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Evaluation of quantum and photoproduct yields in multiple-photon dissociation for isotope separation

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A model is constructed which evaluates the minority isotope photoproduct yield and the number of photons required per unit product for isotope separation via infrared multiple-photon dissociation by a Gaussian beam. Under most experimental conditions, these parameters are optimized if the peak central fluence is about twice the saturation fluence. The quantum yield and the photoproduct yield are then both about half that attainable if the same laser energy were instead delivered by a beam with a flat transverse profile. Specific applications to deuterium separation are also discussed.

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I. INTRODUCTION

Technological and economical evaluation of laser-assisted isotope separation schemes require an accurate characterization and optimization of both the quantum efficiency and net yield of the process. These properties are easily determined by linear extrapolation of the experimental data for single quantum isotope separation techniques, such as for D, ^{13}C , or ^{18}O separation by ultraviolet laser predissociation of formaldehyde.¹ However, for processes utilizing more than a single quantum, such as infrared multiple-photon dissociation (MPD), the quantum yield and net yield of the rare isotope photoproduct are sensitive to the laser fluence (and intensity) and to the transverse beam profile. This study addresses the general characterization of these properties for MPD by an unfocused Gaussian beam.

Using a parameterized functional characterization to describe the laser-dependent dissociation probability and the absorption coefficient for the rare and abundant isotopes, analytic expressions for quantities such as the quantum yield, photoproduct yield of each isotope, and the isotopic enrichment factor are derived in Sec. II. Successful practical isotope separation is shown to be sensitive to a number of laser and molecular parameters. Notably, the nature of the transverse beam profile—Gaussian vs rectangular—can dramatically affect the outcome of isotope separation experiments. In Sec. III the application of these findings to deuterium isotope separation is briefly considered.

II. THE MODEL

The nature of the laser-molecule interaction in multiple-photon absorption and dissociation is becoming increasingly better characterized. For example, the rate equation approximation² is currently believed to well-describe the detailed statistical evolution of an ensemble of molecules undergoing (incoherent) multiple-photon absorption. However, such a detailed picture of the molecular evolution is not required in this study; instead, only empirical models of the molecular dissociation probability and the absorption cross section—which describe the ensemble averaged respective molecular properties—are employed here.

Consider a gas-phase mixture of molecules $X\text{D}$, with density n_{D} that contains the rare isotope D, and molecules $X\text{H}$, with density n_{H} that contains the abundant species H. In the example concerning deuterium separation described below, D and H in fact represent deuterium and hydrogen, respectively. For an unfocused laser beam of given pulse energy E and a given fluence ϕ incident on the mixture, the number of $X\text{D}$ molecules decomposed per pulse N_{D} by MPD in a cylindrical volume of length Δl , may be determined from the model presented below, which incorporates several molecular parameters. Similarly, the total number of photons absorbed by the medium, N_{photon} may be evaluated. Then the ratio, $Q \equiv N_{\text{photon}}/N_{\text{D}}$, equals the number of photons that need to be absorbed by the medium to separate a single rare isotope atom D; $1/Q$ is the quantum yield.

A commonly used model^{3,4} for MPD, valid for fluences sufficiently above threshold, is assumed:

$$D(\phi) = p \left(\frac{\phi}{\phi_{\text{sat}}} \right)^m, \quad 0.1\phi_{\text{sat}} \leq \phi \leq \phi_{\text{sat}} \quad (1a)$$

$$= p, \quad \phi \geq \phi_{\text{sat}}, \quad (1b)$$

where $D(\phi)$ is the local dissociation probability function, which can assume values from 0 to $p (< 1)$; $D(\phi)$ depends on ϕ , the spatially dependent local fluence; ϕ_{sat} , the saturation fluence; and p , a parameter that is usually 1 (but which may lie within $0 < p < 1$ because only a fraction of all $X\text{D}$ molecules present may effectively interact with the laser). For most molecules, the value of m lies within the range 2–4.^{5–8} This characterization of the dissociation probability is appropriate for the critical range of fluences in which D is a rapidly varying function of ϕ , i.e., from threshold, where $D < 1\%$, to “saturation”, where $D > 90\%$.

The number of $X\text{D}$ molecules that dissociate after irradiation by a single pulse in the volume under examination is

$$N_{\text{D}} = n_{\text{D}} \Delta l \int \int D(\phi(r, \theta)) r dr d\theta, \quad (2)$$

where r and θ are the usual cylindrical coordinates. For a Gaussian beam with an electric field effective radius ω , Eq. (2) is readily integrated³ to yield

$$N_D^{\text{Gaus}} = n_D \Delta l p \frac{\pi \omega^2}{2m} \left(\frac{\phi_0}{\phi_{\text{sat}}} \right)^m, \quad \phi_0 \leq \phi_{\text{sat}} \quad (3a)$$

$$= n_D \Delta l p \frac{\pi \omega^2}{2} \left(\ln \frac{\phi_0}{\phi_{\text{sat}}} + \frac{1}{m} \right) \quad \phi_0 \geq \phi_{\text{sat}},$$

where $\phi(r) \equiv (2E/\pi\omega^2) \exp(-2r^2/\omega^2)$ and ϕ_0 is the peak central fluence ($\equiv 2E/\pi\omega^2$).

The number of photons absorbed within this same volume N_{photon} , is

$$N_{\text{photon}} = \frac{\Delta l}{h\nu} \left\{ \iint [n_D \sigma_D(\phi) + n_H \sigma_H(\phi)] \phi(r) r dr d\theta \right\}, \quad (4)$$

where $\sigma_D(\phi)$ and $\sigma_H(\phi)$ are the absorption cross sections for the two molecules, and $h\nu$ is the photon energy. Experimental studies^{4,9} have shown that at low fluences ($\phi \ll 0.01\phi_{\text{sat}}$) σ is independent of ϕ ; however, the net absorption cross section decreases with increasing fluence at higher ϕ . This occurs because the molecular cross section to absorb a photon (at the ground-state resonant frequency) decreases as the energy of the absorbing vibrational level increases. For $\phi \geq 0.01\phi_{\text{sat}}$, the following parameterization^{4,10} is successful in describing the absorption of infrared photons in resonantly absorbing XD molecules interacting with an intense pulsed infrared field:

$$\sigma_D(\phi) = \frac{A}{\phi^\gamma} \quad 0.01\phi_{\text{sat}} \lesssim \phi \leq \phi_{\text{sat}}, \quad (5)$$

where the value of γ lies in the range $0 < \gamma < 1$. (γ must be < 1 since the number of quanta a molecule absorbs $\sigma\phi$ must increase with ϕ .) Judd¹¹ has shown that above a critical fluence, which is $\ll \phi_{\text{sat}}$, many molecules obey Eq. (5) with $\gamma \cong 1/3$.

Since when $\phi = \phi_{\text{sat}}$ all resonant molecules decompose, A may be determined from the number of photons a given molecule must absorb to dissociate, N ; this leads to $A = Nh\nu\phi_{\text{sat}}^{\gamma-1}$. Under collision-free conditions, N equals the number of quanta needed to reach the dissociation barrier plus the additional number of photons that are absorbed in the molecular continuum before the molecule dissociates. This continuum absorption depends on the laser intensity and wavelength, the molecular absorption coefficient, and the level-dependent molecular dissociation lifetime. In a collisional regime, N may be even higher due to energy siphoning from XD to XH . For $\phi > \phi_{\text{sat}}$, σ_D is simply obtained by the condition that XD cannot absorb more than N quanta:

$$\sigma_D(\phi) = Nh\nu/\phi, \quad \phi \geq \phi_{\text{sat}}. \quad (6)$$

The decomposition products have been assumed to be transparent at the laser frequency in this study. Also note that since in well-designed experiments the abundant isotope will absorb very little energy, σ_H will be assumed to be independent of fluence in the following analysis.

Equation (4) is readily evaluated for a Gaussian profile:

$$N_{\text{photon}}^{\text{Gaus}} = n_D \Delta l \frac{\pi \omega^2}{2} N \left[\frac{1}{1-\gamma} \left(\frac{\phi_0}{\phi_{\text{sat}}} \right)^{1-\gamma} + \frac{n_H}{n_D} \left(\frac{\sigma_H}{Nh\nu/\phi_{\text{sat}}} \right) \frac{\phi_0}{\phi_{\text{sat}}} \right], \quad \phi_0 \leq \phi_{\text{sat}} \quad (7a)$$

$$= n_D \Delta l \frac{\pi \omega^2}{2} N \left[\frac{1}{1-\gamma} + \ln \frac{\phi_0}{\phi_{\text{sat}}} + \frac{n_H}{n_D} \left(\frac{\sigma_H}{Nh\nu/\phi_{\text{sat}}} \right) \frac{\phi_0}{\phi_{\text{sat}}} \right], \quad \phi_0 \geq \phi_{\text{sat}} \quad (7b)$$

In this result, Eq. (5) has been assumed to be valid at very low fluences, $\phi < 0.01\phi_{\text{sat}}$, as well as in the indicated range. Since the number of photons a molecule absorbs at these very low fluences is quite small, < 1 , this is a good approximation.

The number of photons that are extracted from the laser per dissociated XD molecule Q is then given by

$$N_{\text{photon}}/N_D:$$

$$Q^{\text{Gaus}} = \frac{Nm}{p} \left(\frac{x^{1-\gamma-m}}{1-\gamma} + \frac{x^{1-m}}{\delta S} \right), \quad x < 1 \quad (\phi_0 \leq \phi_{\text{sat}}), \quad (8a)$$

$$= \frac{N}{p} \frac{1/(1-\gamma) + \ln x + (1/\delta S)x}{1/m + \ln x}, \quad x \geq 1 \quad (\phi_0 \geq \phi_{\text{sat}}), \quad (8b),$$

where $x \equiv \phi_0/\phi_{\text{sat}}$, $\delta \equiv n_D/(n_H + n_D)$ is the rare isotope concentration, and $S \equiv \sigma_D(\phi_{\text{sat}})/\sigma_H = (Nh\nu/\phi_{\text{sat}})/\sigma_H$ is the absorption isotopic selectivity at the saturation fluence.

The photon utilization factor Q and the photoproduct yield N_D are the two most important parameters in isotope separation. A third significant variable is the density of photoproduct χ ; it may be important in considerations of the necessary depletion of the rare isotope (per pulse) and gas pumping speed, and is defined here as

$$\chi = \frac{N_D/\Delta l}{\pi \rho^2}, \quad (9)$$

where ρ is chosen as the radius within which lies, say, 90% of the photoproduct yield. For a Gaussian beam

$$\chi^{\text{Gaus}} = n_D p \frac{m \ln x + 1}{m \ln x + \ln 10 - \ln(1 + m \ln x)}. \quad (10)$$

In some systems, such as in deuterium separation by MPD of 2,2-dichloro-1,1,1-trifluoroethane,⁶ the abundant isotope may noticeably dissociate at fluences not much greater than the saturation fluence for XD . Then Eq. (1), with suitably subscripted (D or H) p , m , and ϕ_{sat} parameters, can be used to describe the dissociation of either XD or XH . In particular, Eq. (3) can be employed to determine the isotope enrichment factor β . For the most significant fluence regime of $\phi_{\text{sat,H}} > \phi_0 > \phi_{\text{sat,D}}$ (ignoring possible isotopic scrambling and chain reactions):

$$\beta \equiv \frac{N_D^{\text{Gaus}}/N_H^{\text{Gaus}}}{n_D/n_H} \quad (11a)$$

$$= \frac{p_D m_H f^{m_H}}{p_H} \left(\frac{\ln x + 1/m_D}{x^{m_H}} \right), \quad 1 < x < f \quad (11b)$$

where $f \equiv \phi_{\text{sat,H}}/\phi_{\text{sat,D}} \gg 1$ and still $x = \phi_0/\phi_{\text{sat,D}}$. Of course, under these circumstances σ_H will no longer be truly independent of fluence, as is assumed throughout this study.

The above results for a Gaussian beam may be compared to those for an idealized circular flat transverse profile of radius ω , characterized by $\phi = \phi_0$ ($r < \omega$), $\phi = 0$ ($r > \omega$), and $\phi_0 = E/\pi\omega^2$. N_D , N_{photon} , and Q are readily obtained:

$$N_D^{\text{Flat}} = n_D \Delta l p \pi \omega^2 x^m, \quad x < 1, \quad (12a)$$

$$= n_D \Delta l p \pi \omega^2, \quad x > 1, \quad (12b)$$

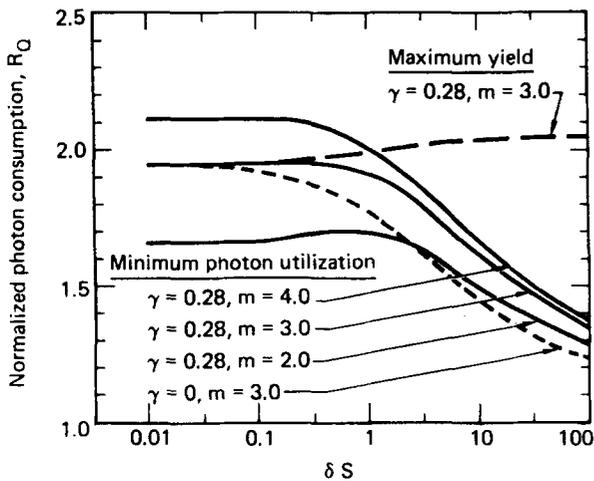


FIG. 1. The number of photons required to produce a single separated minority atom for an incident Gaussian beam, normalized by the number required if instead all the laser energy were concentrated in a flat beam, $R_Q \equiv Q^{\text{Gaus}}/Q^{\text{Flat}}$, is plotted vs δS —subject to either the minimum photon utilization or maximum yield constraint.

$$N_{\text{photon}}^{\text{Flat}} = n_D \Delta l \pi \omega^2 N (x^{1-\gamma} + x/\delta S), \quad x \leq 1, \quad (13a)$$

$$= n_D \Delta l \pi \omega^2 N (1 + x/\delta S), \quad x \geq 1, \quad (13b)$$

$$Q^{\text{Flat}} = (N/p) [x^{1-\gamma-m} + (1/\delta S)x^{1-m}], \quad x \leq 1, \quad (14a)$$

$$= (N/p) [1 + x/\delta S], \quad x \geq 1. \quad (14b)$$

Armed with the above expressions, either the quantum yield or photoproduct yield may be maximized for a specified pulse energy, E , but varying peak central fluence ϕ_0 . Minimizing Q^{Gaus} [Eq. (8)] leads to the implicit equation

$$x \ln x = \delta S \left(\frac{1}{1-\gamma} - \frac{1}{m} \right) + x \left(1 - \frac{1}{m} \right) \quad (15)$$

for the best value of x . For a flat transverse profile, Eq. (14) gives $x = 1$. The alternate restriction, that of maximizing XD decomposition, is obtained from either Eq. (3) or (12). For the Gaussian beam $x = \exp(1 - 1/m)$, while for the flat beam $x \geq 1$. [Maximum density χ occurs at $x = e^{9/m}$ (Gaussian) or $x \geq 1$ (Flat).] These extremum values for x may be inserted into the appropriate expressions to obtain the ensuing values for photon utilization and yield. (σ_H has been assumed to be a constant; extension to a more general fluence dependence is straightforward.)

Figures 1 and 2 portray a general parameterization of photon utilization and yield obtained for a fixed laser pulse energy. In Fig. 1, R_Q , the ratio of the average number of photons required to dissociate a single XD molecule in a Gaussian beam to that in a flat beam, is plotted vs δS . The quantity δS provides a measure of the ratio of absorption in XD to XH at saturation for the flat beam. Specifically, curves are plotted for $\gamma = 0.28$; $m = 2, 3$, or 4 and $\gamma = 0$; $m = 3$ for optimized quantum yield, and for $\gamma = 0.28$, $m = 3$ for maximized yield. The employed range of parameters is typical of isotope separation experiments, and has direct relevance to the example of deuterium separation to be discussed below. Note that the (flat beam) normalization constant is evaluated at ϕ_{sat} , and contains the important factor $(1 + 1/\delta S)$.

Even with optimized photon utilization, Fig. 1 shows

that 1.4 to 2.1 times as many quanta are needed to obtain each separated D minority isotope atom for the Gaussian beam *vis-a-vis* the flat beam. For $\delta S < 0.3$, R_Q is independent of δS , while for higher δS , R_Q decreases (improves). Of course, Q^{Gaus} actually decreases much faster with increasing δS through the entire range of δS than is shown for R_Q due to the normalization constant in R_Q [which is $\propto (1 + 1/\delta S)$]. In contrast, under the constraint of maximized yield, the photon utilization ratio slowly increases with increased δS . For a given pair of (γ, m) , R_Q is the same under either constraint for $\delta S < 0.3$.

Figure 2 exhibits the ratio of the yield for a Gaussian beam to that for a flat beam ($x = 1$) R_D as a function of δS for a given pulse energy. Curves for the parameters $\gamma = 0.28$; $m = 2, 3$, or 4 and $\gamma = 0$; $m = 3$ are plotted for the condition of minimum photon consumption, and for $m = 2, 3$, or 4 under the constraint of maximum yield. For maximum yield, R_D is approximately 0.5, increasing with decreasing m , and is independent of δS and γ . For optimized photon utilization, R_D is also optimized for $\delta S < 0.3$, and is therefore also equal to the value obtained under the yield constraint. However, in this case the yield significantly decreases at higher δS , which is in contrast to the results for the yield constraint. Note that for either constraint $R_D(\delta S = 0) = 1/R_Q(\delta S = 0) = \exp(1/m - 1)$.

It is clear from Figs. 1 and 2 that an idealized flat (or any flatter than Gaussian) beam is always preferable to the Gaussian from both quantum and photoproduct yield considerations. For $\delta S \ll 0.3$, the optimal central Gaussian beam fluence is the same under either constraint [$\phi_0 = \phi_{\text{sat}} \exp(1 - 1/m)$], leading to equal yield and photon absorption for either case. For small δS this central fluence is approximately twice the saturation fluence; specifically $x = (1.65, 1.95, 2.12)$ for $m = (2, 3, 4)$. More generally, when $\delta S \rightarrow 0$, $Q^{\text{Gaus}}(\phi) \propto 1/N_D^{\text{Gaus}}$ and $R_Q = 1/R_D$. At higher values of $\delta S (> 1)$, under either of the two constraints, the nonoptimized variable attains increasingly unfavorable values as δS increases. The question of whether quantum efficiency or photoproduct yield should be sacrificed for the other depends on the conditions of the experiment.

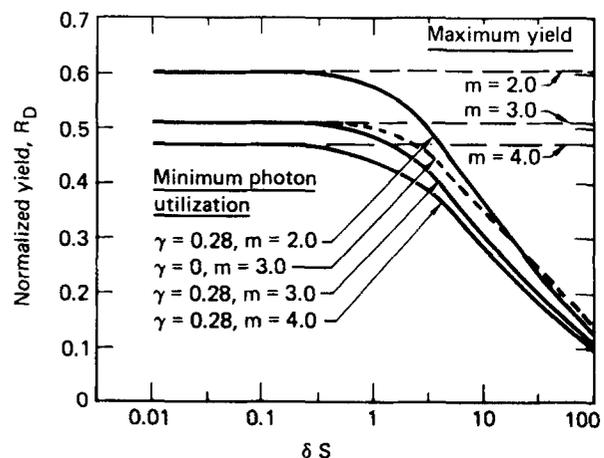


FIG. 2. The number of separated minority atoms produced by a Gaussian beam, normalized by the number formed by a flat beam, $R_D \equiv N_D^{\text{Gaus}}/N_D^{\text{Flat}}$, is portrayed vs δS —subject to either the minimum photon utilization or maximum yield constraint.

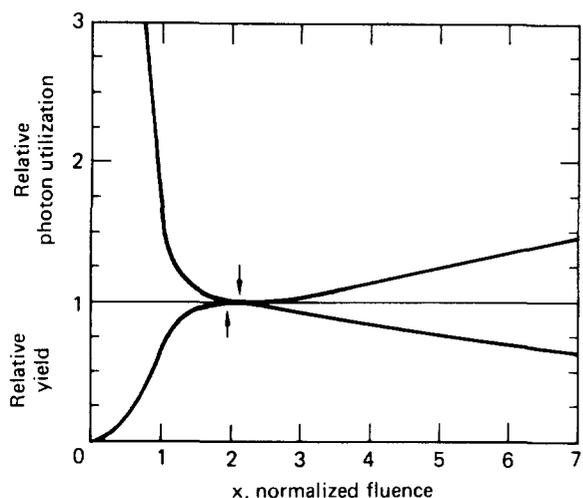


FIG. 3. The yield and photon utilization number for a Gaussian beam are plotted showing the dependence on the normalized peak laser fluence x for a given laser pulse energy. Both variables have been normalized by their optimal values, which occur at a peak central fluence of about twice the saturation fluence ($x \approx 2$), as depicted by the arrows.

The sensitivity of the photon utilization number, Q^{Gaus} and the photoproduct yield N_D^{Gaus} to the exact value of ϕ_0 is portrayed in Fig. 3 for $m = 3$, $\gamma = 0.28$, $S = 1200$, and $1/\delta = 6500$ (typical values in deuterium separation⁴). Though the quantum yield is maximized for $x \approx 2.13$, Q^{Gaus} and N_D^{Gaus} are insensitive to small variations about this value. It should be realized that for $x \gg 2.13$, aberrations from the plotted Q^{Gaus} may occur due to nonlinear absorption by XH , and also to increased values of N due to larger photon absorption in the molecular continuum. In addition, as stated earlier, for $\phi_0 \gg \phi_{\text{sat}}$, XH may begin to dissociate, leading to rapidly decreasing enrichment factors at high fluences.

Another issue which is important in reactor design relates to the depletion factor, i.e., the fraction of all molecules which enter the laser interaction area (in a transverse gas flow arrangement) which are dissociated. For a flat beam, essentially all XD molecules flowing into the target area can be decomposed, i.e., this is very little "dead" cross-sectional area. This is not the case for a Gaussian beam. Even assuming optimized yield, the effective transverse area of dissociated XD molecules is only $\pi\omega^2 p/2$ [$\equiv N_D/(n_D \Delta l)$]. To insure nonlossy propagation through the reaction cell, its effective cross-sectional diameter must be $\geq 6\omega$. Therefore unless gas flow is slow and there is sufficient gas mixing between laser pulses, the net fractional depletion of XD will be small. Maximization of the density of photoproduct χ [Eq. (10)] leads to $x = \exp(9/m)$ and a cross-sectional area of $(\pi\omega^2 p/2)(10/m)$. For $m = 3$ this leads a threefold improvement in depletion compared to the optimized yield case. However, the greatly decreased quantum and photoproduct yields at the required high fluences, combined with an increase in the likelihood of gas breakdown, will usually militate against employing depletion factor maximization. (Of course, if low-loss waveguide propagation were feasible, the depletion factor could be made quite large at fluence levels determined by the yield condition.)

The importance of the net overall deuterium depletion in the photochemical reactor has been analyzed by researchers at Ontario Hydro¹² and has been posed as a tradeoff between high pumping costs and degraded photoproduct parameters. For example, with a high pumping speed, pumping costs will be high but each laser pulse interacts with a fresh reactant mixture containing a relatively high deuterium content. With a slower pumping speed and mixing of the reactants in the reactor between pulses, a much smaller total volume of material needs to be processed suggesting much lower pumping costs; however, in this case the laser interacts with a mixture with a lower average deuterium fractional content δ and possibly also with absorbing photoproducts, thereby hurting the quantum yield. Note that the quantum yield ($1/Q$) varies approximately as δ . Since these researchers have shown that pumping costs are so high that a net dissociation of 80–90% of all molecules entering the reactor is required, the above analysis has quite important implications.

This analysis also shows that a flat beam is to be much preferred over a beam with a smoother transverse profile with long wings, such as the Gaussian beamshape. However, a non-Gaussian profiled laser beam, especially one tailored to have rather sharp edges, will not propagate well for long distances. One way to make the transverse beam shape flatter, thereby significantly improving all the photochemical parameters, is to irradiate the sample with several simultaneous and parallel, yet transversely overlapping independent Gaussian beams, possibly at different wavelengths. For example, consider the case of four independent beams of equal radius each centered at a vertex of a square of length approximately equal to this beam radius. Since MPD is relatively insensitive to the coherence and wavelength (within a given range), the net field is significantly flatter than a Gaussian while still effective for MPD. Therefore the optimal peak central fluence of each beam, as well as the total fluence at any point due to the influence of several beams, may be considerably lower than in the purely Gaussian case. For a given pulse energy, fewer photons are wasted in XH absorption in regions of high fluence—thereby much improving the quantum yield and enrichment factor—and in XD absorption in the wings—where there is little decomposition of XD .

III. APPLICATION TO DEUTERIUM SEPARATION

CO_2 laser multiple photon photolysis of $\text{CDF}_3/\text{CHF}_3$ mixtures at $10.3 \mu\text{m}$ has been studied in detail and has been found to be nearly photochemically ideal for deuterium separation.⁴ Optimal values of the quantum and deuterium-product yields are needed for a meaningful technical comparison to the widely used G - S process ($\text{H}_2\text{S}/\text{H}_2\text{O}$ chemical exchange) and other candidate photochemical routes.¹ Employing the models described in this study, the MPD of CDF_3 using 2 nsec duration, Gaussian profiled CO_2 laser pulses incident on mixtures of $\text{CDF}_3/\text{CHF}_3$ with 1 atm of argon added can be characterized by the following parameters⁴: $\phi_{\text{sat}} = 20 \text{ J/cm}^2$, $p = 1$, $m = 3$, $\gamma = 0.28$, $S = 1200$, and $1/\delta \approx 6500$. N is approximately equal to 28, of which 25 quanta are required to reach the CDF_3 dissociation barrier

TABLE I. Photon utilization and photoproduct yield for D/H separation by CDF₁ IR photolysis.

Case ^a	x ^b	Q ^{Quant}	$N_D^{\text{Quant}}/N_D^{\text{Quant}}(x_{\text{Base}})$
Base ^a	2.13	352	1.000
$m = 2$	1.81	302	1.181
$m = 4$	2.32	380	0.920
$\gamma = 0.23$	2.12	349	1.001
$\gamma = 0.35$	2.16	355	0.999
$\phi_{\text{sat}} = 15$ J/cm ²	2.13	352	1.333
$\phi_{\text{sat}} = 25$ J/cm ²	2.13	352	0.800
$S = 1000$	2.10	411	1.001
$S = 1400$	2.16	309	0.999

^aBase case is $\phi_{\text{sat}} = 20$ J/cm², $p = 1$, $m = 3$, $\gamma = 0.28$, $S = 1200$, $1/\delta = 6500$, and $N = 28$. In each case *only* the noted parameter is varied.
^bValue of x for maximized quantum yield.

and an additional 3 photons are absorbed in the continuum before decomposition; depending on the CHF₃ pressure, N may be slightly larger than 28 because CDF₃ → CHF₃ energy transfer.

For this base case, $x = 2.13$ for maximum quantum yield, corresponding to a peak central fluence of 43 J/cm². 352 infrared photons are required to yield a single deuterium atom, of which an average of 55 quanta are actually absorbed by CDF₃ molecules. This last number should be compared to $N = 28$. For optimized photoproduct yield, $x = 1.95$ (39 J/cm²), which leads to essentially the same photon utilization ($Q = 353$) and yield. Note that this relative insensitivity to ϕ_0 was earlier depicted in Fig. 3 for the same parameter values as used here.

The changes in Q and N_D due to small variations in the base case parameters (for fixed pulse energy) are the same for either the quantum or photoproduct yield constraint, though the optimal fluence may slightly differ. A representative set of variations from the base case is shown in Table I for minimized photon utilization. Note that in this Table the

variations in γ and ϕ_{sat} are constrained by the condition that the optical selectivity maintains the same value at ϕ_{sat} .

IV. CONCLUDING REMARKS

The described model may be further refined, for example, by use of more exact or intensity-dependent models for the dissociation probability D and is easily adapted to variations in experimental conditions, such as the use of two frequency MPD, the inclusion of absorption by photoproducts, or the variation in transverse profile during propagation. The considerations presented in this study should lead to much more meaningful appraisal of MPD isotope separation schemes.

ACKNOWLEDGMENTS

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¹J. Marling, J. Chem. Phys. **66**, 4200 (1977); for another example of single photon (deuterium) isotope separation see: D. S. Y. Hsu and T. J. Manuccia, Appl. Phys. Lett. **33**, 915 (1978).

²See for example, J. Stone and M. F. Goodman, J. Chem. Phys. **71**, 408 (1979); J. R. Barker, J. Chem. Phys. **72**, 3686 (1980).

³I. P. Herman, Opt. Lett. **4**, 403 (1979).

⁴J. B. Marling, I. P. Herman, and S. J. Thomas, J. Chem. Phys. **72**, 5603 (1980).

⁵I. P. Herman and J. B. Marling, Chem. Phys. Lett. **64**, 75 (1979).

⁶J. B. Marling and I. P. Herman, Appl. Phys. Lett. **34**, 439 (1979).

⁷J. D. Campbell, G. Hancock, and K. H. Welge, Chem. Phys. Lett. **43**, 581 (1976).

⁸M. Quack, Ber. Bunsenges. Phys. Chem. **83**, 757 (1979).

⁹J. G. Black, P. Kolodner, M. J. Shultz, E. Yablonovitch, and N. Bloembergen, Phys. Rev. A **19**, 704 (1979).

¹⁰R. A. Lucht, J. S. Beardall, R. C. Kennedy, G. W. Sullivan, and J. P. Rink, Opt. Lett. **4**, 216 (1979).

¹¹O. P. Judd, J. Chem. Phys. **71**, 4515 (1979).

¹²K. B. Woodall and J. O'Neill (private communication); M. F. Kresovic, Ontario Hydro Research Division Report No. E79-85-K, Ontario, Canada, 1980.