF_6 gas to low temperature before infrared excitation, we sought an efficient and practical means of

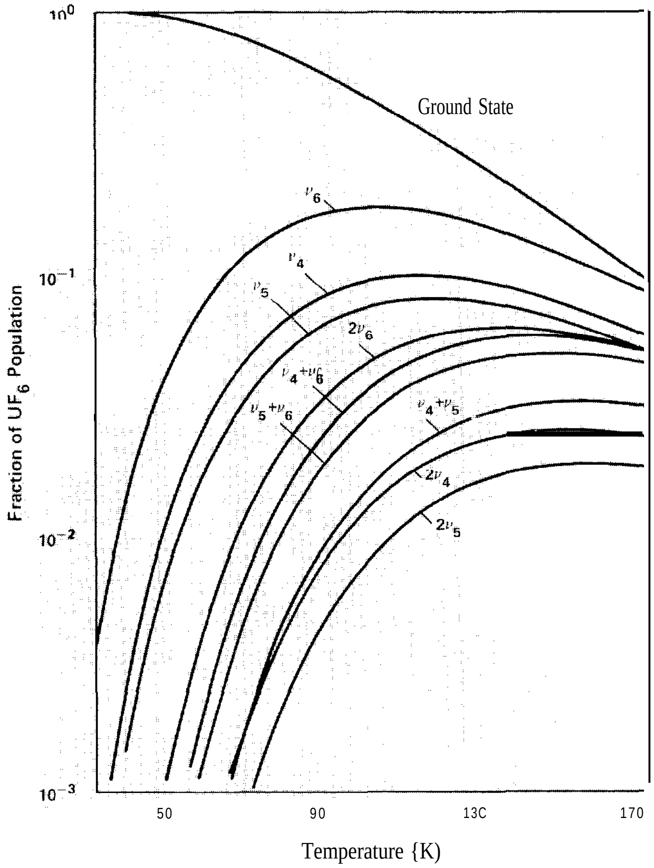

Fig. 14. Calculated thermal populations in the ten lowest vibrational levels of UF_6 as a function of temperature. As the temperature decreases, a greater fraction of the molecules occupies the ground state and the lower vibrational levels. This situation leads to greater selectivity of vibrational excitation and access to a larger UF_6 population.

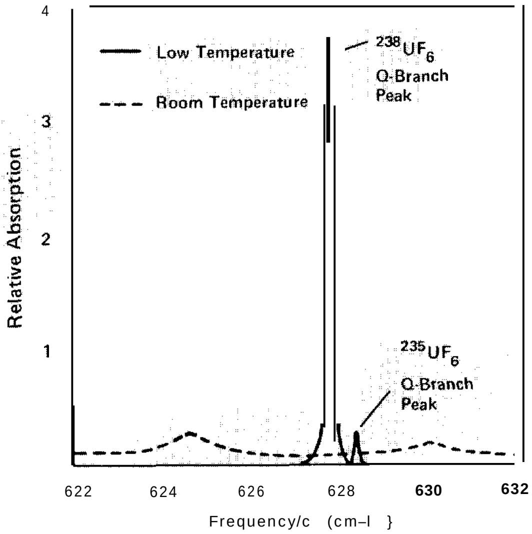

Fig. 15. The v_3 absorption band of expansion-cooled natural-assay UF_6 exhibits narrow, distinct Q-branch peaks for $^{238}UF_6$ and $^{235}UF_6$. In contrast, the room-temperature band is broad and the isotopic features are merged. (For clarity the $^{235}UF_6$ peak is increased in height. The Q-branch peak heights for a sample containing the natural mixture of uranium isotopes are in the ratio of about 140 to I.)

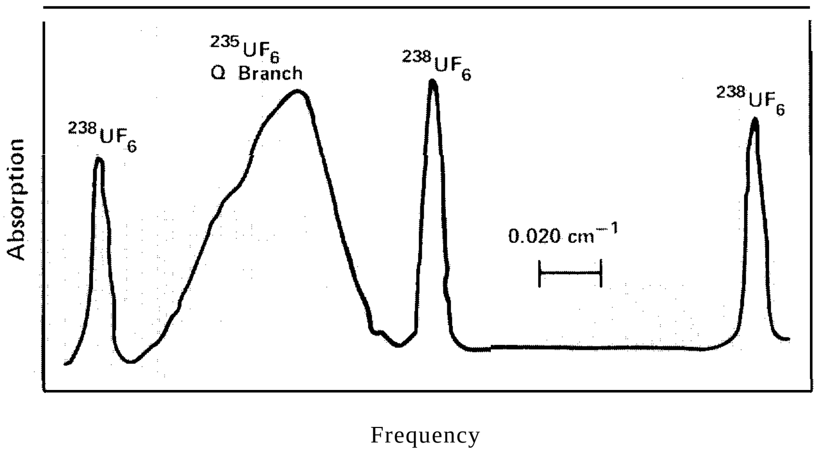

Fig. 16. A small portion of the v_3 absorption band of UF_6 at high resolution. This scan of a sample enriched to 3 per cent in uranium-235 was obtained with a tunable semiconductor diode laser. The sharp peaks labeled $^{238}UF_6$ result from R-branch transitions in $^{238}UF_6$.

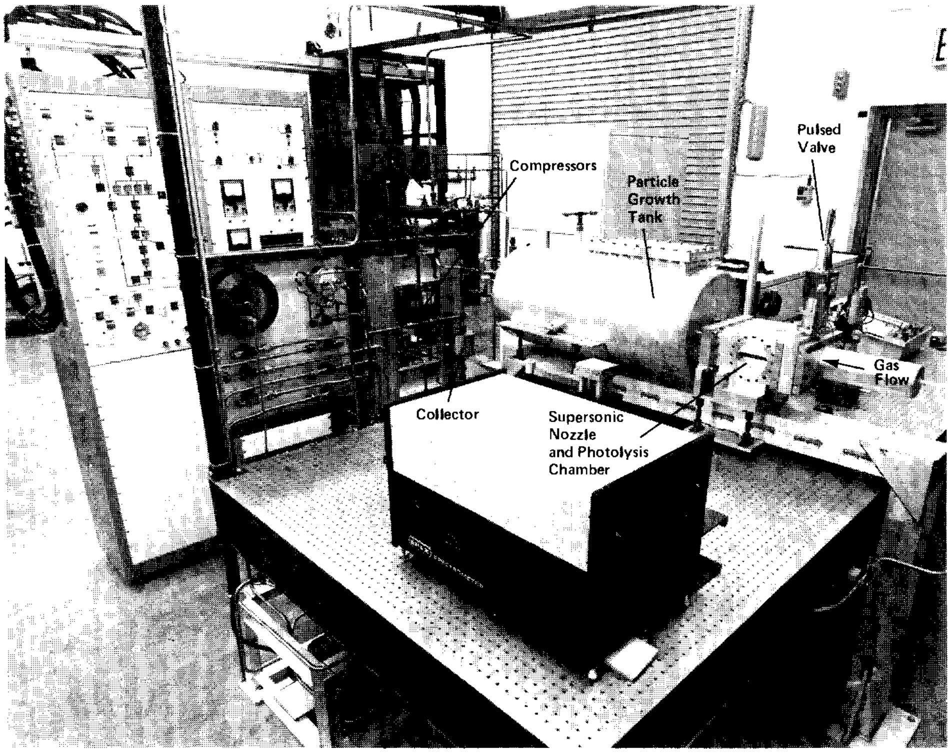

Fig. 17. Photograph of pulsed recirculating loop. This compact system provides a high density of supercooled UF_6 monomers for spectroscopic measurements and enrichments experiments. The system is simple and operates routinely for several hours.

cooling. Static cooling was impossible because the very low vapor pressure of solid UF_6 would provide too few molecules in the gas phase, and it is these molecules on which the laser process is designed to work. Early in the program Theodore Cotter suggested the use of a supersonic nozzle for expansion supercooling, a cooling method that was subsequently used not only in the isotope separation experiments but also in the high-resolution spectroscopy experiments. (Expansion supercooling has since become standard practice in high-resolution spectroscopy.)

The major question concerning this cooling method was whether the gas emerging from the nozzle would remain in the gas phase long enough for the lasers to act on single molecules. After expansion the gas is in a non equilibrium state of supersaturation and has a strong tendency to condense within the flow. At a given temperature the major factor controlling condensation is the UF_6 number density in the flow-cooled region. The theory of homogeneous condensation was not well developed at the start of the project. We have since developed detailed theories and performed extensive experiments on condensation showing that expansion supercooling is a suitable technique. Measurements indicate that the nozzle produces uniform supersonic flow in the central core with only small turbulent-flow boundaries near each wall of the flow channel.

The ratio of final to initial temperature during supersonic expansion is equal to $(P/P_0)^{(\gamma-1)/\gamma}$, where P and P_0 are the final and initial pressures and γ is C_p/C_V, the ratio of specific heats at constant pressure and constant volume. When γ is very nearly unity, as it is for a gas of large polyatomic molecules such as UF_6, the initial pressure and/or the nozzle area expansion ratios must be very large to achieve substantial cooling. To circumvent this constraint, small amounts of UF_6 are mixed with a carrier gas consisting of atoms or small molecules (for example, argon or nitrogen) with a larger γ. Under these conditions substantial gas cooling can be achieved with only modest initial pressure and nozzle area expansion ratios. The carrier gas also provides a collisional environment that ensures continuum fluid flow and thermal equilibrium among the vibrational, rotational, and translational degrees of freedom of the UF_6 before irradiation.

The first infrared absorption measurements on UF_6 at low temperature were accomplished in a blowdown mode in which the supersonic gas flow from the nozzle was dumped into a large (150 cubic meter) evacuated tank. The duration of continuous supersonic flow, which was set by the volume of the dump tank, was about 20 seconds. The time between runs was 2 hours. Despite the slow turnaround time, this setup provided many of the early data on shifts and simplifications in the UF_6 spectrum at low temperature.

Experiments are now done in a closed-cycle system known as a pulsed recirculating loop (Fig. 17). Since the lasers used in the experiments are pulsed at low repetition rates, a continuous gas flow and a large compressor train to move the gas through the system were unnecessary. To produce a pulsed gas flow coincident with the laser pulse, the recirculating loop includes a fast-acting hydraulic valve at the entrance to the nozzle. The valve is actuated at a typical rate of 1 hertz and provides a fully supersonic flow of cooled gas lasting about 2 milliseconds at the nozzle exit, With this system experiments can be performed at UF_6 densities and temperatures that are nearly the same as those for a full-scale plant. The only scaling required is increasing the area of the gas flow and the cross-sectional area of the irradiation zone.

SELECTIVE PHOTODISSOCIATION OF UF_6. After expansion through the nozzle, the cooled gas is irradiated by a sequence of infrared and ultraviolet laser pulses (Fig. 18). Either one or two infrared lasers tuned in the 16-micrometer range provide selective vibrational excitation of $^{235}UF_6$. The two-frequency infrared excitation described above provides higher selectivity than single-frequency excitation. The first

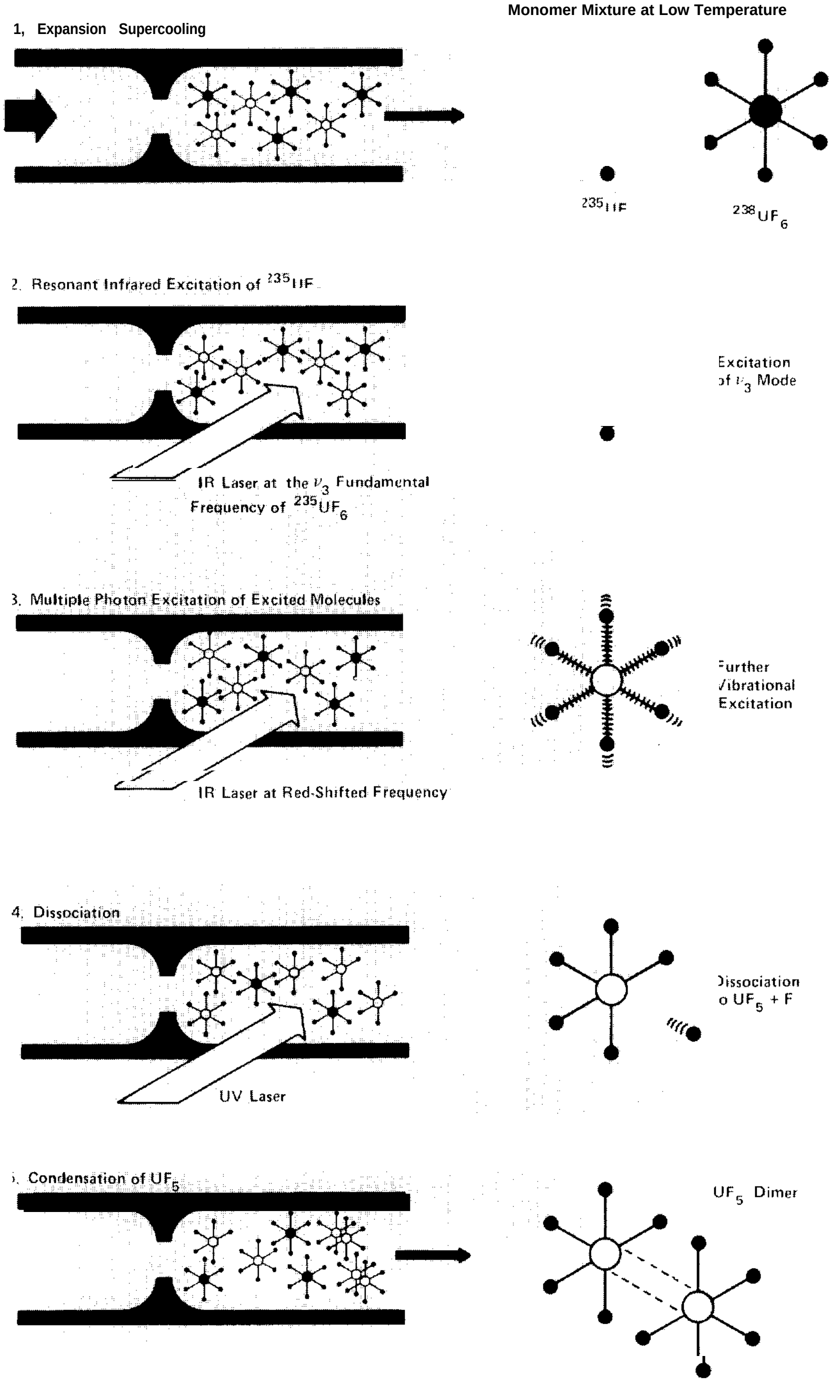

Fig. 18. The Los Alamos uranium enrichment scheme involves irradiating expansion-cooled UF_6 gas with infrared and ultraviolet lasers. The expansion supercooling produces a substantial density of UF_6 monomers at low temperature. Two infrared lasers selectively excite the v_3 vibrational mode of $^{235}UF_6$ molecules, and the excited molecules are dissociated by an ultraviolet laser. The UF_5 product forms particulate that are easily separated from the gas flow.

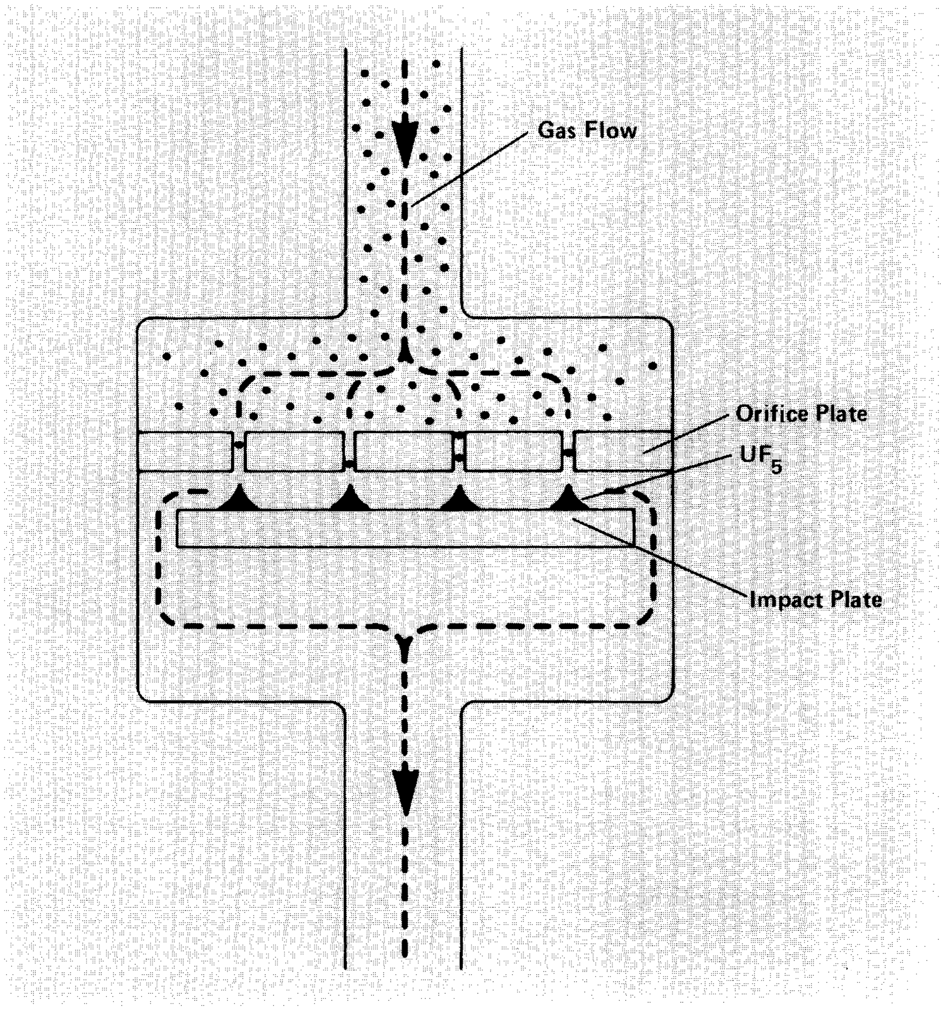

Fig. 19. Cross-sectional view of sonic impactor for collection of enriched product. The UF_5 molecules formed by dissociation of UF_6 aggregate to more massive particulate that are separated from the gas flow in the sonic impactor. The gas reaches sonic velocities as it passes through small holes in the orifice plate and then bends around to the exit port. The massive UF_5 particulate cannot negotiate the bend and instead collect on the impact plate.

low-intensity laser is tuned near the resonant frequency of the $^{235}UF_6$ Q branch, and the second high-intensity laser is tuned far to the red of this peak to achieve maximum excitation of the $^{235}UF_6$ molecules. Since multiple-photon excitation can occur over a fairly wide range of frequencies, especially at high intensity, the second laser will also excite some $^{238}UF_6$ molecules. But the probability for ultraviolet dissociation is substantially higher for the highly infrared-excited $^{235}UF_6$ molecules than for the $^{238}UF_6$ molecules. The physics of the infrared excitation is complex and depends on a number of parameters. These parameters are now being systematically varied to minimize excitation of $^{238}UF_6$ and thereby increase the infrared selectivity even further.

The infrared excitation produces a change in the ultraviolet dissociation spectrum similar to that shown previously for CF_3I. Thus, an ultraviolet laser tuned near the low-frequency edge of the dissociation spectrum of unexcited molecules will provide large dissociation yields for $^{235}UF_6$ and small dissociation yields for $^{238}UF_6$. In addition, ultraviolet dissociation of UF_6 to UF_5 is very efficient, occurring with a near unity quantum yield in the 200- to 300-nanometer wavelength region.

Although ultraviolet dissociation has been chosen for the Los Alamos uranium enrichment process, the intensity of the second infrared laser can be increased to provide dissociation without an ultraviolet laser. At present both methods are being considered.

POSTPHOTOLYSIS CHEMISTRY AND COLLECTION OF ENRICHED PRODUCT. A primary concern regarding this stage of the process was whether the UF_5 and UF_6 molecules might exchange fluorine atoms before being separated. But the UF_5 molecules rapidly form dimers in the supersonic flow; these dimers are relatively immune to exchange of fluorine with UF_6.

After being irradiated, the process gas containing the enriched UF_5 first passes through a supersonic diffuser, which returns the gas to higher pressure and room temperature. The enriched material in the form of particulate is then separated from the gas stream and collected on a simple sonic impactor (Fig. 19). The gas reaches sonic velocities as it passes through a series of small orifices in a flat plate. At the exit of the orifice plate the gas flow bends around to an exit port. The massive particulate traveling at sonic velocities cannot negotiate the turn and impact on a backing plate. A typical run time for a collection experiment is 1 to 2 hours. Figure 20 shows a sample of enriched material collected on the impact plate.

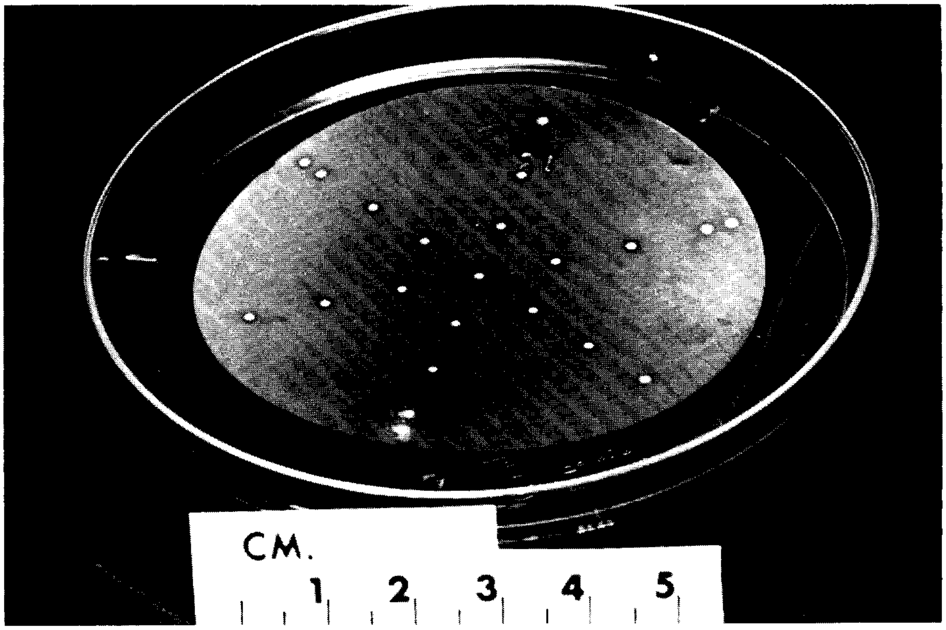

Fig. 20. Sample of enriched material produced by laser irradiation of UF_6 gas and collected in a sonic impactor.

DIAGNOSTICS. The samples collected from this system constitute the major source of data and confidence for projected performance of a full-scale plant. Each collection experiment yields an enrichment parameter for one set of operating conditions, but such experiments give little information about the intermediate steps of infrared excitation, ultraviolet dissociation, and postphotolysis chemistry. Morever, collection experiments are time-consuming and expensive. We have therefore developed a red-time diagnostic technique that does not involve an assay of the solid material.

Based on detection of the fluorescence induced in UF_6 by a low-intensity ultraviolet laser, the technique (Fig. 21) directly measures the number density of UF_6 before and after photolysis and thus the number density of UF_5 produced during photolysis. Experiments are performed separately on each isotopic species as a function of the intensities and frequencies of the infrared and ultraviolet lasers and other important parameters. With this technique we have obtained many of the fundamental data about vibrationally enhanced photodissociation of UF_6. From the ratio of the enhanced dissociation for the two isotopes we can also project the intrinsic enrichment attainable for uranium with the molecular laser isotope separation process.

RESULTS OF THE URANIUM ENRICHMENT EXPERIMENTS. The collection and laser-induced fluorescence experiments clearly show that vibrational excitation of UF_6 produces enhanced ultraviolet photodissociation of the molecule, that uranium can be enriched with this technique, that high values of β can be achieved, and that the enriched materical can be collected with little or no degradation by postphotolysis processes.

But the process must not only work—it must work efficiently and economically. The two parameters used most often to characterize the figure of merit for an isotope separation process are θ, the cut, and α, another measure of enrichment. The cut is the fraction of UF_6 dissociated at each stage of enrichment. Obviously the larger the cut and enrichment the fewer the number of stages needed in a full-scale plant. The enrichment parameter α, unlike β, depends on the cut. For enrichment in uranium-235 it is defined by

$$\alpha = \frac{(^{235}N/^{238}N)_{\text{product}}}{(^{235}N/^{238}N)_{\text{tails}}} = \frac{\beta(1-\theta)}{1-\beta\theta}\ .$$

The economics of the process improves as α and θ increase.

In 1976 milligram amounts of slightly enriched uranium were produced at Los Alamos by the molecular laser isotope separation process. Since then the major experimental efforts have focused on increasing α and θ for this process. But these two parameters are not independent. For example one can increase θ by increasing the intensity of either the infrared or the ultraviolet laser, but this increased intensity will saturate and broaden the absorption features and thereby reduce the selectivity and decrease a.

The process parameters that determine u and θ include the frequencies and intensities of the lasers and the temperature of the UF_6 gas. Currently, enrichment experiments are aimed at determining a set of parameters that optimize α and θ. Values for α and θ achieved in the experiments to date show that the molecular laser isotope separation process is economically competitive with other separation methods. But since the entire parameter space has not been studied

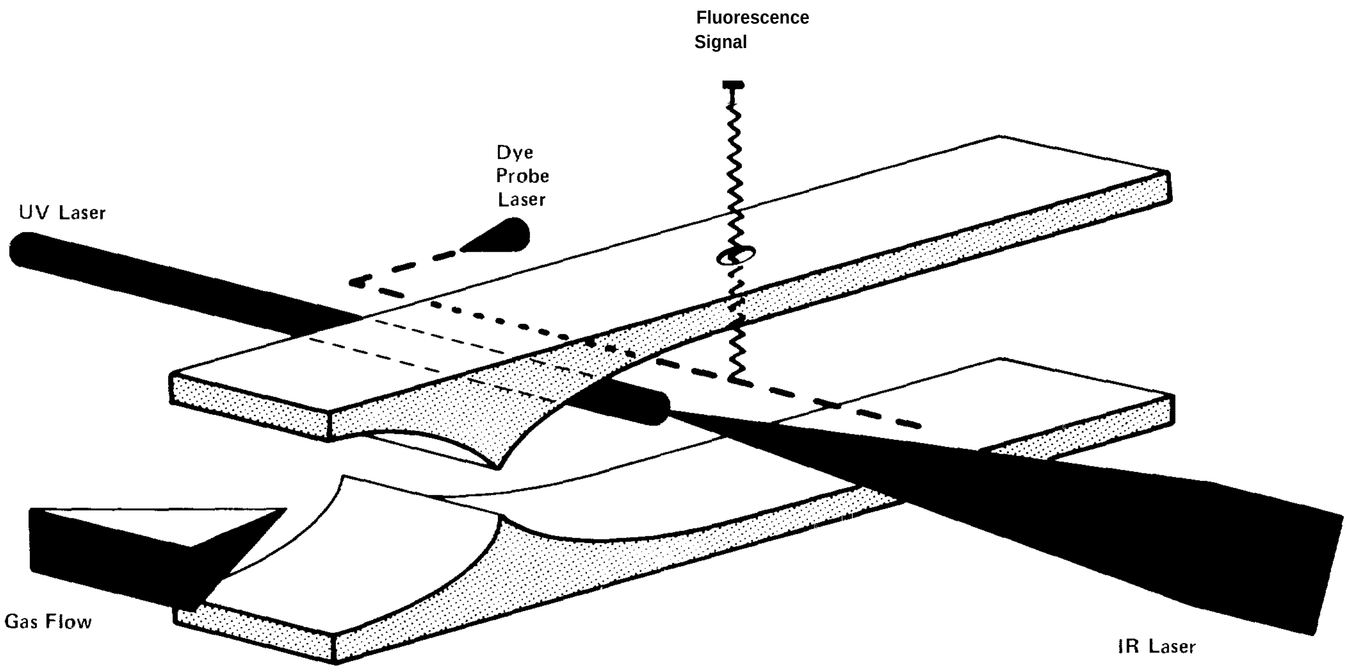

Fig. 21. Real-time diagnostic technique for determining the number density of UF$_5$ produced during photosis. A low-intensity dye laser induces fluorescence in the UF$_6$ molecules within a small volume about 1 centimeter downstream of the photolysis zone. The fluorescence is detected by a high-gain photomultiplier before and after the volume has been irradiated by the infrared and ultraviolet laser pulses. The difference is a direct measure of the UF$_5$ produced during photolysis. In experiments using this diagnostic technique, the infrared laser beam can be focused to provide high fluences.

(in particular, the selectivity of the multiple-photon process as a function of laser frequency and intensity and UF$_6$ temperature is uncertain), additional work will be required before we know with certainty that we have achieved the optimal set of operating parameters.

Engineering Considerations

Concurrent with the experimental research efforts to optimize α and θ, we have undertaken the engineering design studies needed to convert a small-scale laboratory experiment into a full-scale production plant. In these studies we have specified the production plant in as much detail as possible, identified the scaling required, and designed two intermediate-scale facilities in which plant equipment can be developed and the process can be evaluated. One of these facilities, the preprototype, is now assembled; the other, the demonstration module, is still in the design stage. We will first discuss some aspects of the scaling involved in our concept of a production plant and then briefly describe the intermediate-scale facilities.

SCALING UP. The performance goals for a production plant include the following.

- Product assay: $\geq 3.2\%$
- Tails assay: $\leq 0.1\%$
- Capacity: 8.75 MSWU/year
- Availability: $\geq 90\%$
- Product cost: $\leq \$40$/SWU

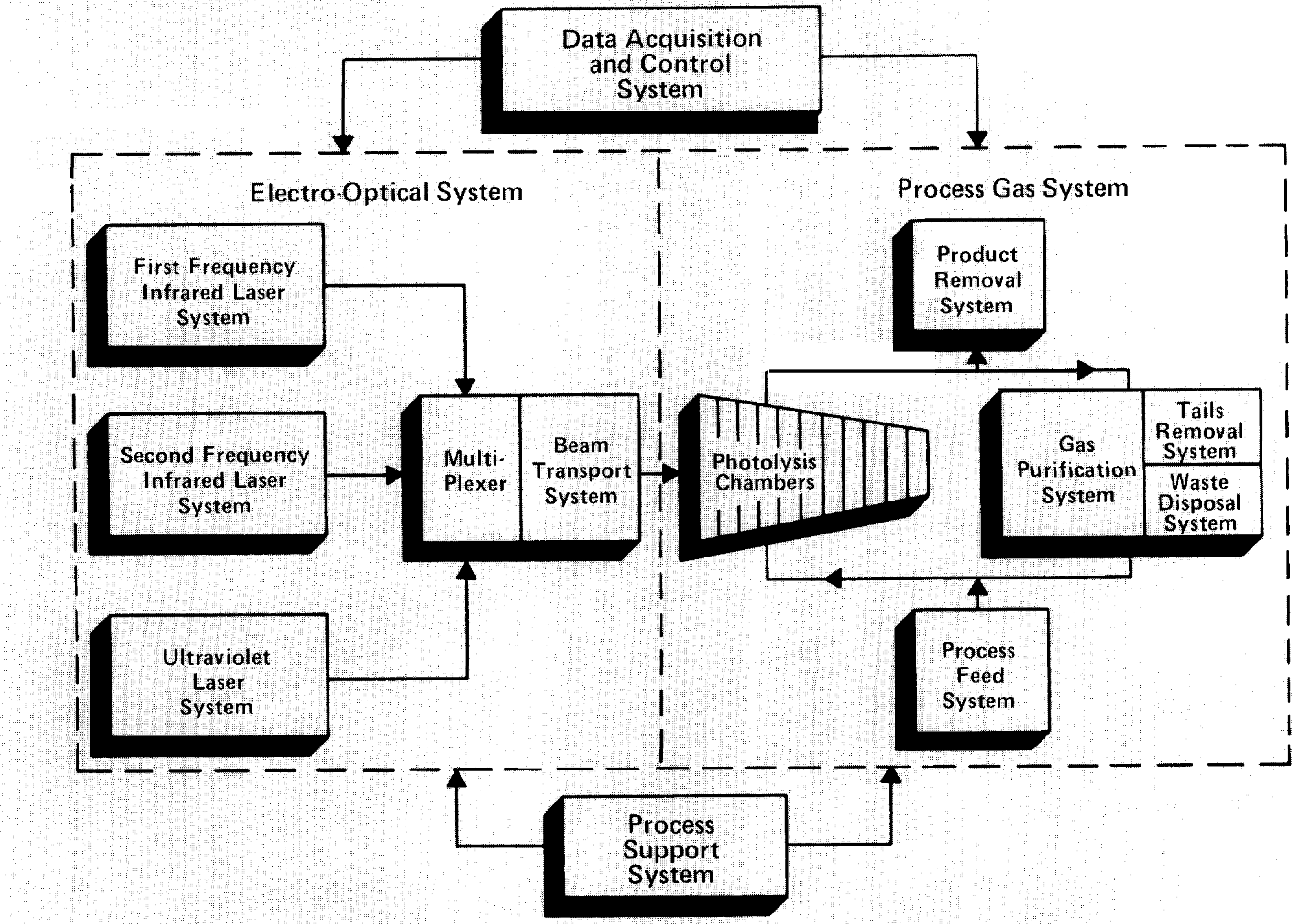

Fig. 22. Four major systems compose a production plant for uranium enrichment by laser irradiation of UF_6 gas. Shown here schematically is the organization of the more important equipment items and subsystems.

In more concrete terms a plant must produce an annual throughput of 1,500,000 kilograms of reactor-grade uranium, with tails depleted to 0.1 per cent, at a cost of about $600 per kilogram. Obviously, developing reliable plant equipment to meet these goals is not a trivial task.

The equipment for a production plant can be grouped into four major systems: the process gas system, which includes the photolysis chambers and the components providing the flow of process gas; the electro-optical system, which includes the lasers and the beam-transport optics; the data acquisition and control system; and the process support system. Figure 22 shows these systems schematically.

The design of a production plant begins with the choice, guided by the product cost goal, of an α and θ combination. To arrive at a product cost less than $40/SWU, current calculations show that α must be greater than 3 and θ must be between 0.05 and 0.30, depending on α. The choice of α and θ strongly influences the design of the photolysis chamber, as does the need to minimize diffraction and other optical losses. Other parameters influencing its design are the UF_6 number density and the temperature and pressure of the process gas.

For the values of α and θ believed to be attainable, a plant must have not one but several photolysis chambers to achieve the desired product assay. The chambers are arranged in what is commonly referred to as an enrichment cascade (Fig. 23); the term

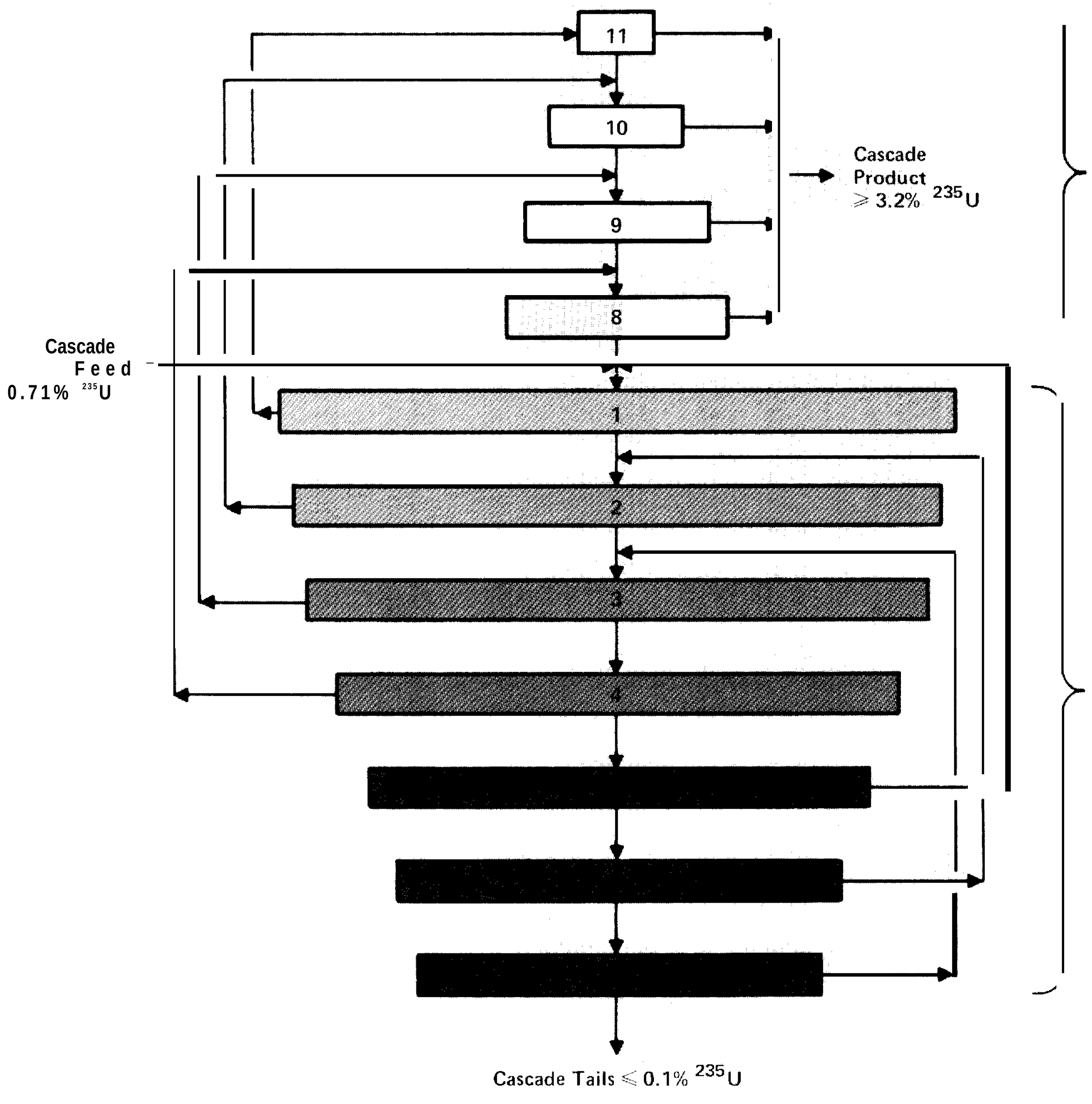

Fig. 23. Schematic gas flow pattern in an 11-stage cascade for uranium enrichment by laser irradiation of UF_6 gas. Each stage consists of a photolysis chamber and associated equipment. The relative volumetric flow through a stage is indicated by the area of the rectangle representing the stage. The incrementally enriched stream from each stage (shown here exiting to the right or left) flows to another stage for further enrichment, and the incrementally depleted stream from each stage flows to another stage for further depletion. This recirculating flow pattern avoids losses of separative work that would occur if streams of unlike assay were mixed.

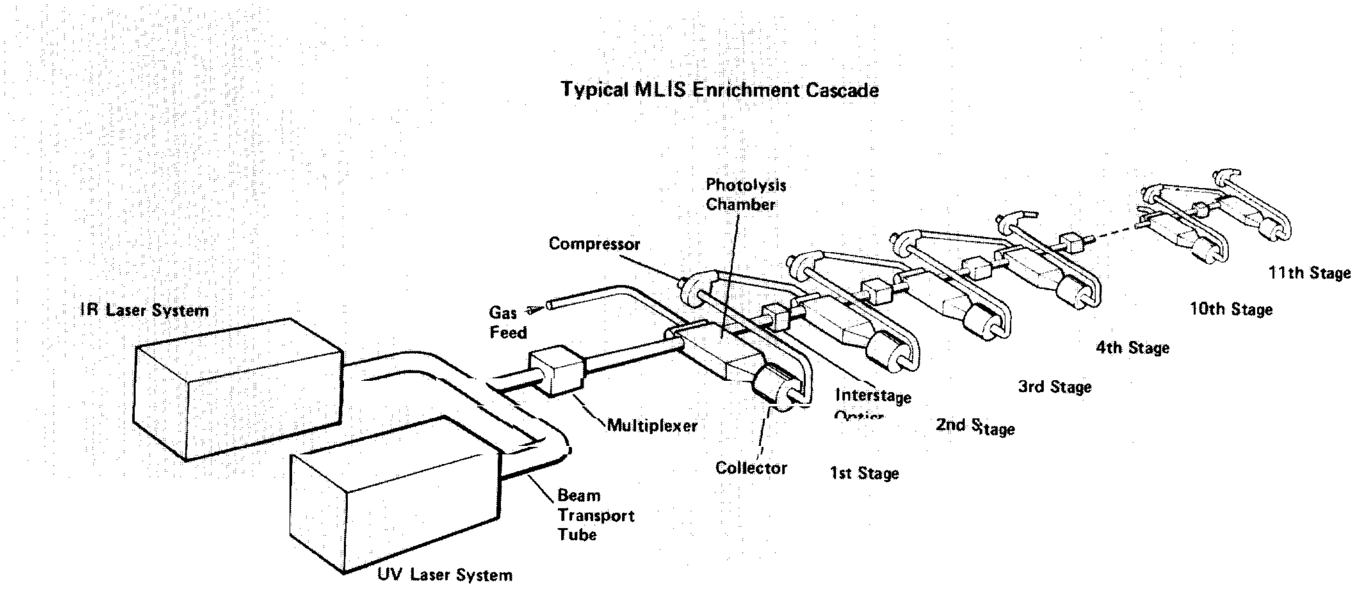

Fig. 24. Possible arrangement for integrating the laser systems and the cascade stages in a production plant for uranium enrichment by laser irradiation of UF_6 gas. Single banks of infrared and ultraviolet lasers service the entire cascade. Interstate optics adjust the fluences of the beams at each stage of the cascade.

stage refers to a single chamber and its associated equipment. The number of stages in an enrichment cascade depends directly on the α and θ combination chosen. In general, low α and θ values lead to a large number of stages, which in turn leads to increased complexity, large size, high energy consumption, and high capital costs for the plant.

Each photolysis chamber in the cascade includes a nozzle that might be as much as 8 meters wide. in contrast to the single 20-centimeter nozzle used in the laboratory experiments. Further, the gas flow though the chambers must be continuous rather than pulsed. Each stage must include a compressor system for moving the gas and equipment for collecting the enriched UF_5, converting it back to UF_6, and returning it either to the cascade or to the final product stream. A feed system, a gas purification system, a tails removal system, and a waste disposal system service the entire cascade.

All of the equipment necessary for the process gas system is within the current state of the art. In particular, the flow equipment developed for gaseous diffusion plants can be translated in a relatively straightforward manner to a molecular laser isotope separation plant.

The electro-optical system for a production plant must be capable of uniformly irradiating the gas flow through each photolysis chamber with the required infrared and ultraviolet laser fluences, The laboratory experiments were performed with a small beam size and a low repetition rate (about I hertz). Both these parameters must be increased considerably in a production plant.

The required increase in beam area implies a similar increase in beam energy to maintain the same fluence. The CO_2 and XeCl lasers used in the experiments can be scaled to higher energies by ganging several laser heads together in what is termed a master oscillator power amplifier chain. Several chains are necessary for each laser type. Individual high-energy beams must then be combined spatially to achieve the required beam area. To irradiate all of the gas flowing through a plant-scale nozzle, the repetition rate of the laser pulses must be about 10,000 hertz. Direct extrapolation of current technology to achieve such high rates from a single laser is not likely. However, the required rate can be achieved by temporally combining reliable, long-lived lasers with repetition rates of about 1250 hertz. A system known as a multiplexer combines the laser beams temporally and a reflective mirror arrangement called a dihedral combiner performs the spatial combination.

The electro-optical system must also compensate for the reduction in beam fluence that occurs as the beam progresses through

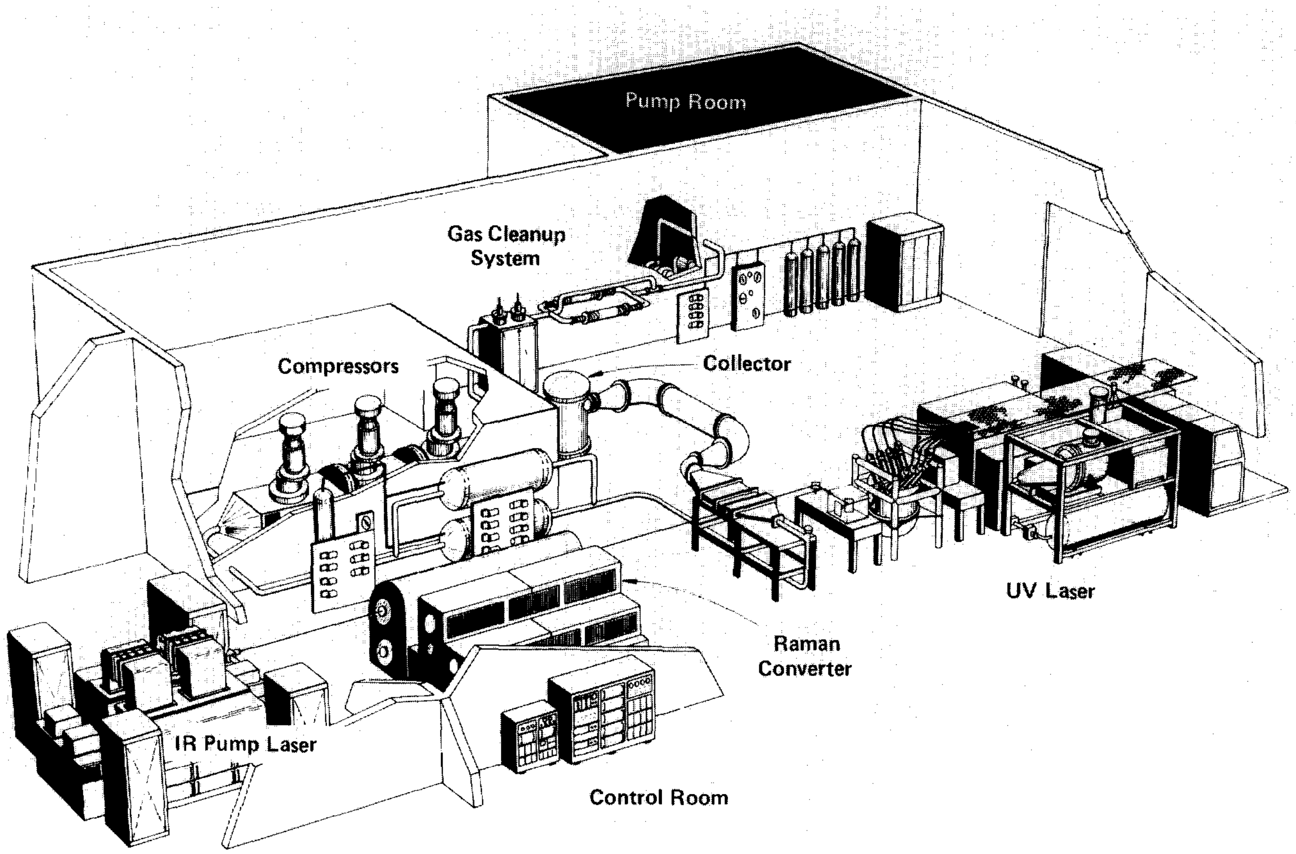

Fig. 2.5. The Laboratory's preprototype for testing the molecular laser isotope separation process at a scale intermediate between that of the laboratory experiments and a production plant.

each photolysis chamber. This fluence reduction, which is due to absorption, degrades the enrichment. It is not large, however, and can be limited by restricting the width of the photolysis chambers. In addition, the beam transport system includes interstage optics that adjust the beam area to the required fluence as it is transmitted from one chamber to the next. With this approach the laser beams can be adjusted to provide optimum fluence at each stage of the cascade.

Data acquisition and process control for a plant demand no new technology, Existing computers and instrumentation can meet all of the requirements for continuously monitoring and controlling the electro-optical and process gas systems. Equipment for the process support system, such as cooling towers, gas liquefaction plants, and electrical power system, is standard and can be obtained in the sizes required.

Integration of the cascade stages with the electro-optical system is a major design and engineering problem. Figure 24 shows schematically how this might be accomplished. A typical production plant might consist of two integrated cascades that share common subsidiary systems.

We have carried out an extensive production plant design at a conceptual level. That is, detailed design of equipment is bypassed in favor of an approach that clearly identifies the function, size, and performance requirements for each piece of equipment and each system. This level of detail is sufficient for reasonable costing, for studying design tradeoffs, and for establishing the goals that can be achieved by scaling the process and the equipment.

THE PREPROTOTYPE. Our first step toward a production plant was design and assembly of a preprototype by the Laboratory's Applied Photochemistry Division. This facility will test the process and equipment at a scale significantly larger than that of the pulsed-flow experiments. The preprototype (Fig. 25) includes a gas flow system capable of continuous operation, lasers designed to operate at 1000 hertz. and a subscale plant-type collector, The short lifetimes of the switching elements in the laser systems will limit the tests primarily to short-duration (lO-minute) runs. The gas flow area in the preprototype is approximately five times greater than that in the pulsed recirculating loop. The repetition rate of the lasers is sufficient to irradiate only about 1 per cent of the available UF_6. The preprototype demonstrates that scaling the process gas system is straightforward and relatively inexpensive, but scaling the photon supply is expensive and will require further engineering.

The preprototype will not address the requirements for spatial and temporal multiplexing, process staging, or interstage optics. Other issues not readily addressed by the preprototype are gas cleanup requirements for recycling and propagation of the laser beams on a plant scale.

THE DEMONSTRATION MODULE. The questions of scale not addressed by the preprototype can be answered with our next step toward a production plant, the demonstration module. The present plan is to complete the module in the late 1980s. It will be capable of demonstrating all critical aspects of a production plant. Most optical equipment and a beam transport system will be demonstrated at plant design conditions. These components will be incorporated into a multinozzle configuration with sufficient design flexibility to permit their optimization and refinement. A fully integrated stage will incorporate full-scale or directly scalable hardware. Data on the performance, reliability, maintenance, and lifetime of the lasers will establish production plant design criteria and realistic economic parameters.

Conclusions

We have concentrated in this article on the use of lasers to separate uranium isotopes. The primary reason for pursuing the development of a laser process for separating isotopes of any element is an economic one. In the case of uranium the cost of the product from more conventional methods is high enough to warrant introduction of the more selective and technology-intensive laser methods. We believe the high cost of the photons involved can be offset by the reduction in capital and operating costs and electric power consumption relative to conventional processes.

The intense research effort in this area has led to significant advances in our fundamental knowledge of photon-molecule interactions and in the technology of lasers. The application of this new knowledge and technology to more general areas in chemical processing—selective chemical synthesis, purification, reaction-rate control, and catalysis-has only just begun. ■

Further Reading

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AUTHORS

Reed J. Jensen received his Ph.D. in physical chemistry from Brigham Young University in 1965. After a postdoctoral appointment at the University of California, Berkeley, he joined the Laboratory's GMX Division. Following a two-year teaching experience with Brigham Young University, he returned to Los Alamos to initiate a program in chemical laser research. He played a key role in advancing the technology of high-energy pulsed chemical lasers. His experience with the interaction of laser radiation and chemical kinetics led him directly into the field of laser isotope separation. During this period he, along with several coworkers, advanced the concept for the molecular laser isotope separation process described in this article. His promotion to the post of Assistant Division Leader of the Laser Division was followed in 1976 by an appointment as Alternate Division Leader of the newly formed Applied Photochemistry Division. In 1980 he was named Division Leader of the Applied Photochemistry Division and Program Manager for molecular laser isotope separation. Under his direction approximately 225 scientists and technicians pursued research and development in laser isotope separation, laser-induced chemistry, applied photochemistry, spectroscopy, and related fields. In 1981 he was named Deputy Associate Director for molecular laser isotope separation. (Photo by LeRoy N. Sanchez)

O'Dean P. Judd received his Ph.D. in physics with a specialty in plasma physics from the University of California at Los Angeles in 1968. For several years he worked at the Hughes Research Laboratory on microwave electronics, plasma physics, and high-energy lasers. He joined the Laboratory's Theoretical Division in 1972 as an Associate Group Leader of its Laser Theory Group. There he did theoretical work on atomic and molecular physics, lasers, and nonlinear optical interactions for the laser fusion and laser isotope separation programs. In 1974 he became Group Leader of the Laser Division's Advanced Laser Group, whose task was the development of high-energy visible and ultraviolet lasers. In 1977 he joined the Applied Photochemistry Division Office and worked on problems related to uranium isotope separation and multiple-photon excitation processes in polyatomic molecules. Currently he is a Project Manager for high-energy laser concepts in the Defense Science and Technology Office. He is a consultant on lasers to the National Oceanic and Atmospheric Administration and is an Adjunct Professor of Physics in the Institute of Modern Optics and the Department of Physics and Astronomy at the University of New Mexico. His theoretical and experimental interests include lasers and quantum electronics, nonlinear optics, atomic and molecular physics, plasma physics, and laser chemistry. (Photo by LeRoy N. Sanchez)

J. Allan Sullivan earned a Bachelor of Science and a Master of Science in aeronautical engineering from the University of Colorado. After receiving a Ph.D. in mechanical engineering from the University of Michigan, he served for a short time as an Assistant Professor at Colorado State University and then joined the Laboratory in 1966. In his first few years with the Laboratory, he worked on advanced nuclear reactor concepts and computer codes for transient reactor behavior. In association with C. P. Robinson, he helped pioneer some of the early research in laser development and isotope separation at the Laboratory. In 1974 he was appointed Group Leader of what is now the LIS Engineering Group in the Applied Photochemistry Division. This group worked on advanced engineering for the then fledgling molecular laser isotope separation program. In 1977 he served a short time as the Alternate Director for the Reactor Behavior Division of EG&G, Idaho Falls and then returned to the Laboratory's Applied Photochemistry Division. There he served as a project leader for novel instrumentation applications of lasers and as an industrial liaison officer. In 1980 he was assigned to the Department of Energy's Office of Advanced Isotope Separation where he represented the Laboratory's interests in formulating the criteria for deciding which advanced isotope separation technology will be scaled to production facilities. At present he is the Program Manager for engineering implementation of the molecular laser isotope separation program. (Photo by LeRoy N. Sanchez)