Measurements of $^{235}\text{U}/^{238}\text{U}$ isotopic ratio in the photoproduct UF$_5$ by multiphoton ionization and time-of-flight mass spectrometry

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Abstract. A MultiPhoton-Ionization Time-Of-Flight Mass Spectrometry (MPI/TOFMS) apparatus was developed for real-time measurement of the uranium isotopic ratio in nascent UF$_5$ formed by the 266 nm photolysis of effusive UF$_6$ ($< 300\text{ K}, \approx 1.3 \times 10^{-4}\text{ Pa}$). The UF$_5$ was selectively and efficiently multiphoton ionized by 532 nm radiation at appreciably low fluences ($< 10\text{ J/cm}^2$). The main ions observed, U$^+$ and U$^{2+}$, were subsequently analyzed with a TOFMS with mass resolution of 1190 to separate $^{235}\text{U}^{n+}$ and $^{238}\text{U}^{n+}$ completely. The isotopic ratio measurements showed good precision resulting from the excellent agreement which was observed between the isotopic ratios in UF$_5$ products and those in a parent UF$_6$ sample. These results suggested that the MPI/TOFMS method can be applied to the real-time analysis of separation factors in the molecular laser isotope separation of uranium by ionization of UF$_5$ following the infrared photodissociation of UF$_6$.

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Molecular Laser Isotope Separation (MLIS) of uranium is based on the isotopically selective Infrared Multiphoton Dissociation (IRMPD) of UF$_6$. A $^{235}\text{UF}_6$/$^{238}\text{UF}_6$ mixture seeded in a rare gas is adiabatically cooled in a supersonic Laval nozzle at an extremely low temperature below 100 K. The decrease in temperature sharpens the $v_3$ band shapes of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ around 16 $\mu$m. Multi-frequency p-H$_2$ Raman lasers are then used to excite and dissociate $^{235}\text{UF}_6$ selectively. The U-235 is thus enriched in UF$_5$ photoproducts. Under limited experimental conditions, we have already accomplished separation factors exceeding 4, which corresponds to the enrichment of $^{235}$U in UF$_5$ to nuclear-fuel grade at one stage [1]. In the multifrequency irradiation scheme, to achieve highly selective IRMPD, we have inherently many irradiation parameters to optimize, e.g., irradiation frequencies, laser fluences, and the time delays between laser pulses. Since the analytical methods used for measurement of separation factors (gas chromatography and conventional mass spectrometry) were extremely laborious and time consuming, the number of our data points was too limited to investigate the optimum irradiation conditions. Date acquisition on a real-time or even a single-shot basis is highly desirable for the purpose of the selectivity optimization.

Stuke et al. [2] first reported that the nascent UF$_5$ products formed by the UV photolysis of UF$_6$ could be selectively multiphoton-ionized by 532 nm radiation to yield mainly U$^+$ and U$^{2+}$ ions.

\begin{align}
\text{UF}_6 + h\nu (266\text{ nm}) & \rightarrow \text{UF}_5 + \text{F}, \\
\text{UF}_5 + h\nu (532\text{ nm}) & \rightarrow \text{U}^{n+} \quad (n = 1, 2).
\end{align}

Following their report, Chou et al. [3] studied the MPI of UF$_5$ in a shorter-wavelength region (433-474 nm) and estimated that the ionization efficiency was approximately two orders of magnitude higher than that at 532 nm. A more detailed wavelength and fluence dependence of the MPI efficiency, although still qualitative, was reported by Dore et al. [4] These results demonstrate that the MPI method can be applied in principle to the real-time measurement of the U-235/U-238 ratio in nascent UF$_5$ formed by the multifrequency 16 $\mu$m irradiation UF$_6$.

It must be noted, however, that we still have two unsolved problems for the actual application of this method to the real system. First, the mass analyzers used by Stuke et al. and by Chou et al. had rather low resolution in discriminating $^{235}\text{U}^{n+}$ and $^{238}\text{U}^{n+}$ ions. Dore et al. measured only ion currents using simple ion collection plates with no mass resolution. The use of an angular-type TOF spectrometer with sufficiently high mass resolution is the most desirable in view of its capability to detect all ions formed in each laser pulse. Up to now,
no measurement of the isotopic ratio in UF₆ on a single-shot basis with good precision by TOF mass spectrometry has been achieved.

Second, IR Multiphoton Excitation (IRMPE) produces an ensemble of hot UF₆ molecules which are vibrationally excited and yet remain undissociated because the excitation level is below the dissociation threshold. These hot UF₆ molecules remain in the system until they are subjected to the following MPI laser radiation, and then may absorb MPI photons which are not absorbed by cold UF₆ molecules. This situation is completely different from the case of the UV photolysis of UF₆ in the B band (240–340 nm) in which the dissociation of UF₆ is direct and extremely fast [5] with a quantum yield of unity [6], i.e., every UF₆ molecule absorbing a single UV photon promptly dissociates and no hot UF₆ is subjected to the MPI laser radiation. Such undesirable MPI of hot UF₆ molecules following IRMPE might occur in shorter-wavelength regions (< 500 nm) and may yield the same ions as those from the MPI of UF₅ products, disturbing the isotopic ratio measurement of the latter. Thus the MPI wavelength must be within the region where hot UF₆ molecules are off-resonant and the MPI efficiency therefore becomes a severe criterion for the sensitivity of the MPI/TOFMS method. The wavelength for the MPI laser has not yet been discussed.

We report in the present paper a MPI/TOFMS apparatus with sufficient mass resolution to distinguish ²³⁵UF₆⁺ and ²³⁸UF₆⁺ ions originating from UF₅. In order to find optimum MPI conditions, we reexamine the MPI of nascent UF₅ at 532 nm, which is far red-shifted from the possible absorption region of hot UF₆. Calibration is made between the isotopic ratios in parent UF₆ molecules and those in UF₅ photoproducts obtained by isotopically non-selective UV photolysis of UF₆.

1 Experimental

Figure 1 schematically shows the experimental apparatus. The MPI/TOFMS system is equipped with an angular-reflection-type TOFMS (R. M. Jordan Co.) and a Laval nozzle with a throat dimension of 3 x 5 mm². Natural or enriched UF₆ gas was used for the irradiation sample. The natural UF₆ was obtained from a laboratory stock with an assay of 0.719 ± 0.002 atom% ²³⁵U. Four kinds of enriched UF₆ samples with different isotopic contents were of certified grade from Cogema Pierrelatte. The isotopic contents of these samples (2.014 ± 0.003, 7.10 ± 0.01, 9.46 ± 0.03, and 19.78 ± 0.09 atom% ²³⁵U) were measured with a magnetic mass spectrometer (Finnigan MAT 271/45) by us. UF₆ gas diluted in Ar (UF₆/Ar = 0.001) was fed into the stagnation region of the nozzle from four pulsed fuel injectors operating at 0.1 Hz. The gas mixture emanating from the nozzle was sampled by a skimmer and admitted to the ionization chamber, which is evacuated to about 2.7 x 10⁻⁷ Pa with a turbo-molecular pump. Pressure changes in the ionization chamber with the opened injectors were measured by means of a fast ionization gauge (Beam Dynamics Inc., Model FIG-1) positioned 40 mm downstream from the ionization point. From measurements with the movable ionization gauge, it was found that the UF₆/Ar gas passing through the skimmer was not a free molecular beam but an effusive one under the employed operating conditions. The maximum partial pressure of UF₆ in the effusive beam was 1.3 x 10⁻⁴ Pa.

The 4th- and 2nd-harmonic beams (at 266 and 532 nm, respectively) from a Nd:YAG laser (Lumonics, HY-750) were separated with a Perin-Broca prism and then used for irradiation. The pulse duration was 12 ns (FWHM). The far-field beam profiles observed were rather flat-top-like. The counterpropagating 266 and 532 nm beams were focused onto the center of the ionization region with 70- and 36-cm-focal-length lenses, respectively. The 266 nm beam was used for the isotopically non-selective dissociation of UF₆. The 532 nm beam, optically delayed by 60 ns with respect to the preceding 266 nm beam, was used for the multiphoton ionization of the UF₅ photoproducts. The pulse energies were measured with energy meters (Scientec 38-IUV5 for 266 nm and Laser Instrumentation 17 AN for 532 nm). Both meters were mutually calibrated within their common wavelength region and further calibrated with other devices.

Ions formed in the space between the repeller plate and the extraction grid (placed 1 cm apart) were accelerated through the ground grid and then deflected by the