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GOVERNMENT OF INDIA

परमाणु ऊर्जा आयोग

ATOMIC ENERGY COMMISSION

LASER SEPARATION OF ISOTOPES OF HYDROGEN

by

S. M. Dave, S K. Ghosh and H. K. Sadhukhan

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भाभा परमाणु अनुसंधान केन्द्र

BHABHA ATOMIC RESEARCH CENTRE

बंबई, भारत

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LASER SEPARATION OF ISOTOPES OF HYDROGEN

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INTRODUCTION

Since the discovery of isotopes and their increasing importance in research, medicine and nuclear power generation, the separation of isotopes has remained a very active field of investigation. Of special importance in the nuclear technology are the isotopes of uranium and hydrogen, viz. ^{235}U and ^2D . Both these isotopes are present in small quantities ($\sim 0.7\%$ for ^{235}U and 0.015% for ^2D) in their natural sources. Isotopes due to their similar chemical properties cannot be separated by using usual chemical methods. However, for light elements like hydrogen, repeated chemical extraction is possible and this leads to desired enrichment; the chemical extraction, which is also known as chemical exchange, takes advantage of the small zero point energy difference between the isotopic molecules. Another method, which is more generally employed is the electrolysis, where the slight difference in overvoltage is utilized in selective discharge on the electrodes for achieving separation. For heavier isotopes, physical methods are generally more suitable. These methods utilize the small difference in mass of the isotopic substances.

Hundreds of methods for separation of different isotopes have been proposed and quite a few of them have been successfully tried in laboratory as well as on the large scale.

The more prominent among these methods are: gaseous diffusion, centrifuge, thermal diffusion, multiple distillation, electromagnetic and chemical exchange. But all these methods are highly capital as well as energy intensive and the cost of the production of isotopes still continues to remain rather high.

Recently, the invention of lasers have provided a very powerful and promising method of isotope separation. This method has some flexibility and provides many advantages over the existing processes.

The separation of isotopes by laser differs significantly from the other conventional methods of isotope separation. Laser can distinguish between atoms of different isotopes or between compounds containing different isotopes not on the basis of mass but through subtle differences in their electronic structure. These differences, even though they are small, affect the wavelengths of radiation absorbed by a substance; each isotope absorbs a radiation of a particular, definite wavelength. Because laser is very pure and monochromatic, it is possible to excite the desired isotope in presence of other isotopes. The separation of the excited isotope then can be easily carried out. This method thus, fulfils the long cherished dream of an isotope producer to selectively extract only the desired isotope from the mixture in a given compound.

Many excellent reviews on the Laser Isotope Separation Process have been published. The purpose of the present article is to outline

this laser isotope separation technique and discuss in details and carry out an exhaustive survey of the various applications of this relatively new process for the production of heavy water.

2. LASER ISOTOPE SEPARATION

The laser method utilizes the small difference in the spectroscopic properties of the isotopic substances. The electronic, vibrational and rotational energy levels are slightly changed due to isotopic substitution. This is called the isotope shift. The nuclear mass difference of the isotopic molecules causes difference in the reduced mass and thus modifies the electronic energy levels. This is very prominent for isotopes of light elements, such as hydrogen and deuterium. For heavier elements, hyperfine interactions and contribution from non-zero volume of the nucleus are more prominent.

The laser separation of isotope is based on the selective excitation of the desired isotopic component by laser, followed by the physical removal of the excited isotopes based on some aspect of interaction between selectively excited atoms or molecules by physical or chemical means. If a mixture of isotopic molecules (or atoms) is irradiated with a light whose frequency exactly corresponds to the excitation energy of the species of a particular isotopic composition, only those particular isotopic species will be selectively excited. For successful selective photoexcitation, the following conditions must be satisfied:

(1) The two isotopic molecules should have the spectral lines of

interest sufficiently separated; in other words, the overlapping should be minimum.

- (2) Since the isotope shift, in general, is very small, the radiation used should be highly nonachromatic.
- (3) The intensity of the radiation should be very high, otherwise the process would be too slow to be of any practical importance.

Laser light which operates by exploiting the quantum - mechanical transition between the energy levels of atoms and molecules, is most suitable for selective excitation because it is highly monochromatic and it can produce light of very high intensity. The availability of tunable lasers also makes it possible to adjust the frequency of light to that required for selective excitation of a particular isotopic species.

Due to selective excitation, one type of isotopes in a given compound are in an excited state while the others are in the ground state. Some of the physical and chemical properties of the molecules (or atoms) are changed due to excitation. The difference in the characteristics of the excited and unexcited species can be conveniently used to effect their separation. The different types of laser isotope separation processes mainly differ in the method employed for separation of the excited species from the unexcited ones. The difference in the physical and chemical properties of the excited and unexcited species can be exploited for this purpose,

It is essential that a suitable photo physical or photochemical method must be found for the removal of the excited species. Before discussing the various isotope separation schemes, let us discuss the efficiency of various methods.

2.1. Separation Selectivity

The quantitative comparison of efficiency of different laser induced separation processes can be carried out by calculating their separation selectivity. Two types of selectivity are defined - optical selectivity and separation selectivity.

2.1.1. Optical Selectivity : The optical selectivity which is sometimes known as excitation selectivity can be defined as⁽⁷⁾

$$S_D = \frac{\sigma(A)}{\sum \sigma'(A')} \quad \dots(1)$$

where $\sigma(A)$ is the absorption cross section for the isotope A for the separation process. Similarly, $\sigma'(A')$ refer to the cross section for the isotopic species A' for absorption and scattering at the laser wavelength. In the isotopic pair A-A', A is the isotope of interest.

The maximum optical selectivity, S_D , obtainable with a process depends on the separation between the absorption lines in the species containing heavier and lighter isotopes as well as on the pressure-broadened line width.

2.1.2. Overall Process Selectivity: Another quantity of interest is the overall process selectivity or separation

selectivity, S , which is defined by the relation⁽⁴⁾

$$S = \frac{R_f (A/A^1)}{R_0 (A/A^1)} \quad \dots(2)$$

where $R_f (A/A^1)$ and $R_0(A/A^1)$ denote the final and initial isotopic ratio, i.e. the ratio of the mole fractions of the two isotopic substances before and after the separation. The various factors which are responsible for the loss of the separation selectivity are given below^(4,5).

- (1) Thermal Nonselective Excitation - The thermal excitation that usually takes place at any temperature is completely nonselective. Hence the laser excitation energy should be significantly higher than the thermal energy, kT . The experiments at low temperature helps in satisfying this condition.
- (2) Resonant Excitation Transfer - The selectively excited isotopes may transfer its energy to the other species due to collision.
- (3) Scrambling Processes - Separation selectivity may be reduced by scrambling processes which are the secondary processes that come into play after the primary separation step of the chemical reaction, dissociation, ionization etc.

3. DIFFERENT LASER SEPARATION METHODS

A common feature of all the laser isotope separation methods lies in the selective excitation of the desired isotopic component by laser irradiation of sufficient monochromaticity and intensity, followed by physical removal of the excited

isotope based on some aspect of interaction between selectively excited atoms and molecules by physical or chemical means. The various proposals for laser isotope separation differ mainly in the method employed to extract the selected atom or molecule after excitation by laser.

The various separation methods which differ mainly in the manner of extraction of the excited atoms or molecules, can be broadly classified into two categories, viz., photophysical and photochemical methods depending on whether the change in the property of atoms and molecules caused by excitation which is used for the extraction of the excited species is physical or chemical in nature. They can also be classified further as an atomic scheme or molecular scheme depending on whether the matter in atomic or molecular states is used.

3.1. Experimental Technique

The experimental scheme is fairly straightforward and simple. It consists of an atomic beam which consists of a stream of atoms moving in the same direction and having a narrow range of speed. This atomic beam is usually produced by evaporating desired substance in an oven inside an evacuated chamber. The collimation of the beam is obtained by passing it through a series of orifices. This has a disadvantage - that it reduces the intensity of the beam. The vacuum helps in minimizing, random collisions and hence the beam travels in a straight line. This atomic beam is exposed to properly attenuated laser

of desired wavelength. The excited species can be isolated by using the following techniques:

- (i) Deflection of the Excited Species
- (ii) Radiation Pressure of the Repeated Photon Absorption
- (iii) Selective Multistep Photoionization
- (iv) Multiple photon Absorption
- (v) Predissociation of Molecules
- (vi) Chemical Scavenging

These techniques will be described in detail in the subsequent section. A schematic diagram for this laser method is given in Fig.1.

The laser method can be applied to atomic or molecular systems. In case of atoms, the difference in the electronic energy levels are made use of for the selective excitation of a particular isotope. In case of molecules, the electronic spectra get complicated due to vibrational and rotational spectra while the vibrational spectra become complicated due to rotational spectra. Thus the isotopic shift is masked and the selective laser action is hindered. However, strong cooling of molecular gas improves this situation considerably.

Selectivity of laser is preserved best when a beam of noninteracting atoms or molecules is irradiated. However, low density of the beam leads to the low yield. In actual practice, a compromise between the requirements of a high separation

coefficient and a high yield is essential and is usually achieved.

With this background now let us discuss briefly the principles involved in the above mentioned extraction methods.

- (i) Deflection of the Excited Species: This method is based on the difference in electric and magnetic properties of the excited atoms as compared to those in the ground state. The atomic beam is irradiated with laser and then subjected to non-homogeneous electric or magnetic field, when the excited atoms are collected in a suitable collector. If however the excited species are short lived, long lived excited species can be formed by illuminating with a second laser.
- (ii) Radiation Pressure of Repeated Photon Absorption: Radiation pressure of repeated photon absorption can also be employed to deflect excited isotopic species. The laser beam is focussed perpendicular to the direction of the atomic beam. The atoms of the desired isotope are excited by photons. These excited atoms decay quickly by fluorescence, again absorbs photon and the process is repeated. Many photons can be absorbed during the passage through the laser beam. At each stage, the atoms acquire a small but definite increment in momentum in the direction of the laser light and thus form a beam separate from the unexcited ones. Finally, they can be collected into a collector.

(iii) Selective Multi-step Photo-ionization: This is a photophysical method and is usually performed at an atomic level. This consists of two processes; (a) isotopically selective excitation and (b) ionization of the excited species.

The selective ionization can be made with a finely-tuned laser, whereas the ionization of the excited atoms can be effected by another more precise laser or by some other source of energy. The overall process may be a twostep or multistep process.

The atoms lying only in the metastable state (lying slightly above the ground state) are susceptible to laser excitation. The second laser can ionize this excited atoms. The ionized atoms can be more easily deflected and collected by using appropriate electric or magnetic fields.

(iv) Multiphoton Absorption: This is a selective twostep photo-dissociation process⁽⁸⁾. Molecules which have an unstable excited electronic state with energy less than 8 to 5 eV can be used for twostep photo-dissociation by a combined action of IR and UV laser. The first photon, usually IR, induces transition between vibrational stages and causes selective vibrational excitation (either onestep or multistep depending on the molecule). The second photon, UV or visible causes transition to the unstable excited electronic state leading to dissociation.

In an alternate procedure, a molecule may absorb many IR photons in rapid succession, increasing its vibrational energy till the bond breaks. Only the initial IR transitions are isotopically selective. This method is especially suited for large molecules made up of several atoms.

- (v) Selective Predissociation of Molecules: This method requires a molecular excited state that exhibits a resolvable isotope shift, when irradiated by a laser. The excited molecule should decay spontaneously and primarily by dissociation and the dissociation products should be stable and should not undergo chemical side reactions. The stability of the dissociation products is an important criterion, because otherwise they will react again. This is usually a very difficult condition to achieve, as the free radicals and fragments are normally highly reactive. (In predissociation, a molecule dissociates at an energy much below the threshold of the dissociation energy).
- (vi) Chemical Scavenging: The fact that the excited state of a molecule is more reactive than its ground state may be exploited for the separation of the desired isotopes. A scavenger is mixed with the substance before excitation with laser. This scavenger does not react with the substance when it is in ground state. In excited state, it reacts with the scavenger molecule leading to its separation. In practice,

it is often difficult to find a suitable chemical scavenger and hence the use of scavenger technique is rather limited.

The most outstanding feature of the application of the vibrational photochemistry to isotope separation is the utilization of the lower energy IR photons from an efficient molecular laser to achieve a reasonable separation of the desired isotope. Since 1 mole of photons at 3000 cm^{-1} is equivalent to 10^{-2} KWh and some of the available IR lasers are about 10% efficient, processing of bulk chemicals for the purpose of isotope separation could prove to be economic (41)

There are, however, many problems to be solved. These are: thermal reaction rates, vibrational energy transfer, surface catalysed reactions and so on. The methods which rely on V-V transfer to enhance the excitation of heavy isotopes appear quite promising for systems with anharmonicities and isotopic shifts larger than kT at temperatures where vapor pressures are sufficient. While for lighter isotopes, methods, based on selective photodissociation, selective photopredissociation and chemical scavengers should yield encouraging results.

4. DEUTERIUM SEPARATION BY LASER METHODS

Heavy Water is used as a moderator and coolant in the CANDU reactors where natural uranium is used as fuel. The low natural abundance (0.015%) and large overall concentration

of D_2O (99.8%) make heavy water production both capital and energy intensive proposition. Laser separation of deuterium is receiving increasing attention from different establishments in Canada, U.S.A. and Israel. The general goal is to produce heavy water at a much cheaper rate and/or to stretch the supply of uranium.

Any hydrogen-bearing molecule is a source of deuterium and hence in principle deuterium separation with laser can be attempted by using any convenient compound of hydrogen. The method of radiation pressure has not been found suitable for deuterium separation, although it can be profitably utilized for tritium separation⁽¹⁰⁾. As stated earlier, for deuterium separation the following three methods have been found to be acceptable:

- (i) Selective twostep photodissociation,
- (ii) Onestep Selective Photopredissociation, and
- (iii) Chemical Scavenging ,

Some of the methods of laser separation of hydrogen isotopes have been investigated and reviewed by several authors, e.g., Miller⁽¹¹⁾, Andridge et.al⁽¹²⁾, Marling et.al.⁽¹³⁾ and Vanderleeden⁽⁷⁾. A detailed spectroscopic and photochemical evaluation for more than one hundred organic compounds in the continuing search for the most suitable working material for deuterium separation has been reviewed by F.T. Aldrige, I.P. Herman, J.B. Marling and L.L. Wood⁽¹²⁾.

4.1. Requirements of the Process

Any laser isotope separation scheme to be acceptable for heavy water production should meet the following requirements:

(1) The large scale production of heavy water is possible only if virtually inexhaustible hydrogenous feed streams e.g. water, methane and syngas are available. Hence, the working material from which deuterium is to be extracted by laser irradiation, should be capable of being easily redeuterated by exchange with H_2O , methane or syngas, the available abundant sources of hydrogen.

(2) The low natural abundance of deuterium (~ 150 ppm) requires a 1000-to-1 or greater D/H optical selectivity to be achieved in multiphoton absorption for acceptable photon utilization. This rather stringent condition restricts the use of multiple photon absorption method for the separation of deuterium.

(3) The deuterium-bearing dissociation products, either obtained directly by exposure to laser or after scavenging, must be stable and should not lose their deuterium by exchange with the remaining protonated hydrogen molecules, or with walls of the container or with moisture.

(4) At present, only CO laser and $^{12}C^{16}O_2$ lasers satisfy the optical requirements of $\geq 10\%$ overall electrical efficiency and ≥ 100 KW average power capability in the high peak power pulsed mode. Several kilowatts average laser power

is required per ton/year D₂O production. The molecules therefore, should be selected in such a way that acceptable photon utilization accessible by efficient high power in lasers is achieved. For this, the multiphoton bands should occur at 4.9-5.5 μ capable of excitation by a CO laser or at 9.2 - 10.8 μ capable of excitation by a ¹²C ¹⁶O₂ laser.

(5) The working molecule should be relatively inexpensive and should have low toxicity, reasonable chemical stability and sufficient volatility for gas phase operation.

(6) Considerable simplification results if the photoproducts are such that they can be easily separated from the feed-stream by simple physical means.

(7) For large scale production, it is desirable to employ higher reactant pressures (from about 100 torr to one atmosphere), This scaling-up of the pressure must be consistent with isotopically selective absorption as well as highly selective dissociation and/or reaction.

4.2. Economics of Deuterium Separation by lasers.

Since heavy water is a relatively more cheaper commodity than U²³⁵, the economic viability of the laser method of heavy water has to be established beyond any doubt, if the method is to be employed for large scale production of heavy water. At present either UV or IR lasers are available

which fulfil our requirements. The important characteristics⁽⁷⁾ of a laser process for deuterium separation with UV and IR photons are:

- (a) the laser photon energy ϵ (in electron volts),
- (b) Overall laser efficiency η , and
- (c) the Process's photon utilization, Q , which denotes number of deuterium atoms separated per photon put out by the laser.

The electrical energy input and the laser capital cost vary as a function of $\epsilon/\eta Q$, while $1/Q$ is a process-independent quantity. Because of this reason, it is possible to trade off the laser related ratio ϵ/η against the process-independent quantity $1/Q$. Based on this ratio, ϵ/η , it is possible to divide laser separation processes into the following two classes:

- (1) those with large ϵ/η and large Q e.g. ultraviolet photo predissociation reactions, and
- (2) those with small ϵ/η and small Q , e.g. infrared photocatalysis reactions.

Typical parameters like energy consumption, capital cost etc. for the two types of laser processes for deuterium separation are given in Table 1.

The laser power cost, or the energy required to separate the deuterium in one Kg of D₂O will be given by

$$C_{\text{elec}} = \$ 2.67 \times 10^{-2} (\epsilon/\eta) Q, \quad \dots(3)$$

where the electricity costs have been assumed to be 1 cent

per kilowatt hour. For both the methods, this leads to

$$C_{elec} \sim \$ 20 / \text{Kg } D_2O.$$

The average optical power needed to separate one kilogram of D_2O per year is given by

$$P \approx 0.303 \text{ } \epsilon / Q \text{ Watts/kg per year} \quad \dots(4)$$

corresponding to $P \sim 3$ to 10 watts per kilogram per year for the cases in Table 1. The minimum size of an optimum plant would be about 100 tons per year, so that the average laser output would be 300 Kilowatts to one megawatt. The larger systems must, therefore, cost no more than \$ 3.00 per watt of electrical input. At that price, the laser capital cost to produce one kilogram of D_2O per year is

$$C_{laser} = 0.918 \text{ } \epsilon / \eta \text{ } Q \text{ dollars/kg per year}$$

or about \$ 600/Kg per year for the cases in Table 1. Depending on the depreciation and interest rates, this would correspond to about \$ 70 per kilogram of heavy water produced. This should be compared with the current canadian price of \$ 130/Kg for heavy water produced by the GS process, of which 60 per cent is due to capital charges 25 percent due to energy and 15 per cent for operations and maintenance⁽¹⁰⁾.

Thus there is ample ground for optimism for the laser separation of heavy water. However considerable breakthrough in achieving better laser efficiency and photon utilization

has to be obtained and it is quite possible that the efforts in this direction will be successful.

5. LASER METHODS OF DEUTERIUM SEPARATION

In recent years, many compounds have been tried for laser irradiation and some of them have been investigated rather extensively. Some of these investigations hold out good promise to culminate into a successful future heavy water production processes. The investigations carried out by different group of workers will be described in this section.

5.1. Photobromination of Methanol

The first successful application of continuous wave (CW) hydrogen fluoride laser to separate deuterium from hydrogen by specific photo-catalysis of reaction of methanol with bromine was reported by Meyer, Kook, Grose and Spencer⁽¹⁴⁾. The strong absorption of CH₃OH was demonstrated for HF laser lines, while no absorption by deuterio methanol of HF beam was observed. Excitation of CH₃OH by the absorbed laser beam increased its rate of removal by reaction with bromine. Irradiation at 90W for 60 sec with CW HF laser of a 1:1 mixture in the presence of bromine produced deuterium enrichment of more than 95% (i.e. D₃CO₂). The following reaction takes place^(15,16)

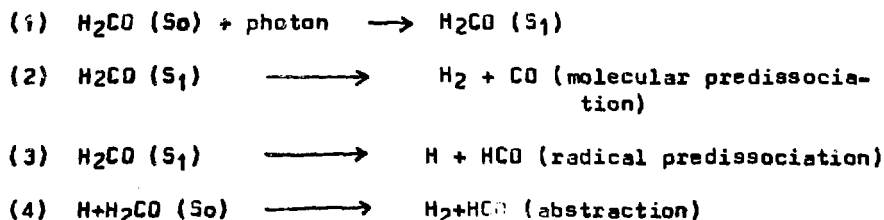


However, apart from historical significance of being the first process to establish that laser method can be used to

enrich deuterium, this method as such is not suitable for heavy water production, because, here, the hydrogenated methanol is excited and is extracted with the scavenger. This would lead to the processing of tremendous amount of feed material, thereby increasing very significantly, the cost of heavy water production. The better and more effective approach would be to pick out atoms or molecules containing deuterium and selectively excite them. In all the subsequent methods, this has been the case.

5.2. Photopredissociation of formaldehyde

The first successful deuterium enrichment resulting from the photopredissociation of formaldehyde was reported by Yeung and Moore⁽¹⁷⁾ in 1972. They used an equimolar mixture of H_2CO and D_2CO and irradiated it with frequency - doubled ruby laser light of wavelength 3472 Å with a spectral width of 3 cm^{-1} . The D_2CO molecules are excited and dissociated according to the following scheme:



Only the scheme (2) gives the desired product. The enrichment $\text{D}:\text{H} = 6:1$ in the product was observed by them. However by using narrower wavelengths this factor can be enhanced.

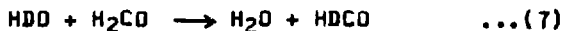
Different parameters for this process, such as the rate of formation of the products by photopredissociation, the selectivity, the efficiency of the process etc. have been discussed by Letokhov⁽¹⁸⁾. He has carried out mathematical analysis and has derived theoretical expressions for these quantities.

Marling⁽¹⁹⁾ reported experimental observations with H₂CO and D₂CO in their natural mixtures using CW He-cd Laser line at 325.03 μ m, giving rise to a selectivity coefficient, S of 14. Using Xe (III) ion laser, he has reported enrichment factor of 58⁽²⁰⁾.

Recently Mannik, Keyser and Woodall⁽²¹⁾ have reported highest enrichment factors upto 254 ± 30 , using tunable ultraviolet dye laser, starting from a 4 Torr sample of natural formaldehyde.

Although formaldehyde has been extensively studied^(17, 18, 19, 20, 21) the main drawback for its use as a potential process material is the problem of redeuteration of the depleted residue. Aldrige et.al.⁽¹²⁾ have suggested to replace formaldehyde by some other similar compound e.g. propargyl aldehyde where redeuteration can be easily achieved. Also, investigations are in progress to obtain a better method for redeuteration of formaldehyde. Recently, theoretical investigations on the exchange reaction of formaldehyde with hydrogen as well as water have been reported by Dave et.al^(22, 22) and the values of the equilibrium constants and

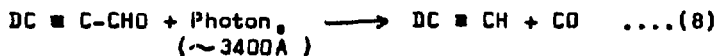
the separation factors are encouraging. Vanderleeden⁽⁷⁾ has also reported that the chemical exchange reaction



occurs rapidly in the presence of platinum catalysts at 125°C. However, further investigations are necessary to establish the feasibility of this process.

5.3. UV Laser Dissociation of Propynal

As stated in the earlier section, the formaldehyde has a distinct disadvantage in having unresolved difficulties in its redeuteration. Another promising compound belonging to the same class is propargyl aldehyde, HCCCHO and UV laser-induced predissociation of this material has been reported⁽²⁴⁾. The advantages of this method include: resolvable isotopic shifts, availability of efficient near UV lasers, probable molecular break up into stable molecules and simple aqueous phase redeuteration of the propynal feed stream. The process proceeds as follows:



Further experimental evaluation of propynal should be thoroughly investigated. Some of the studies of IR laser-based processes have, however, disclosed intractable difficulties to the practical implementation^(25,26).

5.4. Multiphoton Dissociation of 2,2, - dichloro- 1,1,1, - trifluoroethane (Freon 123).

Recently a highly promising working material for the laser separation of deuterium has been reported by Marting and Herman⁽²⁷⁾. The compound 2,2-dichloro-1,1,1-trifluoroethane, CF_3CHCl_2 or commonly known as Freon 123, was selected by them as the starting material for the laser separation of isotopes of hydrogen. The compound CF_3CDCl_2 undergoes isotopically selective absorption near 10.2 and 10.6 μm , which is accessible with the normal CO_2 laser. They have used commercial CO_2 TEA laser. The laser excited molecules undergo dissociation to give $\text{CF}_2 = \text{CFD}$ as the main product, which is a stable deuterium bearing compound.

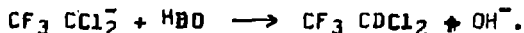
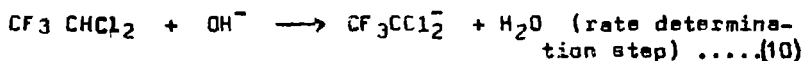
The selectivity or the enrichment factor for this process is given by

$$S = \frac{[\text{CF}_2 = \text{CFD}] / [\text{CF}_2 = \text{CFH}] \quad (\text{Photo product}) \dots (9)}{[\text{CF}_3\text{CDCl}_2] / [\text{CF}_3\text{CHCl}_2] \quad (\text{Starting Material})}$$

S has been observed to be as high as 1400. The probability for CF_3CDCl_2 dissociation into $\text{CF}_2 = \text{CFD}$ photoproduct occurs with a fluence threshold near 1.5 J/cm^2 and appears to saturate near 100% yield above 15 J/cm^2 .

The main advantage of this working material is that the depleted material can be redeuterated easily by chemical exchange with water in presence of NaOH as catalyst. The

liquid phase base-catalysed, H/D exchange occurs rapidly with water without hydrolysis to permit redeuteration of CF_3CHCl_2 working material by the following steps:



The aqueous H/D exchange rate is about $0.07 \text{ sec}^{-1}/\text{mole litre}$ at 20°C according to Hine, Wiesboeck and Ramsey⁽²⁸⁾. The deuterium separation factor for the above reaction at 20°C has been found to be 1.26.

Theoretical calculations of these separation factors as well as the investigation of the kinetics of the base-catalysed exchange reaction of Freon 123 with water are in progress in our laboratory.

The Freon 123 is commercially available in large quantities and it holds out a promise of being exploited by laser separation to yield heavy water.

The other investigations necessary for the adaptation of this process for heavy water manufacture are :

- (1) The recovery of deuterium from $\text{CF}_2 = \text{CFD}$
- (2) The possibility of reconvertng the residual compound after D extraction to original Freon 123, to make this process commercially more attractive.

5.4. Photodissociation of Polyvinyl Chloride

Recently Sydney Benson⁽²⁹⁾ has investigated the possibility of using dichloroethane, which is contained in polyvinyl chloride, as the working material for a laser process for producing heavy water at a much reduced cost.

This process involves tuning a laser beam to a suitable frequency at which it will be absorbed by deuterium bearing molecules in dichloroethane gas (contained in polyvinyl chloride). The laser beam decomposes the gas into hydrogen chloride and vinyl chloride. The vinyl chloride fraction contains the deuterium. The material is then heated and the product containing 25% heavy water is obtained.

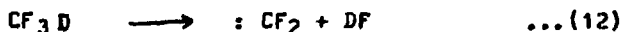
The starting feed material polyvinyl chloride is abundantly available and has all the advantages of a suitable starting material for the laser process.

Benson claims that his method is much simple, less expensive, and can be very well adapted to an existing chemical plant and by using this process, the cost of heavy water production may be reduced by a factor of 3 to 10 compared to GS process.

5.5. Selective Dissociation of Fluoroform-d.

Recently Tuccio and Hartford⁽³⁰⁾ have reported deuterium enrichment with a new starting material, Fluoroform-d. This

compound undergoes multiphoton dissociation when irradiated with a pulsed CO_2 laser tuned to $10.6 \mu\text{m}$ (971.9cm^{-1}) and dissociates to yield DF by unimolecular elimination. This dissociation scheme can be represented by



followed by



The DF generated upon CF_3D dissociation can be easily removed from the feed material stream by reaction with NaF. Heating of the resulting NaDF_2 would then yield the enriched DF. The comparison of DF and HF fluorescence intensities yield an upper bound of 19000 for the dissociation selectivity of CF_3D over CF_3H at a pressure of 1.3. The deuterium enrichment factor of greater than 5000 is obtained in the natural fluorocarbon form.

This method because of its very high enrichment factor may provide a basis for an improved deuterium enrichment scheme which can be scaled to commercial size.

However, the major problem which remains to be solved is the re-deuteration of the depleted fluorocarbon. The theoretical study of the thermodynamic as well as the kinetic aspects of the exchange of fluorocarbon with water is under active consideration in our laboratory. We have found⁽³¹⁾ that the separation factors for the exchange reaction



is of the order of 2.46 at 30°C . The entire temperature

dependence is reported by us⁽³¹⁾.

6. CONCLUSION

As stated earlier, since heavy water is a much cheaper commodity as compared to U^{235} and also so much investment has been made in other heavy water processes, such as GS and ammonia-hydrogen exchange processes, the prospects for the economic viability of producing heavy water by laser separation method appear much more uncertain. However, considerable efforts in different laboratories in U.S.A. and Canada are continuing and many schemes which we have discussed earlier have been proposed and some of them look really feasible and are undergoing testing on the pilot plant scale.

Eventhough formidable engineering problems remain to be solved⁽³²⁾, considerable investment in laser technology will be made by the end of the next decade and it is possible that significant progress would be made to overcome these problems.

With the cost of energy escalating at an unpredictably faster rate, a breakthrough in the heavy water technology is very badly needed which may lead to significantly lower capital cost and lower energy consumption. Let us hope that the laser separation method will provide such an alternative.

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Table 1. Typical Parameters for Economical Separation of Deuterium with Laser Method*

Parameter	Laser Process	
	UV Photopredissociation	IR Photocatalysis
Photon Energy	3.5	0.35
Laser Efficiency	0.02 (to be achieved)	0.05 (available)
Photon Utilization, Q	0.3 (within reach)	0.01 (to be achieved)
Laser output power (W/Kg D2O per year)	3.6	10.7
Laser Power cost (US \$/Kg D2O)	15	20
Laser Capital Cost (US \$/Kg D2O per year)	550 (to be achieved)	650 (within reach)

* J.C. Vanderleeden, Laser Focus Magazine, 51 (1977).

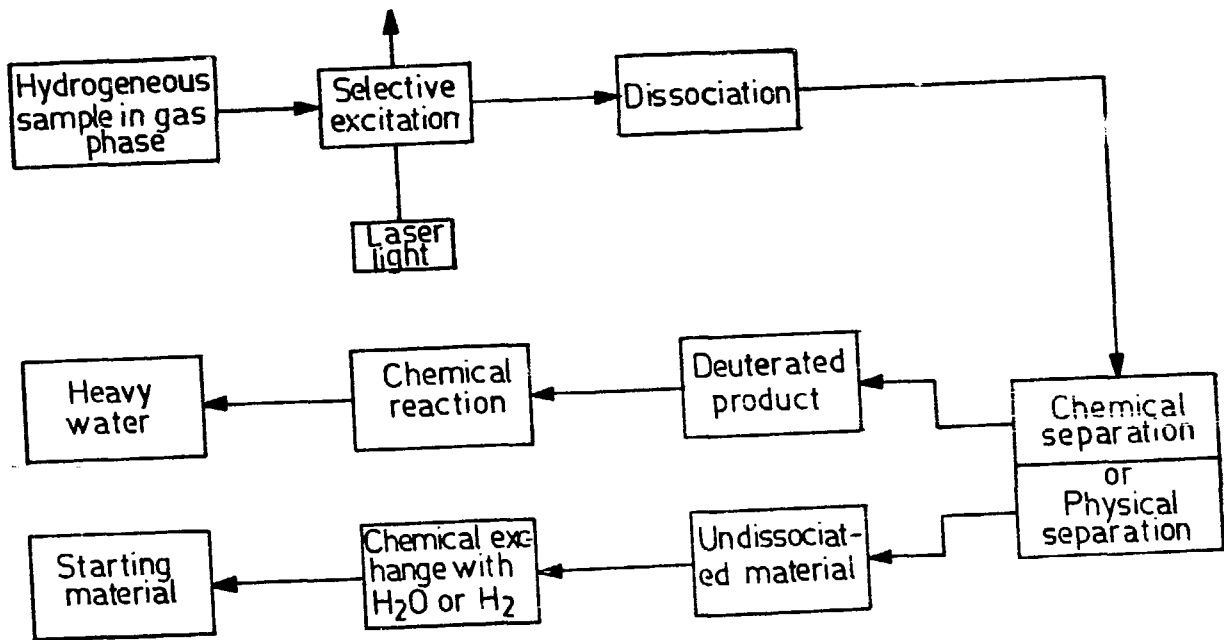


Fig.1. Schematic diagram for Heavy water production using selective photodissociation by laser.