THE PRODUCTION OF HEAVY WATER BY PHOTODESORPTION: *

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Abstract

Research from all over the globe has recently brought attention to the laser as a tool for isotope enrichment. So far the main thrust of this effort has been toward uranium enrichment; however, numerous successes in other areas have been demonstrated. Isotopes of boron, sulfur, chlorine, and carbon have been separated.

A new technique is proposed for laser isotope enrichment. The technique, referred to as photodesorption, involves selective isotopic excitation of molecules adsorbed on a surface such that an enrichment results from subsequent physical or chemical events undergone by the excited molecules. The specific processes of concern here are the physical photodesorption enrichment of heavy water from light water and tritiated water from heavy water. The ability to work directly with water molecules has significant advantages for a commercial process.

A photodesorption enrichment process has been formulated and some analyses have been performed. This process is described and some preliminary cost estimates are made which assume successful accomplishment of the major R&D objectives of the new process. The results indicate that the process has the promise of a significant reduction in the cost of heavy water and that further study is warranted.

Introduction

The application of photoexcitation to the separation of isotopes dates back to the early 1930's; (1,2) however, only recently have isotopic separations, based on laser-induced photochemical and photophysical excitation been demonstrated. The excitations are possible because the frequencies of the lines in the spectrum are generally unique for most isotopes. Successful separation has generally employed the isotopically specific absorption of narrow band radiation by one isotopic species in the vapor state. (1-7)

The energy crunch of recent years has spurred interest in all alternative energy-related technologies. In particular, the success of the CANDU reactor concept has stimulated a demand for a cheaper heavy water supply, since heavy water accounts for approximately one-fourth of CANDU's present capital cost. The possibility of a thermal breeder, based on a thorium heavy water concept, could serve as a backup for the LMFBR, even though such a breeder would have a lower breeding ratio. In addition, significant pharmaceutical and military markets could develop in the near future, which would add to the incentive for producing cheaper D_2O .

The Canadians, who at present lead the world in heavy water production, have had to limit the expansion of their CANDU industry because of a lag in heavy water enrichment. The English, using slightly enriched uranium, have recently developed an efficient reactor moderated with heavy water and cooled with light water. Indeed, if the cost of heavy water could be significantly reduced, its use throughout the world would certainly be more widespread.

One of the first photochemical attempts at separating hydrogen isotopes was that of Nayer et al. (3) They used a CW hydrogen fluoride laser to stimulate a H_2COH reaction with bromine gas while leaving some of the D_2COH unreacted. Yeung and Moore (4) separated deuterium from hydrogen by using selective laser photodissociation of formaldehyde. The present concept of achieving enrichment via molecular excitation on a surface has subtle advantages over gas phase processes. The basic concept of photodesorption has been successfully demonstrated for selective desorption of HD from H_2/HD mixtures. (5)

Concept

A new approach to isotope separation based on the ability of lasers to selectively deliver large numbers of photons to a molecule adsorbed on a solid surface is evaluated. Selective photodesorption of a given isotope from a transparent or reflective solid surface may be accomplished by exciting the isotope with the appropriate infrared wavelength. Recent results on selective photodesorption of HD and H_2 in a low-temperature Vycor glass system using a filtered quartz-halide lamp have shown that the concept not only works but yields extremely encouraging efficiencies. (5)

A major advantage of isotope photodesorption over gas-phase isotope enrichment techniques is the higher concentration of adsorbed molecules per unit volume attainable on solid surfaces. In the gas-phase approach the isotope partial pressure must be kept low to avoid energy transfer, which would spread the excitation energy over all the isotopes. That is, the number of isotope molecules per unit volume is limited by the mean

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free path for collision. However, much higher isotope densities can be tolerated on a solid surface since the translational motion of a molecule is restricted by its adsorption interactions with the solid matrix.

The photodesorption technique can be thought of as involving an equilibrium shift in the population of the water molecules between the vapor phase and adsorbed phase. The Gibbs phase rule⁽⁸⁾ provides a general relationship among the degrees of freedom of a system f , the number of phases p and the number of components c :

$$f = c - p + 2 \quad (1)$$

For HOD/H₂O vapor mixtures adsorbed on a surface under equilibrium conditions we have a two component, two phase system. Thus there are two degrees of freedom, that is the system is bivariant, and temperature and pressure can be independently varied. This tells us that for example at a given pressure we can shift the vapor/adsorbed state equilibrium of the HOD molecules by changing the temperature of the HOD molecules. Furthermore the extent of the equilibrium shift is limited only by the attainable temperature change.

As shown in Figure 1, the O-D bond of water has a unique series of vibrational absorption bands in the 3.70 to 3.50 micron region in the adsorbed state on silica glass^(9,10) and alumina which are very far from the corresponding bands for H₂O in the 2.78 to 2.63 micron region. To achieve the selective heating of the HOD molecule in a HOD/H₂O mixture a laser photon source would be used. The value of a laser source for photodesorption is not in its monochromaticity (since the O-D and O-H vibrational bands are well separated) but is in its superior photon output (wall plug efficiency) as compared to filtered polychromatic sources.

The total energy content of a water molecule E_T can formally be broken down into

$$E_T = E_t + E_v + E_r + E_{el} \quad (2)$$

where E_t , E_v , E_r and E_{el} are the translational, vibrational, rotational, and electronic energy content of the molecule. The isotope mass difference between the water molecules H₂O, DOH and D₂O has a significant effect on the vibrational energy term E_v . The fundamental infrared stretching band for the O-H and O-D bonds of water molecules adsorbed on solids are separated by ~9000 Å (see Figure 1). The present photodesorption concept proposes to utilize the O-D band to selectively excite the HOD molecules and thereby increase their temperature.

For a vapor phase/adsorbed phase equilibrium system, the probability of an adsorbed molecule detaching from the surface⁽¹¹⁾ is

$$P = e^{-E_0/E} \quad (3)$$

where E is the energy content of the molecule and E_0 is the surface binding energy. This energy, E_0 , required to break the adsorption bonds holding a molecule at a given site on a solid is equal to the heat of adsorption ΔH_{ad} . The heat of adsorption is ~2 to 3 times the heat of vaporization, ΔH_{vap} , for a given compound at low coverage and approaches ΔH_{vap} for monomolecular coverages. The probability of an excited, adsorbed molecule detaching is

$$P^* = e^{-E_0/E^*} \quad (4)$$

where E^* is the energy content of the excited molecule. The ratio of the probability for detachment of excited and equilibrium molecules is

$$\frac{P^*}{P} = \exp\left(E_0 \frac{E^* - E}{E E^*}\right) \quad (5)$$

To the first approximation, one can consider the ratio just after vibrational excitation

$$\frac{P^*}{P} = \exp\left(E_0 \frac{E_v^*}{E E^*}\right) \quad (6)$$

This equation relates the extent of vibrational excitation to the relative probability of finding a selectively excited molecule, for example DOH, in the vapor phase. The ratio can be interpreted in terms of an effective enrichment factor. Note that the larger the binding energy E_0 is the larger the ratio.

For a mole of bent triatomic molecules (i.e., water) in their ground electronic state at 300°K:

$$\begin{aligned} E_T &= E_t + E_v + E_r \\ &= 3(1/2RT) + 3(1/2RT) + 3RT \\ &= 6RT \\ &= 3.6 \text{ kcal/mole} \end{aligned} \quad (7)$$

Excitation of the O-D stretch band at 3.6 microns imparts

$$E_v^* = \frac{2.895 \times 10^5}{3600 \text{Å}} = 7.9 \text{ kcal/mole} \quad (8)$$

to the DOH molecules. The heat of absorption for water on silica glass surface is, for monolayer coverage, approximately 12 kcal/mole. (12) Substituting into the probability ratio equation gives an enrichment factor of 9.9. Table 1 shows the results of the calculations on DOH and TOD for excitation of the stretch and combination bands of these adsorbed molecules.

Table 1. Effective Enrichment Factors

	HO-D			DC-T		
	$\lambda(\mu)$	E_v^*	$\frac{P}{P}$	$\lambda(\mu)$	E_v^*	$\frac{P}{P}$
Stretch	3.6	7.9	9.9	4.2	6.8	8.8
Combination	1.83	15.5	15.0	2.53	11.3	12.5

Now consider the effect of the absorption of the infrared photon by an adsorbed DOH molecule in terms of the surface residence time τ described by the Frenkel equation (13)

$$\tau = \tau_0 e^{\frac{E_0}{RT}} \quad (9)$$

where τ_0 is a constant determined by the adsorption interactions and is typically of the order of 10^{-13} seconds. For the water molecules at ambient temperature (300°K) the residence time is $\sim 5 \times 10^{-13}$ seconds. For a DOH molecule vibrationally excited by a 3.6 micron photon the resonance time could be as short as 5×10^{-13} seconds. Even for a large loss (90%) of the vibrational energy, the excited DOH molecule τ would be $\sim 3 \times 10^{-13}$ seconds. Thus, we find the excited DOH molecules reside on the adsorption surface a much briefer time than those molecules at ambient conditions.

For present purposes, let us focus on photodesorption of DOH using the 3.6 to 4.1 micron stretching band. The following treatment uses the 3.85 micron midpoint of this region for calculations which corresponds to a photon energy of 7.4 kcal/Einstein.

At present, two laser systems, one based on existing technology and the other on theoretical grounds, (14) would emit in this region. The DF laser output fits this DOH photodesorbing region quite well. A suitable DF laser system should be attainable with existing technology. The second photon source would be a tripled carbon dioxide laser. (14) The technology for the tripled CO₂ laser system would have to be developed. Considering the importance of this spectral region for military laser applications other lasers will more than likely be developed which will be applicable to the present process.

The output requirement for the laser system can be estimated if one makes certain assumptions about the photodesorption process. First assume three Einsteins per mole of DOH (i.e., 0.16 Einstein/g) are required for the photodesorption process. That is, assume only 1 out of every 3 photons is successfully utilized in photodesorbing DOH molecules. This arbitrary photon loss factor is imposed from considerations of the three processes a photon can undergo: 1) absorption by DOH, 2) absorption by impurities, and 3) scattering. The implied assumptions are that the three processes are equally probable and only the first leads to photodesorption of the DOH molecule. We will further assume that the quantum yield for photodesorption is unity. The validity of such arbitrary assumptions must be experimentally investigated. Taking into account this 33% photon utilization efficiency, a ~ 5 kilowatt laser system would be required to photodesorb one gram of DOH per second.

One limitation on the physical photodesorption process, perhaps the most severe, is the readorption of the enriched phase. To be economically viable multiple photodesorption of the DOH molecules in a single stage must be avoided. Two methods to minimize readorption would utilize a carrier gas (CG in the schematic of Figure 2). One method would be to use an inert carrier gas to sweep the enriched phase through the honeycomb structure. The second approach would be to use a reactive carrier gas which would scavenge the deuterium atoms of the excited DOH molecules. The deuterium rich carrier gas would then be subsequently processed. Both approaches would be sensitive to the nature of the high surface area material, honeycomb dimensions, gas pressure and vessel temperature. However the inert CG system would probably be much more sensitive to these parameters.

Another factor to consider is over what surface area must the photons be spread to photodesorb one gram of DOH. As a model case, assume a solid surface having the water adsorption properties of Vycor glass. At 75% relative humidity one gram of Vycor glass adsorbs 0.2 grams of water (15), which corresponds to ~ 16.9 moles of water per meter of glass surface for 1-cm-thick plates. Taking the natural abundance of DOH to H₂O

as 1 in 3000 gives 5.6×10^{-3} moles of DOH/m² of glass. To photodesorb 1 g of DOH at this coverage of 0.11 g/m² of glass would require irradiation of 9.4 m² of glass surface.

Commercial Feasibility of the Photodesorption Enrichment Process (PEP)

The upper part of Figure 3 shows the conceptual flowsheet for the PEP process which consists of three photodesorption stages and a vacuum distillation where it is assumed that an enrichment factor of ~ 10 (i.e., 9.9 in Table 1) is achieved in each photodesorption stage. This process for removing heavy or enriched water is based on the ability of IR light to selectively excite the vibrational mode of the desired species while adsorbed on a solid surface. As discussed in the preceding section, when the excited molecule absorbs this energy, the probability of the molecule detaching itself from the surface and entering the gas phase is enhanced. A stream of carrier gas can then be used to remove the isotopically selected molecule from the area, carry it to further stages as required, and finally collect the product.

The schematic in Figure 2 shows the structure and operation of the conceptual PEP photodesorption units upon which cost estimates are based. At the heart of the photodesorption process is the adsorption/desorption surface and its structural configuration. A photodesorption structure of the spiral wound corrugated foil was assumed. These honeycombs could be assembled in stacked modular units to form the honeycomb photodesorption sub-sections I through N.

As shown, the PEP procedure would involve 4 separate operating steps in a complete cycle: 1) adsorption of H₂O/DOH mixture, 2) photodesorption and collection of enriched deuterium phase, 3) surface heating for removal and collection of spent deuterium phase, and 4) cooling of surface. Carrier gases would be utilized to carry out these various steps. The number of subsections N to a vessel required for smooth operation would be determined by the process times for steps 1 through 4. For example, there might be 10 of these sub-sections in a vessel, operating in parallel at slightly staggered steps of the cycle to avoid any abrupt changes in momentum.

Several geometric forms can be employed to accomplish this separation task depending on the type of adsorption surface used. Keeping in mind the need for rapid removal of the desorbed species, one must try to avoid tortuous paths created by such high surface area configurations as packed columns. Parallel path configurations created by tubes, fibers (including fiber optics), or honeycomb structures look promising for photodesorption processes. Two major categories of substrates are possible. The first is a high surface area substrate transparent to IR light. Unfortunately, at the wavelength of the vibrational modes most useful for exciting DOH and TOH (3.6 μ and 4.2 μ , respectively), very few materials of reasonable cost are transparent enough to allow development of a commercial process. The second major category is a reflective substrate coated with high surface area material. At 3.6 microns, copper possesses good reflective properties (99%). The probability of photodesorbing a molecule adsorbed on the interior coating of a chamber having mirrored coppered walls is greatly increased because of the multiple reflection path of the photon. Such chambers can be constructed as honeycomb-type structures made from copper foil.

The more promising honeycomb structure consists of corrugated foil laid alternately with plain foil. A modular unit can be constructed by spiral winding or stacking the corrugated and plain foil as shown (view A-A) in Figure 2 to form a structure with a high surface area per unit volume that will be suitable for rapid gas flow and for admitting light. The effective surface area of the foil can be increased by at least a factor of 10³ by applying a rough coating of a transparent high surface area material such as MgO. The coating should be such that it minimizes the water adsorption energy and photon losses and perhaps shifts the O-D spectra to improve the overlap with the laser output.

The best mass produced honeycomb structure presently available has a surface area of ~ 302 sq ft/cu ft of structure. Placing the corrugated foil in a configuration such as those shown in Figure 2, with a foil thickness of 0.002 in. and wave height or amplitude of 3.012 in., will yield a surface area of 4323 sq ft/cu ft of structure, an increase of a factor of 12.6. For natural abundance levels it was calculated that by using the latter corrugated structure with a high surface area coating (i.e., 2×10^3 area factor) one gram of DOH would be monomolecularly adsorbed in each cubic meter of honeycomb structure.

The difficulties of preparing cost estimates for a system at this stage of development are recognized as being quite serious. The objective of a cost analysis at this point in time is primarily to determine whether the technology has a chance of reducing costs compared with current systems or even being competitive assuming that the physical chemistry works and that the R&D program is successful in achieving its objectives. The key assumptions in the cost estimate are a CO₂ triple laser at 10% efficiency and a photodesorption separation factor of 10 for DOH from natural water. The capital costs for the process were estimated for both CF and CO₂ laser systems. Recycle costs of the DF based on existing DF electrolytic cell technology were included for the DF laser system. The capital and operating costs were compared with the figures proposed by the Canadians from an 800 ton/year H₂S gaseous separation process.^{10b} In terms of capital costs it is estimated that the PEP plant might be from one fifth to one tenth the cost of the GS plant. The production cost per pound of heavy water from a PEP plant might be one-sixth that of the proposed GS plant if the assumed rates, yields and other objectives are achieved.

The PEP scheme should also be applicable to the removal of TOH from D₂O and TCH from H₂O. One advantage of the PEP scheme over present tritium recovery technology is the elimination of T₂ or P₂ gas handling which presents safety problems.

Other Applications

A photochemical desorption technique should be applicable to $^6\text{Li}/^7\text{Li}$ laser isotope enrichment. Exchange of Li for the H of surface hydroxyl groups is known to occur on solids subjected to Cl_2Li vapor (17,18). The products of this surface reaction are methane gas and surface Li-O-Si groups. By selective laser infrared excitation of the Li-O vibrational band one may be able to photoreact, react, and sweep the ^6Li with a carrier gas. A possible separation scheme would then involve (1) subjecting a glass surface to Cl_2Li vapor to exchange Li for H, (2) removing the remaining Cl_2Li vapor, (3) introducing photoactive carrier gas, (4) photoexciting the ^6Li which reacts with and is removed by the carrier gas, and (5) recovering the enriched Li phase from the solid and preparing the spent surface for a new cycle. This final step could involve either a wash procedure to replace the residual Li-O with H-O groups or perhaps a high temperature exchange. Photophysical desorption of ^6LiF from a NaCl surface at high temperatures offers another possible separation scheme.

Extension of the photodesorption technique to other isotope separations should be feasible. Modifications of gas phase laser isotope procedures to fit the proposed photodesorption technique are possible and should lead to improved enrichment because of the superior isotope densities attainable on solids. This increased density could result in better utilization of the photons, superior enrichment per pulse, more efficient processing, and lower cost.

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**Fig. 1. Infrared at Absorption Spectra of
D₂O and H₂O Adsorbed on Alumina.**

**Fig. 2. Flowsheet for the Photodesorption
Enrichment Process in Schematic of a Photo-
desorption Unit**

SCHEMATIC: