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A NEW DECONVOLUTION TECHNIQUE IN BATCH ISOTOPE SEPARATION BY LASERS

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A new procedure has been proposed to investigate the effect of irradiation geometry and extract unbiased data from focused beam experiments in laser-induced photolysis and isotope separation. The model proposed here is shown to be advantageous over previous models experimentally and theoretically. The accuracy of this model was verified by comparing the parallel beam results and deconvoluted focused beam results using photolysis of CF_3Cl with O_2 added.

As a second step, the effectiveness of this method was tested for a binary system ($\text{CTF}_3/\text{CHF}_3$). By comparing the results with lenses of different focal length, the effect of focusing on selectivity was mathematically well described for two extreme cases: (1) tight focusing sufficient to produce cores with complete dissociation by one pulse near the focal spot for CTF_3 and CHF_3 , and (2) mild focusing without such cores. The advantage of performing the experiments with tightly-focused beam geometry before deconvolution experiments was also shown.

Introduction

The use of isotopically selective dissociation reactions induced by infrared laser beam is currently under investigation for such practical application goals as separation of ^{235}U , ^{13}C , ^2H (deuterium) and ^3H (tritium). For the development of this new technique, the following steps will be necessary. First, the most suitable working substance must be selected. Secondly, in batch experiments, reaction kinetics must be fully studied to obtain the best performance for the chosen working substance. In this step, such controllable variables as irradiation

wavelength, laser pulse duration, buffer gas pressure, gas temperature and pulse energy must be chosen to optimize the objective functions such as selectivity, operating pressure and reaction rate. At the same time, a study of a novel continuous reactor will be necessary for large-scale production. The continuous reactor should be so designed as to minimize deterioration of batch performance due to reflectivity loss, beam fluence inhomogeneity, back mixing, wall-catalyzed reaction and so on. Although the state of progress may vary from one isotope to another, the search for the optimal working substances is converging to a few substances, and most efforts are currently concentrated on the second step: optimization of reaction performance.

For ^{13}C separation, selectivity exceeding 60 at 13

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Table 1. Studies on the effects of irradiation geometry on multiphoton dissociation results

Authors	Beam profile	Geometry	Photon absorption	Scheme*	Ref.
Speiser Jortner	Homogeneous	Truncated double cone with cylinder (dog-bone) Eq. (1)	Optically thin $q = (\Phi/\Phi_c)^n$ $q = 1$	$\Phi < \Phi_c$ $\Phi \geq \Phi_c$	17
Fuss, Cotter	Homogeneous	Dobule-cone	Optically thin $q = (\Phi/\Phi_c)^n$ $q = 1$	$\Phi < \Phi_c$ $\Phi \geq \Phi_c$	4
Lyman Rockwood Freund	Homogeneous	Double-cone	Optically thin $q = 1 - \exp[-(\Phi/\Phi_c)^n]$ $q = 1$	$\Phi < \Phi_c$ $\Phi \geq \Phi_c$	12
Herman	Gaussian	Real envelope Eq. (5)	Optically thick $q = (\Phi/\Phi_c)^n$ $q = 1$	$\Phi < \Phi_c$ $\Phi \geq \Phi_c$	8
Hanazaki	Homogeneous	Real envelope	Optically thick $q = k_1 \Phi^n$ $q = k_2 \Phi^n$		6
This work	Homogeneous	Real envelope Eq. (5)	Optically thin $q = (\Phi/\Phi_c)^n$ $q = 1$	$\Phi < \Phi_c$ $\Phi \geq \Phi_c$	

* Intensity dependency of q assumed by some authors was rewritten as fluence dependency for comparison.

kPa was reported with CF_3Br by means of a specially designed short-pulse (2 ns) laser. This is considered a significant breakthrough in low to medium enrichment of ^{13}C .¹⁴⁾ Similar success was reported with a selectivity exceeding 10^4 for deuterium enrichment.¹⁶⁾ Tritium isotope separation by this method was first reported by our group,¹³⁾ and its unique feature lies in the achievement of high selectivity ($>10^3$) above 13 kPa with well-engineered standard pulse duration (1 μs).

In bath experiments of isotope separation by means of infrared multiphoton dissociation, it is quite often necessary to adopt focused beam geometry, since the dissociation threshold of most working substances is higher than the damage threshold of the window crystals, typically 3–6 J/cm². Consequently, the primary information obtained from such an experiment is the averaged quantities over the cell volume where the beam fluence is inhomogeneous.

For the analysis of batch experimental data for continuous reactor design, a more intrinsic relation has to be obtained from the volume-averaged results. This procedure can be called a deconvolution of batch data in laser isotope separation. **Table 1** summarises the models for the explanation of geometrical effects proposed by other groups. Since the multiphoton dissociation rate is primarily dependent on the fluence rather than the peak intensity, the intrinsic fractional conversion per pulse q is written as a function of the fluence in power-low fashion ($q \propto \Phi^n$).

Fuss and Cotter⁴⁾ and Hancock *et al.*⁷⁾ have shown that the specific dissociation rate becomes proportional to the 3/2 power of the pulse energy. But no procedure is shown to deconvolute the distributed-parameter results. Although Lyman *et al.*¹²⁾ showed such a deconvolution procedure, their procedure is based on a rather crude description of the irradiation geometry without finite diffraction-limited spot size.

Besides, as we will discuss later, the least-square fitting to obtain two necessary parameters in the 3/2-power region leads to an ambiguity in estimation.

Herman⁸⁾ derived an analytical solution for deconvolution when the absorbing gas is optically thick and the beam pattern is Gaussian. Since the multimode beam pattern is not Gaussian but rather close to a uniform profile,⁹⁾ his model cannot be applied to our case.

Hanazaki⁶⁾ and Speiser and Jortner¹⁷⁾ adopted non-zero spot size models. But Hanazaki's model is not suitable for deconvolution due to two reasons: (1) dependence of q on Φ he used does not correspond to our situation and (2) the suggested experimental technique cannot be applied to multi-component systems such as for isotope separation.

Although Speiser's model includes the finite spot size, his focused beam geometry is described with two truncated cones connected with a cylinder (so-called 'dog-bone' geometry). Though his model is originally not aimed for deconvolution, a deconvolution procedure can be considered. Consequently, Speiser's model is the only model to be compared with the model we propose for the case with optically thin media and uniform transverse profile. Therefore, in this paper, comparison will be made between our model and Speiser's model.

The relation between the volume-averaged conversion X and the number of irradiation pulses t was shown previously for the case of $\text{BCl}_3 + \text{H}_2\text{S}$.²⁰⁾ Multiphoton dissociation of CF_3Cl was chosen as a next model substance²³⁾ since it can be reacted by parallel laser beam and it is very convenient to study the intrinsic relations among the fluence Φ , the absorbed energy E_{abs} and the intrinsic fractional conversion per pulse q .

Meanwhile, in our recent paper¹⁹⁾ on laser tritium isotope separation, we first proposed a new decon-

Table 2. Conditions of batch irradiation experiments

	Reaction system	Partial pressure	Laser line	Pulse duration	Cell length	Focal length of lens	Laser
(I)	CF ₃ Cl O ₂	4 Torr 10 Torr	1090 cm ⁻¹	~ 1 μs	45 cm	52 cm	Lumonics 103
(II)	CHF ₃ CTF ₃	5 Torr 1 μ Torr	1075 cm ⁻¹	~ 1 μs	10 cm	7.5 cm	Lumonics 821
(III)	CHF ₃ CTF ₃	5 Torr 1 μ Torr	1075 cm ⁻¹	~ 1 μs	45 cm	38 cm	Lumonics 821

volution procedure, and it is needed to study the advantage of this method over other methods. The first object of the present report is to verify the validity of our method with the CF₃Cl system where both parallel and focused beam experiments are possible.

In such a case as removal of trace amount of tritium, direct tabulation of multiphoton absorption data of neat tritium compound (such as CTF₃) is not possible due to its high radioactivity. Our deconvolution procedure is thus inevitably for dilute isotopic mixture and is based on the empirical relation between the fluence and the fractional conversion per pulse to cope with such a restriction. Therefore, at first it is necessary to investigate the effect of this approximation in relation to a more intrinsic relation.

The second aim of this paper is to elucidate the geometrical bias on the measurement of the selectivity, which clarifies the roles of tight and mild focused experiments in kinetic studies.

1. Experimental

The reaction systems used were CF₃Cl/O₂ and CHF₃/CTF₃, and the experimental conditions are summarized in Table 2. The procedures of measurement were similar to those described in ref. 23 (infrared spectrophotometer) and ref. 19 (radio-gas chromatography).

Trifluorochloromethane CF₃Cl and trifluoromethane CHF₃ were obtained from Daikin Kogyo Co., Ltd. and purified by bulb-to-bulb distillation before use. Tritiated trifluoromethane CTF₃ was synthesized by isotopic exchange reaction with tritiated water HTO in the presence of NaOH and dimethylsulfoxide. The isotopic exchange rate was sufficiently fast even at 50°C.

Pulse energy is measured with a pyroelectric detector (Lumonics 20D). The standard deviation of the pulse energy measurements was typically 3% and long-term drifting of the laser energy during the irradiation period was usually less than 5%. The reproducibilities of radio-gas chromatography and spectroscopy measurement were 0.5% and 5%, respectively.

2. Mathematical Description

2.1 Speiser's model

Figure 1 illustrates the dimensions of the focused beam geometry. Speiser approximated the beam envelope with two truncated cones connected with a cylinder. It can be given by

$$r = r_f \quad Z < a' \quad (1a)$$

$$r = R(Z/L) \quad Z \geq a' \quad (1b)$$

To describe the fluence dependence of the intrinsic fractional conversion we may, like Speiser, use the mathematical expression given by

$$q = (\Phi/\Phi_c)^n \quad \text{for } \Phi < \Phi_c \quad (2a)$$

$$q = 1 \quad \text{for } \Phi \geq \Phi_c \quad (2b)$$

The specific dissociation rate b is a quantity averaged over the cell volume as defined by $-\ln(1-X)/t$ where X is the dissociated fraction after t -pulse irradiation. Let the dimensionless reaction volume and dimensionless fluence be defined by $Y = bV_{\text{cell}}/V_f$ and $F = \Phi/\Phi_c$ respectively, and the solution of Speiser's model is given by

$$Y = \left(1 + \frac{1 - \xi^{2n-3}}{2n-3}\right) \cdot F^n \quad \text{for } F < 1 \quad (3)$$

$$Y = \frac{2}{3} + \left(\frac{1}{3} + \frac{1}{2n-3}\right) F^{3/2} - \frac{\xi^{2n-3}}{2n-3} F^n \quad \text{for } F \geq 1 \quad (4)$$

where $\xi = r_f/R$ and $V_f = 2\pi r_f^2 a'$.

2.2 Our modified approach

Instead of Eq. (1), we adopt a more intrinsic description for the beam profile given by

$$r^2 = r_f^2 (1 + Z^2/a^2) \quad (5)$$

where a is the Rayleigh range.

Other assumptions are unchanged, except that V_f is redefined as $2\pi r_f^2 a$. The solution of our model is given by

$$Y = \Theta \cdot F^n \quad \text{for } F < 1 \quad (6)$$

$$\Theta = \int_0^{L/a} (1 + k^2)^{1-n} dk \quad (7)$$

and

Fig. 1. Dimensions of focused beam geometry for mathematical description by our model and by Speiser's model.

$$Y = (F-1)^{1/2} + \frac{1}{3} (F-1)^{3/2} + \Psi F^n \quad \text{for } F \geq 1 \quad (8)$$

$$\Psi = \int_{(F-1)^{1/2}}^{L/a} (1+k^2)^{1-n} dk \quad (9)$$

2.3 Comparison of the models

As stated in the preceding sections, the only difference in premises between Speiser's model and our approach lies in the way of describing the beam profile (Eqs. (1) and (5)). But the results of the deconvolution exhibit a significant difference. A numerical example is illustrated in Fig. 2 for the cases where n in Eq. (2a) is either equal to 4 or allowed to approach infinity.

First, Speiser's model and our model are compared for $n=4$. For $F > 3$, the difference of the two models is within a few percent and the slope in a bilogarithmic plot approaches $3/2$. The $3/2$ -power dependence ($Y \propto F^{3/2}$) can be expected from either Eq. (4) or Eq. (8), since the second term dominates the first term while the third terms in Eq. (4) or in Eq. (8) never become significant when $n > 2.5$ and $L/a > 3$. Speiser's mathematically simpler model can give a limiting form in the $3/2$ -power region as given by

$$Y \approx \left(\frac{1}{3} + \frac{1}{2n-3} \right) F^{3/2} \quad (10)$$

Equation (10) clearly shows that the least-square fitting in the $3/2$ -power region cannot give uniquely determined values for both n and Φ_c simultaneously. The slope of our model continuously increases from $3/2$ with decreasing F , while that of Speiser's model decreases from $3/2$ until F reaches unity and the slope increases below $F=1$. Thus, our model can be used to explain the experimentally observed slope between n and 1.5 , while Speiser's model cannot. The error in Φ_c due to Speiser's model can be seen as the horizontal distance between the curves for given Y in Fig. 2; for $n=4$ the error remains 19% for $F < 1$, increases for $1 < F < 1.3$, decreases for $F > 1.3$ and becomes negligible for $F > 3$.

It should be noted that 19% error in Φ_c results in 103% error in q for the same value of F in the n -th power region.

Fig. 2. Comparison of Speiser's model and our model for $n=4$ and $n \rightarrow \infty$ (simple dissociation threshold scheme).

If we set $n \rightarrow \infty$ in Eqs. (3) to (4) or in Eqs. (6) to (9), we can obtain solutions for both models based on the so-called simple dissociation threshold scheme (SDT scheme) where $q=1$ for $\Phi \geq \Phi_c$ and $q=0$ for $\Phi < \Phi_c$. Although this assumption is very crude, the simple dissociation threshold scheme is the simplest and is often used to estimate Φ_c .^{5,21)}

Another advantage in comparison of the cases for $n=4$ and $n \rightarrow \infty$ is that the fraction of reaction outside the 'core' region (where $q=1$) can be evaluated. In the $3/2$ -power region, from Eq. (10) the fraction reacted outside the core (where $q=1$) can be approximated by $\frac{1}{3} / \{ \frac{1}{3} + 1/(2n-3) \}$. More rigorous treatment with our model (Eqs. (8)–(9)) gives a general relation of the fraction reacted outside the core as a function of F and n as shown in Fig. 3 where V_1 and V_2 are reacted volume inside the core and outside the core, respectively.

The application of this SDT scheme underestimates the critical fluence Φ_c considerably. But as we show later, the beam geometry to enable this $3/2$ -power dependency can be easily attained by a short cell and a short focal length lens where $F \gg 1$. Therefore, before more rigorous experiments for deconvolution for $F < 1$, it is advantageous to perform an experiment in tightly focused geometry to design the batch experiment with roughly estimated Φ_c .

2.4 The effective spot size

It is not always very easy to measure the spot size of a tightly focused laser beam experimentally.

In this paper, therefore, we use a method to determine the spot size by means of the reaction rate measurement itself. This is of course possible when the slope of $\ln b$ vs. $\ln E_0$ plot varies from n of Eq. (2b) to $3/2$, since the simultaneous determination of the three parameters, n , Φ_c and r_f (or a) is possible. In the high E_0 region where the $3/2$ -power law holds,

Fig. 3. Generalized relation between the fraction of dissociated volume outside the core and F for different values of n .

Eq. (10) is a sufficiently good approximation of the asymptote for $F \rightarrow \infty$ as stated in 2.3. On the other hand, for low E_0 limit, our model should be used since Speiser's model gives quite erroneous results. Fortunately, the upper limit of finite integral L/a in Eq. (7) can be substituted with infinity without introducing a serious error for $n > 2.5$. It was numerically confirmed that the error due to such approximation is 4% at most for $L/a=3$ and $n=2.5$ and it decreases rapidly with increasing L/a and/or n . The values of L/a in the conditions (I), (II) and (III) (4.9, 34.5 and 7.3 respectively) and the values of n (5.2 for CF_3Cl , 2.5 for CTF_3 and 2.8 for CHF_3) satisfy such criterion. Such approximation is equivalent to assuming that there is no significant reaction occurring near the cell window. The intersection of the asymptotes in the plot of b vs. E_0 for both high and low E_0 limits gives the solution of Eqs. (6) and (10), from which the value a or the spot radius r_f can be determined.

2.5 Procedure of the deconvolution

The advantage of our model over Speiser's in describing the geometrical effect was illustrated in the preceding section. But a procedure to convert the experimentally obtained relation between b and E_0 into a more intrinsic relation between q and Φ has to be considered independently. This procedure is equivalent to determining the numerical values of n and Φ_c in Eq. (2a). After the relation (b, E_0) is obtained over a wide range, there should be a region where the slope in $\ln b$ vs. $\ln E_0$ plot is much larger than unity for small E_0 . The n in Eq. (2a) can be obtained as this slope. Since the value for the Rayleigh range a can be obtained through the procedure described in section 2.4, the dimensionless

reaction volume Y can be calculated. With known Y , F can be obtained from either Eq. (6) or Eq. (8). The latter case requires numerical iteration. And once F is known, q can be calculated from Eqs. (2a) or (2b) as a function of the fluence Φ at the beam waist. Thus, a set of data (b, E_0) can be converted to a set (q, Φ) .

3. Verification of Our Model: Photolysis of CF_3Cl

As in the case of the parallel beam experiment,²³⁾ the concentration of CF_3Cl decays in a pseudo-first order fashion with respect to the number of pulses. In the preceding report,²³⁾ it was confirmed that the sample gas is completely mixed after each pulse in this pressure range.

Figure 4 indicates the pulse energy (E_f) dependence of the specific dissociation rate b for $\text{CF}_3\text{Cl}/\text{O}_2$ system. The effective spot size was obtained as 0.012 cm^2 by the procedure mentioned in the previous section.

The value of n in the low E_0 region was found to be 5.2 while the slope in the $\ln b$ vs. $\ln E_0$ plot approaches 1.5 in the high E_0 region. Unfortunately, in this case, only an optically thick experiment is possible when experimental conditions such as the focal length of the lens and the cell length have to be designed so that the slope of the $\ln b$ vs. $\ln E_f$ plot covers from $3/2$ to n when the available pulse energy from the laser is given.

But the zone where the reaction actually takes place is relatively very small near the focal spot, and when the fluence at the focal spot is known, an optically thin treatment does not significantly affect the result. The multiphoton absorption of this system was investigated in the previous report²³⁾ and the result was summarized by the equation written as

$$-\frac{d\Phi}{dl} = A\Phi^m \quad (11)$$

where $m=1.3$ for this case and

$$A = \alpha P_{\text{CF}_3\text{Cl}}(1 + \beta P_{\text{O}_2}) \quad (12)$$

with $\beta = 0.30 \text{ kPa}^{-1}$ and $\alpha = 1.28 \times 10^{-2} \text{ J}^{1-m} \cdot \text{cm}^{2m-3} \cdot \text{kPa}^{-1}$ Figure 5 shows the calculated fluence profiles for three cases: (a) the one under optically thick condition as calculated with Eqs. (11), (12) and the beam envelope Eq. (5) by a stepwise calculation; (b) the profile based on the optical thin assumption with the same fluence at the focal spot as in case (a); and (c) the optically thin profile with the same fluence based on Speiser's model. Case (b) is a good approximation of case (a), while case (c) differs significantly from both cases.

Each point in Fig. 4 is converted by the deconvolution procedure described in the preceding section and the results are plotted in Fig. 6. The critical fluence Φ_c was obtained pointwise as shown in Fig. 7 and the averaged value according to our model (13

Fig. 4. Dependence of specific dissociation rate b on pulse energy E_f for $\text{CF}_3\text{Cl}/\text{O}_2$ system.

Fig. 5. Calculated fluence profiles along beam axis for three cases: (a) optically thick media with our model; (b) optically thin media with fluence equal to fluence at the focal spot in case (a) with our model; and (c) optically thin media with Speiser's model.

J/cm^2) was compared with that according to Speiser's model ($16 \text{ J}/\text{cm}^2$). Also shown in Fig. 6 is the result of the parallel beam experiment for the same gas mixing ratio.²³⁾ Agreement between the two cases is fairly good considering the approximate nature of the mathematical expression of the fluence dependence of q in Eqs. (2a) and (2b).

In the low fluence region, the deconvoluted results are slightly lower than the parallel beam data. This can be reasonably attributed to the mathematical description of the relation between q and Φ . Since q is expected to approach unity asymptotically with increasing Φ in reality, a model based on Eqs. (2a) and (2b) tends to overestimate q in the high Φ range while

Fig. 6. Deconvoluted results of focused beam experiments compared with parallel beam experiment: intrinsic conversion per pulse q as a function of fluence Φ .

Fig. 7. Critical fluence values for $\text{CF}_3\text{Cl}/\text{O}_2$ system.

it tends to underestimate q in the low Φ range.

When it is taken into consideration that an analytical solution can give a very clear-cut image of the limiting cases and assessment of the error involved, our modified approach is shown to be sufficiently accurate and convenient to use.

4. Application of Our Model to Isotopic Mixture ($\text{CTF}_3/\text{CHF}_3$)

For the two-component ($\text{CTF}_3/\text{CHF}_3$) system, the experimental conditions can be classified into three ranges: (1) $F_T < 1$, $F_H < 1$, (2) $F_T \geq 1$, $F_H < 1$, and (3) $F_T \geq 1$, $F_H \geq 1$.

A mildly focused geometry can be defined as one where the maximum fluence at the beam waist is close to or less than the critical fluences when the maximum available pulse energy is given.

A tightly focused geometry is the one where the condition F_T , $F_H > 1$ can be achieved at maximum pulse energy. While the condition $F_T < 1$ and $F_H < 1$

Fig. 8. Relation between dimensionless reaction volume Y_T ($\equiv b_T V_{\text{cell}}/V_f$) and fluence at beam waist for tightly and mildly focused geometries.

can be achieved by reducing E_0 for both geometries, the determination of the value n in Eq. (2a) in this region is prohibitively difficult in tightly focused geometry, since the specific rates become much smaller compared with those in mildly focused geometry.

Consequently, an experiment planned to be analysed with the deconvolution technique has to be performed under mildly focused geometry. On the other hand, tightly focused geometry ($F_T, F_H > 1$) is advantageous for a preliminary study since it does not require a series of experiments with different pulse energy. Since the pulse energy dependence of the specific dissociation rates b_T and b_H is clear ($b \propto E_0^{3/2}$) in this region, it is easy to normalize the pulse energy dependence and compare the results under different conditions on the same E_0 basis. The tightly focused geometry can be satisfied almost always without knowing the actual values of Φ_{cT} and Φ_{cH} with sufficiently short focal length lens.

In section 4.1, the usefulness and the limitation of the tightly focused geometry in estimation of Φ_c will be discussed.

The application of our deconvolution procedure to a two-isotopic component system gives insight in understanding the nature of experimentally obtained selectivity S as defined by b_T/b_H . In section 4.2, the geometrical bias on the selectivity will be discussed.

4.1 Estimation of the critical fluence

The pulse energy dependences of the specific dis-

Fig. 9. Deconvoluted result of Fig. 8: intrinsic conversion per pulse q as a function of fluence.

Fig. 10. Values of critical fluence Φ_{cT} obtained from results in Fig. 9 with $n=2.5$ as compared with Φ'_{cT} based on simple threshold assumption ($n \rightarrow \infty$).

sociation rates for CTF_3 and CHF_3 for experimental conditions (II) and (III) (Table 2) are shown in a bilogarithmic plot in Fig. 8. To conjugate different geometries, the dimensionless reaction volume Y ($\equiv b V_{\text{cell}}/V_f$) rather than b is plotted on the ordinate. The spot size of the tightly focused geometry was estimated on the basis of the assumption that the beam divergence obtained in mildly focused geometry remained unchanged. The slopes for CTF_3 and CHF_3 in Fig. 8 for a tightly focused geometry (condition (II)) approach 1.5 while those for mildly focused geometries are 2.5 and 2.8, respectively. Figure 9 shows the result of deconvolution: q as a function of Φ . Meanwhile, the critical fluence Φ_{cT} was calculated and is plotted against the fluence Φ in Fig. 10 according to our model. Φ_{cT} based on Speiser's model is shown for comparison. Speiser's model overestimates the value of Φ_{cT} by 20%.

The average value of Φ_{cT} according to our model obtained from the mildly focused geometry experiment is 136 J/cm^2 . If the value for n_T obtained from a

mildly focused geometry is adopted, an averaged value for Φ_{cT} can be calculated as 119 J/cm² for the tightly focused geometry experiment. Since these values are close, our model and the deconvolution procedure were shown to be consistent and applicable to different geometries. Since the value for n in Eq. (2a) cannot be determined from a tightly focused geometry, the simple dissociation threshold scheme ($n \rightarrow \infty$) is suited for preliminary survey as a first step and its limitation must be quantitatively evaluated.

The critical fluence based on this assumption Φ'_{cT} was also plotted against Φ in Fig. 10. The values for Φ'_{cT} are independent of the fluence and are approximately 40% less than the average value for Φ_{cT} with $n=2.5$. This difference corresponds to the fact that the application of the simple threshold assumption ($n \rightarrow \infty$) underestimates Φ_c by a factor of $[(1/3)/\{(1/3) + (2n-3)^{-1}\}]^{2/3}$ according to Eq. (10). The difference between Φ_{cT} and Φ'_{cT} in Fig. 10 suggests that the experiments in tightly focused geometry are of limited value in estimation of the critical fluence without knowing the exact value of n .

Consequently, this geometry is good for rough estimation of Φ_c for the design of a more rigorous experiment for deconvolution, but is not suited for accurate measurement of Φ_c .

4.2 Geometrical bias on the selectivity

The selectivity in the region $F_T, F_H < 1$ can be written as

$$S = Y_T/Y_H = \zeta S_0 \quad (13)$$

where

$$\zeta = \frac{\Theta_T}{\Theta_H} = \frac{\int_0^{L/a} (1+k^2)^{1-n_T} dk}{\int_0^{L/a} (1+k^2)^{1-n_H} dk} \quad (14)$$

So long as $n_T \sim n_H$, ζ does not deviate significantly from unity. This fact ensures that $S (=b_T/b_H)$ under the condition $F_T, F_H < 1$ is an acceptable approximation for the intrinsic selectivity $S_0 (=q_T/q_H)$. The values of S_0 and S are compared in Fig. 11.

The selectivity S directly obtained from experiments tends to overestimate the intrinsic selectivity S_0 by 20% in this case.

The apparent selectivity for tightly focused geometry $S_{t.f.} (=b_T/b_H)$ can be approximated by

$$S_{t.f.} = Y_T/Y_H = \left(\frac{\frac{1}{3} + \frac{1}{2n_T - 3}}{\frac{1}{3} + \frac{1}{2n_H - 3}} \right) \left(\frac{\Phi_{cH}}{\Phi_{cT}} \right)^{3/2} \quad (15)$$

while $S_0 (=q_T/q_H)$ in this region is obviously unity. Since n_T and n_H do not differ very much in most cases, Eq. (15) is further simplified to

$$S_{t.f.} \simeq (\Phi_{cH}/\Phi_{cT})^{3/2} \quad (16)$$

Fig. 11. Comparison of S_0 and S for $F_T, F_H < 1$.

Fig. 12. Comparison between experimentally obtained values for $S_{t.f.}$ for $F_T, F_H < 1$ and theoretical value based on Eq. (16).

Information with respect to the intrinsic selectivity at $F_T=1$ is of practical significance in design for tritium removal. The intrinsic selectivity at $F_T=1$ (S_0^*) can be roughly estimated from this result, since it is given by

$$S_0^* = (\Phi_{cH}/\Phi_{cT})^{n_H} \simeq S_{t.f.}^{2n_H/3} \quad (17)$$

Even if the value of n_H is not precisely known, the possible range of value of S_0 at $F_T=1$ can be estimated since the value of n_H is typically between 3 and 6 for an isotopically selective pressure region.¹⁹⁾

Using previously obtained values for Φ_{cT} and Φ_{cH} in mildly focused geometry,¹⁹⁾ $S_{t.f.}$ was calculated from Eq. (16), which can be compared with experimental selectivity in Fig. 12. The agreement of the experimental data with calculation is within the range of error in measurement.

Concluding Remarks

Our deconvolution technique was shown to be sufficiently accurate and convenient in obtaining the intrinsic relation between the fractional conversion per pulse and the fluence from the results in focused beam experiments. The critical fluence for a resonant isotopic compound such as CTF₃ (Φ_{cT}) obtained through this procedure is an important factor in assessing the scale of the laser required for given separative work, since it gives the minimum required fluence to remove tritium nearly completely by one

irradiation. This technique can also be used to evaluate the bias in batch selectivity measurement. The intrinsic selectivity at the critical fluence of CTF_3 (S_0^*) thus obtained gives the maximum enrichment factor.

When the data for Φ_{cT} and S_0^* in various experimental conditions are tabulated, the optimum condition for a given working substance will be clarified. For such a purpose, this new technique will become a very useful tool.

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Nomenclature

a	= Rayleigh range defined by Eq. (5)	[cm]
a'	= Half-length of the central cylinder of Speiser's geometry	[cm]
b	= $-(1/t) \ln(1-X)$ = specific dissociation rate	[—]
E_f	= pulse energy at the focal spot	[J]
E_0	= incident pulse energy	[J]
F	= Φ/Φ_c = dimensionless fluence	[—]
k	= integration parameter in Eqs. (7) and (9)	[—]
l	= axial distance	[cm]
L	= cell half-length	[cm]
m	= parameter in Eq. (11)	[—]
n	= parameter in Eq. (2a)	[—]
$P_{\text{CF}_3\text{Cl}}$	= CF_3Cl partial pressure	[kPa]
P_{O_2}	= O_2 partial pressure	[kPa]
q	= intrinsic fractional conversion per pulse	[—]
R	= beam radius at the window	[cm]
r	= radius of the beam	[cm]
r_f	= focal radius	[cm]
S	= b_T/b_H = apparent selectivity	[—]
S_0	= q_T/q_H = intrinsic selectivity	[—]
$S_{t,f}$	= b_T/b_H for $F_T, F_H > 1$ = apparent selectivity in tightly focused geometry	[—]
t	= number of pulses	[—]
V_1	= reacted volume inside the core ($q=1$)	[cm ³]
V_2	= reacted volume outside the core ($q<1$)	[cm ³]
V_{cell}	= cell volume	[cm ³]
V_f	= $2\pi r_f^2 a'$ for Speiser's model, $2\pi r_f^2 a$ for our model = focal volume	[cm ³]
Y	= dimensionless dissociation volume	[—]
Z	= axial distance from the focal spot	[cm]
α	= parameter in Eq. (12)	[J ^{1-m} ·cm ^{2m-3} ·kPa ⁻¹]
β	= parameter in Eq. (12)	[kPa ⁻¹]
A	= parameter in Eq. (11)	[J ^{1-m} ·cm ^{2m-3}]
Φ	= fluence	[J/cm ²]
Φ_c	= critical fluence	[J/cm ²]
Φ_c'	= critical fluence based on simple dissociation threshold assumption	[J/cm ²]

Θ	= defined by Eq. (7)	[—]
Ψ	= defined by Eq. (9)	[—]

<Subscripts>

H	= CHF_3
T	= CTF_3

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