

LASER ISOTOPE SEPARATION
- A NEW CLASS OF CHEMICAL PROCESS

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ABSTRACT

Lasers are being used industrially in applications that include cloth cutting, semiconductor annealing, metal welding, cutting and drilling and even the etching of identifying marks on bottle caps. Lasers may soon find several applications in chemical processing as well. The applications that have attracted the most research funding to date involve isotope separation for the nuclear industry. These isotopes have an unusually high value (\$1,000/kg) compared to bulk chemicals (~\$1/kg) and are generally required in very large quantities. In a laser isotope separation process, light is used to convert a separation that is very difficult or even impossible by conventional chemical engineering techniques to one that is readily handled by conventional separation technology. For some isotopes this can result in substantial capital and energy savings. A uranium enrichment process developed at the Lawrence Livermore National Laboratory is the closest to commercialization of the large scale laser isotope separation processes. Of particular interest to the Canadian nuclear industry are the laser separation of technetium, tritium, zirconium-90 and carbon-14. In this paper, the basic principles behind laser isotope separation are reviewed and brief descriptions of the more developed processes are given.

1.0 INTRODUCTION

The rapidly expanding industrial market for lasers is evidence for the fact that industry is gaining confidence in the reliability of laser technology. Many of these applications such as cloth cutting, semiconductor annealing, metal welding, cutting, drilling, and laser marking (placing identifying marks on packaging) to name only a few examples, make use of the laser's ability to deliver a well-defined and, if desired, an intense beam of energy to a precise location. But lasers have another property which can make them useful in chemical processing. They can deliver light energy with a very narrow frequency or wavelength range.

2.0 EXPENSIVE LASERS PRODUCE EXPENSIVE CHEMICALS

Laser energy is considerably more expensive than process heat because lasers are driven by electricity rather than heat and they convert electricity to visible, infrared, or ultraviolet light with an efficiency that, in the future, is unlikely to exceed 20%, even in the most efficient lasers. (Efficiencies of up to 40% have been predicted for one special class of laser called the free electron laser²). The most efficient high power laser available today is the carbon dioxide laser⁴. Its efficiency is currently less than 10%. In general, laser photons can be considered to be very expensive, costing at least \$1/mole^{4,5}. By contrast, almost no high volume industrial chemicals sell for as much as \$1/mole. Bulk chemicals typically sell for about \$1/kg. For this reason, the development of chemical processes using lasers have focussed over the last ten years on the production of very high value and high volume products such as the separation of isotopes for the nuclear industry. For example, uranium nuclear fuel enriched from 0.7% ²³⁵U to 3% ²³⁵U has a value of approximately \$1,000/kg (~\$250/mole)⁶, and annual sales between \$1 and \$10 billion per year. The CANDU reactor does not use enriched uranium but instead uses water enriched from 0.0148% deuterium to 99.91% deuterium as neutron moderator and coolant. The heavy water is valued at about \$300/kg of D₂O or about \$1500/kg of deuterium.

Canadian heavy water production capacity is about 1.2 million kg/a. Uranium enrichment costs represent 5 to 10% of the cost of producing power from light water reactors. Deuterium enrichment costs represent nearly 20% of the capital cost of CANDU nuclear reactors or about 10% of the cost of producing power from heavy water reactors. Considerable research^{8,11}, particularly in the case of uranium, has gone into the development of laser based processes as a lower cost alternative to conventional isotope separation techniques.

3.0 LASER ISOTOPE SEPARATION - HOW DOES IT WORK?

In a laser isotope separation process light is used to convert a separation which is very diffi-

sult or even impossible by conventional chemical engineering techniques into one that is readily handled by conventional separation technology. Many of the laser isotope separation processes being studied involve the use of a laser to selectively break up or dissociate molecules containing the desired isotope while leaving molecules containing the other isotope untouched.

Molecules vibrate with one or more characteristic frequencies. They absorb light at these frequencies and transmit light of other frequencies. An infrared absorption spectrum is a record of the characteristic vibrational frequencies of a molecule. If a laser is tuned to one of these frequencies, the laser energy will be absorbed. If the laser energy is intense, the molecule will absorb enough energy to dissociate into fragments that have physical and chemical properties that differ greatly from those of the original molecule.

Just as placing a lump of putty on one prong of a tuning fork lowers the characteristic vibrational frequency of the tuning fork, substituting one atom of a molecule with a heavier isotope changes the characteristic vibrational frequencies of the molecule. A small portion of the absorption spectra¹⁰ of CF_3H and CF_3D , illustrates this isotopic shift (Figure 1). In principle a laser can be selectively tuned to preferentially dissociate molecules containing the low abundance isotope. Unlike conventional separation processes where energy is expended equally on all molecules, a laser isotope separation process expends laser energy preferentially on the minor component in the mixture. Because of this, expensive laser radiation can be considered for chemical processing.

4.0 EXAMPLES OF ISOTOPE SEPARATION PROCESSES

4.1 Deuterium Separation

Research at Lawrence Livermore Laboratories¹⁰ and Allied Chemical¹¹ in the United States, and at Atomic Energy of Canada Limited¹² and Ontario Hydro³ in Canada has contributed to the development of laser deuterium separation processes. The most attractive separation process is based on the dissociation of trifluoromethane (CF_3H) with carbon dioxide laser radiation.

The reaction $CF_3D + nh\nu \rightarrow CF_2 + DF$ has been shown to be at least 10 000 times more probable than the reaction $CF_3H + nh\nu \rightarrow HF + CF_2$ when the carbon dioxide laser is tuned to a wavelength in the 10.2 μm to 10.3 μm region. About 30 laser photons are required for each dissociation. The CF_2 radicals combine to form tetrafluoroethylene, a valuable chemical byproduct. In a single step a stream of CF_3H molecules containing 0.019% CF_3D can be converted to a stream of CF_3H molecules containing about 0.0019% CF_3D mixed with a stream of HF molecules containing approximately 50% DF. Simply by exposing the trifluoromethane stream to intense infrared radiation, an extremely difficult separation of two nearly identical molecules (CF_3H and CF_3D have boiling points differing by only a few tenths of a degree) is converted to the much simpler separation of highly polar molecules (HF or DF) from a trifluoromethane stream with an almost 100°C lower boiling point. It has been shown at

Ontario Hydro Research that better than 90% of the HF/DF mixture can be extracted from the trifluoromethane by flowing the stream over a bed of sodium fluoride pellets. The trifluoromethane is unaffected. Note that this process applies laser energy selectively to the desired isotope by proper tuning of the laser. This is the key to making high cost laser light competitive with low cost process heat.

Figure 2 illustrates some of the other key details of the process. The supply of trifluoromethane is far too small to provide the large quantities of deuterium required for a single CANDU nuclear reactor. (Approximately 5×10^7 kg of heavy water are required.) The deuterium content of the trifluoromethane must be replenished by deuterium exchange with an abundant deuterium source, water. $CF_3H + H_2O \rightarrow CF_3D + H_2O$. This can be done in a counter-current flow exchange tower using sodium hydroxide as a catalyst. The exchange can take place at moderate temperatures (70°C) if a rate enhancing solvent (dimethyl sulfoxide) is added to the exchange liquid or at higher temperatures (130°C) without the solvent¹⁴. In order to avoid separating the components of the exchange liquid loop, the deuterium content of this stream can be replenished by passing water vapour counter-current to this liquid stream in another multiplate counter-current flow contacting tower.

This process is in a relatively early stage of development. The steps in Figure 2 have been demonstrated on a laboratory scale only.

4.2 Comparison With Conventional Deuterium Separation Technology

Deuterium is currently separated from lake water in a process involving deuterium exchange between hydrogen sulphide and water. Advantage is taken of the fact that the distribution of deuterium between hydrogen sulphide and water varies with temperature. Hundreds of separation stages are required in large (90 m high by 9 m in diameter) counter-current flow exchange towers which contain 20 atmospheres of toxic, corrosive hydrogen sulphide gas. The laser process uses a non-toxic, non-corrosive process gas and strips four times more deuterium from lake water than the hydrogen sulphide process does and enriches it in a single separation stage. Cost estimates based on computer modelling and bench scale experiments predict that heavy water could be made for as low as half the cost of heavy water from an as-yet unbuilt hydrogen sulphide plant. However, costs of three or four times this low level cannot be ruled out because of many uncertainties involved in scaling up this process. Larger cost reductions are not thought possible because a substantial fraction of the total process cost must be used to transfer deuterium to the process gas using conventional technology. It will be difficult to achieve large cost breakthroughs via laser isotope separation for isotopes valued at substantially below \$1,000/kg, especially when process gas recycle is required.

Development of new deuterium separation technology has slowed considerably due to the recent drop in electrical load growth throughout Canada

which has resulted in large projected heavy water surpluses for the remainder of this century.

4.3 Uranium Enrichment

By far the most advanced and most successful laser isotope separation process is the uranium enrichment process being developed for the US Department of Energy at the Lawrence Livermore National Laboratory. This process is now undergoing large scale engineering development. The frequencies at which atomic uranium absorbs light are shifted many times the laser line width when ^{235}U is substituted for ^{238}U . ^{235}U atoms can be selectively ionized by the absorption of three photons from copper vapour laser pumped dye lasers. Other lasers are also being considered for this process⁹. Isotopic selectivity greater than 10% is possible. A schematic representation of this process is given in Figure 3.

4.4 Comparison of Uranium Laser Isotope Separation With Other Uranium Enrichment Processes

Although details of the US government uranium enrichment programs are classified, some information has been released¹³ which indicates that a substantial cost breakthrough is predicted using laser technology.

Table I

Comparison of Uranium Enrichment Costs

Process	Relative Capital Costs	Relative Energy Requirements	Operating Costs
Gaseous Diffusion (Conventional Technology)	high (=1.0)	high (=1.0)	low
Gas Centrifuge (Developmental Technology)	high (~1.33)	low (~0.042)	moderate
Laser Isotope Separation (Developmental Technology)	low (~0.10)	low (~0.042)	low

The two new processes (gas centrifuge and laser isotope separation) are expected to substantially lower the energy requirements of uranium enrichment. The laser based process also offers the prospect of substantially reduced capital costs as well.

Even though there is surplus uranium enrichment capacity available today, development of advanced uranium enrichment technology is proceeding rapidly because of the potential for very large cost reductions with these new processes.

5.0 OTHER ISOTOPES

Several other isotope separation processes are being studied. Many of these have applications within the nuclear power industry.

5.1 Zirconium

Nuclear reactors use zirconium alloys for internal reactor parts (fuel cladding in light water reactors and fuel cladding, pressure tubes and calandria tubes in heavy water reactors). Removal of ^{91}Zr from the alloy substantially reduces the neutron absorption of the alloy and leads to increased power production per kilogram of uranium fuel⁴. Unpublished calculations from Atomic Energy of Canada Limited indicate that in CANDU reactors this laser processed alloy is worth up to an additional \$2,000/kg. A Waterloo University Research group is developing an infrared laser process based on the selective dissociation of zirconium bearing molecules. The key to the development of this process will be the synthesis of a suitable volatile zirconium compound. Use of the relatively efficient and low cost carbon dioxide laser is desirable but not essential. Preliminary studies are also underway at Atomic Energy of Canada Ltd on a similar process. No conventional process exists for zirconium isotope separation.

5.2 Tritium

The tritium separation processes that are being studied closely resemble the deuterium separation process described earlier. Separation of trace quantities of tritium from large amounts of hydrogen is required to treat the waste streams of nuclear fuel reprocessing plants and future nuclear fusion plants. Highly selective dissociation of CF_3T in the presence of CF_3H has been demonstrated¹⁵. T/H separations with other fluorocarbons ($\text{C}_2\text{F}_5\text{T}$ and CF_3CFClT) are also being studied^{10,17}.

Nuclear reactors that use heavy water moderator accumulate inventories of tritium. In order to reduce the radiological hazard of chronic and accidental leaks, processes are required that separate T from D. A laser process has been developed at Lawrence Livermore National Laboratories based on the selective laser dissociation of chloroform, CCl_3T , which shows some promise of being superior to conventional cryogenic distillation technology¹⁸. The recovered tritium has a value of \$10,000,000/kg. It is used as a fuel in fusion research and to illuminate watch faces and airport signs.

5.3 Carbon 14

Heavy water reactors produce substantial quantities of ^{14}C as a waste product. Carbon 14 enrichment by selective dissociation of formaldehyde, $^{14}\text{CH}_2\text{O}$, has been demonstrated at Ontario Hydro Research¹⁹. Recovered carbon 14 has a value of greater than \$10,000,000/kg. It is used as a tracer in medical and biological research.

5.4 Carbon 13

A Russian process based on selective dissociation of CF_3I has been reported²⁰. Considerable cost reduction compared to the conventional method of producing carbon 13 by cryogenic distillation of carbon monoxide has been claimed but no laser produced carbon 13 has reached North America as yet.

Development of an alternative process using a lower cost feed material is being studied at the National Research Council of Canada²¹.

5.5 Plutonium

The plutonium recovered from spent commercial reactor fuel can be reused as nuclear reactor fuel. However the ratio of plutonium isotopes present is not well suited for military uses of plutonium. A classified US government program to separate plutonium isotopes using lasers is underway²². No details of this process are available. However, a production facility is expected to be operational by the late 1980's⁶.

5.6 Lithium

A Japanese research group has demonstrated the separation of ⁶Li and ⁷Li using a laser photoionization technique similar to that described previously for uranium²³. ⁶Li absorbs thermal neutrons to form tritium, an important fusion reactor fuel. Fission reactors use ⁷Li (>99%) as a pH adjuster for preventing hydrogen embrittlement.

5.7 Isotopes for Medical Research and Treatment

It may be possible to produce small quantities of many isotopes which have high value as medical diagnostics and relatively small demand (<1 kg) on a small scale using low cost lasers. Several radioisotopes (eg, thallium-203 and zinc-68) currently separated by high cost calutrons (electromagnetic separators) at Oak Ridge are candidates for laser isotope separation process development²⁴.

5.8 Other Isotopes

The isotopes of oxygen, nitrogen, and sulfur are examples of stable isotopes required in small quantities for research purposes. Laser isotope separation may lead to reduced costs for some of these isotopes.

CONCLUSIONS

1. Laser radiation can be used to promote separations that are extremely difficult by conventional technology. It is particularly applicable to isotope separation where the product produced has a very high value (ie, >\$1,000/kg).
2. The first large scale industrial use of lasers for isotope separation is expected to be the uranium enrichment process developed at Lawrence Livermore National Laboratory. This process is planned to be operational in the 1990's.
3. An attractive research area for the 1980's will be the development of processes to separate small quantities (<1 kg) of high cost isotopes with lasers. These processes will in most cases not require any improvements or scale-up of existing laser technology.

4. Over the next 10 years we can look for improvements in laser reliability and efficiency and reductions in capital and operating costs, spurred on in part by very large US government research programs in isotope separation and in other laser applications and in part by the rapidly expanding industrial use of lasers. By the mid-1990's, lasers are expected to become an accepted tool for some special classes of chemical processing.

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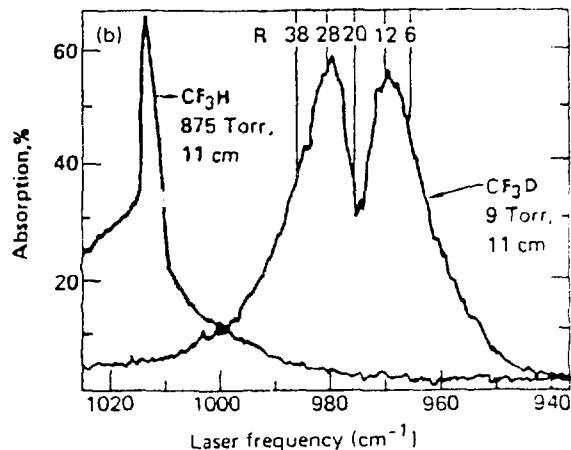


Figure 1

Infrared Absorption Spectra of CF₃H and CF₃D

The large isotopic shift associated with substitution of a D atom for a H atom is shown. Note that the spectrum of CF₃H has been amplified by 100 times by recording it at a much higher pressure. The positions of some carbon dioxide laser lines are also indicated.

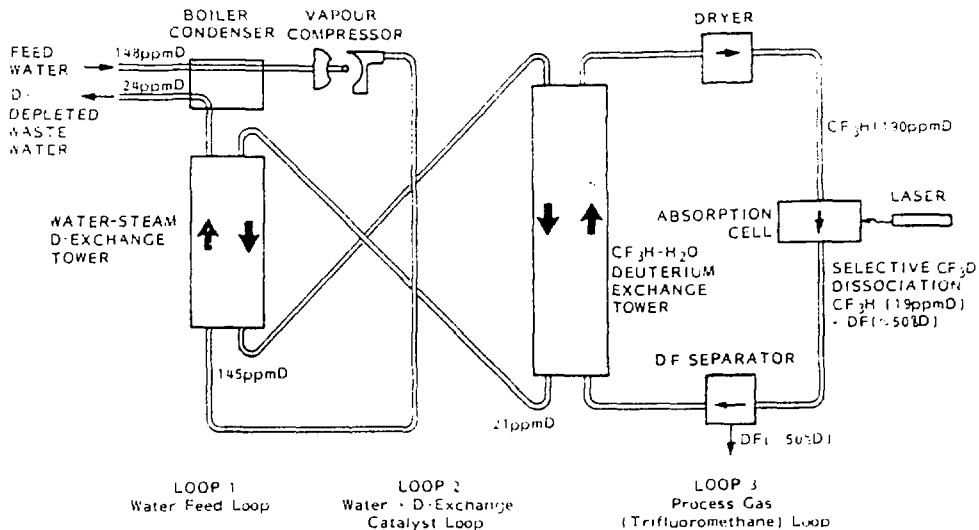


Figure 2

Trifluoromethane Laser Heavy Water Process

The three loops in the trifluoromethane laser deuterium separation process. In loop 3, the CF₃D molecules are selectively dissociated to DF and CF₂. The DF is recovered by selective absorption on sodium fluoride pellets and then chemically converted to water and distilled to 99.9% reactor grade heavy water. Loops 1 and 2 are required to replenish the deuterium content of the trifluoromethane by deuterium exchange with water.

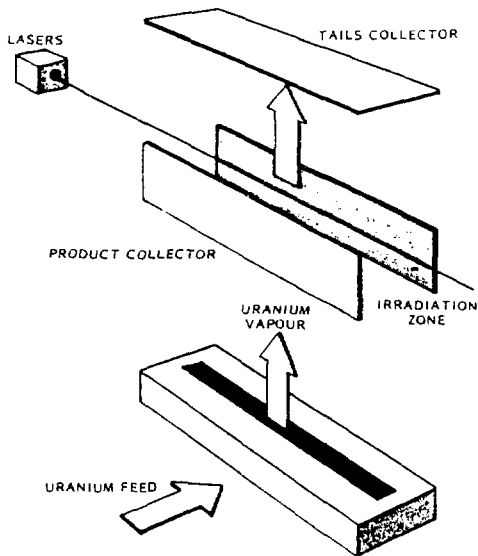


Figure 3

Livermore Uranium Enrichment Process

A beam of uranium vapour intersects a laser beam which selectively photoionizes the ²³⁵U component. An electromagnetic field collect the ions at the product collector while the unionized ²³⁸U atoms pass through the field unaffected and freeze out on the tails collector.