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LASER ISOTOPE SEPARATION OF URANIUM

Allen Hartford

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LASER ISOTOPE SEPARATION OF URANIUM*

Allen Hartford
Lawrence Livermore Laboratory
Livermore, California

Abstract

The known capacity through gaseous diffusion to produce isotopically enriched uranium for nuclear reactor usage is thought to be adequate through the mid 1980's. After that time however, the projected demand will sharply exceed the supply if additional enrichment facilities are unavailable. Economic factors suggest the serious consideration of other enrichment approaches for the future.

Laser isotope separation (LIS) is a possible alternative to the more conventional technologies (diffusion and gas centrifuge). It is the object of the research at Lawrence Livermore Laboratory (LLL) and several other laboratories to decide whether LIS is practical and economically competitive for large scale separation of uranium isotopes.

All photo-separation processes are based on the well known spectroscopic isotope effect. Selective excitation of one isotope of the feed, either atomic or molecular in form, is feasible with available lasers. The excited isotope is then isolated from the unexcited isotopes by either a physical or chemical extraction. An example of the former would be the electromagnetic extraction of ions formed by photoionization of the selectively excited species. A typical chemical extraction would be the use of a photo-induced chemical reaction.

It is the intent of the LLL effort to develop a broad technical data base for the evaluation of a variety of LIS schemes. This necessarily requires extensive efforts in the fields of atomic and molecular spectroscopy as well as chemical kinetics. The fundamental spectroscopic and kinetic parameters required are described. Finally, an experiment demonstrating selective photoionization of ^{235}U in a beam of the metal vapor is reviewed.

Separation of Uranium

For over 40 years there has been interest in the photo-induced separation of isotopes. Following the initial investigations of Sauer in 1935, Gunning and others during the 1950's convincingly demonstrated the laboratory scale photo-separation of U isotopes. Yet today no isotope commercially available is produced by a photoexcitation method. This is not too surprising. Conventional light sources do not possess the tunability, narrow linewidths, and directionality required for commercial scale separations. Attempts to increase the power of so called resonance lamps lead to broadening of

emission lines, so that isotopically selective excitation required is not longer possible. On the other hand the use of lasers is rapidly changing this situation. The rapid progress in laser technology is partly illustrated by the fact that laser isotope separation (LIS) of at least six elements has been demonstrated in the last several years. Figure 1 summarizes these results.

Some advantages of LIS for many elements are high separation factors, high efficiencies, and costs significantly reduced from present enrichment techniques. A successful LIS scheme for enrichment of uranium could have enormous economic impact, while for lighter elements significant cost reductions could open new applications of isotopes in research and technology.

All isotope enrichment schemes based on photoexcitation depend on the well-known spectroscopic isotope effect. These effects are generally observable only in the vapor phase. Consequently, attention will be focused on vapor phase LIS schemes. Under appropriate conditions, an isotope within a mixture of isotopes may be selectively excited by narrow wavelength radiant energy. The excited isotope possesses different properties than the unexcited ones. Advantage may then be taken of these different characteristics to either physically or chemically separate the excited isotope.

One physical technique for separation of isotopes is depicted in a simplified manner in Figure 2. The process is selective photoionization. The first photon is preferentially absorbed by one isotope due to the isotope shift. This shift may be as small as one part in 10^5 or less of the transition energy. Tunable and fixed frequency lasers are available which have bandwidths on the order of one part in 10^4 , so the selective excitation may be quite efficient. A second quantum of energy can photoionize the selectively excited species, but does not affect the unexcited isotopes. Product ions may be separated from the neutrals by application of an electromagnetic field.

If the feed material for the isotope separation is a molecular vapor, a selective two step photo-dissociation may be accomplished. Such a scheme is shown in Figure 3. One isotopic component is selectively excited by an infrared photon which induces vibrational excitation. This component is then dissociated with a second photon of energy insufficient to dissociate the unexcited isotopic molecular species. Separation of the dissociated fragment may be accomplished either physically or chemically. If the fragment is itself a stable species with vapor pressure substantially different than the starting material, isolation is rather simple. If the species is reactive, a chemical scavenging method can be devised.

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One photon LIS processes are in general more attractive than multi-photon schemes. Two examples are molecular predissociation and a photo-induced chemical reaction. The latter represents a chemical extraction and is based on the strong reactivity dependence on reactant internal excitation.

In summary the three major requirements for a successful LIS scheme are:

- a. An absorption spectrum with clearly resolved isotope effects.
- b. A sufficiently monochromatic laser to excite only a single isotopic species.
- c. A physical or chemical process which operates on only the excited species but not the unexcited.

Also, it is important that secondary processes, such as energy transfer from the selectively excited isotope to the undesired isotope and chemical or charge exchange reactions are of minimal importance during the actual separation.

The remainder of this talk will be devoted to the LIS of uranium isotopes employing the general schemes discussed previously. First, I will mention the motivation for finding an alternative to the present separation technologies of gaseous diffusion and gas centrifuge. An overview of some of the work at the Lawrence Livermore Laboratory will then be presented, followed by a description of a successful LIS of uranium via two step photoionization.

In Figure 4 the projected relationship between supply and demand for enriched uranium for power reactors between 1980 and 2000 is shown. The uranium required for power reactors contains about 3% ^{235}U compared to 0.7% in natural uranium. Commencing in the mid 1980's a new enrichment facility having twice the capacity of the present Oakridge Gaseous Diffusion plant will be required every 1 1/2 years. Each of these installations requires a capital investment of two to three billion dollars, which could constitute a total expenditure of tens of billions of dollars by the end of the century. The gas centrifuge has greater capital costs, but the power requirements are somewhat less.

LIS represents a possible alternative to these techniques. The purpose of the research at LL and other laboratories is to determine whether laser photochemistry is practical for large scale enrichment of uranium. There are a number of advantages recognizable in a uranium LIS scheme. First, an LIS process has an inherently high separation factor which allows high enrichment in one or a few stages rather than a cascade. Consequently, capital investment for LIS plants could be relatively inexpensive. In addition separative work costs for a laser process are expected to be low due to electrical power requirements. An LIS plant may consume as low as 100 keV per separated ^{235}U atom compared to 3 MeV for gaseous diffusion. Finally, ore utilization should be increased. Gaseous diffusion removes about 60% of the ^{235}U from the feed material, whereas an LIS procedure could extract almost

all of it.

Associated with the various types of LIS schemes discussed earlier is the determination of a variety of fundamental physical parameters. At LL we have established a broad based experimental program to measure these parameters in both atomic uranium vapor and uranium containing molecular vapors. Among the parameters needed to determine the viability of any LIS scheme are:

- a. Absorption cross sections for both the atomic and molecular species.
- b. Photoionization cross sections from an excited level in the atomic vapor.
- c. Photodissociation cross sections for molecular species.
- d. Energy transfer, charge exchange, and chemical exchange cross sections.
- e. The evaluation of photo-induced chemical reactions.

Let us consider first LIS schemes based on the uranium atomic vapor. Although the generation of the atomic vapor poses some problems due to the corrosive nature of the molten metal and the high temperatures involved (typically in excess of 2000°C), the spectroscopy and isotope effects are better characterized than for molecular species. Additionally, selective excitation may be readily accomplished with currently available narrowband, tunable dye lasers. Although the spectral positions and isotope shifts for many uranium transitions were previously known, absorption cross sections were not accurately determined. An apparatus for these measurements and based on a narrowband (~ 30 MHz), tunable CW dye laser is shown in Figure 5. The beam from the laser is split, one beam passing through a uranium vapor of known density and path-length the other serving as a reference beam. The ratios of the beam intensities are taken electronically. Hence, as the laser is scanned through a transition (Doppler width ~ 2 GHz) a precise value of the percentage of absorption is found. This allows very accurate determination of the absorption cross section. A typical scan is shown in Figure 6. Typical cross sections have been found to be in the range of 10^{-13} to 10^{-15} cm².

In a selective photoionization scheme it is vital to know the photoionization cross section from the laser pumped level of uranium. A number of these intermediate transitions accessible with our narrowband width lasers are given in Figure 7. Measurements of relative photoionization cross sections from these levels are currently being made.

A schematic of the apparatus for these experiments is shown in Figure 8. A beam of uranium atoms issues from a tungsten oven into an interaction chamber. Here they are excited by a single mode dye laser which yields a large population in the intermediate level. UV light of variable wavelength then ionizes the uranium atoms. This tunable radiation is generated by a combination of 3/4-meter spectrometer and 2.5 kw Xe-Hg arc. Detection is accomplished by an ion counting technique.

The uranium ions pass through a quadrupole mass spectrometer and onto a channeltron electron multiplier. The ion signal is pulsed as a result of chopping the laser beam. When the chopper allows the laser beam to pass, the signal is fed into one channel of a dual channel scalar. As the beam is blocked, the signal is fed into the other channel. This signal is due to unsuppressed thermal ions, etc. and causes a background signal. The two signals are subtracted yielding a relative photoionization cross section. By scanning the UV wavelength an entire spectrum can be mapped. The results of such a measurement are shown in Figure 9 in which the 5935 Å transition has been laser excited. The two features to note are the distinct autoionizing peaks at 3010 Å and 2960 Å.

Another important parameter to measure for economic evaluation of any scheme based on the atomic vapor is the intermediate state lifetime. The most convenient way to perform this experiment is to excite the transition of interest with a narrowband, tunable pulsed dye laser and monitor the fluorescence decay. A laser with pulse length of about 6 nsec and 300 MHz bandwidth is available. The dominant problem associated with this measurement is minimizing the blackbody radiation from the uranium oven source which is orders of magnitude larger than the expected fluorescence level.

LIS schemes based on molecular systems are attractive for a number of reasons. First, the volatility is often orders of magnitude greater than the atomic vapor, making lower temperature operation possible. Additionally, many of the often molecular species present far less restrictive materials compatibility than the atomic vapor. Finally, molecular species present the possibility of selective excitation with an infrared photon. Some of the molecular species which have been chosen as possible feed materials for an LIS scheme are given in Figure 10. These were chosen on the basis of volatility and reported thermodynamic stability, in addition to computer modeling of the rotational structure in vibrational and electronic transitions.

One serious problem encountered with polynuclear uranium compounds is the so-called "thermal confusion" or "hot band" problem. This phenomenon stems from the low frequency vibrations found in many of the compounds of interest. For UF_6 at room temperature only a few tenths of a percent of the molecules are in the ground vibrational level. Figure 11 shows the relative populations of vibrational levels up to 1000 cm^{-1} in energy. Over 80% of the thermal population exists above this energy. This situation makes it extremely difficult to isotopically excite UF_6 in the low energy infrared active modes. A similar situation exists for other molecular systems.

Since little or no spectroscopic information existed for the molecular species of interest, a facility was established to carry out moderate resolution spectroscopy in the $0.25\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$ range. The results of these investigations are presented in Figure 12. As may be seen UO appears to be the most promising molecular system investigated to date. A portion of the visible emission spectrum is displayed in Figure 13. The most notable feature is the vibronic band at 5935 Å.

Further high resolution absorption studies of this molecule are currently underway. Spectra of both ^{235}UO and ^{238}UO are being recorded to ascertain isotope effects. In Figure 14 the method of UO generation for the absorption studies and its volatility compared to uranium are depicted. It may be noted that UO has a higher vapor density than uranium at a comparable temperature. Also materials compatibility is superior to that of the atomic system.

A final comment is in order on an experiment to demonstrate the feasibility of uranium LIS. The particular technique employed was selective photoionization. Figure 15 shows a top view of the apparatus. Uranium atoms from a tungsten oven were collimated into a molecular beam. A dye laser entering from the top chamber and UV ionizing radiation entering from the side, intersect the beam at the same point. The dye laser operated at 5915 Å and had a bandwidth of 30 MHz and a power of 40 mw. UV radiation was provided by a filtered Xe-Hg arc. The two isotopically shifted transitions involved are shown in Figure 16. The photoions passed into a mass spectrometer for isotopic analysis. With the laser tuned to either the ^{238}U or ^{235}U absorption mass scans were performed. The results are given in Figure 17. It is evident that when one isotope is selectively excited, only photoions of that isotope may be detected. This vividly demonstrated the possibility of uranium enrichment via a laser technique.

DEMONSTRATED LASER ISOTOPE SEPARATIONS

<u>Element</u>	<u>Method</u>
H	Molecular predissociation
B	Two step photodissociation
N	Two step photodissociation
Ca	Two step photoionization
Br	One photon excitation followed by collisional dissociation
Ba	Photodeflection (multiphoton)
U	Two step photoionization

ISOTOPE SEPARATION BY PHOTOIONIZATION

1. Irradiation of gaseous isotopic mixture with $h\nu_1$ selectively excites isotope "A"
2. Irradiation with $h\nu_2$ produces "A" ions, leaves "B" unaffected
3. Ions can be separated from neutrals by electromagnetic fields

ISOTOPE SEPARATION BY MOLECULAR DISSOCIATION

1. Isotopically selective step is $h\nu_1$
2. $h\nu_2$ dissociates molecule
3. Molecular fragment containing U is the enriched product

Problems:

Vibrational levels at $h\nu_1$ and above may be thermally populated

Rotational line density prevents selective excitation of a single isotope

PROJECTED DEMAND ON U.S. ENRICHMENT FACILITIES

ATOMIC URANIUM ABSORPTION APPARATUS

**ABSORPTION CROSS SECTIONS AND ESTIMATED LEVEL LIFETIMES
IN URANIUM VAPOR**

Level (cm^{-1})	λ Res ($\text{\AA}$)	I.S. (mk)	HFS (cm^{-1})	τ (nsec) Estimated	σ (10^{-16}cm^2) at 2500°K
15631	6395.45	+305	—	300	336
15638	6392.78	+190	—	170	106
16505	6056.81	-280	—	530	70
16900	5915.38	-280	0.21	300	1030
17361	5758.14	-160	—	330	110
18932	5280.53	-230	—	100	359
19885	5027.38	-411	—	100	946
22582	4426.93	-280	<0.08	75	430
22919	4362.05	-235	Sharp	66	2750
23212	4306.81	-170	<0.12	—	—

Data compiled by E. Worden

AUTOIONIZATION APPARATUS

AUTOIONIZATION FROM $7M_7$ AT 591.5 nm IN ATOMIC URANIUM VAPOR

CANDIDATE MOLECULES FOR LASER ISOTOPE ENRICHMENT

- 1. Uranium tetrahalides (UX_4 , $X = F, Cl, Br$)**
- 2. Uranium mixed tetrahalides (UX_3Y)**
- 3. Uranium oxyhalides (UOX , UOX_2 , UO_2X_2 , $X = F, Cl$)**
- 4. Simple uranium molecules (UO , UO_2 , etc.)**

POPULATION OF LOW-LYING VIBRATIONAL LEVELS IN UF_6 AT 300°K

SUMMARY OF SURVEY SPECTROSCOPIC RESULTS

<u>Molecule</u>	<u>Observations</u>	<u>Conclusion</u>
• UBr_4 , UBr_3Cl UBr_2Cl_2	Molecular bromine absorption sets in at 350°C	Thermal decomposition
• UI_3 , UBr_3 UCl_3	Formation of UI_4 , UBr_4 , UCl_4	Disproportionation
• UO_2Cl_2	Formation of UO_2 and Cl_2	Thermal Decomposition
• UO	Discrete emission bands	Stable molecule

MATERIALS COMPATIBILITY AND VOLATILITY OF UO

Simple vapor production of UO

Pressure of UO > pressure of U

PHOTOIONIZATION VACUUM CHAMBER

ISOTOPE EFFECT IN URANIUM

NATURAL URANIUM SAMPLE

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