IR-LASER ISOTOPE SEPARATION STUDIES AT RIKEN

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The study of molecular laser isotope separation at Riken is reviewed historically and the current research objectives are shown in relation to the research programs on MLIS at RIKEN.

1. Tritium

Separating tritium from light- and heavy-water contaminated in fission plant operation and reprocessing is of international interest for two reasons. Removal of this radioactive element from the plant is necessary for worker and environmental safety. Futhermore, after recovery of this fission by-product, the tritium can be used as fuel for nuclear fusion.

A large quantity of tritium is produced by the ternary fission of ^{235}U and is accumulated in the nuclear fuels of most widely operated light-water reactors at a rate of about 25 kCi/yr per 1-GWe reactor. The world capacity of atomic power generation is currently about 250 GWe/yr, and therefore about 6 MCi of tritium are formed worldwide per year. In the near future it will be necessary to remove the tritium from the effluent of fuel reprocessing plants (0.1 to 10 Ci/1, 0.06 to 6 ppm HTO/H_2) for safety and to protect the environment. It is estimated that approximately 1 MCi/year of tritium has to be treated in a nuclear fuel reprocessing plant, which has the capability of 1500 tons U/yr.

Aside from the relatively inefficient laser sources and photon utilization inherent in the approach to dissociate HTO by lasers, the extremely fast vibrational relaxation in water vapor destroys the isotopically selective absorption of the excitation step. Consequently, another hydrogen-bearing molecule must be chosen as the photoseparated source of tritium for laser separation. However, this molecule, the "working" molecule, must be able to pick up tritium from the original source of tritium, water (HTO or DTO), by rapid catalyzed liquid-phase hydrogen exchange, without undergoing any "hydrolysis-type" reactions. This exchange of tritium is depicted in the process flow diagram of Fig.1.

The tritiated compounds studies to date as working molecules for isotope separation of tritium by IR laser-induced multiphoton dissociation are listed in Fig.2. These compounds are all halogenated alkanes (C_1-C_4) containing only a single hydrogen atom in the molecule (with one exception).

These highly halogenated hydrocarbons have been selected because they are chemically inert, volatile, nonflammable, nontoxic, and inexpensive; some of them are produced commercially in large quantities. They have strong IR absorption peaks (C-H bends, C-F stretches, etc.) in the emission regions of the most efficient and most highly developed IR lasers (e.g., 9 to 11 μm for the CO_2 laser and 11 to 13 μm for the CO_2-laser-pumped NH_3 laser), and their linear absorption cross sections are larger than those of nonhalogenated hydrocarbons. The isotope shifts resulting from hydrogen atom replacement (T-for-H, T-for-D, etc.) in these compounds are extremely large, ~100 to 1000 cm⁻¹ for some bands. It is essential that
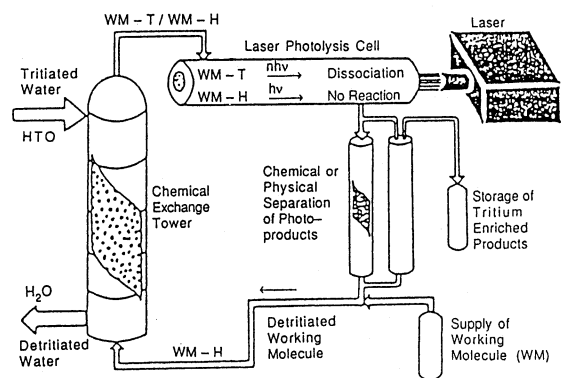

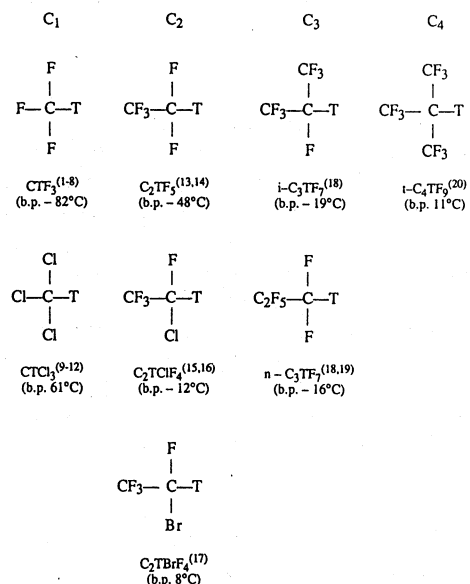Fig.1 Process flow for laser isotope separation of tritium

Fig.2 Compounds with one hydrogen site that have been studied as working molecules for laser isotope separation of tritium

these shifts be larger than the rotational line contour width (~10 cm^{-1}) to achieve absorption selectivity.

The first laser separation of tritium-from-hydrogen was demonstrated by TEA CO_2-laser-induced MPD of trifluoromethane-T (CTF_3) present in a CTF_3/CHF_3 mixture at RIKEN.

The dependence of the dissociation yields for CTF_3 (d_T) and CHF_3 (d_H) on laser frequency are shown in Fig.3 together with the IR spectrum of synthesized neat CTF_3 for comparison. The peak in the MPD spectrum of CTF_3 (~1073 cm^{-1}) is near the peak in the linear absorption spectrum of CTF_3 (1077 cm^{-1}), being red-shifted by 4 cm^{-1}.
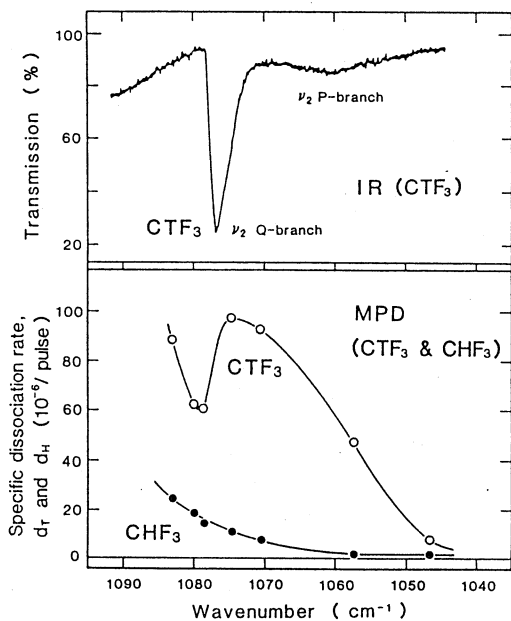

Fig.3 Multiphoton dissociation (MPD) spectra of CTF_3 and CHF_3 (lower) and infrared spectrum of synthesized CTF_3 (upper)

Following these first successful experiments, extensive studies were conducted to examine the dependence of the CTF_3 and CHF_3 dissociation probabilities on laser frequency, pulse energy, pulse duration, irradiation geometry, tritium concentration, sample pressure, buffer gas pressure, and temperature. Further increases in the enrichment factor and an increase in operating pressure were attained by using "mild" focusing instead of "tight" focusing, the addition of argon buffer gas, lowering sample temperature, and using lower frequency laser lines.

2. Uranium Isotopes

Natural uranium contains 0.7% of uranium-235. Light water reactors for commercial electricity generation now used in Japan require the enrichment of U-235 up to 3%.

In the molecular laser isotope separation (MLIS) of uranium, gaseous UF_6 is cooled in a supersonic Laval nozzle to extremely low temperatures such as 100 K in order to suppress the hot band absorptions. Multi-frequency p-H_2 Raman lasers emitting around 16 μm are used for the isotopically selective infrared multiple-photon dissociation (IRMPD) of the supercooled UF_6. Under some well-controlled experimental conditions, we reported dissociation selectivities exceeding 4 for $^{235}UF_6/^{238}UF_6$ at 70 K. The results are summarized in Table 1. These selectivities correspond to the production of 3% enriched uranium-235 at one stage. We also reported that CH_4 was an excellent scavenger gas which reacted rapidly with F atoms formed via the reactions (1) and (2), and yet did not seriously deteriorate the primary dissociation selectivities.

$$^{235}UF_6 \xrightarrow{nh\nu} {}^{235}UF_5 + F \qquad (1)$$

$$^{238}UF_6 \xrightarrow{mh\nu} {}^{238}UF_5 + F \qquad (2)$$
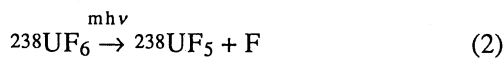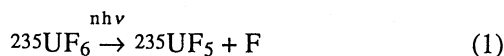
When the dissociation probability in Eq.(1), q_5, is greater than that in Eq.(2), q_8, U-235 is enriched in the product UF_5. The UF_5 particles can be separated from the unreacted UF_6 gas.

Table 1

Typical values of separation factors

UF_6 temperature (K)	IR laser for excitation	IR laser for dissociation	separation factor S	
160	line-tunable	line-tunable	1.6	(1.7)
100	line-tunable	line-tunable	2.1	(2.3)
70	continuously tunable	line-tunable	4.2	(4.7)
			average	maximum

These results were obtained with time-consuming, off-line analytical methods for reaction yields (gas chromatography) and isotopic ratios (conventional mass spectrometry). Since the reaction yields and the selectivities may depend complexly on various irradiation parameters such as frequencies, fluences and the pulse delay in the multi-frequency irradiation scheme, we must acquire the data on a single-shot basis with real-time analytical methods in order to explore better conditions for the MLIS process. Thus we developed highly sensitive methods for real-time determination of the reaction yields and the selectivities using HF infrared emission and MPI/TOFMS (multiphoton ionization/time-of-flight mass spectrometry), respectively. The experimental set-ups are schematically shown in Figs. 4 and 5.
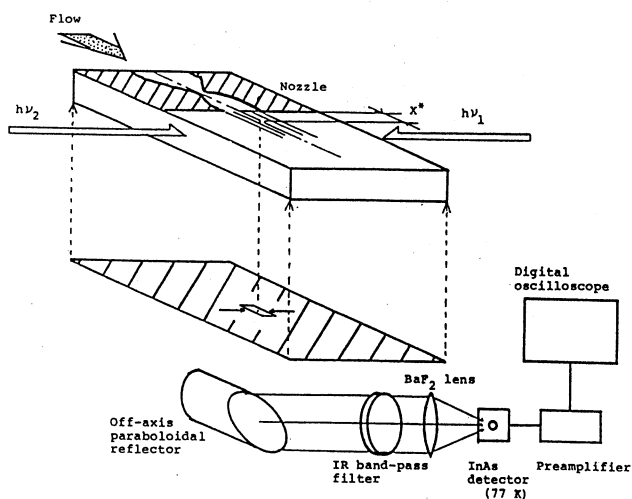
Fig.4 Schematic diagram of a supersonic nozzle reactor and
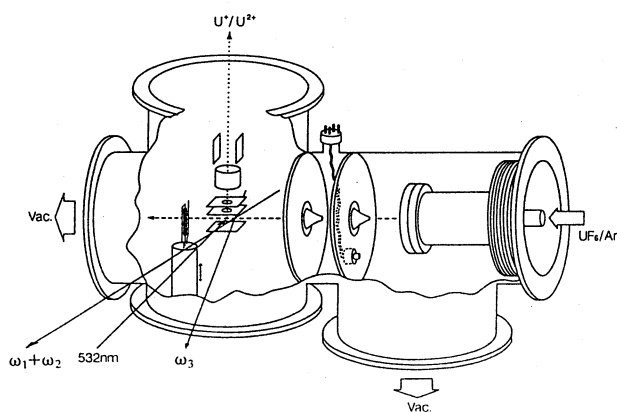the detection system for infrared emission measurement

Fig.5 Schematic diagram of MPI-TOF/MS on-line
measurement system

3. Germanium and Zirconium Isotopes

Germanium has five isotopes of atomic mass 70, 72, 73, 74, and 76. One of the germanium isotopes is used in the medical market. Zirconium has five isotopes of atomic mass 90, 91, 92, 94, and 96. In view of the fission power market and the future fusion power market, great benefits are anticipated for the uses of enriched or depleted zirconium.

In the MLIS of heavy elements, the selection of working substances is one of the most essential factors. We chose the metal alkoxide compounds $(M(OR)_n$; M: metal element, R: alkyl group). The advantages of metal alkoxides as the working substances for MLIS (1) are as follows.
(1) Alkoxide compounds are available for most of the heavy elements. (2) Metal alkoxides have relatively high volatility compared with other organometallic compounds. (3) They have strong and isotope-selective infrared absorptions corresponding to the $\nu(C-O)M$ and $\nu(M-O)$ bands within the emitting regions of CO_2, NH_3, and para-H_2 Raman lasers. The criterion (3) is essential since the use of the most efficient IR laser is most desirable.

We investigated the MLIS of germanium and zirconium by TEA CO_2 laser-induced IRMPD of germanium tetramethoxide $(Ge(OCH_3)_4)$ and zirconium tetra-tert-butoxide $(Zr[OC(CH_3)_3]_4)$. These alkoxide compounds are more volatile than the other alkoxides of corresponding elements. After a careful handling procedure was developed to treat these relatively unstable compounds by excluding contamination of H_2O or O_2, we demonstrated the enrichment of relevant isotopes experimentally.