Laser Separation of Isotopes

The isotopes of an element, ordinarily indistinguishable, can be sorted out in the monochromatic light of a laser. The process may make isotopes plentiful for medicine, research and nuclear power

by Richard N. Zare

In nature most elements are mixtures of isotopes: they are made up of atoms that all have the same number of protons and electrons but that differ in number of neutrons. Ordinarily the fact that an element is a mixture of several kinds of atoms matters little because the various isotopes are all but indistinguishable in most of their properties. For that very reason, however, when we do want to separate the isotopes of an element, the task can be exceedingly difficult. Some recent investigations into the absorption of laser light by the isotopes of elements and by compounds containing those elements now promise to make the separation both easier and cheaper.

In isolating an element from a compound or a mixture of elements it is common to rely on differences in the chemical properties of atoms. These properties are determined almost entirely by the electron clouds that surround the nucleus; the atoms of each element, of course, have a characteristic number of electrons. The isotopes of a single element, on the other hand, have virtually identical electron clouds: the electrons are identical in number and differ only slightly in their geometric configuration. As a result the separation of isotopes by single-step chemical extraction has not proved practical.

For light elements isotope separation by repeated chemical extraction is possible, but for all those heavier than oxygen only physical methods have been developed. The physical methods all depend ultimately on the small discrepancies in mass per atom that result from variations in the number of neutrons in the nucleus. The best-known of these methods is gaseous diffusion, in which isotopes are distinguished by the slightly different rates at which they diffuse through a porous barrier; lighter atoms pass through the barrier somewhat faster than heavier ones. Gaseous centrifugation, multiple distillation and electromagnetic separation take advantage of other properties that depend on atomic mass. All these procedures are tedious and cumbersome, with the result that

the products of separation—isotopically pure or enriched elements—are extremely costly. The enriched uranium that serves as the fuel for nuclear fission reactors is the most important of these products; other isotopes, employed in small quantities in research, in medicine and in other fields, are many times more expensive.

The separation of isotopes by laser light differs fundamentally from other methods. It distinguishes between atoms of different isotopes or between compounds containing different isotopes not on the basis of mass but through subtle differences in electronic structure. These differences, even though they are small, affect the wavelengths of light absorbed by a substance; each isotope absorbs light of a slightly different color. Because a laser emits light of very pure color it can be employed to "tag" the atoms or compounds of one isotope while leaving all others undisturbed.

One of the first principles of quantum mechanics is that an atom or a molecule can absorb energy only in discrete units. That is because the atom has only a finite number of discrete energy states, each one representing a particular configuration of its electron clouds. By absorbing or radiating away energy the atom can move abruptly from one state to another, but intermediate energies are forbidden.
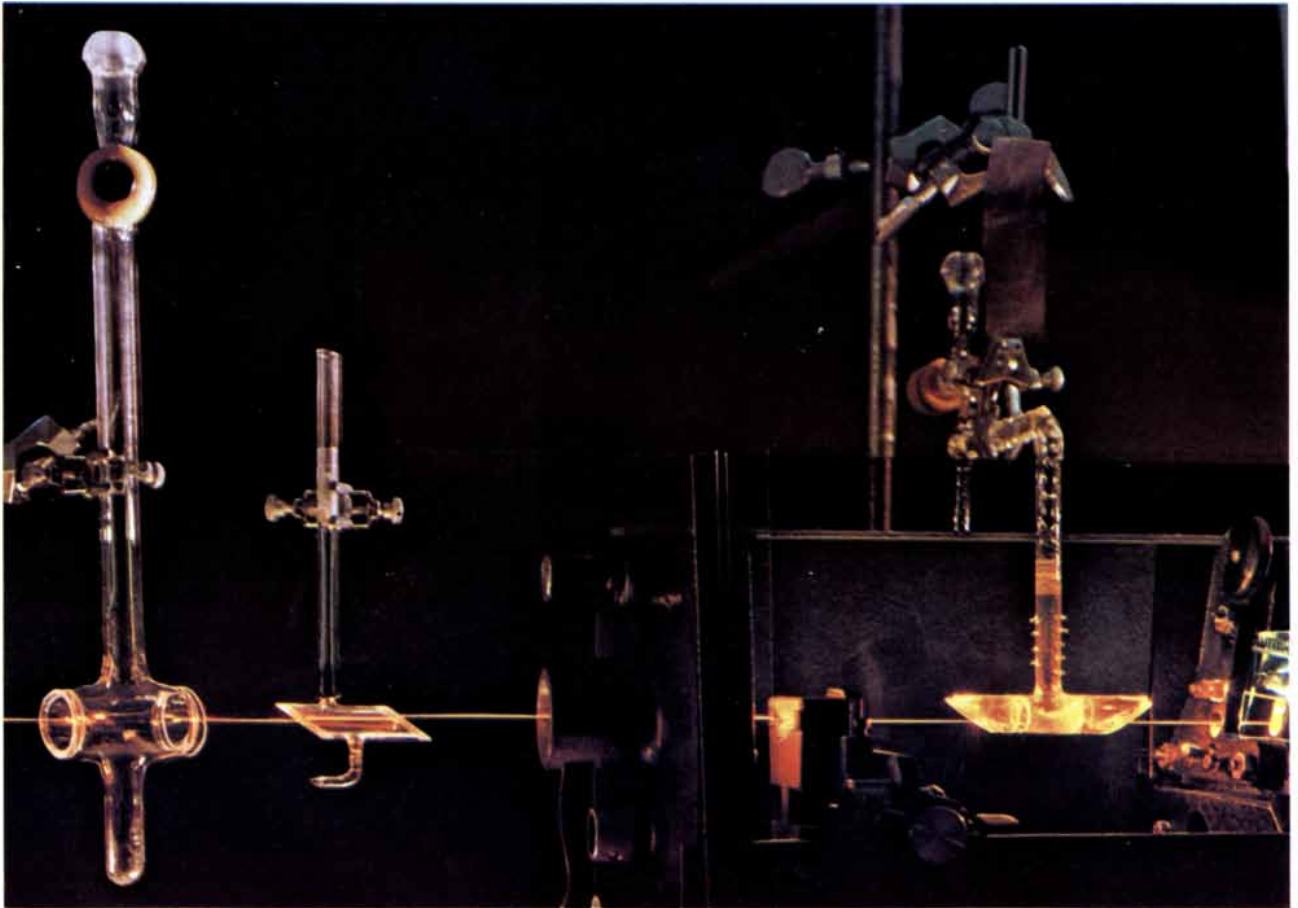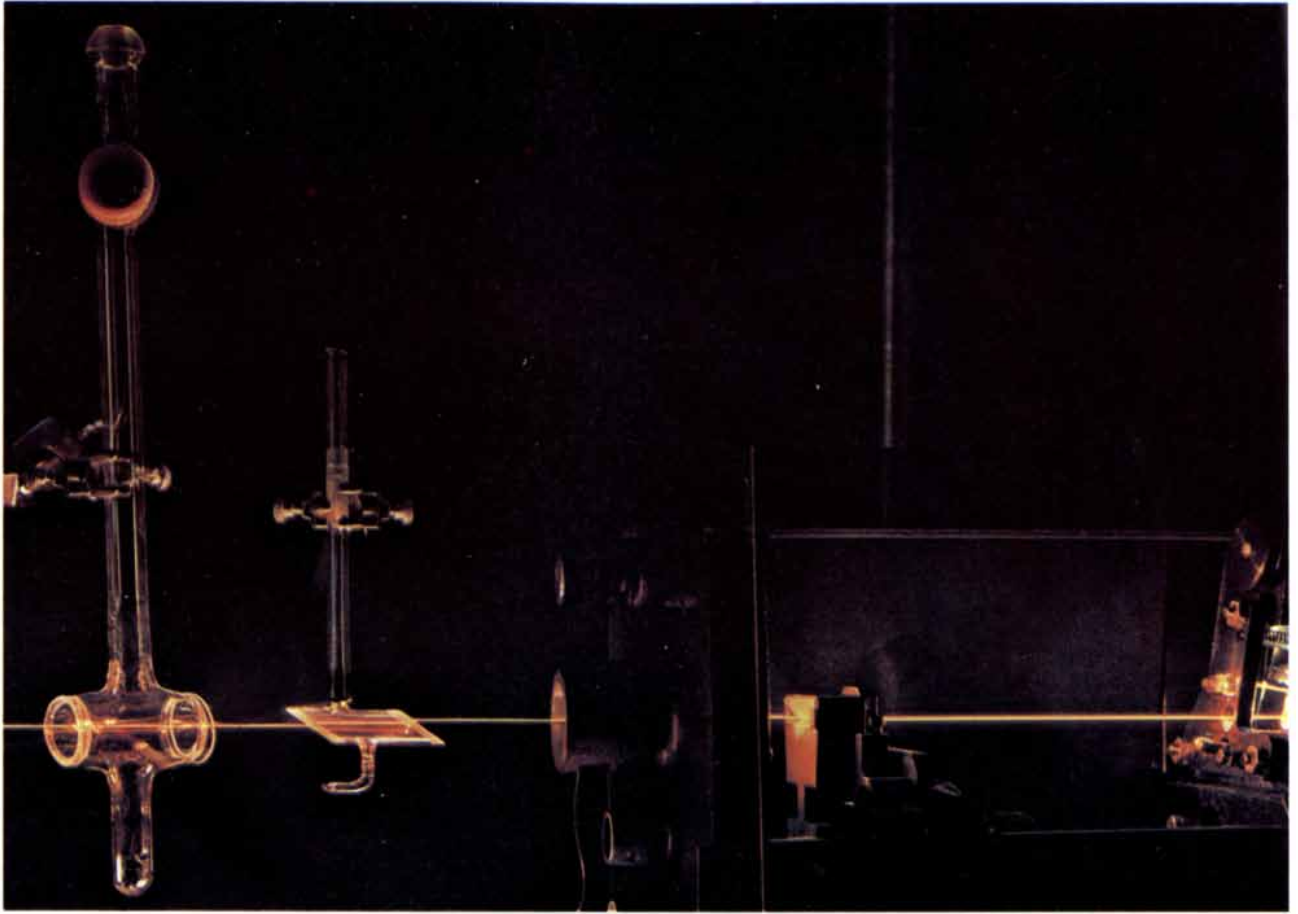
Atoms can make these abrupt transitions by absorbing or emitting light

or other electromagnetic radiation. It is only a matter of convenience whether the radiation is regarded as a stream of particles or as a system of waves; the two expressions are formally equivalent. The particles, called photons, each have a definite energy, inversely proportional to the wavelength of the corresponding wave. Photon energy (and wavelength) is unaffected by the intensity of a light source; increasing the intensity simply increases the number of photons. Within the visible portion of the spectrum the energy or wavelength of a photon is perceived by the eye as color.

Light can be absorbed by matter only when the energy of a photon corresponds to the difference in energy between two of an atom's allowed states; photons of other energies simply fail to interact with the atoms and the light is transmitted. When a photon is absorbed, it induces a change in the atom's electronic structure: a single electron is promoted to a state of higher energy and the atom is said to have entered an excited state. On the average the excited electron is farther from the nucleus. Additional photons (of the appropriate energy or wavelength) can elevate the electron to still higher energy levels, and as the energy increases so does the density of the allowed states. The ultimate level is the ionization limit, where the electron is torn loose from the atom; ionization can be regarded as a continuum of allowed states.
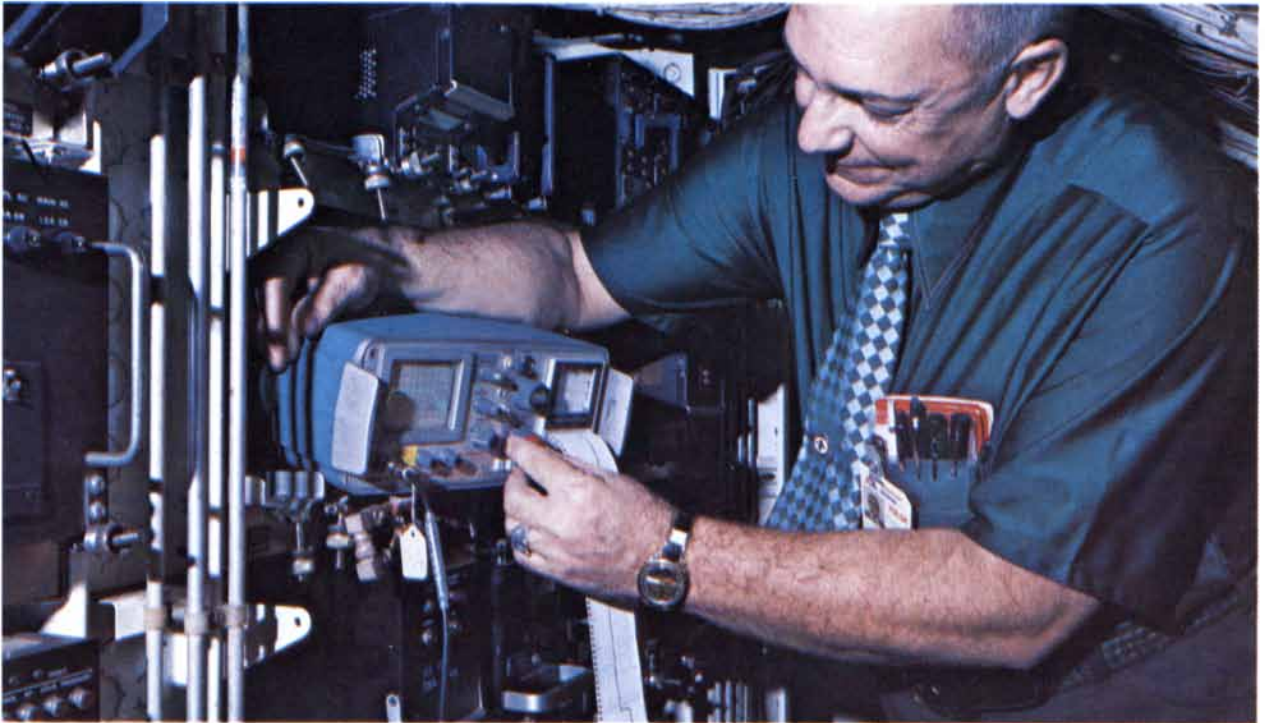
After an atom has absorbed a photon

"With TDR*cable testing at American Airlines, we're finding cable disturbances long before they cause system failures."

Aubrey Thomas, American Airlines
Maintenance and Engineering Center, Tulsa, Oklahoma

Aubrey Thomas checks a cable and antenna by looking at their signatures on the screen of a TEKTRONIX TDR cable tester in a 747's electronic equipment bay, from which most routine avionics troubleshooting can now be done. Not only can he spot subtle changes in systems—if there is a problem, he quickly knows what it is and precisely where.

*Time Domain Reflectometer

Aubrey Thomas points out that "anybody who has had to pull panels throughout an airplane to find a cable fault will understand why we appreciate the TDR's* ability to quickly identify the nature of the problem and to tell where it is—often to the inch, or closer.
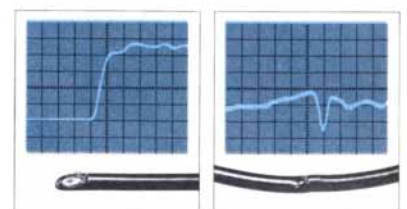
"But even more impressive is a situation where, let's say, you might have to figure out why a pilot was getting strong navigation signals close to a station, but not farther away. If you used a meter and it showed continuity in the system, you might waste hundreds of man-hours and change thousands of dollars worth of components, and still not be any better off.

"But by using the TDR in the equipment bay, you would know immediately that the problem was, let's say, six feet of corroded cable shield, starting at the vertical-fin disconnect and coming back toward the inside fuselage. That's the beauty of the TDR, it's not limited to identifying shorts or opens —it points out any disturbances."

Back in 1971 Aubrey Thomas and two other people at American Airlines were looking for a better way to test the miles of cable that carry radio, navigation, and instrumentation information, as well as power for complex basic electrical systems. "I knew that the TV industry used time domain reflectometry a lot," Aubrey says, "and couldn't see why it wouldn't work on airplanes."

They started by using a TEKTRONIX oscilloscope and plug-in TDR unit, on a roll-around cart. But because work quarters on aircraft are often either cramped or relatively inaccessible, what they really needed was something much smaller and battery powered.

Recognizing these needs, Tektronix had been developing TDR units that were not only small, portable, and battery operated—but were also simple to use, had chart-recording capabilities, could be used in hostile environments (rain, snow, extremes in temperature and altitude), and on a wide variety of cable types.
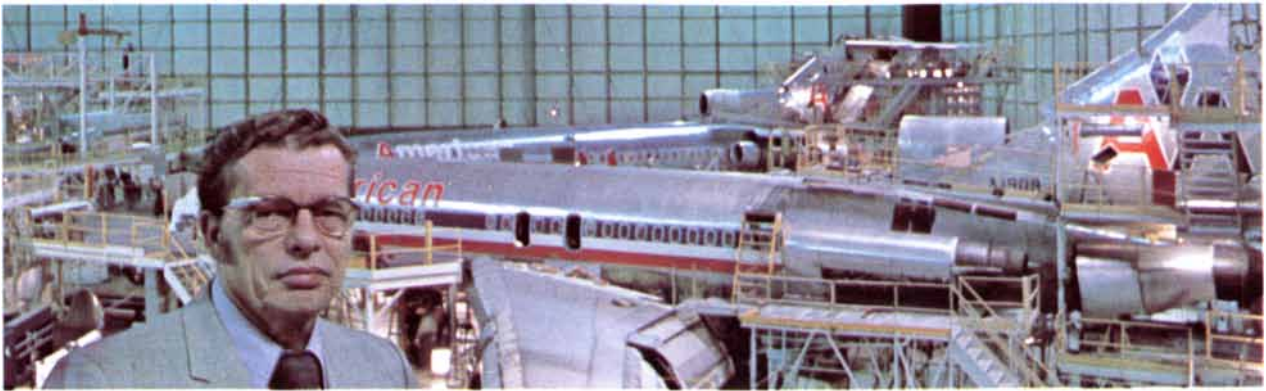

Open cable produces this characteristic signature. Detectable by other methods, but a TDR gives the precise location.

Crimped cable signature. One example of a potential problem virtually impossible to detect by conventional methods.

What an avionics tech sees

A time domain reflectometer (TDR) works in a manner similar to radar. It generates repetitive pulses of energy that are sent down a cable and displayed on a cathode-ray tube screen. Any cable faults (impedance changes) cause pulse reflections. The shape of the reflection (the signature) allows the type of problem to be identified. Distance to the fault is determined by measuring the elapsed time between the pulse and reflection. Entire lengths of cable

DEFLECTION OF EXCITED ATOMS is perhaps the most obvious method for the laser separation of isotopes. The atoms, a mixture of two isotopes (*black dots and colored dots*), issue from an oven to form an atomic beam. They are then irradiated by a laser tuned to excite the atoms of one isotope but not those of the other. Excited atoms often have electrical and magnetic properties different from those of atoms in the lowest energy state, and the excited atoms can be extracted from the beam by an inhomogeneous electric or magnetic field.

RADIATION PRESSURE of repeated photon absorptions can also be employed to deflect one isotopic species. Again the laser is tuned to excite one isotope, but in this case the excited state decays quickly (by fluorescence), so that many photons can be absorbed during the brief transit of the atoms through the laser beam. With each photon absorbed the atom acquires a small increment of momentum, and so it is gradually pushed out of the atomic beam; atoms of the other isotope, which do not absorb the laser photons, are not deflected.

RECOIL OF DISSOCIATING MOLECULES represents a third means of separating isotopes by deflection. The molecules, which are made up of one element that has two isotopes (*black and colored dots*) and another with only one isotope (*gray dots*), have absorption bands that depend on isotopic composition. The laser excites and dissociates only molecules that include one isotope (*color*). Part of the energy of the broken chemical bond pushes the fragments apart; the lighter fragment (*color*) is deflected through a larger angle and can be collected.

90

it can give up its energy of excitation in any one of several ways. The simplest route is for it simply to emit a photon of the same energy as the one it absorbed; this is the process of fluorescence. Some excited atoms can decay to a metastable state, which persists for a relatively long period before the energy is reemitted. The energy can also be dissipated through a series of small transitions and thereby be converted to random kinetic energy, or heat. Ultimately the atom returns to its lowest allowed energy state: the ground state. Since an atom can occupy only designated energy states, it absorbs and emits light only in narrow lines of precisely defined wavelength, each line corresponding to a particular atomic transition. The collection of all such lines is the spectrum of the atom.

Like atoms, molecules have electronically excited states. In addition, they have vibrational and rotational energy states, corresponding to various possible modes of oscillation and rotation of the constituent atoms around their common center of mass. Transitions between vibrational states are also associated with the absorption and emission of electromagnetic radiation, although the wavelengths involved are generally longer than those of atomic spectra. Most transitions between the electronic energy levels of atoms or molecules are in the visible and ultraviolet regions of the spectrum, whereas transitions between molecular vibrational states are in the infrared.

The characteristic spectra of both atoms and molecules are subtly influenced by the details of nuclear structure. Electrons are bound to an atom by the positive charge of the nucleus, and their motions are determined primarily by the number of protons in the nucleus. Neutrons do have an influence on the electron cloud, however; by changing the mass, volume and shape of the nucleus, changes in neutron number can subtly alter the trajectory of an electron. In a molecule differences in nuclear mass can have somewhat larger effects, by altering the frequency of the molecular vibrational states. All these effects are small and they play no part in most interactions of matter. They are nonetheless crucial for the laser separation of isotopes. They give each isotope of an element and each molecule composed of different isotopes a different set of energy levels, leading to small shifts in absorption and emission spectra.

Several mechanisms for the laser separation of isotopes have been proposed, but all of them have as their basis the same principle. A collection of atoms or molecules containing more than one isotope is irradiated by a laser whose wavelength has been adjusted so that it excites the atoms of one isotope but has no effect on the others. In this way the various species of atoms are distinguished from one another. Several methods are then available for actually sorting them into different "bins."

Laser light is essential to the technique; no other light source would do. Lasers themselves operate by exploiting the quantum-mechanical transitions between the energy levels of atoms and molecules. In a laser a substantial fraction of all the atoms in a population of atoms are promoted to the same excited state; the atoms return to a lower energy state by emitting light coherently, or in phase. The coherence is ensured by bouncing a portion of the light back and forth between two mirrors so that it passes through the laser medium repeatedly, stimulating atoms to radiate as it passes. The two mirrors form a resonant cavity, a kind of organ pipe for light. In some cases the cavity can be "tuned" in order to adjust the wavelength of the light emitted.

Two properties in particular recommend the laser for the work of isotope separation. First, it can produce a light of high intensity, that is, a beam with a large flux of photons; with dimmer sources separation would probably be too slow to be practical. Second, laser light can be made highly monochromatic, so that all the photons emitted have very nearly the same energy. Emission over a narrow range of wavelengths is essential for the excitation of one isotope to the exclusion of others, since the spectral lines of isotopes are generally close together.

The various proposals for laser isotope separation differ mainly in the method employed to extract the selected atoms or molecules after they have been excited by the laser. One of the most straightforward techniques simply exploits intrinsic physical properties that distinguish excited species from those in the ground state. For example, in the excited states of many atoms the electron cloud is more readily distorted in an electric field or it has a larger magnetic moment than it does in atoms in the ground state.
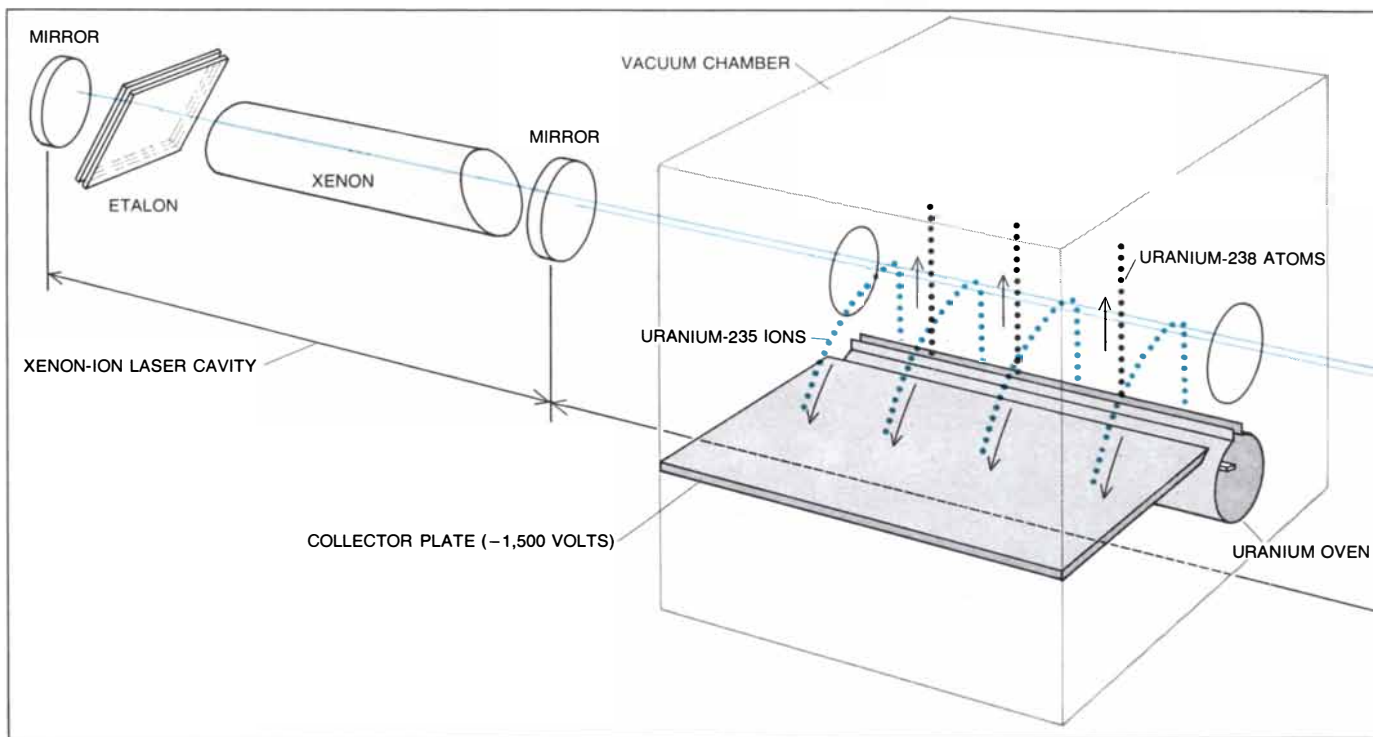
For experiments in isotope separation it is often convenient to employ an atomic beam: a stream of atoms that all move in the same direction and have a relatively narrow range of speeds. The beam is created by evaporating the substance in an oven inside an evacuated chamber; the resulting thermal motions of the atoms are random, with the average velocity determined by the temperature. Atoms that happen to be moving in a particular direction pass through a small opening in the oven, and the beam can be further collimated by passing it through a series of orifices, although only at the cost of reduced intensity. Because the beam travels in a vacuum, collisions that would disturb the straight-line motion of the atoms are minimized. The same technique can be employed to prepare a beam of molecules.

An experiment in the separation of isotopes by the deflection of excited atoms might begin with a beam of some arbitrary element A, which might consist of two isotopes, designated A_1 and A_2. The beam is irradiated by a laser tuned to some feature of the spectrum of the isotope A_1, so that many A_1 atoms make a transition to an excited state (denoted by A_1^*) whereas almost all the A_2 atoms remain in the ground state. The A_1^* atoms are thus conspicuously labeled and can be separated from the rest. The separation is accomplished by passing the atomic beam through an inhomogeneous electric or magnetic field, which deflects those atoms that are more readily polarized or have a larger magnetic moment. The deflected atoms are then collected, for example by condensation on a cooled surface. It should be emphasized that the selective step in this procedure is not the deflection in an inhomogeneous field; the field would deflect excited A_2^* atoms as well as A_1^* atoms. The isotopes are separated because of the selective laser excitation of the A_1 species.

For this process to be successful two conditions must be met: a substantial fraction of all the A_1 atoms must be "pumped" by the laser, and the excited state must survive long enough for the field to cause a measurable deflection. Unfortunately these two requirements are contradictory. A large proportion of the atoms can be made to undergo a particular transition only if that transition is a highly probable, or favored, one, but in that case the reverse transition to the ground state must also be favored. In other words, if an atom is likely to absorb a photon of a given wavelength, then it is also likely to emit such a photon. The excited atoms decay rapidly by fluorescence.

One possible way to resolve this dilemma might be to illuminate the atomic beam with a second laser (or some other source of energy) that would convert the excited A_1^* atoms into a longer-lived, metastable species that could be labeled A_1^{**}. The metastable atoms, which also commonly bear distinctive electrical and magnetic traits, could then be deflected.

Alternatively the short radiative lifetime of the excited species A_1^* might be turned to advantage. That could be achieved by actually pushing the atoms out of the beam with the radiation pressure of the laser light. For this purpose the laser must intersect the atomic beam at a right angle. Each atom that absorbs a photon then acquires from it a small increment of momentum that tends to propel it away from the laser source. The momentum is proportional to the energy of the laser photons, but it is always very small, so that for any appreciable deflection each atom must absorb many photons. The short lifetime of the

SELECTIVE IONIZATION of atoms was employed in the laser enrichment of uranium in a technique demonstrated at the Lawrence Livermore Laboratory. Two lasers, one operating with a medium of xenon ions, the other employing krypton ions, were arranged on a common axis and a beam of uranium atoms was introduced into the cavity of the krypton-ion laser. By means of an etalon, a device that narrows the bandwidth of a laser, the xenon laser was adjusted so that its wavelength corresponded to one of the absorption lines of the isotope uranium 235. In this way uranium-235 atoms were promoted to an excited state, whereas atoms of the commoner isotope uranium

excited atoms is essential so that they can quickly return to the ground state to absorb another laser photon. It should be noted that each time an excited atom returns to the ground state by emitting a photon the atom recoils with a momentum exactly equal to that gained when light is absorbed. The recoil momentum is randomly oriented, however, with the result that after many recoils the average momentum from the reemissions is zero. The momentum of the absorbed laser photons always pushes the atoms in the direction of the laser beam.

The first successful application of this technique was reported in 1974 by Anthony F. Bernhardt, Donald E. Duerre, Joe R. Simpson and Lowell L. Wood of the Lawrence Livermore Laboratory. They prepared an atomic beam of barium and tuned a laser to a line in the barium spectrum at a wavelength of 5,535 angstroms, which falls in the green part of the visible spectrum. The absorption of a single photon of this wavelength changes the transverse velocity of a barium atom by about .8 centimeter per second. That speed is about 50,000 times smaller than the longitudinal velocity of the atoms in the beam, so that repeated absorption and reemission is clearly essential. The number of photons that can be captured is limited by the transit time of the barium atoms in the laser beam, by the finite time required for the excited state to decay and

by the loss of excited atoms that decay not to the ground state but to metastable states from which another photon cannot be absorbed. Even under the best conditions the angular deflection is small, and a highly collimated beam of atoms is necessary.
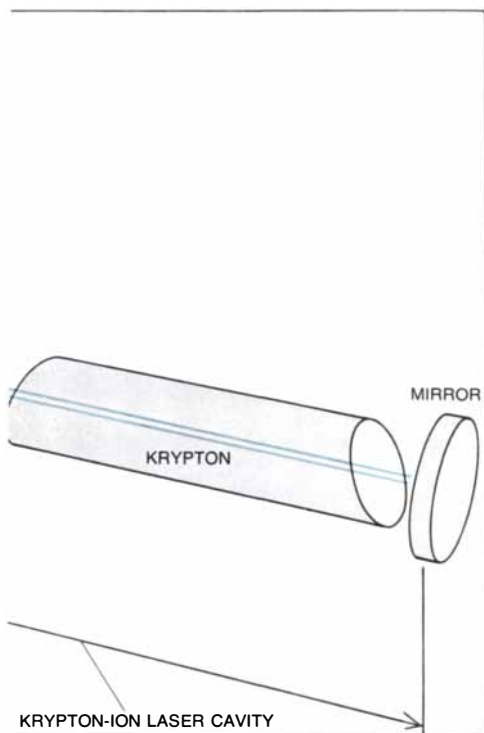
Barium has a number of stable isotopes, of which the most abundant one, making up about 72 percent of the natural element, is the isotope with an atomic mass number of 138. The atomic mass number is the sum of the number of protons (in this case 56) and the number of neutrons (82) in the nucleus. By selective excitation the Lawrence Livermore group was able to produce barium enriched in this isotope by a factor of two or three.

One disadvantage of the technique is that it requires many laser photons, each of relatively high energy, for each atom separated. A third proposed method of separation by deflection overcomes this difficulty by obtaining part of the energy required from another source: the laser-induced rupture of a chemical bond in a molecule.

The technique relies on choosing a molecule that is stable in the ground state but decomposes spontaneously when it is promoted to an excited state. For the sake of simplicity it can be assumed that the molecule is diatomic and can be represented by the arbitrary symbols AB, where A again has two isotopes

A_1 and A_2. If a laser can be tuned so that it excites only those molecules that incorporate A_1 atoms, then only those molecules will be dissociated. The energy of the chemical bond is dissipated in both the internal excitation of the products and in their motion; the recoil motion, which is much larger than the recoil associated with photon absorption, deflects the atoms from the beam. There is the potential for a substantial deflection triggered by a single photon, but so far the technique has not been successfully demonstrated.

Instead of deflecting atoms that are excited but electrically neutral, another approach to isotope separation converts them into ions, which are much more easily manipulated. A strong electric field can efficiently sweep the charged particles from a beam of neutral atoms in the same way that an electron beam is swept across the face of a cathode-ray tube. The ionization can be accomplished in two steps: first one isotopic species is selectively excited with a finely tuned laser, then the excited atoms are ionized with another, less precise laser or even with some other source of energy. The method was demonstrated in 1974, when the isotopes of calcium were separated by investigators at the University of Cologne, and when the isotopes of uranium were separated by a group at the Lawrence Livermore Labo-

238 were not affected. Each excited atom could then be ionized by a photon from the krypton-ion laser; atoms that had not been excited could not be ionized. Ions were swept out of beam by an electrically charged plate.

ratory. The commercial application of the technique is now being considered.

In the experiments in Cologne and at Livermore only microscopic quantities of material were separated, but there is reason to believe the devices and techniques can be scaled up. In 1975 Sam A. Tuccio, Richard J. Foley, James W. Dubrin and Oscar H. Krikorian at Livermore reported the enrichment of milligram quantities of uranium, and it subsequently became apparent that similar work had been started earlier by Richard H. Levy and G. Sargent Janes at the Avco Everett Research Laboratory. Avco Everett and the Exxon Corporation are now building a pilot plant for the laser enrichment of uranium at Richland, Wash. Because of security considerations and proprietary secrecy many of the details of this process (as well as those of other uranium-isotope-separation methods) remain obscure, but a major portion of the work at Livermore has been made public.

In the Livermore experiments a beam of uranium atoms emerges from an oven at a temperature of 2,600 degrees Kelvin. At this temperature 45 percent of the atoms are in the lowest possible energy state and 27 percent are in a metastable state of only slightly higher energy. (This metastable state is not an independent, excitational energy level, and it is not reached by radiative transitions; it is formed by the splitting of the

ground state into sublevels, giving a "fine structure" to the atomic spectrum.) It is the atoms in the metastable state that are excited and ultimately ionized and isolated.
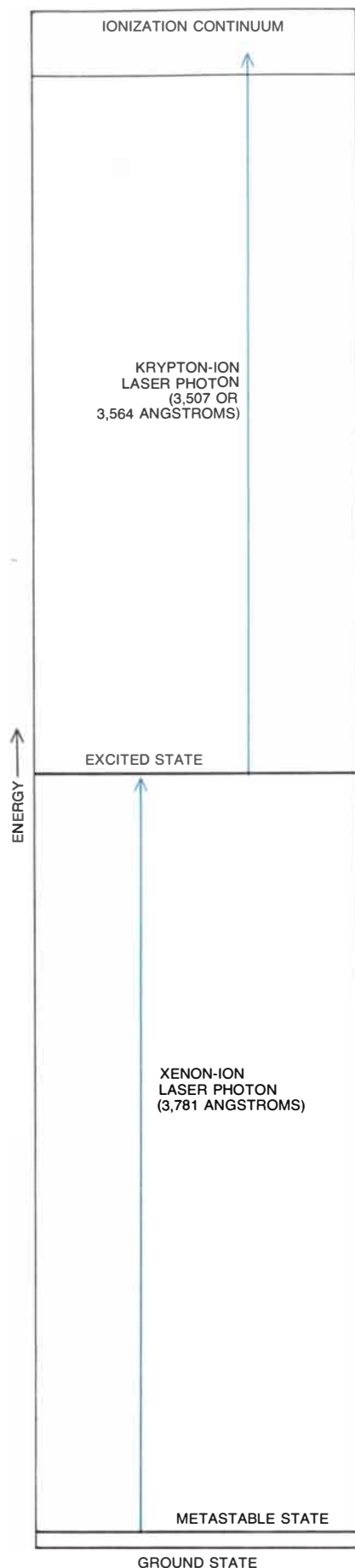
The excitation is provided by a laser whose operating medium is a gas of xenon ions; its radiation at a wavelength of 3,781 angstroms (in the ultraviolet region of the spectrum) excites only the lighter and easily fissionable uranium isotope of atomic mass number 235 and only those atoms of uranium 235 that happen to be in the low-lying metastable state. Atoms of the heavier isotope uranium 238 are not affected, whether they are in the ground state or in the metastable state.

To ionize an atom a specific wavelength is not needed; any photon with enough energy to overcome the ionization potential barrier will suffice. In this case the uranium atoms excited by the xenon laser have only to absorb another photon with a wavelength less than 4,400 angstroms in order to be ionized. The photons are supplied by a second laser, employing krypton ions rather than xenon, with two strong emission lines at 3,507 and 3,564 angstroms. The second laser is not isotopically selective; it would ionize excited states of either uranium 235 or uranium 238.

The excited state of uranium 235 has a brief lifetime (235 nanoseconds), and so it is important that the second photon be supplied immediately after the atom is excited. That is ensured by arranging the two lasers on a common optical axis, with the beam of uranium atoms inside the cavity of the krypton laser. The ionized atoms, which are stripped of one electron and hence have a positive charge, are attracted to and deposited on a collector plate with a negative charge of 1,500 volts.

The system was run continuously for about two hours, with the xenon-ion laser operating at a power of 70 milliwatts and the krypton-ion laser at 30 watts. The much higher power of the second laser was required to compensate for the small probability that a given excited atom would absorb a photon and be ionized. The yield is somewhat reduced by

IONIZATION of uranium atoms in the Livermore experiment was accomplished in two steps, only one of which was isotopically selective. The atoms susceptible to laser excitation were those in a metastable state lying only slightly above the lowest possible energy level, the ground state. Atoms of uranium 235 in the metastable state were stimulated by the xenon laser to make a transition to an excited state, but uranium-238 atoms were not excited. Any atom in the excited state could then be ionized by absorbing a photon with a wavelength of less than 4,400 angstroms. The krypton-ion laser, emitting photons with wavelengths of 3,507 and 3,564 angstroms, was capable of ionizing excited atoms of either uranium isotope.
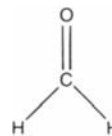

93

the fact that some uranium atoms are thermally ionized in the oven, a process that is not isotopically selective. Nevertheless, four milligrams of uranium were obtained with a uranium-235 content of about 3 percent. That is four times the abundance of uranium 235 in natural uranium and is approximately the level of enrichment required for nuclear power reactors.

Several variations on the method of selective ionization have been proposed. For example, instead of a two-stage process several or many photons could be employed. Another appealing idea is the creation of very highly excited states, lying just below the threshold of ionization, so that the final ionization step would require only a gentle electric field or collisions with charged particles. On the other hand, certain parasitic processes must be suppressed. Collisions between positively charged uranium-235 ions and neutral uranium-238 atoms can transfer the charge to the heavier isotope, thereby scrambling the isotopic content of the product. A more dramatic failure would be the creation of a population inversion among the excited uranium atoms; under some circumstances the atoms might be stimulated to emit radiation as they drop to a lower energy level. In other words, the uranium vapor could itself become the medium of a laser. Nevertheless, these experiments represent the first steps toward the commercial development of a new method of uranium isotope separation. It remains to be seen whether or not this particular method will turn out to be the most economical.
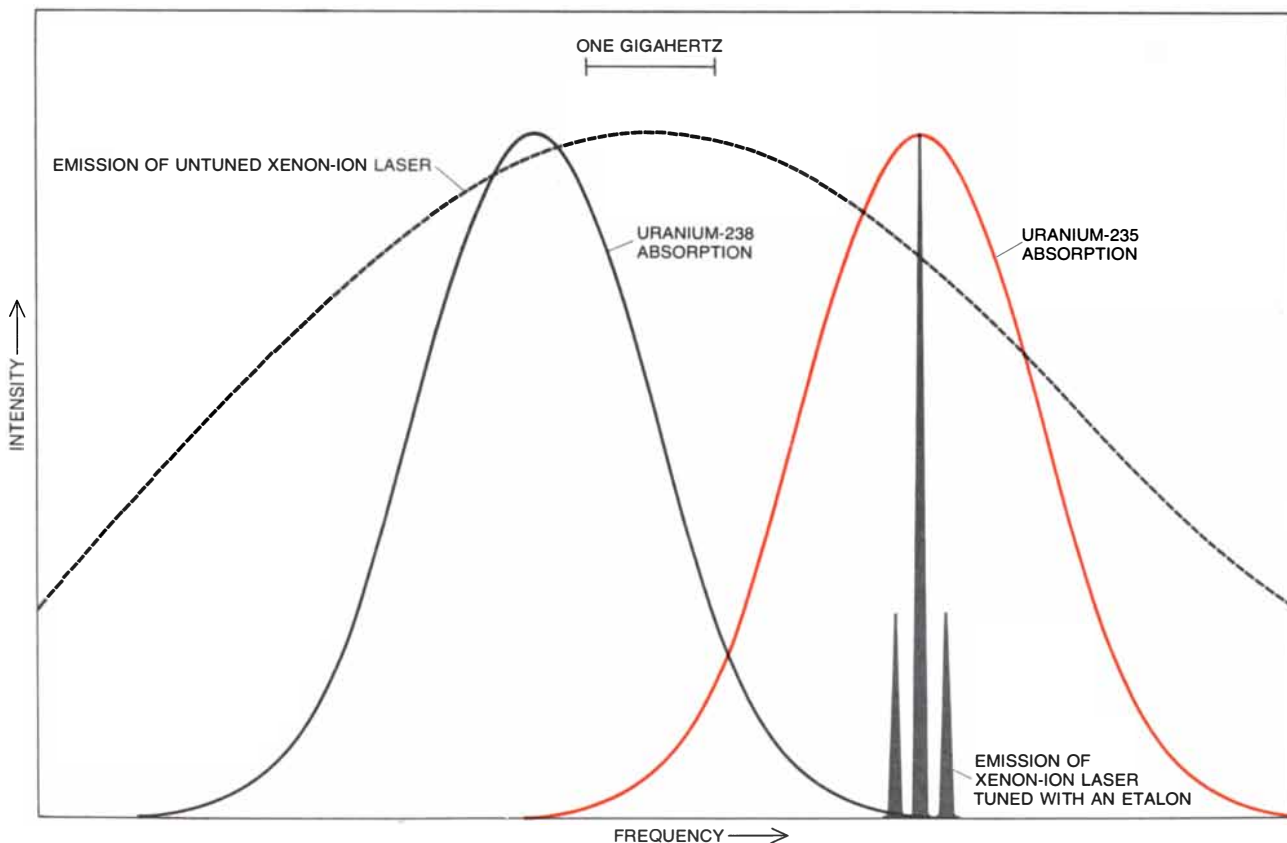
A class of isotope separation techniques that has the attraction of great simplicity is the decomposition of molecules into stable products that can then simply be removed from the mixture. A prerequisite, however, is a molecule that satisfies a rigorous list of specifications: it must be possible to excite the molecule with laser photons, the molecule must then dissociate spontaneously and the products of the dissociation must be stable, so that there are no further chemical reactions. The last requirement is a particularly difficult one to satisfy; many molecules that can be decomposed by electromagnetic radiation give rise to free radicals, fragmentary molecules that are highly reactive.

For the purposes of isotope separation the reaction that has probably been studied most extensively is the laser decomposition of gaseous formaldehyde, an organic molecule with the structure

When formaldehyde is decomposed by laser irradiation, it can yield two distinct sets of products, molecular hydrogen (H_2) and carbon monoxide (CO), or the free radicals H and HCO. The free radicals are unstable and react promptly with one another or with other substances present. The molecular products, on the other hand, are stable and could easily be separated by chemical means, with the result that any isotopic composition they might be given by selective excitation would be preserved.

The photochemistry of formaldehyde decomposition is quite complex, but the relative yield of molecules and free radicals apparently depends on the wavelength of the light absorbed, so that the

ABSORPTION SPECTRUM of uranium isotopes can be closely matched by the emission spectrum of the xenon-ion laser. The absorption spectrum includes two adjacent peaks, the one at higher frequency (or shorter wavelength) representing the absorption of uranium 235. The natural emission spectrum of the laser is comparatively broad and encompasses the absorption peaks of both isotopes, so that it w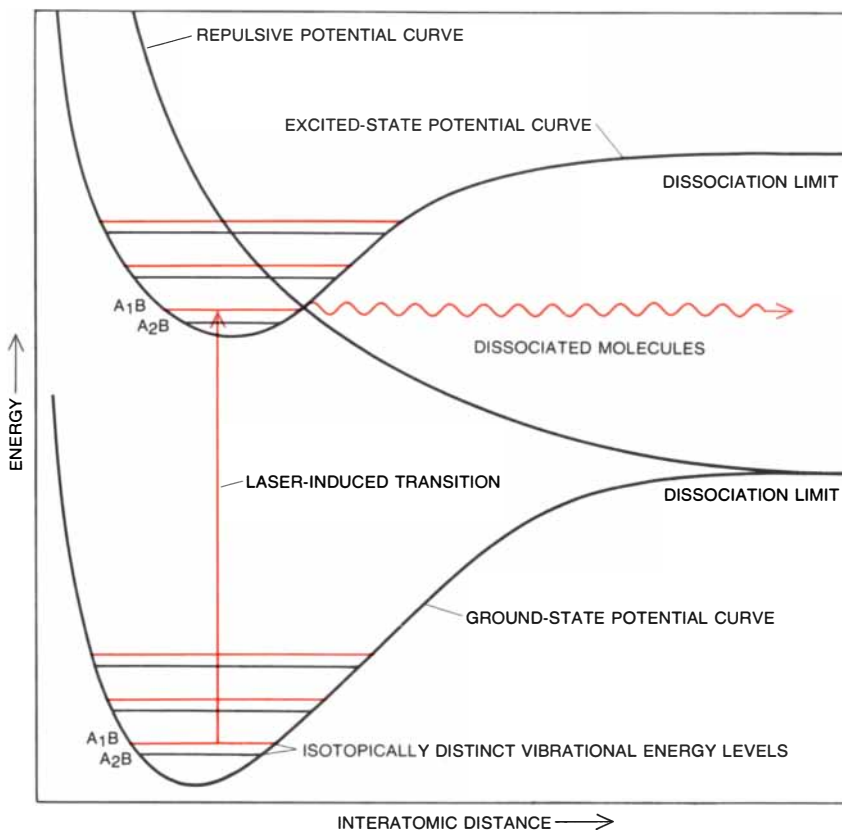ould not be suitable for discriminating between them. The emission of the laser is narrowed by inserting an etalon into the laser cavity; the etalon confines the laser to only a few modes of resonance, giving rise to a spectrum of distinct spikes. The sharpened emission can be tuned so that it coincides with the maximum uranium-235 absorption and lies outside the range of uranium-238 absorption.

process may be amenable to experimental manipulation. Three groups of investigators have already reported the successful application of this procedure to the separation of hydrogen isotopes.

Hydrogen has two stable isotopes, the common one with a mass number of 1 (^1H or merely H), which has a solitary proton as its nucleus, and the much rarer deuterium (^2H or D), with a mass number of 2 and a nucleus that consists of one proton and one neutron. Formaldehyde can be prepared with pure hydrogen (H_2CO) or with pure deuterium (D_2CO). Employing a mixture of equal quantities of these gases, Edward S. Yeung and C. Bradley Moore of the University of California at Berkeley achieved a deuterium-enrichment ratio of six to one in 1972, and with the same starting materials other workers later reached a ratio of nine to one. In 1975 John B. Marling of Livermore succeeded in selectively exciting HDCO, the form of formaldehyde in which both hydrogen isotopes are present; the deuterium content of the products, in the form of HD, was 14 times that of the starting materials.

Dissociation of the formaldehyde molecules does not come about through excitation all the way to the dissociation continuum. If photons with sufficient energy to achieve that result were supplied, they would be absorbed by all formaldehyde molecules, without isotopic selectivity. Instead the molecule is disassembled at a lower energy through a phenomenon called predissociation. It is raised to a precise energy level where the force between the constituent atoms can change from attractive to repulsive; even though the energy supplied is less than that ordinarily required to break the chemical bond of the molecule in that electronic energy state, the molecule comes apart.

The separation of deuterium from hydrogen is facilitated by the comparatively large differences between the spectra of these isotopes, which can be attributed to the large ratio of the atomic masses. The isotopes of carbon and oxygen display much smaller spectral shifts, but recently they too have been separated by the photodecomposition of formaldehyde. John H. Clark, Yehuda B. Haas, Paul L. Houston and Moore of the University of California at Berkeley, working with the carbon isotopes of atomic mass 12 and 13, have increased the abundance of carbon 12 in carbon monoxide to 81 times its normal value, thereby enriching the undecomposed formaldehyde in carbon 13. Their experiment employed laser light with a wavelength of 3,032 angstroms, where the creation of free radicals predominates. Nitric oxide, which combines with free radicals, was added to the reaction mixture in order to achieve these enrichment factors. More recently Mar-

PREDISSOCIATION OF MOLECULES into chemically stable fragments offers another approach to laser isotope separation. The energy of the chemical bond in a molecule is a function of the distance between the atoms, and the curve describing this relation is called a potential curve; in a stable molecule the curve has an energy minimum where the forces of attraction and repulsion are in balance. Actually a molecule can have a number of potential curves, each curve associated with an electronic energy state, and some of them may not have a stable minimum; on such a curve the force between the atoms is always repulsive. The absorption of a laser photon can induce a transition from one potential curve to another. If this excited-state curve is intersected by a repulsive potential, the molecule may then dissociate. The process is called predissociation because it takes place at an energy below the usual threshold for dissociation on that potential curve. It can be made isotopically selective by tuning the laser so that only one isotopic species is promoted to the excited-state potential curve. Within a bound potential there are a finite number of molecular vibrational states (*horizontal lines*), and the positions of these energy levels are slightly different for each isotopically distinguished molecule.

ling has shown that wavelengths greater than 3,300 angstroms suppress the creation of free radicals; 80 percent or more of the yield is in the form of molecular products. He has been able to enrich oxygen 17 and oxygen 18, both of which are rare, as well as carbon 13 and deuterium. Of particular importance, he was able to achieve enrichments by a factor of three or four with formaldehyde made up of elements in their natural isotopic abundances. When rare isotopes are being separated, most of the effort required in conventional methods is often exerted in reaching the enrichment level of a few percent. Marling's results illustrate one of the potential benefits of laser technology: large single-step separation factors for the very rare isotopes.

Studies of separation by photodecomposition have centered on, in addition to

formaldehyde, symmetric tetrazine, an unstable organic molecule with the structure

When tetrazine is irradiated, it decomposes into two molecules of molecular nitrogen (N_2) and two molecules of hydrogen cyanide (HCN). Robert R. Karl and K. Keith Innes of the State University of New York at Binghamton

have shown that each photon absorbed by tetrazine leads to the decomposition of one molecule. The process has been employed to separate the isotopes of hydrogen, carbon and nitrogen.

Robin M. Hochstrasser and David S. King of the University of Pennsylvania have also demonstrated isotopic enrichment through the photolysis of tetrazine, but their method differed in an important respect from that of most other experiments. Instead of exciting molecules in the gas phase they irradiated a crystal of symmetric tetrazine cooled to 1.6 degrees K. (1.6 degrees Celsius above absolute zero). When the laser was tuned to spe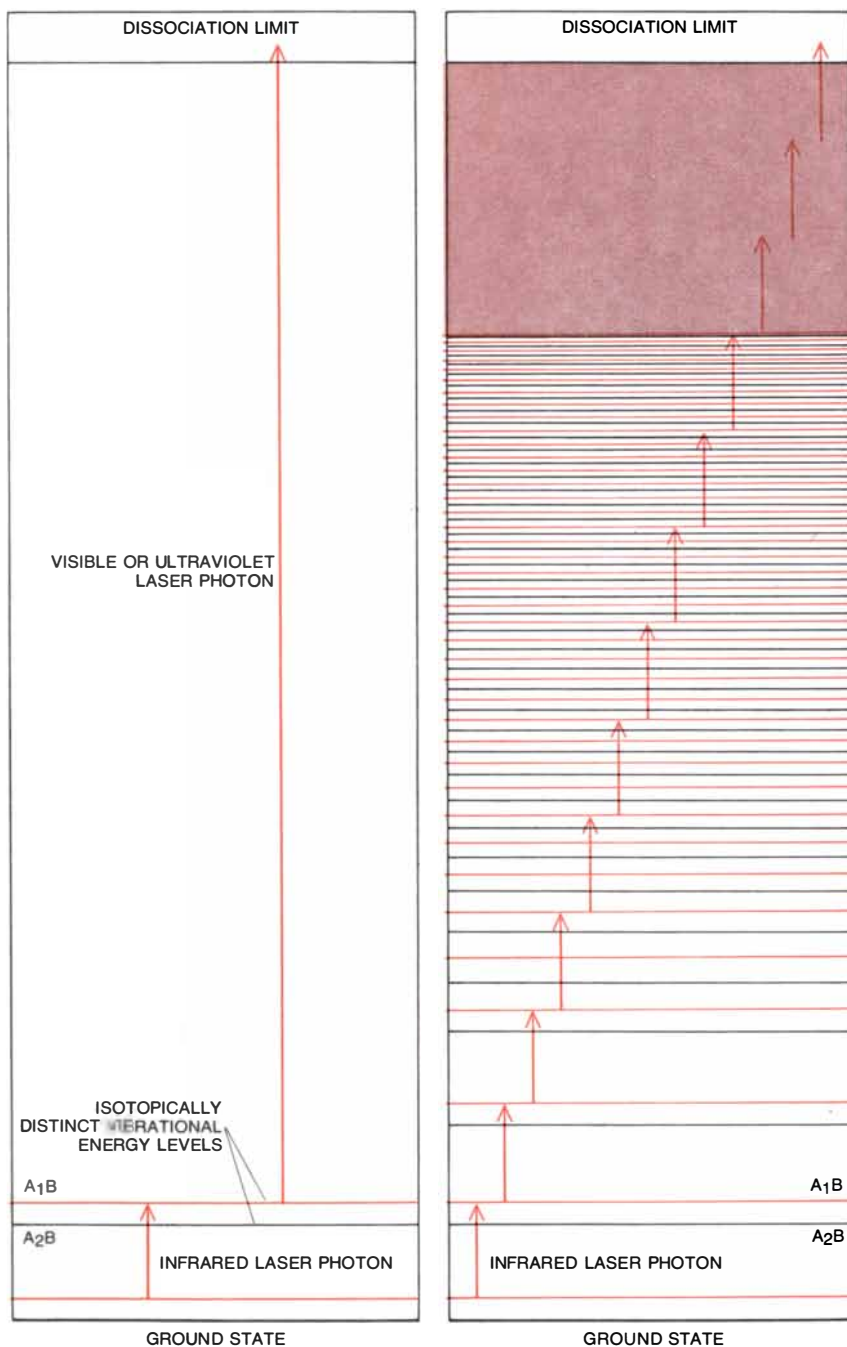ctral features of molecules with a particular isotopic composition, the selected molecules completely decomposed. Irradiation for a few minutes enriched the crystal in nitrogen 15 and carbon 13 by a factor of 1,000 or more.

Not all molecules can be made to predissociate into stable fragments; it is often necessary to work with substances whose properties are not so convenient for the chemist. In many cases dissociation requires a two-photon process, in which a molecule is first excited, then induced to make a second transition either to the dissociation continuum or to another excited or metastable state that decomposes. Such a two-step process for the separation of uranium isotopes is being investigated at the Los Alamos Scientific Laboratory. An infrared photon selectively excites molecules of uranium hexafluoride gas that contain an atom of uranium 235 but not those with the heavier isotope. An ultraviolet photon then decomposes the excited $^{235}UF_6$ but not the unexcited feedstock. The products of the decomposition are $^{235}UF_5$ and atomic fluorine; the $^{235}UF_5$ subsequently precipitates from the gas. To aid in the selective excitation of $^{235}UF_6$, the absorption spectrum of the molecule is simplified by expanding the gas through a nozzle, causing it to cool but not to condense.
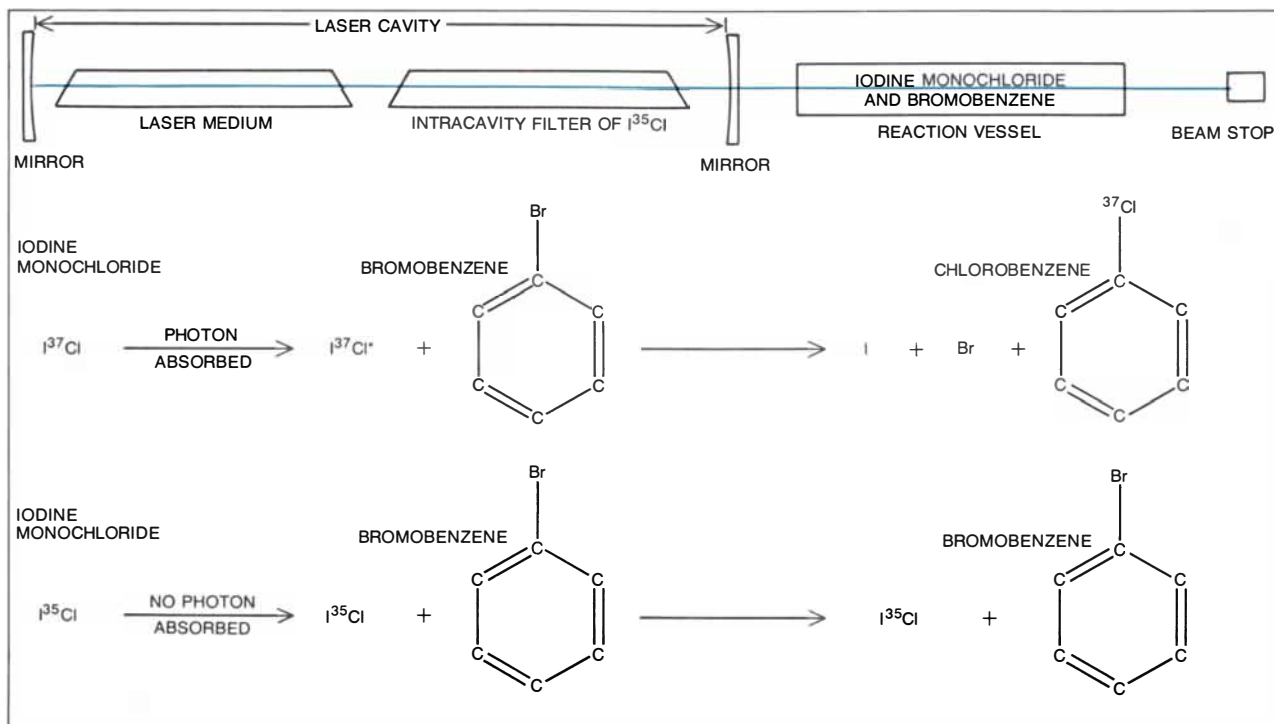
In still another technique dissociation is induced by the absorption of many low-energy infrared photons, rather than just one or two of rather high energy. Indeed, the discovery of this process is one of the most exciting to emerge from research into laser separation. An example of its application is the separation of the isotopes of sulfur, sulfur 32 and sulfur 34, by the decomposition of sulfur hexafluoride (SF_6).

In an experiment conducted by R. V. Ambartzumian and V. S. Letokhov of the Institute of Spectroscopy in Moscow sulfur hexafluoride was irradiated with a pulsed carbon dioxide laser supplying a power of between one and two billion watts per square centimeter. The laser was tuned to an infrared wavelength coinciding with a vibrational excitation of $^{32}SF_6$. Virtually all the $^{32}SF_6$ was decomposed, and the residual gas was enriched in $^{34}SF_6$ almost 3,000-fold. When the laser was adjusted to another wavelength, which excited $^{34}SF_6$, that molecule was decomposed. Essentially the same results were obtained independently by John L. Lyman, Reed J. Jensen, John P. Rink, C. Paul Robinson and Stephen D. Rockwood at Los Alamos.

Subsequent molecular-beam studies have confirmed an early conclusion that the sulfur hexafluoride molecule decomposes without collisions after it has climbed a "ladder" of successive vibrationally excited states up to the dissociation continuum. The process is not yet well understood, but it has already been employed in the enrichment of isotopes

MULTIPLE PHOTON ABSORPTION is another method for separating isotopes by the dissociation of molecules. In a two-stage process (*left*) one photon selectively excites molecules containing a particular isotope; a second photon then dissociates the excited molecules. The first photon is usually an infrared one, causing a transition between vibrational states, whereas the second photon is in the visible or ultraviolet region of the spectrum. In an alternative procedure (*right*) a molecule absorbs many infrared photons in rapid succession, increasing its vibrational energy until a chemical bond breaks. This method has been applied successfully only with comparatively large molecules made up of several atoms; such molecules have many closely spaced vibrational states. Only the first few infrared transitions are isotopically selective.

Figure labels: DISSOCIATION LIMIT; VISIBLE OR ULTRAVIOLET LASER PHOTON; ISOTOPICALLY DISTINCT VIBRATIONAL ENERGY LEVELS; A_1B; A_2B; INFRARED LASER PHOTON; GROUND STATE; DISSOCIATION LIMIT; A_1B; A_2B; INFRARED LASER PHOTON; GROUND STATE

of hydrogen, boron, carbon, silicon, chlorine, titanium, molybdenum, tungsten and osmium as well as sulfur. So far it has been observed only in molecules made up of more than three atoms, suggesting that the high density of excited states characteristic of these molecules may be needed for the chain of photon absorptions to continue unbroken all the way to dissociation.

As a rule excited states of atoms are chemically more reactive than the ground state, and this distinguishing trait suggests still another method for isotope separation. The method consists in mixing with the feedstock a scavenger molecule, one that does not react with the atom or molecule to be separated when that atom or molecule is in the ground state but combines irreversibly with it when it is in an excited state. Finding such an ideal scavenger is not a trivial undertaking, but when one is available, it offers a significant benefit. No additional photons, and thus no additional energy, are required to ionize or dissociate the excited states.

Chemical scavenging has been employed by Douglas M. Brenner and Saswati Datta at Columbia University in separating the isotopes of chlorine. In their experiment a mixture of iodine monochloride (ICl) and bromobenzene

(C_6H_5Br) was irradiated with a dye laser operating at a wavelength of 6,050 angstroms (in the orange-red). At this wavelength the laser excited molecules of iodine monochloride containing chlorine 37 but not those containing the other stable isotope, chlorine 35. In subsequent collisions of the excited $I^{37}Cl^*$ molecules with bromobenzene the bromobenzene abstracted the chlorine-37 atom to form an unstable radical intermediate, $^{37}ClC_6H_5Br$, that rapidly expelled bromine to yield the stable product chlorobenzene $(C_6H_5^{37}Cl)$. After irradiation for about two hours several milligrams of C_6H_5Cl was produced; it was enriched sixfold in chlorine 37.

A special feature of the Columbia work is the use of an isotope to tune the laser for the selective excitation of another isotope. A sample of $I^{35}Cl$ was placed in the cavity of the dye laser, where by its absorption spectrum it quenched the output of the laser at precisely those frequencies that would excite $I^{35}Cl$. By the use of this intracavity filter $I^{37}Cl$ molecules were selectively excited without taking extraordinary measures for narrowing the emission line of the laser and locking it onto a particular $I^{37}Cl$ transition. The method offers the selective excitation of an isotopic species without detailed knowledge of its spectrum.

The Columbia work has also shown that an understanding of the scavenger mechanism may make possible the direct preparation of isotopically labeled compounds. Since many isotopes are employed not as pure elements but as compounds, the technique could increase the utility of laser isotope separation. Indeed, research on isotopically selective photochemistry not only promises to yield practical methods for isotope separation and isotope labeling but also may provide a means for following and understanding the chemistry of excited-state reactions.

Widespread interest in the laser separation of isotopes derives largely from its possible application to the nuclear power industry. At present the dominant technology for the enrichment of uranium is gaseous diffusion. A brief review of this process suggests incentives for developing alternatives.

In a gaseous-diffusion plant vapors of uranium hexafluoride (UF_6) are pumped through a porous barrier, the lighter $^{235}UF_6$ diffusing more rapidly than the heavier $^{238}UF_6$, so that the transmitted vapor becomes slightly enriched in uranium 235. The enrichment in passing through a single stage is small, and so hundreds of stages must be linked together in a cascade, where the

97

feed to each stage consists of the enriched stream from the stage below combined with the depleted stream from the stage above. In order to separate a quantity of UF_6 containing one kilogram of uranium enriched to 3 percent uranium 235, with waste UF_6 at .2 percent uranium 235 discarded, almost 1,500 kilograms of natural uranium must enter the cascade at the first stage and more than two million kilograms of uranium must be pumped and recirculated through the cascade. An energy of about five million electron volts is expended for each atom of uranium 235 that is separated.

The present cost of obtaining uranium 235 of 90 percent purity by gaseous diffusion is about 2.3 cents per milligram. This compares favorably with the cost of from $1 to $10 per milligram of most other isotopes at the 90 percent enrichment level, but a more familiar standard of economic value shows immediately that all purified isotopes are quite precious. The present price of gold is about .3 cent per milligram.

The U.S. has three gaseous-diffusion plants capable of separating 3,960 metric tons of 3 percent uranium 235. The capital cost of a new plant with an annual capacity of about 2,050 metric tons of 3 percent uranium 235 is estimated to be about $3 billion with an annual operating cost of about $500 million. Estimates of the demand for enriched uranium are uncertain, but domestic consumption could require a capacity equivalent to between four and eight new plants by the end of the century, and foreign demand could double or triple that number. The adoption of other physical separation techniques, such as gaseous centrifugation, might reduce the cost of uranium-isotope separation by from 10 to 30 percent. If large-scale laser separation proves feasible, it offers the potential of much greater savings.

The energy required to generate visible photons or infrared photons for laser separation might be from one to 10 electron volts per uranium-235 atom separated. Even if the efficiency of the laser in converting electrical energy into light is no greater than .002, the energy cost of the process is between 500 and 5,000 electron volts per uranium-235 atom. That is at least 1,000 times less than the energy cost of gaseous diffusion. Because the laser is also expected to make possible a high separation factor in each stage, the potential exists for removing almost all the uranium 235 in the ore. Gaseous diffusion can economically extract only 60 to 70 percent of the uranium 235 in the feedstock, leaving uranium containing .2 to .3 percent uranium 235 as "tails," or waste. Higher extraction efficiency would effectively increase useful uranium reserves. Indeed, a laser separation plant might be able to reprocess the stored wastes from gaseous diffusion plants; these wastes represent between 30 and 40 percent of all the uranium 235 that has ever been mined! Although a more sophisticated economic analysis might be less optimistic, it would seem that a savings of several hundred billion dollars could be realized by the end of the century if the laser technology works.

These calculations assume the continued use of light-water reactors like those now operating in the U.S. Another type of reactor eliminates the need for uranium isotope separation by "burning" a fuel of natural uranium. These heavy-water (D_2O) reactors, however, require large quantities of deuterium: about one ton of D_2O per megawatt of electrical capacity. The widespread adoption of heavy-water reactors would therefore motivate another kind of laser isotope separation program.

Uses of isotopes in fields other than nuclear power generation are diverse, but much smaller amounts are consumed. Isotopes are important as tracers in research, medicine and agriculture, but because they are so costly there is little incentive for finding new applications. This may change dramatically if laser isotope separation techniques can reduce the present cost by a factor of 100 or 1,000. For example, in chemistry an abundant supply of low-cost isotopes might lead to the widespread adoption of isotopically labeled compounds for structural analysis, for analytical detection and for kinetic studies.

The separation of isotopes is an important process, which the intense, monochromatic light of the laser may soon make cheaper and therefore commoner. It is possible that the application of the laser to chemistry may ultimately have even greater significance, a possibility made plain when the laser itself is viewed in the light of history.

The origins of chemistry are customarily traced to the alchemists, whose work was funded by royal patrons eager to transform lead into gold. The alchemists of course failed to achieve that transformation, but in their efforts they assembled a body of knowledge that provided a factual basis for much of modern chemistry. Today the royal patrons of the sciences are government agencies, which urge the development of new methods for separating isotopes, again with the prospect of economic rewards. This time the goal will probably be achieved. As before, however, the ultimate reward may prove to be of far greater value than the immediate object being sought. By understanding the mechanism of laser isotope separation we may be laying the foundation for a new chemistry, one in which compounds are made not by supplying the random energy of heat but by exciting only those internal motions of molecules that facilitate the transformation of reactants into products.

Waveform fidelity.
If you don't understand it,
you could be making a $350 mistake.

Today a good amp and tuner can easily cost you $350, $500, $700 or even more. But no matter how much a component costs, if it doesn't have waveform fidelity, the music that's put into it won't be the music that comes out. And that's an expensive mistake to make.

It's also a mistake Technics won't let you make. Because Technics' two new integrated amps, the SU-7600 and the SU-8600, as well as our two new tuners, the ST-7600 and the ST-8600, have superb waveform fidelity.

With both tuners, the waveform being broadcast will be the waveform you'll receive, with virtually no distortion or cross modulation. Because both have flat group delay filters in the IF sections. So the time delay is constant for all frequencies.

There's also a Phase Locked Loop IC in the MPX sections. That's why, for example, with the top of our line, the ST-8600, you'll get stereo separation of 45dB at 1kHz and 35dB at 10kHz. And a frequency response that's as flat as it is wide, 20Hz to 18kHz (+ 0.2dB − 0.8dB).

And with an 8-ganged tuning capacitor (5 for FM and 3 for AM) and a Technics developed 4-pole MOS FET, broadcasts with the ST-8600 will sound more like master tapes than FM.

You'll also find waveform fidelity in both amps. Including our most powerful one, the SU-8600. *With 73 watts per channel, minimum RMS, both channels driven into 8 ohms from 20Hz to 20kHz, with no more than 0.08% total harmonic distortion.*

And the SU-8600 will stay 73 watts regardless of the power-hungry transient bursts found in many musical waveforms. The reasons: Sixfold independent power supplies for the control voltage and power amplifiers. The results: Virtually no transient cross-talk distortion. And optimum waveform fidelity.

So before you make a $350 mistake, or an even more expensive one, listen to our new amps and tuners. Your Technics dealer has them. Along with Technics waveform fidelity.

Cabinetry is simulated wood.

Technics
by Panasonic