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ISOTOPE SEPARATION USING TUNABLE LASERS

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MASTER

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ISOTOPE SEPARATION USING TUNABLE LASERS*

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Summary

The recent development of tunable lasers has made possible the serious consideration of photochemical, and photophysical processes for the separation of isotopes on a commercial scale. Photoseparation processes are, in principal, applicable to the isotopes of all elements, though the major economic motivation is for the enrichment of uranium for power reactors.

Various processes for laser isotope separation based upon the use of the spectroscopic isotope effect in atomic and molecular vapors are discussed. Emphasis is placed upon processes which are suitable for uranium enrichment.

A demonstration process for the separation of uranium isotopes using selective photoionization is described.

The first successful processes for the photochemical separation of isotopes were demonstrated more than 20 years ago. The processes have remained as laboratory curiosities, however, because light sources suitable for scaling these processes to a commercially significant size have not been available. The recent development of tunable lasers now makes it possible to consider photochemical separation of isotopes on a commercial scale.

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Photochemical techniques are applicable in principle to the isotopes of any element. At present, however, the greatest economic motivation is associated with the enrichment of uranium for power reactors. The three gaseous diffusion plants operated by the U.S.E.R.D.A. are capable of producing approximately 5400 tonnes of enriched uranium per year at an enrichment level of about 3% ^{235}U , the enrichment required for most light water reactors. It is predicted that by the year 2000 approximately 25,000 to 30,000 tonnes will be required per year. To meet this demand new enrichment facilities must be constructed. It appears that it will be necessary to construct every 18 months a new enrichment plant with a capacity larger than that of the present Oak Ridge Gaseous Diffusion Plant. Ten or eleven new plants of this size will be required by the turn of the century. Each of these plants is expected to cost between 3 and 4 billion dollars with its associated power plant. The tremendous cost of these plants is in itself a strong motivation for finding alternative processes which use less expensive equipment. This is only one of several incentives for the development of new enrichment processes. Others are the cost of electrical energy associated with the gaseous diffusion process and the more effective utilization of ^{235}U from natural uranium ore.

There are a number of laser isotope separation processes. They have some common features however. The most attractive processes at present are based on vapor phase photophysical and photochemical processes.

In a typical laser isotope separation process we would expect to find three components. The introduction of an isotopically mixed vapor is followed by a laser excitation step which is the isotopically selective step. Finally, in the extraction step, the selectively excited isotope is separated from the feed stream by one of several possible processes.

This reasoning can be carried further to define essentially four different types of processes. Atomic vapor process based upon the physical or chemical extraction of the excited isotope represent two alternatives. Two additional alternatives are available for processes based on molecular vapors.

At present several photophysical processes based on the selective excitation of atomic vapors have been demonstrated. Research is being carried on in a number of laboratories to discover chemical processes which can be based upon molecular vapors but the development of such processes is far more difficult than the development of photophysical processes based on atomic vapors.

All laser isotope separation processes have a common physical basis. The spectroscopic isotope effect is utilized to provide isotopically selective excitation. It is well known that different isotopes of the same atom have slightly different absorption and emission spectra due to the fact that their energy levels are slightly different. This difference in energy levels is called the isotope effect, or shift, and is illustrated in Figure 1 for a mixture of "A" and "B" isotopes. If we have a precisely tuned laser with photons of energy $h\nu_1$, we can selectively excite isotope "A" while leaving isotope "B" unexcited. This step is the same for all laser isotope separation processes.

Laser isotope separation processes are differentiated from one another by processing subsequent to the isotopically selective excitation. In Figure 1, the isotopically selective excitation has left isotope A in the energy level " α ". Following this step, we have a number of choices. A second photon of energy $h\nu_2$ can be absorbed to produce an ion, in which case isotope "A" is selectively photoionized. We could well cause state α to undergo a chemical reaction to form a product which would be enriched in isotope "A". Another possibility is that the momentum of photon $h\nu_1$ could be transferred to the atoms of isotope A in a beam of isotopes "A" and "B". Isotopes "A" are then deflected away from isotopes "B" and can then be collected to provide the enriched product.

A variation on the selective photoionization possibility is that a photon of $h\nu_2$ can raise the energy level of isotope "A" not to the continuum but rather to an energy level which lies slightly below the ionization continuum and the atom can be subsequently ionized by an infrared photon. This scheme can, under some circumstances, have some advantages with respect to the direct photoionization mentioned above.

In the third step of a photophysical process ions are extracted by a combination of electric and magnetic fields to produce the enriched product.

If the product of the laser excitation is a chemical reaction or a chemical product then this product can be collected by condensation or some other means.

The isotope shift in atomic systems is generally in the range of $1:10^6$ to $1:10^8$. It is not possible to use conventional thermal light sources to produce the necessary intensity for large scale separation processes with the sort of selectivity required for isotopically selective excitation. Suitable linewidth and stability are well within the state-of-the-art of tunable lasers however.

On the basis of Figure 1 we can set down the conditions which must be met for the laser separation of isotopes. First of all we must have a resolvable isotope effect. Recent laboratory results have shown that it is possible to resolve an isotope effect for virtually any atom in the periodic chart using tunable lasers. It's also necessary that only one isotope can absorb the laser light. Thus, the laser linewidth must be less than the isotope shift and the laser must be so stable that its frequency does not vary by more than the isotope effect. There must also be no competing mechanism for excitation, that is, there must be no other mechanism in the system which can produce the same excitation as that provided by the laser.

So far, only processes based on atomic vapors have been considered. All of the possibilities which have been mentioned exist as well for molecules. However, molecules provide some additional possibilities. In Figure 2 is shown a schematic energy level diagram for a mixture of isotopic molecules. In addition to the isotope effect involving electronic excited states, there is also an isotope effect associated with vibrational excitation which can be very much larger than the electronic

effect. The vibrational isotope effect can be as large as $1:10^4$ to $1:10^3$. In Figure 2 the vibrational isotope effect has been used to selectively excite isotope "A" with photons of energy $h\nu_1$. Vibrational excitation energies are generally very much smaller than the energies associated with electronic excitation. It is more difficult to use this small energy in subsequent processes for extracting the excited isotope than it is if the isotopically selective excitation is an electronic transition.

Assuming that isotopic selectivity has been produced by the photon, $h\nu_1$, there are again a number of choices for subsequent steps. Possibilities other than the selective chemical reaction and selective photoionization processes described for the atomic system are photodissociation, for instance by photons of energy $h\nu_2$.

In a process in which $h\nu_2$ dissociates the molecule, the enriched product can be removed by virtue of a difference in vapor pressure between the dissociated fragments and the initial molecules. The various possibilities for molecular isotope separation processes are tabulated in Figure 2.

Assuming that isotopically selective excitation has been carried out, there are a number of ways in which the selectivity can be lost. One of the dominant mechanisms for the loss of isotopic selectivity is resonant energy exchange. If one molecule is selectively excited using the isotope shift, the excited energy level is very nearly resonant with the corresponding level of the undesired isotope. The cross section for resonant energy exchange is very large, in fact it can be much larger than the collision cross section. In order to make use of the isotopically selective excitation it is necessary to remove the selectively excited isotope before it has a chance to undergo resonant energy exchange. The same arguments apply to resonant charge exchange in processes which are based on the selective production of an ion. Cross sections for charge exchange can be several hundred square angstroms.

The cross sections for energy and charge exchange limit the density, and therefore the throughput, of large scale isotope separation systems.

Isotopically selective excitation can also be lost by scrambling processes. "Enriched" molecules can exchange the desired isotope with undesired isotopes which exist elsewhere in the system to destroy the enrichment. This can happen in one of two ways. In the first of these processes the desired isotope itself is exchanged. A similar process can occur with the addition or the exchange of another atom of a polyatomic molecule to destroy the enrichment. Another means by which isotopically selective excitation can be lost is by the process of chaining.

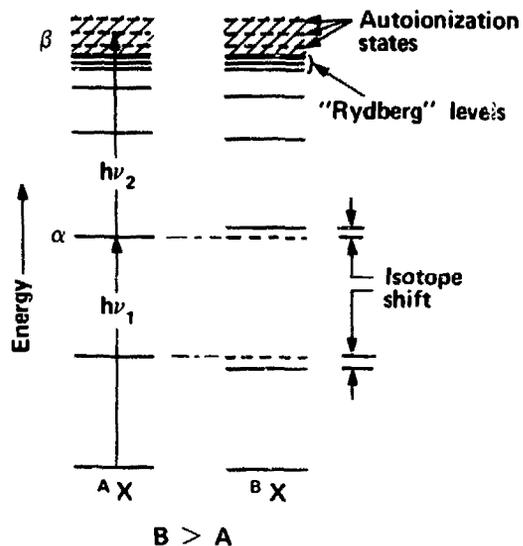
Experimental demonstration of laser isotope separation has been carried out in several laboratories. A schematic diagram of an experiment in which the isotopes of uranium were separated is illustrated in Figure 4. In this experiment a beam of uranium atoms produced by an oven at the left of the diagram enters a region in which it is excited by the tunable output of a dye laser. This is the isotopically selective excitation step. The dye laser beam is tuned to excite only the ^{235}U atoms. Excited atoms are then ionized by the output of a mercury arc. The output is filtered so that there is insufficient energy to ionize the ground state of uranium but there is sufficient energy to ionize the atoms which have been excited by the dye laser. The beam, which is a mixture of ^{235}U ions and ^{238}U neutral atoms, enters an ion lens where the ions are focused onto the entrance slit of a quadrupole mass spectrometer which measures the mass of the ions which have been produced by the selective excitation. After passing through the mass filter the ions are collected by an electric field and the ion current is measured by a Channeltron electron multiplier. In this experiment the laser beam was tuned to either the ^{235}U or ^{238}U absorption lines using an absorption cell which was independent of the separation apparatus. At the top of Figure 4 the mass spectrum of the collected ion current is shown with the laser tuned to the ^{238}U absorption line. There is a mass peak only at 238, virtually no atoms of mass 235 were detected. When the laser was tuned to the absorption line of ^{235}U , as shown in the lower curve, an ion signal corresponding only to mass 235 was seen. The difference of three orders of magnitude in the heights of these mass peaks comes about from two causes. A factor

of 140 is due to the isotopic abundance ratio and an additional factor of 8 is related to the hyperfine splitting of the ^{235}U line.

In Figure 5 is plotted the absorption spectra of the ^{235}U and ^{238}U lines on the same wavelength or energy axis. These were obtained by setting the mass spectrometer to mass 235 or mass 238, as is appropriate, and varying the frequency of the laser. As the laser frequency is scanned through the ^{235}U line, the eight peaks of the hyperfine spectrum of the 5915 Å are clearly seen. This structure maps perfectly onto the emission structure of the same line as attained from a Fabry-Perot interferometer trace of the 5915 Å line. The ^{238}U line has no hyperfine structure. This isotope effect shown in Figure 5 is typical of many of the uranium absorption lines. For comparison, the laser linewidth is shown in the same diagram. The laser linewidth is very much smaller than the linewidth associated with any of hyperfine components of the ^{235}U atom. This also presents a problem for the efficient use of a laser in separating isotopes. It thus makes it difficult to access all the atoms in a vapor with a laser tuned to a particular frequency.

In this discussion some of the problems and techniques related to laser isotope separation have been discussed. A considerable amount of research will be required to bring these processes to commercial application.

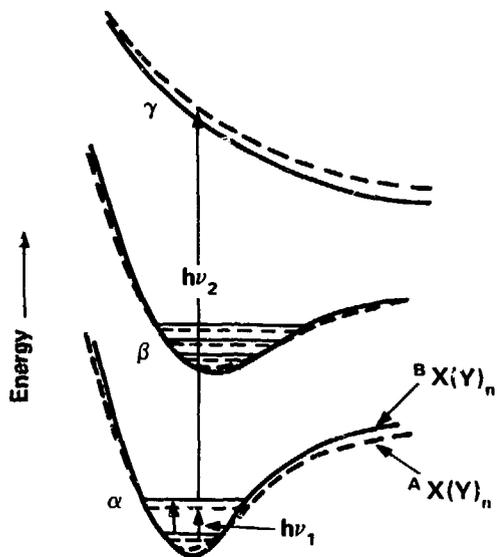
LASER PROCESSES FOR ISOTOPE SEPARATION (ATOMIC VAPORS)



- 1st step: selective absorption of $h\nu_1$ by ${}^A X$
- 2nd step: any of following
 - a. Photoionization by $h\nu_2$
 - b. Chemical reaction of state α
 - c. Deflection of atomic beam by $h\nu_1$
 - d. Absorption of $h\nu_2$ to Rydberg level followed by ir photoionization
- 3rd step: extraction by
 - a. Electric and magnetic fields for ions
 - b. Condensation for chemical reaction products

FIGURE 1

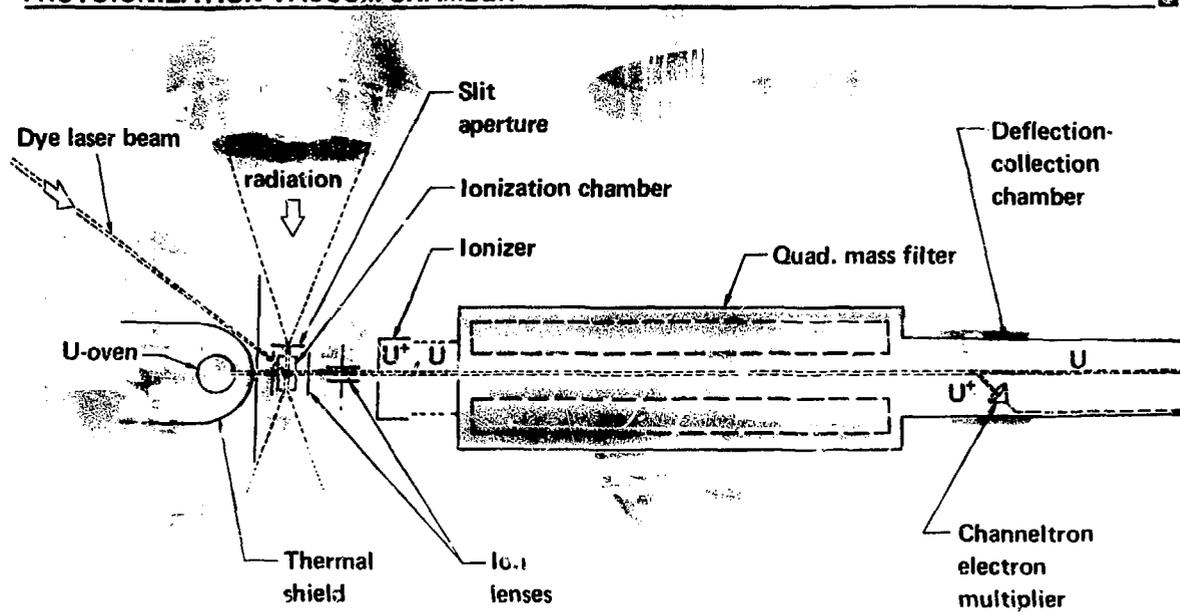
LASER PROCESSES FOR ISOTOPE SEPARATION (MOLECULAR VAPORS)



- 1st step: selective absorption of $h\nu_1$ by $A X(Y)_n$ ($h\nu_1$ may excite vibrational or electronic transitions)
- 2nd step: any of following –
 - a. Photoionization by $h\nu_2$
 - b. Photodissociation by $h\nu_2$
 - c. Chemical reaction of state α
 - d. Chemical reaction of state β (β produced by $h\nu_2$)
- 3rd step: extraction by
 - a. Electric and magnetic fields for charged fragments
 - b. Condensation for neutral fragments
 - c. Chemical scavenging

FIGURE 2

PHOTOIONIZATION VACUUM CHAMBER



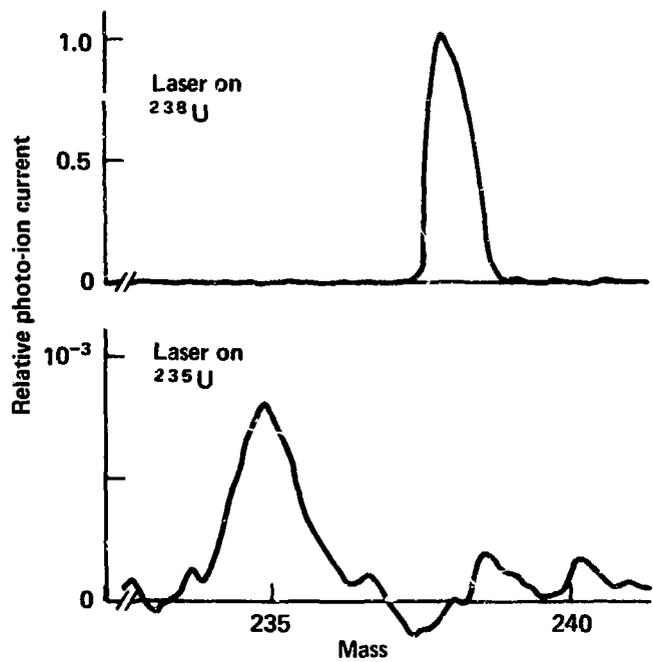


FIGURE 4

ISOTOPE EFFECT IN URANIUM

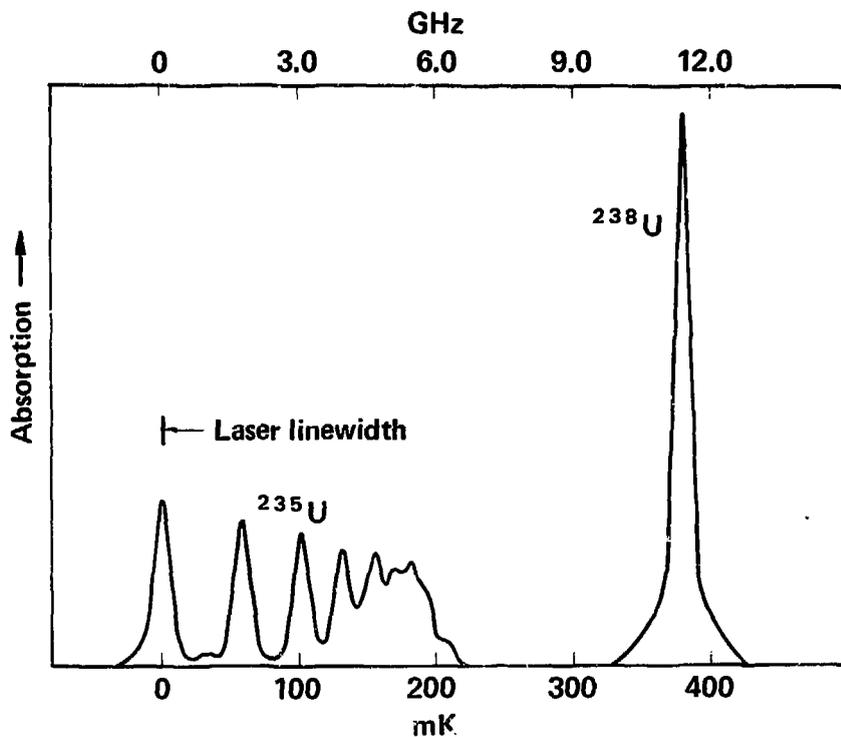


FIGURE 5

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