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Contrast ratio and separation factor in multiphoton dissociation of supercooled UF_6 irradiated with multifrequency 16 µm Raman-laser radiation

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Abstract. In infrared multiphoton dissociation of supercooled UF_6 irradiated with multifrequency para-H_2 Raman laser beams, separation factors and contrast ratios were measured by selective multiphoton ionization of the photoproduct UF_5 at 532 nm followed by time-of-flight mass spectrometric analysis. The relationship between separation factor and contrast ratio is discussed theoretically and quantitatively investigated in the experiments. From this relationship, we obtain the irradiation conditions of the laser-beam fluences for attaining a high separation factor and estimate the value of the intrinsic separation factor in multifrequency dissociation of UF_6.

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The isotopically selective multiphoton dissociation of UF_6 with a 16 µm infrared laser has been studied for its application to uranium enrichment [1–6]. The laser radiation which is resonant with the ν_3 vibrational frequency of $^{235}UF_6$ allows the dissociation product UF_5 to be enriched in ^{235}U. We attained [4] a separation factor higher than 4 by multifrequency dissociation of UF_6 cooled to 70 K. This value of the separation factor indicates that the multifrequency irradiation process can, in a single stage, produce UF_5 enriched above 3% in ^{235}U which can be used for nuclear fuel in light-water reactors.

In InfraRed MultiPhoton Dissociation (IRMPD) of UF_6, we used multifrequency irradiation and spectrum narrowing in UF_6 supercooled by adiabatic expansion to obtain a high separation factor while overcoming the problem of the UF_6 molecule having a considerably small isotope shift (0.6 cm^{-1}) [7]. When the vibrational temperature of UF_6 is high, large values of the separation factor cannot be obtained no matter how optimally the irradiation conditions of laser beams are chosen. Furthermore, even when the UF_6 temperature is low, the separation factor deteriorates if the laser irradiation conditions related to laser frequencies or fluences deviate from the optimal ones. In the multifrequency irradiation scheme for achieving high isotopic selectivity, there are too many inherent parameters to optimize experimental conditions. It should be noted that no theoretically established method of determining the optimum conditions for obtaining high separation factors has been reported for multifrequency IRMPD of UF_6.

Let us consider the separation factor as a function of the following two parameters: first, an intrinsic separation factor which corresponds to the upper limit of the isotopic selectivity, and second, a deteriorating factor which reduces the isotopic selectivity from the value of the intrinsic separation factor. The intrinsic separation factor is the highest separation factor attainable at given reactant conditions (UF_6 temperature, its pressure, etc.) when the laser irradiation conditions are chosen to be optimal so as not to deteriorate the selectivity. The deteriorating factor is dependent on the irradiation conditions such as laser frequencies and fluences, but independent of the reactant conditions. The most logical approach to obtain a high separation factor is to determine simultaneously the reaction conditions under which the intrinsic separation factor is large and the deterioration factor is small.

In the present paper, we define the contrast ratio as a parameter representing the extent of deterioration in isotopic selectivity, and attempt to relate quantitatively the separation factor with the intrinsic separation factor and

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Abbreviations: $C_R(235)$: contrast ratio with respect to $^{235}UF_6$; q_{S5}: yield of isotopically selective dissociation with respect to $^{235}UF_6$; q_{S8}: yield of isotopically selective dissociation with respect to $^{238}UF_6$; q_{N5}: yield of isotopically non-selective dissociation with respect to $^{235}UF_6$; q_{N8}: yield of isotopically non-selective dissociation with respect to $^{238}UF_6$; S: separation factor; S_0: intrinsic separation factor; Φ_i: fluence of individual beam Ω_i [J/cm^2]; Ω_1: Raman-laser beam for exciting $^{235}UF_6$ molecules selectively; Ω_2: Raman-laser beam for pumping UF_6 molecules excited by Ω_1; Ω_3: Raman-laser beam for pumping excited UF_6 molecules further to a dissociative state contrast ratio in a functional form. Using this quantitative relation, we present a method for evaluation of the upper limit of the separation factor for individual separation schemes.

1 Model description

Previously, we experimentally studied the dissociation characteristics in IRMPD induced by multifrequency 16 μm Raman-laser beams and pointed out that the isotopically non-selective dissociation channel is not negligible [8]. The separation factor is deteriorated by the non-selective dissociation. This deterioration can be quantitatively evaluated as follows. Let us define q_{N5} and q_{N8} as the yields of isotopically non-selective dissociation of $^{235}UF_6$ and $^{238}UF_6$, respectively, as shown in Fig. 1. We note that q_{N5} is equal to q_{N8} because this dissociation is non-selective. Let q_{S5} and q_{S8} denote the yields of isotopically selective dissociation of $^{235}UF_6$ and $^{238}UF_6$, respectively. When the conditions are favorable for enrichment, q_{S5} is larger than q_{S8}. The fractional conversion for each of the isotopic UF_6 species ($^{235}UF_6$ and $^{238}UF_6$) is the sum of the yield of isotopically selective dissociation and that of the non-selective one.

In multifrequency IRMPD, $q_{Ni} (i = 5$ or $8)$ corresponds to the yield of dissociation by the beams excluding the beam for selective excitation (we call it first-frequency beam here). $q_{Si} (i = 5$ or $8)$ is due to the dissociation by the beams including the first-frequency beam. When the first-frequency beam does not excite $^{238}UF_6$ at all, q_{S8} is zero. The observed separation factor S is given by

$$S = (q_{S5} + q_{N5})/(q_{S8} + q_{N8}). \tag{1}$$

Let us express the contrast ratio with respect to $^{235}UF_6$, $C_R(235)$, by the following equation:

$$C_R(235) = (q_{S5} + q_{N5})/q_{N5}. \tag{2}$$

$C_R(235)$ corresponds to the ratio of the total dissociation yield to the non-selective one for $^{235}UF_6$. The value of $C_R(235)$ is observable in the experiments where we measure the ratio of the yield obtained with the first-frequency beam for $^{235}UF_6$ to the yield without it. We define the intrinsic separation factor S_0 as

$$S_0 = q_{S5}/q_{S8}. \tag{3}$$

If the laser irradiation conditions were ideal and non-selective dissociation was completely prevented ($q_{N5} = q_{N8} = 0$), S_0 would equal S. In reality with non-selective dissociation, the experimentally observed value of S is smaller than S_0, and the value of S_0, therefore, cannot be directly observed.

With (1), (2) and (3), the separation factor S can be expressed as a function of $C_R(235)$ and S_0:

$$S = C_R(235)/\{[C_R(235) - 1]/S_0 + 1\}. \tag{4}$$

Figure 2 shows the dependence of S on $C_R(235)$ obtained from (4) in the cases of $S_0 = 5$, 10, 15 and 20 as examples. S is close to unity when $C_R(235)$ is small. It approaches S_0 as $C_R(235)$ increases. The figure indicates a criterion on the value of $C_R(235)$ for S larger than a certain value. For instance, in order to obtain S larger than 4 for reactor-grade enrichment, $C_R(235) > 16$ for $S_0 = 5$ or $C_R(235) > 6$ for $S_0 = 10$.

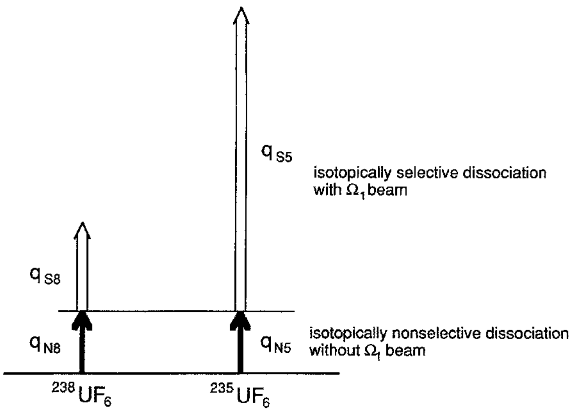

Fig. 1. Relationship between dissociation yields q_{S5}, q_{S8}, q_{N5} and q_{N8}

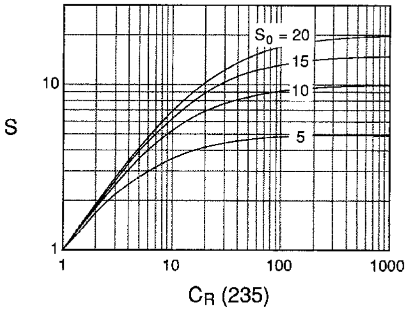

Fig. 2. Separation factor S as a function of contrast ratio $C_R(235)$ in the cases of $S_0 = 5$, 10, 15, and 20

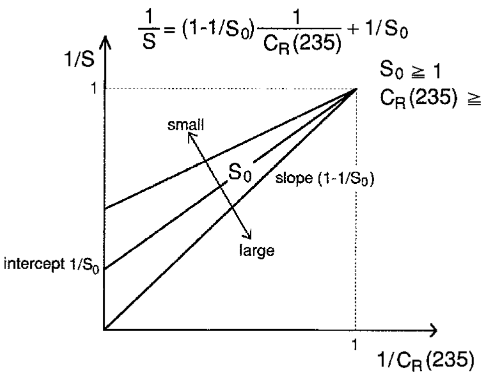

Fig. 3. $1/S$ as a function of $1/C_R(235)$

Equation (4) can be rewritten as

$$1/S = 1/S_0 + 1/C_R(235) - 1/S_0C_R(235). \tag{5}$$

It should be noted that (5) is symmetrical with respect to the variables S_0 and $C_R(235)$. We notice from this relation that the values of S_0 and $C_R(235)$ are equally important in obtaining high separation factors. Figure 3 shows that the relation between $1/S$ and $1/C_R(235)$ can be expressed by

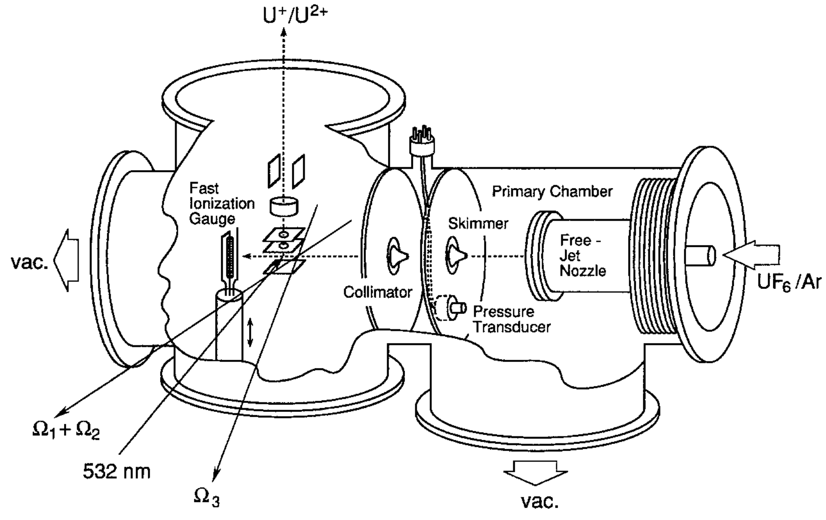

Fig. 4. Schematic diagram of the molecular beam experimental apparatus for MPI (at 532 nm)/ TOFMS of nascent UF_5 formed by the dissociation of UF_6 in a supercooled molecular beam with three-frequency para-H_2 Raman-laser pulses (Ω_1, Ω_2 and Ω_3)

a straight line with the slope of $(1 - 1/S_0)$ and the intercept of $1/S_0$. We note that one can estimate the value of S_0 from the value of the slope or intercept by plotting the data in a $1/C_R(235)$ vs $1/S$ plane.

2 Experimental

The experimental setup for real-time measurement of the separation factors is schematically shown in Fig. 4. The details of the apparatus have been described elsewhere [9,10]. Briefly, 20% enriched UF_6 gas diluted in Ar was supplied from the stagnation region of a pulsed nozzle. The molar fraction of UF_6 was 0.5%. The UF_6/Ar free-jet expansion was formed in a primary chamber through the nozzle orifice. A skimmer (1 mm hole diameter) and a collimator (2 mm hole diameter) formed a molecular beam which was admitted to the dissociation and ionization chamber. The supersonic molecular beam was crossed with the 16 μm Raman-laser beams which induced the isotopically selective IRMPD of UF_6.

The 16 μm laser radiation was generated by stimulated Raman scattering of CO_2 radiation in para-H_2 [11,12]. We used three focused infrared beams with different frequencies: a continuously tunable beam for selective excitation of $^{235}UF_6$ molecules (Ω_1), a second beam near 16 μm (Ω_2) for boosting the molecules already excited by Ω_1 to higher vibrational states, and a third one at 17 μm (Ω_3) for pumping the excited molecules to a dissociative state. The transverse profiles of all three beams were Gaussian with a $1/e^2$ radius of about 2.0 mm. The pulse energy of each beam was measured with pyroelectric detectors (Gentec ED-500 and ED-200). The Ω_1 and Ω_2 beams irradiated the molecular beam simultaneously, whereas the Ω_3 beam was delayed by ≈ 80 ns relative to the Ω_1 and Ω_2 beams.

Mass spectra of UF_5 produced by IRMPD of UF_6 were obtained using a MultiPhoton Ionization (MPI) technique with second-harmonic generation (at 532 nm) from a Nd: YAG laser (Lumonics, HY-750). Selective ionization of UF_5 was induced at a position 2.5 mm downstream from the point of Raman-laser irradiation. The isotopic ratio between ^{235}U and ^{238}U in the dissociation product UF_5 was measured from U^+ and U^{2+} ion signals using a reflectron-type Time-Of-Flight Mass Spectrometer (TOFMS) (R. M. Jordan) on a single-shot basis.

3 Results and discussion

3.1 IRMPD of UF_6 by three-frequency Raman-laser radiation

Under our experimental conditions, it was found that UF_6 was dissociated by two beams Ω_2 and Ω_3 without beam Ω_1. As mentioned above, this is an isotopically non-selective dissociation. In addition, we observed no dissociation when UF_6 molecules were irradiated by one frequency, either Ω_2 or Ω_3. This indicates that beam Ω_2 plays a role in the second stage of excitation (boosting the molecules selectively excited by beam Ω_1 to higher vibrational states where they are subsequently dissociated by Ω_3) while inducing the non-selective dissociation together with beam Ω_3. It is reasonable to believe that there are two dissociation channels in this three-frequency IRMPD of UF_6: the isotopically selective dissociation of UF_6 where it is excited stepwise by the three beams (Ω_1, Ω_2 and Ω_3) and the non-selective dissociation by the two beams Ω_2 and Ω_3 (without Ω_1).

In our previous paper [8], we proposed a mathematical model for multifrequency IRMPD of UF_6. In this model, the dissociation probability was expressed by a functional form based on the product of power-law terms for individual fluences. From the theoretical study using this model, we discussed the dependence of contrast ratio or separation factor on the fluence, Φ_2, of beam Ω_2. When Φ_2 was larger than the value required to boost all the molecules excited by the beam Ω_1 to higher states, the non-selective dissociation probability increased while the selective one was saturated, and, as a consequence, both contrast ratio and separation factor decreased.

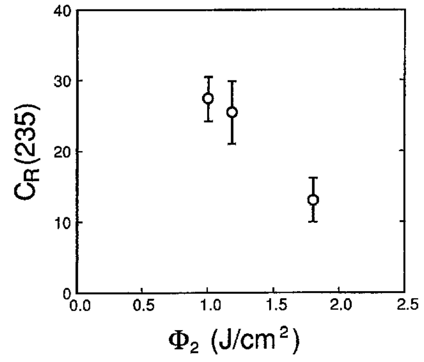

Fig. 5. Φ_2 dependence of the contrast ratio $C_R(235)$ obtained by dissociation of supercooled UF_6 with three-frequency laser radiation

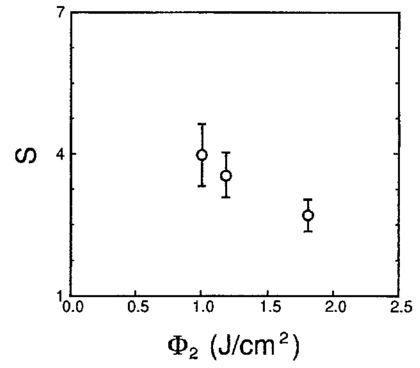

Fig. 6. Φ_2 dependence of the separation factor S obtained by dissociation of supercooled UF_6 with three-frequency laser radiation

Figure 5 shows a typical result of the Φ_2 dependence of $C_R(235)$. We found that $C_R(235)$ decreased as Φ_2 was increased when the laser frequencies and fluences for beams Ω_1 and Ω_3 were fixed at constant values. This experimental result is consistent with the qualitative argument based on the multifrequency IRMPD model, where the selective dissociation is saturated and the non-selective one increases with sufficiently high values of Φ_2. According to (4) or (5), the enhanced non-selective dissociation decreases S as $C_R(235)$ decreases with Φ_2. This is certainly the case in our experiment, as shown in Fig. 6. From these experimental results and the theoretical interpretation based on the model (4, 5), we found that higher values of S result from large values of $C_R(235)$.

3.2 Evaluation of the intrinsic separation factor in multifrequency IRMPD

The intrinsic separation factor S_0 depends on such parameters as the molecular temperature, gas pressure, UF_6 concentration, and frequency and intensity of beam Ω_1. For optimization of the separation factor, we must determine the conditions for obtaining a high intrinsic separation factor while estimating the unobservable value of S_0.

Let us evaluate the value of S_0 using the data shown in Figs. 5 and 6 as an example. We replotted the data on the plane of $1/C_R(235)$ vs $1/S$, as shown in Fig. 7. The solid lines in this figure indicate the dependence given by (5) for several values of S_0. The fact that the data points are positioned near the $1/S$ axis denotes that the deterioration of the separation factor is not very serious because of the large values of the contrast ratios. Although the data deviate from theoretical values to a small extent, we found from this figure that the value of S_0 is around 4 under the present conditions. As shown in Fig. 7, fitting a straight line representing (5) to the data makes it possible to obtain the value of S_0 from the value of the intercept on the vertical axis or the slope of that line.

If one attempts to search for the maximum value of the separation factor randomly to estimate the value of S_0, it takes much time and effort because the parameters for the search (frequencies and fluences of beams Ω_2 and Ω_3, time delays between laser pulses, etc.) are too numerous. In addition, there is no theoretical evidence that the highest value of the separation factor obtained in such a manner is really the maximum. In contrast, the method presented here for the evaluation of the value of S_0 has the great advantage that we can evaluate it readily using a definite number of data points.

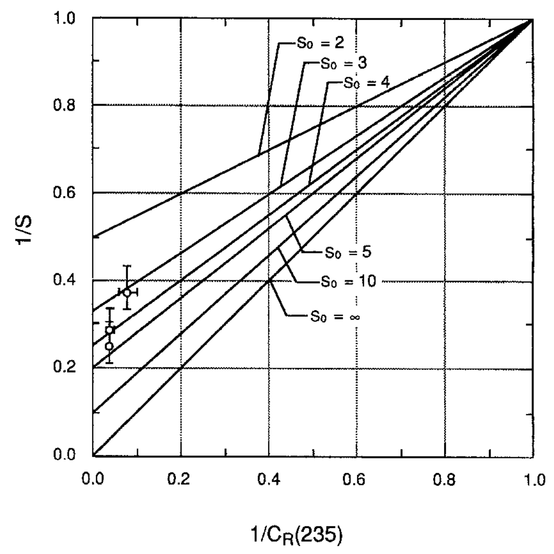

Fig. 7. Dependence of $1/S$ on $1/C_R(235)$ obtained by replotting the data shown in Figs. 5 and 6. The *solid lines* indicate the dependence given by (5) for several values of S_0

We believe that the following method is very useful for optimizing a separation scheme consisting of reactant conditions and irradiation conditions, in view of the fact that the values of both the separation factor and fractional conversion are simultaneously larger than the corresponding desired values. First, perform experiments to obtain several data points for S and $C_R(235)$ under fixed reactant conditions. Then estimate the value of S_0 from those data using the method proposed in this paper. If this value of S_0 is larger than the desired value of S, under the same reactant conditions, search for irradiation conditions that yield higher conversions than required, paying particular attention to the frequency and fluence of the Ω_2 because the conversion is strongly dependent on its frequency and fluence conditions. Then check whether the value of $C_R(235)$ obtained under the determined irradiation conditions is adequately large and that of S obtained is larger than the desired value. If they are satisfactory, one can finally decide the separation scheme (namely, reactant and irradiation conditions). If not, then change reactant conditions to attain a higher value of S_0 and repeat the procedure under those conditions.

4 Conclusions

We presented a functional equation which expresses how the separation factor in multifrequency IRMPD depends on the contrast ratio and intrinsic separation factor. From this relationship, it was found that the values of the contrast ratio and intrinsic separation factor are equally important for obtaining high separation factors, and the contrast ratio can be used as an index for quantifying the deterioration of the separation factor. The fluence conditions which raised the contrast ratio led to an increase in the separation factor.

Furthermore, this functional equation allows one to readily estimate the value of the intrinsic separation factor under definite reactant conditions. By using this estimation, we can evaluate the highest attainable value of the separation factor for the individual separation schemes in the laser isotope separation of UF_6 and consequently optimize the separation scheme.

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