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DEVELOPMENT OF ADVANCED CONCEPTS FOR IMPROVED HEAVY WATER PRODUCTION TECHNOLOGY I.

Quarterly Progress Report for the Period
October 1, 1976 - December 31, 1976

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MASTER

January 1977

MASTER

Prepared for the Advanced Isotope Separation Technology Office, Division of
Nuclear Research and Applications under the U. S. Energy Research and Development
Administration under Contract No. W-7405-Eng-48.

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Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

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DEVELOPMENT OF ADVANCED CONCEPTS FOR
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ABSTRACT

Three strongly differing processes for deuterium isotope separation continued under development during the reporting period which may lead to improved heavy water production technologies. Compound characterization continued and promising alloys were evaluated for rare-earth-transition metal hydrides suitable for chromatographic hydrogen isotope separation. Equilibrium pressure curves for hydrogen and deuterium over these compounds were measured; the single-step deuterium enrichment ratios of 30% were observed for the most promising compounds. Spectroscopic studies suggested that deuterium halide-olefin addition reactions accelerated by IR lasers can be verified by Nd-YAG laser excitations of HBr and DBr overtone bands. Compounds suitable for CO₂ laser multi-photon deuterium-selective dissociation were determined. The most promising compounds have dissociation barriers of less than 2 eV and extremely high frequency factors, which should permit high quantum efficiencies to be attainable.

Two patents originated by project staff members and assigned to ERDA were allowed for advanced isotope separation techniques: Ion laser dissociation of formaldehyde, and IR laser-accelerated deuterium halide-olefin addition reactions.

- * Work performed under the auspices of the U.S.E.R.D.A. Contract No. W-7405-Eng-48.

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I. RARE-EARTH/TRANSITION METAL HYDRIDES SUITABLE FOR CHROMATOGRAPHIC HYDROGEN ISOTOPE SEPARATION

Work is continuing on the preparation and characterization of LaNi_5 -type alloys for use in deuterium separation chromatographic columns. We have recently installed a mass spectrometer especially designed to measure very low levels of deuterium and thus can now measure deuterium/protium separation factors at natural abundance levels. The alloy LaNiCu_4 has been determined to have a separation factor of 1.3, the best measured so far of several intermetallic compounds of this family. Substantial quantities of LaNiCu_4 has been prepared and suitable chromatographic columns are being loaded with it for laboratory scale studies of chromatographic separation of deuterium from hydrogen gas feed streams.

Other LaNi_5 -type alloys are being prepared with lanthanum replaced by calcium to lower the cost of the intermetallic compound, which early analyses suggest may be a dominant item in the economics of this approach to heavy water production. The alloy CaNi_3Cu_2 shows a separation factor about half that of LaNiCu_4 , and is the best calcium-containing compound studied thus far. The lanthanum nickel-copper compounds show increasing separation factors as the copper content is increased, but the calcium-nickel-copper alloys with high copper content are not observed to form hydrides at sufficiently low enough pressures to be useful for chromatography. The calcium substitutes work will be continued, in the expectation that at least a major part of the lanthanum can be replaced.

II. MULTI-PHOTON CO₂ LASER DISSOCIATION OF ORGANIC MOLECULES: COMPOUND SELECTION.

This process is a most promising one for deuterium laser isotope separation (LIS) because of the ready availability of economical and industrially proven, high average power and high peak power CO₂ lasers. Several molecular systems have been chosen which promise high process throughput and high deuterium isotopic selectivity. The excellent gas-phase kinetic data available for these systems also suggest that usefully high process quantum efficiencies will be attainable.

Previous isotopically selective multi-photon dissociation studies produced radicals by dissociation of SF₆¹ or H₂CO², which necessitated bond breaking and hence high energy barriers. Unimolecular elimination of stable molecules by four- and six-center processes has activation energy barriers which are several times lower. Tertiary butyl compounds seem an ideal choice. Activation energies are only 40-45 kcal/mole (1.8-2.0eV), and also offer very high frequency factors (i.e., A or pre-exponential factor.)

Unimolecular thermal dissociation is described by the Arrhenius rate expression

$$k(\text{sec}^{-1}) = Ae^{-E_a/RT} \quad (1)$$

Since the A factor is typically 10¹³sec⁻¹ for these compounds, dissociation can occur after sufficient excitation in a time scale much less than the quenching or scrambling time (typically 10-1000 nanosec), which can permit much more efficient photon utilization and higher isotope selectivity.

Table I lists kinetic data for selected compounds.

TABLE I⁴COMPOUNDS SUITABLE FOR UNIMOLECULAR DISSOCIATION

<u>NAME</u>	<u>NUMBER AVAIL. HYDRO- GEN ATOMS</u>	<u>BOILING POINT °C</u>	<u>A (10¹³sec⁻¹)</u>	<u>E_a kcal/mole</u>
Ethyl Acetate	3	77	0.4	48.0
Isopropyl Acetate	6	90	1	45.0
t-Butyl Acetate	9	98	2.2	40.5
Ethyl Chloride	3	12	1.6	56.5
Isopropyl Chloride	6	36	4	51.1
t-Butyl Chloride	9	52	6	45.0
t-Butyl Bromide	9	73	6	41.8

Ethyl chloride illustrates use of this process for deuterium isotope separation:

Vibrational excitation of the ethyl chloride molecule near 10 μ causes molecular elimination of HCl yielding a deuterated olefin (ethylene-d₁). When using t-butyl compounds, the deuterium will appear as deuterated isobutene (2-methylpropene-d₁). Separation easily occurs due to the ~ 100°C difference in boiling points, and combustion then yields water for final heavy water purification by standard fractional distillation techniques.

The suitability of this class of molecules for CO₂ laser multi-photon dissociation was verified using sec-butyl chloride⁵. Only the HCl and olefin products were observed⁵. The suitable wavelength for the t-butyl halides is 9-10 microns³, where the deuterated species absorb and the normal

species are very transparent³.

The notable advantages of this approach to deuterium separation include the presence of nine identical hydrogens on t-butyl compounds which effectively increases process deuterium throughput nine-fold. The data in Table I also shows that atmospheric operation at somewhat above room temperature is feasible.

Effort in this project during the remainder of FY77 will be concerned with establishing scientific feasibility of deuterium production via multi-photon dissociation of t-butyl and related compounds by CO₂ laser. Parameters to be established are reaction quantum yield, quenching and overall photon utilization efficiency. These data then permit accurate estimation of laser-related costs for heavy water production via this process, and provide some basis for estimating other costs of the overall process.

III. DEUTERIUM HALIDE-OLEFIN ADDITION REACTIONS

Spectroscopic and kinetic details for this process were described earlier.⁶ Basically this process utilizes the highly efficient CO laser to excite DBr or DCl to higher vibrational levels, where a greatly enhanced reaction rate is enjoyed by the isotopically selected olefins via the steps

It is now clear that process (4) is just the opposite of process (2) as it involves dissociation instead of addition. Activation energies for this process can be chosen to be extremely low: ≈ 15 kcal/mole, or the equivalent of 3 CO laser quanta. Table II indicates Arrhenius kinetic parameters which describe the thermal reaction (for which published data is available) via the rate equation:

$$k(\text{sec}^{-1}) = [\text{olefin concentration}] \cdot A \left(\frac{\text{liters}}{\text{mole} \cdot \text{sec}} \right) \cdot e^{-E_a/RT} \quad (5)$$

TABLE II

Arrhenius parameters for HX + olefin addition reactions

Compound	$\log_{10} A (\text{liters/mole} \cdot \text{sec})$	E_a , Activation Energy (kcal/mole)	
		HCl	HBr
1,3-butadiene	8.8	28	24
2-methyl-1,3-butadiene	7.5	22	17
2-methyl-1,3-pentadiene	7.5	17	13

Table II shows the very low activation energies attainable in hydrogen halide reactions with conjugated olefins, which appear to be the best choices for this process. One potential problem is the low frequency factor (A), which will allow quenching to occur at rates comparable to the reaction rate. This needs further evaluation.

This process can be conveniently tested by using the Nd-YAG laser to excite the 3-0 (second overtone) vibrational band, as shown in Table III.

TABLE III

Nd-YAG laser match to HBr 2nd overtone absorption

Nd-YAG laser Wavelength	Measured Output Power	HBr Absorption Line
1.3350 μ	5 watts	H ⁷⁹ Br R(7)
1.356 μ	4 watts	H ⁷⁹ Br, H ⁸¹ Br P(2)

Table III shows the measured performance of a CW Nd-YAG laser system created for this experiment. At the wavelengths used the excited HBr molecule carries 21 kcal/mole of vibrational energy, sufficient for reaction with the reagents of Table II. Important questions to be answered during the remainder of FY 77 are

1. Does vibrationally excited HX lead to rapid, isotopically selective reaction?
2. What fraction of laser-supplied vibrational energy is available to lower the reaction activation energy barrier?
3. How fast is the isotopically selective reaction compared to quenching and energy transfer?

If positive responses are obtained to these questions in FY 77, then an actual demonstration process can be designed and operated in FY 78, using a high peak and average power pulsed CO laser, to determine the basic process parameters needed to guide conceptual engineering design and overall cost estimation for this deuterium production approach.

A patent application describing this process was filed in June, 1976. The application was allowed in December, 1976, and will thus mature into a patent to be issued during 1977.

IV. OTHER PHOTOCHEMICAL PROCESS

Ultraviolet laser photo-predissociation of formaldehyde was thoroughly studied in a highly successful fashion during FY 76, yielding 180-fold deuterium enrichment and $\geq$ 30-fold single step C-13, O-17, and O-18 enrichment.^{6,7} The primary thrust of ongoing research is therefore currently oriented toward IR photochemical processes, for which performance proven, economic, high average power laser exist. During the present reporting period two papers were completed^{6,7} describing the high single step enrichment isotope separation of deuterium, C-13, O-17, and O-18. These papers noted the present conomic superiority of LIS for the majority of these isotopes, relative to currently employed production techniques.

A patent was filed on isotope separation by ion laser photo-predissociation of formaldehyde, was allowed to ERDA early in December, 1976, and will mature into a patent and be issued in 1977. This patent covers the presently commercially attractive routes to carbon and oxygen isotope separation noted above.

Potential routes to carbon and nitrogen isotope separation via IR laser-induced chemistry were described in internal technical memos^{8,9} forwarded to ERDA/NRA staff members in November, 1976. These are being considered for patent application by ERDA and involve HCN addition into olefins⁸ and photodissociation of hydrozoic acid HN_3 .⁹

V. SUMMARY

In the Fall Quarter reporting period of FY77 three very promising routes to deuterium separation were studied, to develop data for evaluating their potential application in improved (less expensive) heavy water production.

Hydrides of intermetallic compounds of rare-earths and transition metals were evaluated to determine hydrogen isotope shifts, with hydrogen pressure vs. hydrided mole fraction curves showing significant deuterium isotope effects. The most promising compounds tested have yielded 30% single-step gas phase enrichment in HD. Further compound optimization is in progress and should be largely completed during the remainder of FY77. Initial chromatographic enrichment results should also be available in this period. The chromatographic approach, if successful, is expected to be economically very competitive.

IR laser-induced chemical processes for deuterium separation appears promising for two approaches currently being studied. CO laser-accelerated DBr or DCl addition into olefins can occur with activation energies as low as 15 kcal/mole (0.6ev). Multi-photon dissociation of large organic molecules appears optimal for t-butyl compounds^{3,10}. Activation energies are low ($\leq 2.0\text{ev}$) and frequency factors are very high ($\sim 10^{13}\text{sec}^{-1}$), thereby insuring very rapid dissociation after CO₂ laser excitation. Deuterium throughput in the process can be very high, due to the nine hydrogen atoms carried per molecule.

The scientific feasibility of both of these processes is scheduled to be established during the remainder of FY77, along with basic process data to guide overall engineering cost estimates. Each of them satisfy basic screening criteria for processes offering at least a 2-fold reduction in overall heavy water production cost.

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Available from
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Springfield, VA 22161
Price: Printed Copy \$; Microfiche \$3.00

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