

Modelling of multifrequency IRMPD for laser isotope separation

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Abstract. The process of infrared multiple photon dissociation (IRMPD) of molecules is of great fundamental importance and has practical significance, such as isotope separation etc. Unfortunately, a clear insight into the process has been hindered by the bewildering array of important variables affecting MPD. The dissociation probability $g(f)$ i.e. the yield has been found to be a sensitive function of laser fluence f along with numerous other parameters like laser frequency, gas pressure etc. We have shown that in single frequency IRMPD, an accurate quantitative characterization of the dissociation probability can be adequately expressed by a 'power law' model with two fitting parameters namely critical fluence, f_c and multiphoton order, m . This model was exploited in analysing our MPD results on various systems. However, the small isotope shift encountered in heavy elements and the sticking phenomenon observed in small light molecules restrict respectively the separation factor and the dissociation yield. These problems can effectively be tackled by irradiation with multifrequency laser beams which can be chosen appropriately on the basis of spectroscopic features. Based on our success in single frequency model, multifrequency IRMPD is modelled by a functional form containing the product of power law terms for individual fluences on irradiation frequencies. This model is successfully benchmarked with our experimental results on multifrequency LIS of tritium. Such knowledge can be utilized for appropriate separation process design, evaluation and optimization.

Keywords. Multifrequency multiphoton dissociation; laser isotope separation; tritium separation.

1. Introduction

A most exciting discovery in nonlinear laser chemistry is the phenomenon of infrared multiple photon excitation (IRMPE) and dissociation (IRMPD) of molecules.^{1–4} In MPE or MPD a molecule could be highly excited and eventually dissociated through frequency selective absorption of tens of photons from an IR laser. The process is of great fundamental importance and has far reaching scientific and practical significance, such as isotope separation, purification of materials, synthesis of novel molecules and even mode-selective chemistry. Currently, the main thrust is aimed at developing a workable separation method for ²³⁵U, the fissile isotope of uranium needed to fuel light water reactors. In addition there is promising market for isotope of light elements such as D, T, ⁶Li, ¹⁰B, ¹³C, ¹⁸O, ³³S etc., some in connection with energy production and others as tracers in analytical, medical and environmental studies. Unfortunately, a clear insight into the process has been hindered by the bewildering array of important variables

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affecting MPD. Therefore, the research in understanding the principles involved remains an ongoing endeavour.

Currently one of the viable enrichment method is provided by irradiation of a low pressure gas sample with a high intensity pulsed IR laser, causing MPD. For this often the laser beam has to be focused to obtain the necessary fluence for MPD and this causes a fluence variation over many orders of magnitude within the irradiation volume. The dissociation probability $g(f)$, i.e. the yield has been found to be a sensitive function of laser fluence along with other parameters like laser frequency, gas pressure etc. To assess the spatially averaged data obtained in MPD experiments, an accurate quantitative characterization of the dissociation probability is necessary by a suitable deconvolution procedure.

Such accurate quantitative modelling of the fluence dependence of the fractional dissociation per pulse is necessary to attain high separation factors and high fractional yields at the same time. We have shown that for single frequency IRMPD⁵, the fractional dissociation per pulse, q can be adequately expressed by a 'power law' model with two fitting parameters. This model was exploited in analysing our MPD results on various systems.⁶ It has been verified experimentally that the values of the parameter n are nearly identical for both resonant and off-resonant excitation in several molecules. In such cases the fluence dependence of conversion, both for a desirable isotope and for an undesirable one, can be easily determined from a small number of data points. As a consequence, the model allows to determine readily the condition for desired fractional yields and separation factors.

However, the small isotope shift encountered in heavy elements and also the sticking phenomenon observed in small molecules⁷ restrict the separation factor and the dissociation yield respectively. These problems can effectively be tackled by irradiation with multifrequency laser beam which can be chosen appropriately on the basis of spectroscopic features. In absence of a model function, very large amounts of data in multi-dimensional space are necessary to find the fluence conditions for desired yields and separation factors. Even when sufficient data are gathered after considerable effort, it may be difficult to interpret the fluence dependence inductively and find the desired condition systematically. Here, we present a model for multifrequency IRMPD using a uniform transverse profiled and focused laser beam for an optically thin sample. The dissociation probability is expressed by a functional form based on the product of power law terms for individual fluences of irradiation frequencies. Then this model is applied to our experimental results on multifrequency laser isotope separation of tritium.

2. Experimental

We present briefly the experimental arrangement as it has been described in detail elsewhere.^{8,9} Trifluoromethane-T (CTF₃) was prepared by hydrogen isotope exchange of CHF₃ with tritiated water in the presence of dimethyl sulphoxide and NaOH. Typically, the CHF₃ samples used in our experiment had 0.2 ppm of CTF₃.

A commercial CO₂ laser (Lumonics TEA103-2) was used for irradiation experiments. The 2.2 m long cavity of the laser (discharge cross section = 9 cm²) was formed with a Littrow mounted blazed grating and a Ge output mirror ($R = 10$ m). Typically when the grating is tuned to resonate for a particular rotational line, the resonance condition may as well hold for a few neighbouring rotational lines provided the output mirror has a concave geometry. The low gain lines, owing to their smaller population inversion,

saturate at the slower rate, thus resulting in an overall reduction in competition among themselves. Hence, even with a partial spatial overlap, a group of neighbouring low gain lines may simultaneously grow to give multifrequency output. Thus, by an appropriate tuning of the grating angle to satisfy the resonance condition, different sets of lines can be made to lase simultaneously. The pulse energy was measured by a pyroelectric joule meter and frequencies were measured by a spectrum analyser. The transverse profile of the laser beam was found to have uniform profile.

All irradiations were carried out at room temperature in a pyrex cell (30 cm in length and 3.5 cm in diameter) equipped with polished KCl windows. Focussing of the laser beam was done at the centre of the cell by a BaF₂ lens ($f=25$ cm).

Irradiated samples were cryogenically transferred to a radio-gas chromatograph (GC) for analysis. The radio-GC consisted of a commercial GC (Shimadzu GC-R1A) equipped with thermal conductivity detector (TCD) and an indigenously built proportional counter (10 ml, 3 kV) for the analysis of tritium bearing species. A Porapak Q column (80–100 mesh, 2 mm id, 2 m long) was used at 35°C with He carrier gas (flow rate 25 ml/min) to separate the only photoproduct C₂F₄ from the starting tritiated fluoroform. The depletion in CTF₃ and CHF₃ could be simultaneously measured by the counter and TCD respectively. The C₂F₄ peak was also used to countercheck the CHF₃ dissociation.

3. Model for single frequency excitation

In a typical MPD experiment, a laser beam propagates centrally and axially through a cylindrical cell and is focused in the centre of the cell, while keeping the fluence at the cell windows lower than the damage threshold (typically 3–5 J cm⁻² for KCl or KBr windows). The schematic diagram of the focused beam geometry is shown in figure 1. The experimental dissociation yield may be expressed in terms of reaction volume V_R , which is defined as the product of the observed cell averaged specific dissociation rate, d and the cell volume V_{cell} : $V_R = d \times V_{\text{cell}}$. Now the data analysis consists of derivation of parameters specific to the molecule from the values of V_R which are the result of both molecular effect and the details of the geometry of the focused laser beam used. Ideally, this would involve the determination of the molecular dissociation probability, $g(f)$ as a function of the fluence f which is related to V_R by

$$V_R = \int_{\text{cell}} g(f) dV. \quad (1)$$

At least four different models^{10–14} have been reported for such evaluation. We have shown that in single frequency IRMPD, such deconvolution can be effectively performed by a ‘power law’ model with two fitting parameters namely critical fluence, f_c and order of the process, n .

$$q = g(f) = (ff_c)^n, \text{ for } f < f_c \\ = 1, \quad \text{for } f \geq f_c. \quad (2)$$

where q is the local dissociation probability function and f_c is the critical fluence.

In this model, two important criteria such as optical thickness of the sample and transverse profile of the laser beam need to be considered. Since most LIS experiments

involve excitation/dissociation of minor isotope, the sample can be treated as optically thin. Single transverse mode (TEM_{00}) laser provides Gaussian beam profile while multi-mode laser has uniform or flat-top beam profile. Therefore, this model in an optically thin medium can be evaluated depending on whether the laser beam is Gaussian or uniform. The transverse and axial distribution g and f are shown in the figure 1 for both the beam profiles. Since our working laser beam profile is closer to uniform, here we present only the treatment for uniform beam profile.

The beam envelope in the reaction cell can be expressed by

$$r^2 = r_f^2 (1 + z^2/a^2), \quad (3)$$

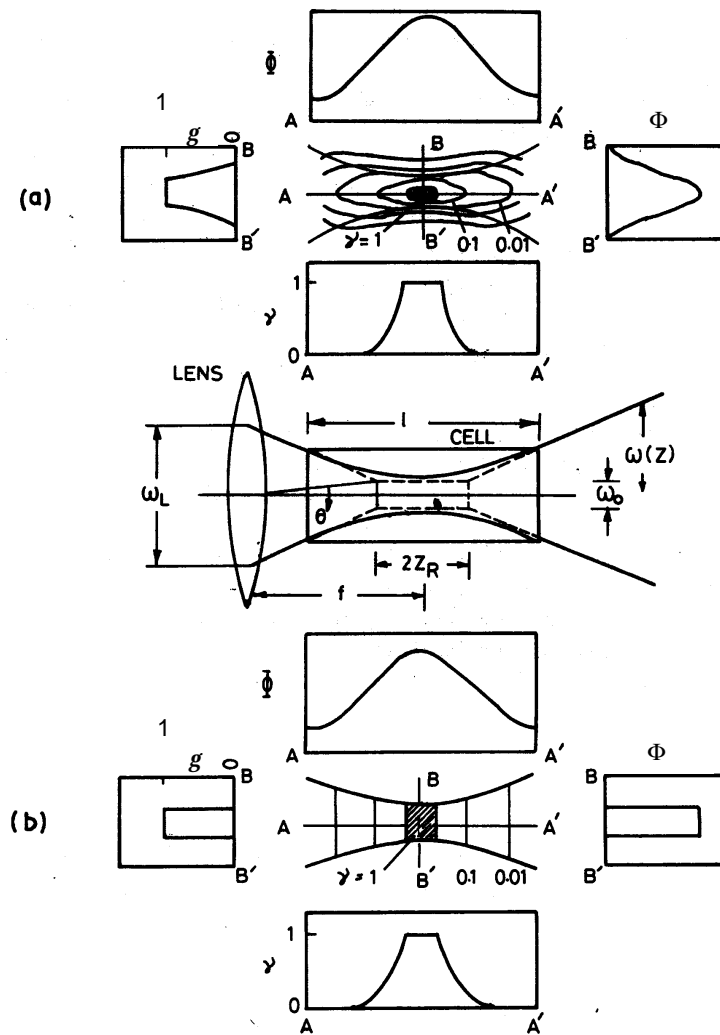


Figure 1. Schematic diagram of the focused beam geometry used in MPD experiments (middle). The transverse and axial distribution of g and f are also shown for (a) Gaussian and (b) uniform profiled beams.

where a is the Rayleigh range, r_f focal spot radius and r is the radius of the irradiated zone at a distance z from the focal point. The dimensionless reaction volume, Y is defined as (V_R/V_f) where the reaction volume V_R normalized by the focal volume, $V_f = 2\mathbf{p}_f^2 a$. The dimensionless fluence F is defined as the fluence \mathbf{f}_0 at the beam-waist normalized by the critical fluence \mathbf{f}_c , $F = \mathbf{f}_0/\mathbf{f}_c$. Denoting $\mathbf{g}(\mathbf{f})$ as q and $2L$ as the cell length

$$V_R = \int_{\text{cell}} q dV = 2 \int_0^L q \mathbf{p}^2 dz. \tag{4}$$

Under the condition of $\mathbf{f}_0 < \mathbf{f}_c$, using expression for beam envelope for r and the relation $\mathbf{f}_0 \mathbf{p}_f^2 = \mathbf{f} \mathbf{p}^2$, and putting $z/a = k$,

$$Y = F^n \int_0^{L/a} (1+k^2)^{1-n} dk. \tag{5}$$

However, for $\mathbf{f}_0 \geq \mathbf{f}_c$ the region of focusing beam envelope can be split into two regions; from $z=0$ to $z=l_c$ where $\mathbf{f} \geq \mathbf{f}_c$ and from $z=l_c$ to $z=L$ where $\mathbf{f} < \mathbf{f}_c$, and the reaction volume is given by:

$$V_R = 2 \left(\int_0^{l_c} q dV + \int_{l_c}^L q dV \right). \tag{6}$$

Using expressions for q in the two regions and replacing z/a by k , for the case of $\mathbf{f}_0 \geq \mathbf{f}_c$

$$Y = (F-1)^{1/2} + 1/3(F-1)^{3/2} + F^n \int_{(F-1)^{1/2}}^{L/a} (1+k^2)^{1-n} dk. \tag{7}$$

First, we present some sample calculations to examine the sensitivity of fluence to the dissociation yield. This is to examine whether the pulse profile dependence predicted by the model actually holds to an acceptable degree for realistic cases. The result of sample calculations is presented in figure 2 which shows the n and \mathbf{f}_c dependence. In a separate study⁶ the evaluation with a Gaussian beam profile was carried out and is incorporated in the above figure, for $n=3$. Comparing the two curves for $n=3$ it is evident that in the region of $F < 1$ (or $\mathbf{f} < \mathbf{f}_c$), the agreement is good, however the Gaussian beam treatment yields about a 10% higher value of critical fluence. From the above exercise, two important conclusions can be drawn. Firstly, it shows how the fluence dependence can change over to finally give a 3/2 power dependence which is generally observed under tight focusing irradiation geometry. Secondly, the approximate independence of the pulse profile for fixed fluence condition indicate that it may not be very critical for data analysis if the laser sometimes unpredictably gets mode-locked.

After this fruitful exercise, the model was applied in analysing results of IRMPD of various systems investigated in our laboratory. Here, we present the results on tritium removal from contaminated reactor water. Table 1 gives the yields and selectivities for

IRMPD of 8.5 Torr of $\text{CHF}_3/\text{CTF}_3$ with and without 20 Torr of Ar under single and quadruple frequency irradiation.

The important finding is almost a ten-fold increase in selectivity by distributing 1J of energy of a single line over four lines. Distributing the total laser fluence over several frequencies led to a reduction of intensities on each frequency required for the individual excitation steps. In addition, one can in principle build up the selectivity by taking advantage of multiplication of the selectivity attained in the individual excitation step.¹⁵

4. Model for multiple frequency excitation

Based on our success on single frequency work, we present a model for such multi-frequency IRMPD. In this model, the dissociation probability is expressed simply by the product of power law terms for individual fluences on irradiation frequencies, ($\Omega_1, \Omega_2, \dots, \Omega_N$). In this case the function $g(\mathbf{f}_i)$ can be given as

$$q = g(\mathbf{f}_i) = \begin{cases} (\mathbf{f}_i / \mathbf{f}_{ci})^n, & \text{for } \mathbf{f}_i < \mathbf{f}_{ci} \\ 1, & \text{for } \mathbf{f}_i \geq \mathbf{f}_{ci} \end{cases} \quad (8)$$

where \mathbf{f}_i is the fluence of the individual beam Ω_i ($i = 1, 2, \dots, N$) and \mathbf{f}_{ci} is the critical fluence for each beam where the value of g saturates to unity. Then for a system with one dissociation channel, q is expressed by the product of the functions $g(\mathbf{f}_i)$:

$$q = \prod_{i=1}^N g(\mathbf{f}_i), \text{ where } N \text{ is the total number of frequencies.} \quad (9)$$

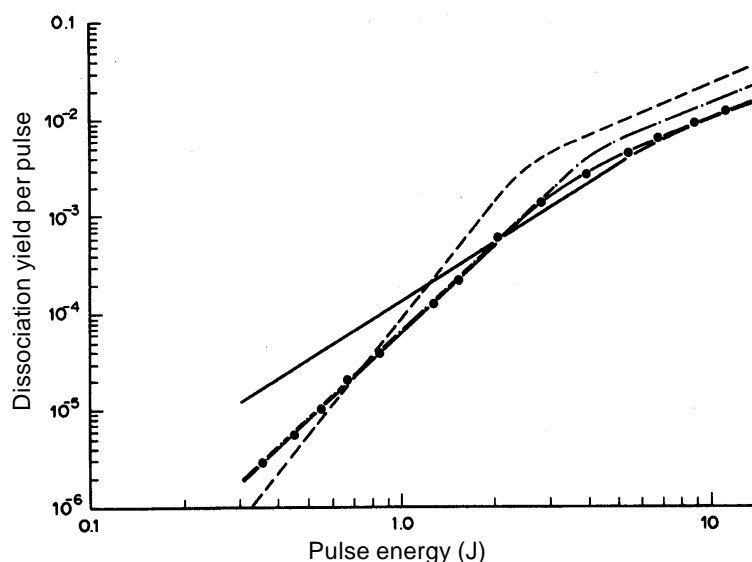


Figure 2. Model calculations of the dissociation yield with a uniform profiled laser pulse as a function of incident pulse energy; (----) $n = 4$, $f_c = 25 \text{ J cm}^{-2}$, (-.-.-) $n = 3$, $f_c = 40 \text{ J cm}^{-2}$, (—) $n = 2$, $f_c = 70 \text{ J cm}^{-2}$. Also shown is the yield curve for a Gaussian laser beam with $n = 3$, $f_c = 44 \text{ J cm}^{-2}$.

Table 1. Yields and selectivities for IRMPD of 8.5 Torr of CHF₃/CTF₃ with and without 20 Torr of Ar under single and quadruple frequency irradiation.

Line/E (J)	Line/E (J)	Line/E (J)	Line/E (J)	P_{Ar} (Torr)	d_H ($\times 10^5$)	d_T ($\times 10^5$)	S (T/H)
9R (8) 1.0	–	–	–	–	1.44	5.38	3.74
9R (8) 1.0	–	–	–	20	3.60	14.57	4.05
–	–	9R (12) 1.0	–	–	4.40	10.60	2.41
–	–	9R (12) 1.0	–	20	3.43	9.09	2.65
9R (8) 0.22	R (10) 0.26	R (12) 0.25	R (14) 0.27	–	0.34	4.73	13.91
9R (8) 0.22	R (10) 0.26	R (12) 0.25	R (14) 0.27	20	0.28	10.73	38.32
9R (20) 0.25	R (22) 0.30	R (24) 0.23	R (26) 0.22	–	0.38	1.98	5.21
9R (20) 0.25	R (22) 0.30	R (24) 0.23	R (26) 0.22	20	0.34	4.31	12.69

Generally speaking we have to consider the possibility of more than one channel for dissociation induced by different combination of frequencies. For instance, in two frequency (Ω_1, Ω_2) irradiation the molecule may be dissociated through three channels: dissociation only by Ω_1 , only by Ω_2 and by Ω_1 plus Ω_2 . However, all these three channels may not be always significant. Expressing the dissociation yield for each of these three channels by q_1, q_2 and q_3 , and because the dissociation through these channels occurs independently, q can be related to q_i 's by the equation:

$$(1-q) = (1-q_1).(1-q_2).(1-q_3). \quad (10)$$

For values of q_i much smaller than unity, this becomes

$$q = \sum_{j=1}^M q_j, \quad (11)$$

where M is the number of dissociation channels and q_j 's can be evaluated following the earlier prescription.

If the focal fluence of each individual frequencies is less than \mathcal{F}_{ci} , then as in the single frequency case, since q_1 and q_2 are due to single frequency,

$$Y_1 = F_1^{n1} \int_0^{L/a} (1+k^2)^{1-n1} dk, \quad (12)$$

$$Y_2 = F_2^{n2} \int_0^{L/a} (1+k^2)^{1-n2} dk, \quad (13)$$

where $F_1 = \mathbf{f}_{0,1}/\mathbf{f}_{c,1}$ and $F_2 = \mathbf{f}_{0,2}/\mathbf{f}_{c,2}$. The third channel is due to two frequencies Ω_1 plus Ω_2 and yield is given by

$$Y_3 = 2F_{11}^{n_1'} \int_0^{L/a} (1+k^2)^{1-n_1'-n_2'} dk, \quad (14)$$

where $F_{11} = \mathbf{f}_{0,1}/\mathbf{f}_{c,1}$ and $F_{22} = \mathbf{f}_{0,2}/\mathbf{f}_{c,2}$. The primed quantities $\mathbf{f}_{c,i}$ and n_i' designate the third dissociation channel. The addition of Y_1 , Y_2 and Y_3 gives the normalized dissociation yield for two frequencies with three dissociation channels.

Now applying this model to our present investigation, four frequencies were used for excitation (Ω_1 , Ω_2 , Ω_3 and Ω_4). The fluence in the irradiation zone was such that there would be negligible dissociation due to individual single frequency or with any combination of two frequencies. This leaves four channels of dissociation due to the combination of three frequencies and one channel due to all the four frequencies. Let the dissociation probabilities of these five channels be q_1 , q_2 , q_3 , q_4 and q_5 respectively. Since the exciting frequencies were neighbouring laser lines, we can assume $q_1 = q_2 = q_3 = q_4$. Hence overall q can be approximated as $(4q_1 + q_5)$. Putting this in the expression for V_R and solving for Y we get,

$$Y = 12F_1^{n_1} F_2^{n_2} F_3^{n_3} \int_0^{L/a} (1+k^2)^{1-n_1-n_2-n_3} dk + 4F_{11}^{n_1'} F_{22}^{n_2'} F_{33}^{n_3'} F_{44}^{n_4'} \int_0^{L/a} (1+k^2)^{1-n_1'-n_2'-n_3'-n_4'} dk. \quad (15)$$

A large number of parametric experiments need to be carried out to determine the values of F_i , F_{ii} , n_i and n_i' for evaluation of Y . Under the limited number of present experiments, further simplifications can be done by assuming F_i and F_{ii} 's to be equal since the total energy of $1J$ is distributed almost equally and also by taking a single value n (n') for all n_i (n_i') for neighbouring four frequencies.

Table 2 represent the model parameters for IRMPD of 8.5 Torr of $\text{CHF}_3/\text{CTF}_3$ with 20 Torr of Ar under single and quadruple frequency irradiation. It can be seen that the

Table 2. Model parameters for IRMPD of 8.5 Torr of $\text{CHF}_3/\text{CTF}_3$ with 20 Torr of Ar under single and quadruple frequency irradiation.

Line	\mathbf{f}_{cT} (J/cm ²)	\mathbf{f}_{cH} (J/cm ²)	n	n'	Y (Expt.)	Y (Theor.)	S (T/H)
9R (8)	48	—	3.0	—	5.8	5.66	
	—	144	2.5	—	1.43	1.45	4.05
9R (12)	66	—	3.0	—	3.62	3.67	
	—	150	2.5	—	1.37	1.36	2.65
9R (8)–R (14)	60	—	1.5	0.6	4.2	3.6	
	—	175	1.5	0.6	0.12	0.16	36.8
9R (20)–(26)	63	—	1.4	0.5	1.7	1.6	
	—	172	1.4	0.5	0.14	0.13	12.3

yield and selectivity are satisfactorily evaluated using the model. The increase in critical fluence for the undesired species (in this case CHF_3) in multiple frequency irradiation compared to single frequency case improved the selectivity of the process.

5. Conclusions

The present model has a simple form based on the model established for single frequency dissociation and at the same time has the flexibility to be applicable to multi-channel dissociation. Having successfully extracted the values of the fitting parameters for a specific molecule, the expected yield and selectivity can be accurately calculated for varying experimental conditions. Such knowledge can be utilized for appropriate design, evaluation and optimisation of laser separation process.

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