

# Carbon isotope separation by multiphoton dissociation of $\text{CF}_3\text{I}$

S. Bittenson and P. L. Houston

Department of Chemistry, Cornell University, Ithaca, New York 14853  
(Received 7 July 1977)

A selective multiphoton dissociation process has been used to enrich carbon-13 in  $\text{CF}_3\text{I}$ . A separation factor of nearly 600 has been achieved for irradiation of 0.1 torr of  $\text{CF}_3\text{I}$  at  $-80^\circ\text{C}$  with the  $R(14)$  line of the  $9.6\ \mu\text{CO}_2$  laser transition. An investigation of the dependence of the enrichment factor on pressure indicates that collisions during the dissociation are effective in destroying the selectivity. The multiphoton dissociation is quite efficient. At laser energy fluences of  $1.2\ \text{J}/\text{cm}^2$ , one in every 11 absorbed photons contributes its energy to the breaking of the C-I bond.

## I. INTRODUCTION

Multiphoton dissociation of molecules using pulsed infrared lasers has been the object of extensive investigation<sup>1-9</sup> following the observation by Isenor and Richardson<sup>10</sup> of dissociation in the intense field of a TEA  $\text{CO}_2$  laser. An important application of this technique is to the separation of isotopically labeled molecules, as reviewed in Refs. 11-14. Enrichment in the isotopes of H,<sup>15,16</sup> B,<sup>17-20</sup> C,<sup>20,21</sup> Si,<sup>20</sup> Cl,<sup>21</sup> S,<sup>21-23</sup> and Os<sup>24</sup> has been reported.

In this paper we report the multiphoton dissociation of  $\text{CF}_3\text{I}$ .<sup>25</sup> We have used this dissociation to separate carbon isotopes. Multiphoton dissociation in the structurally similar molecules  $\text{CCl}_3\text{F}$  and  $\text{CF}_3\text{Cl}$  has recently been reported by Dever and Grunwald.<sup>7</sup> These authors used a focused  $\text{CO}_2$  laser to obtain up to 1.6% conversion of the parent molecule per flash at about 60 torr of pressure. No investigation of the isotopic selectivity was reported. Lyman and Rockwood<sup>20</sup> enriched carbon-13 by multiphoton dissociation of  $\text{CF}_2\text{Cl}_2$  (Freon-12). The  $^{13}\text{C}/^{12}\text{C}$  ratio of the starting material was increased by a factor of 1.65 by selectively dissociating  $^{12}\text{CF}_2\text{Cl}_2$ . Our use of  $\text{CF}_3\text{I}$  for investigation of the multiphoton process offers several advantages. Carbon is the only element of this molecule for which more than one isotope occurs naturally. This property considerably simplifies the mass spectral analysis. In addition,  $\text{CF}_3\text{I}$  can be dissociated at intensities as low as  $5\ \text{MW}/\text{cm}^2$ . An unfocused TEA  $\text{CO}_2$  laser gives sufficient power so that a measurable fraction of starting material may be dissociated in fewer than 100 shots at one torr in a reasonable cell volume. Finally, very high isotope separation factors may be achieved in  $\text{CF}_3\text{I}$ . In excess of 15% of the molecules in the beam can be dissociated per laser pulse at high intensities, and enrichment factors of nearly 600 have been obtained.

The interaction of  $\text{CO}_2$  laser radiation with  $\text{CF}_3\text{I}$  has been reported previously. By using a microwave-infrared double resonance scheme, Jones and Kohler<sup>26</sup> have shown that the  $R(16)$  line of the  $9.6\ \mu\text{CO}_2$  band is coincident with the  $R(7)$ ,  $K=2$ ,  $F=19/2-21/2$  transition of the  $\nu_1\text{CF}_3\text{I}$  band. The absorption coefficient can be inferred from their data to be on the order of  $0.23\ \text{cm}^{-1}\text{torr}^{-1}$ . By using an infrared-infrared double resonance scheme, Petersen *et al.*<sup>27</sup> have observed an increase in absorption at  $1052\ \text{cm}^{-1}$  following the excitation of  $\text{CF}_3\text{I}$  at  $1075\ \text{cm}^{-1}$

with a pulsed  $\text{CO}_2$  laser. This observation indicates that an appreciable excited state population in  $\text{CF}_3\text{I}$  may be obtained.

## II. EXPERIMENTAL

$\text{CF}_3\text{I}$  dissociation was achieved with a grating tuned  $\text{CO}_2$  TEA laser (Tachisto Corporation model 215 laser head) producing a maximum of 1 J single line output in 60 nsec FWHM. Roughly half of the total energy appears in a 400 nsec tail following the main pulse. A 30 cm focal length sodium chloride lens was used to focus the radiation through polished NaCl windows into cylindrical Pyrex sample cells. The dimensions of the cells were adjusted to meet requirements of individual experiments. Cell lengths ranged from 5 to 30 cm when focusing was used, and from 5 to 114 cm when the laser was used unfocused. Species identification, concentrations, and isotope ratios were determined with a Perkin Elmer model 521 grating infrared spectrometer and a Consolidated Engineering Corporation type 21-103A mass spectrometer.

Laser power was measured with a Scientech model 360001 laser power meter. The pulse intensity was taken to be one-half of the measured energy per pulse in 60 nsec over the mean irradiated area of a sample. Beam areas were recorded on thermal sensing paper stock and were not corrected for laser mode structure or external diffraction effects. An intracavity aperture near the output mirror was used to restrict lasing to low order transverse modes, and an external aperture was generally used to reduce the beam area to  $0.5\ \text{cm}^2$ .

Trifluoromethyl iodide was used as supplied by PCR Incorporated after out-gassing at  $77^\circ\text{K}$ , and sample pressures were measured with an MKS Instruments capacitance manometer.

## III. RESULTS AND DISCUSSION

### A. Definitions

For pressures below 1.0 torr, the multiphoton process selectively dissociates  $^{12}\text{CF}_3\text{I}$ . We define below the parameters necessary to describe this selectivity.

Following Lyman and Rockwood<sup>20</sup> and Benedict and Pigford,<sup>28</sup> let  $\beta$ , be the ratio of reactant isotope abundances before and after irradiation:

$$\beta_r = [n_{13}/n_{12}]/[n_{13}(0)/n_{12}(0)], \quad (1)$$

where  $n_{13}$  ( $n_{12}$ ) is the number density of <sup>13</sup>CF<sub>3</sub>I (<sup>12</sup>CF<sub>3</sub>I) molecules and  $n_i(0)$  refers to the initial number of the  $i^{\text{th}}$  species. The laser preferentially dissociates <sup>12</sup>CF<sub>3</sub>I so that  $\beta_r$  increases as the bulk dissociation proceeds.

In a similar fashion, we define  $\beta_p$  as the isotope ratio in the products,  $p_{12}$  and  $p_{13}$ , compared to the ratio expected for a nonselective process:

$$\beta_p = [p_{12}/p_{13}]/[n_{12}(0)/n_{13}(0)]. \quad (2)$$

Both  $\beta_r$  and  $\beta_p$  increase with increasing selectivity.

The parameters  $\beta_p$  and  $\beta_r$ , whose values depend on the number of laser pulses, are useful macroscopic indicators of the selectivity. The microscopic information concerning the selectivity is contained in the parameter  $\alpha$ , defined as follows. After each laser pulse, small increments  $dn_{12}$  and  $dn_{13}$  of  $n_{12}$  and  $n_{13}$  will be converted to the products  $p_{12}$  and  $p_{13}$ , respectively. The isotope ratio in this increment of products will thus be given by  $dn_{12}/dn_{13}$ . Since a completely nonselective process would give an incremental isotope ratio equal to the current value of  $n_{12}/n_{13}$ , we can measure the microscopic selectivity by the parameter

$$\alpha = [dn_{12}/dn_{13}]/[n_{12}/n_{13}]. \quad (3)$$

If <sup>12</sup>CF<sub>3</sub>I molecules are preferentially dissociated, then  $\alpha$  will be larger than one.

We define  $f$  to be the fraction of starting material remaining after irradiation of the sample with several pulses,

$$f = [n_{12} + n_{13}]/[n_{12}(0) + n_{13}(0)] \approx n_{12}/n_{12}(0), \quad (4)$$

where the approximate holds for  $n_{12} \gg n_{13}$ . Assuming that  $n_{12} \gg n_{13}$  and that  $\alpha$  is constant during the course of the photolysis, the quantities  $f$ ,  $\alpha$ , and  $\beta_r$  are related<sup>20</sup> by the equation

$$\beta_r = f^{(1-\alpha)/\alpha}. \quad (5)$$

Combination of Eqs. (2) and (3) and integration from  $f' = 1$  to  $f' = f$  to obtain  $\beta_p$  yields

$$\beta_p = \frac{\alpha^2}{2\alpha - 1} [(1 - f^{(2\alpha-1)\alpha})/(1 - f)]. \quad (6)$$

In principle,  $\alpha$  may be calculated from  $\beta_r$  and  $f$ , from  $\beta_p$  and  $f$ , or from  $\beta_p$  and  $\beta_r$ .

Finally, we will need to know how  $f$  varies with  $N$ , the number of laser pulses. Let us at first assume that the fraction of CF<sub>3</sub>I dissociated in the beam per pulse,  $\Delta f$ , is constant throughout the irradiation. For a cell of volume  $V_c$  and a homogeneously irradiated volume  $V_{\text{irr}}$ ,  $\Delta f$  is related to  $f$  by

$$f = (1 - r\Delta f)^N, \quad (7)$$

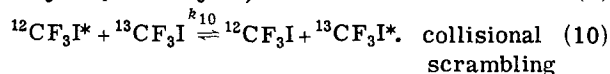
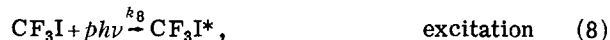
where  $r = V_{\text{irr}}/V_c$  and  $N$  is the total number of laser pulses.

## B. Kinetic scheme

The CF<sub>3</sub> and I radicals formed by multiphoton dissociation of CF<sub>3</sub>I recombine to yield CF<sub>3</sub>I, C<sub>2</sub>F<sub>6</sub>, and I<sub>2</sub>.

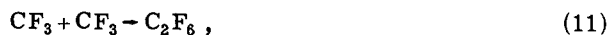
These are the only species observed in either infrared or mass spectra of samples irradiated at intensities below 25 MW/cm<sup>2</sup>. In particular, CF<sub>2</sub>I<sub>2</sub> and other products which arise from breaking a C-F bond are not observed. We propose below a kinetic scheme for the purpose of discussing our results. While this scheme is not exhaustive, it completely accounts for our observations.

The dissociation is described by three processes:

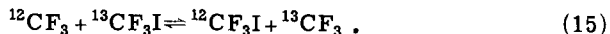


In these equations  $p$  and  $q$  are integral numbers of photons totalling enough energy to break the C-I bond ( $\Delta H_{298}^0 = +55$  kcal/mole;  $p+q \geq 18$  photons). Equations (8) and (9) may actually consist of several individual steps.

Dissociation is followed by recombination of radicals to yield products or reactants:



Two other radical reactions are also of importance:



## C. Isotopic selectivity as a function of pressure

A summary of the experimental results is given in Table I. Runs 1-12 investigate the dependence of  $\beta_p$  on pressure. As shown in Fig. 1,  $\beta_p$  increases dramatically from unity as the pressure of CF<sub>3</sub>I is reduced below 1.0 torr. The R(14) line of the 9.6  $\mu$  CO<sub>2</sub> laser transition selectively dissociates <sup>12</sup>CF<sub>3</sub>I. It may be noted from the table that the fraction of CF<sub>3</sub>I remaining undissociated,

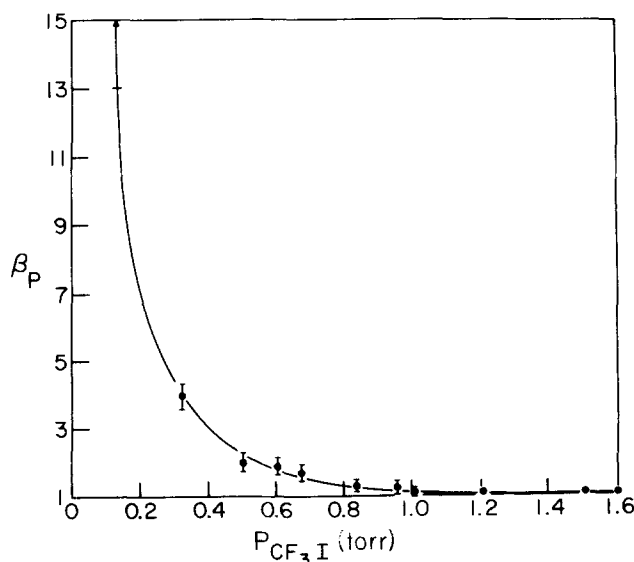


FIG. 1. Selectivity of product formation as a function of pressure. Laser intensity was 5.5 MW/cm<sup>2</sup>.

TABLE I. Summary of experimental results.<sup>a</sup>

Run	P (torr)	I <sup>b</sup> (MW/cm <sup>2</sup> )	β <sub>r</sub>	β <sub>p</sub>	f <sup>c</sup>	r <sup>d</sup>	Δf	α	E <sub>abs</sub> (hν/mol)	Eff. (%)	N
1	0.14 <sup>e</sup>	5.5	1.7	>13	0.77	0.86	<0.001	>13			400
2	0.15	5.5	1.5	>8	0.75	0.86	<0.001	>8			400
3	0.32	5.5	1.0	4	0.95	0.86	<0.001	4			170
4	0.50	5.5	1.0	2	0.95	0.86	<0.001	2			100
5	0.60	5.5		1.9		0.86		1.9			200
6	0.67	5.5	1.0	1.7	0.94	0.86	<0.001	1.7			170
7	0.83	5.5	1.0	1.3 <sup>3</sup>	0.92	0.86	<0.001	1.3			170
8	0.95	5.5		1.2 <sup>3</sup>		0.86		1.2			100
9	1.00	5.5	1.0	1.1 <sup>2</sup>	0.92	0.86	0.001	1.1			100
10	1.20	5.5		1.1 <sup>1</sup>		0.86		1.1			100
11	1.50	5.5		1.0 <sup>8</sup>		0.86		1.1			100
12	5.00	5.5	1.0	1.0 <sup>2</sup>	0.73	0.86	0.004	1.0			100
13	0.15 <sup>f</sup>	25(max)	180	5.3	0.02	0.078	0.05	9.8			1000
14	0.10 <sup>f</sup>	25(max)	590	6.4	0.015	0.078	0.03	12			2000
15	0.10 <sup>f</sup>	3.5	8.1	>25	0.20	0.414	0.004	>41			1080
16	0.50	0.8			1.	0.077	0		2. <sup>6</sup>	0	200
17	0.50	1.5			0.99	0.077	0.001		4. <sup>7</sup>	0.3	200
18	0.50	3.3			0.90	0.077	0.007		8. <sup>1</sup>	1.5	200
19	0.50	5.2			0.56	0.077	0.038		11. <sup>2</sup>	6.1	200
20	0.50	6.1			0.65	0.042	0.051		12. <sup>3</sup>	7.5	200
21	0.50	7.0	1.7	4.4	0.45	0.077	0.052	5.7	13. <sup>2</sup>	7.1	200
22	0.50	10	1.6	4.7	0.63	0.011	0.084	5.6	16. <sup>6</sup>	9.1	500
23	0.50	13	3.2	4.0	0.33	0.042	0.13	5.6			200
24	0.50	16	1.9	3.6	0.59	0.007	0.15	4.3			500

<sup>a</sup>For dissociation with the R(14) line of the 9.6 μ CO<sub>2</sub> laser transition.<sup>b</sup>Energy/cm<sup>2</sup> = I(0, 12).<sup>c</sup>f = (<sup>12</sup>CF<sub>3</sub>I + <sup>13</sup>CF<sub>3</sub>I) / (<sup>12</sup>CF<sub>3</sub>I + <sup>13</sup>CF<sub>3</sub>I)<sub>initial</sub>.<sup>d</sup>r = V<sub>irr</sub>/V.<sup>e</sup>MeOH-LN<sub>2</sub> slush on side arm.<sup>f</sup>– 80 °C dry ice jacket on cell.

$f_r$  is always greater than 0.73 for these runs. Expansion of Eq. (6) under the condition that  $f > 0.73$  yields that  $\beta_p = \alpha$  to within 14%. Thus, for CF<sub>3</sub>I,  $\alpha$  increases as the pressure,  $P$ , decreases.

For dissociation of SF<sub>6</sub> a proportionality between  $\ln\beta_r$  and  $P^{-1}$  has been noted by Ambartzumian *et al.*<sup>29</sup> An increase in  $\beta_r$  as  $P$  decreases has also been observed for dissociations of CF<sub>2</sub>Cl<sub>2</sub>, BCl<sub>3</sub>, and SiF<sub>4</sub>.<sup>20</sup> From Eq. (5) it may be shown that, at a given fractional dissociation, the fact that  $\beta_r$  increases as  $P$  decreases implies that  $\alpha$  increases as  $P$  decreases. Since this behavior seems to be common to a variety of multiphoton systems, one might reasonably conclude that the dependence of  $\alpha$  on  $P$ , shown for CF<sub>3</sub>I in Fig. 1, is related to the mechanism of multiphoton dissociation and not to the specific case at hand. This implies that Reaction (10) must be at least partly responsible for the scrambling.

The differential equations corresponding to Reactions (8)–(10) may be used to predict the dependence of  $\ln\beta_r$  on  $P$ . These equations can be solved to yield the time dependence of <sup>12</sup>CF<sub>3</sub> and <sup>13</sup>CF<sub>3</sub>. The amounts of each radical formed per laser pulse of duration  $t_0$  may then be solved by integration of the equations for <sup>12</sup>CF<sub>3</sub> and <sup>13</sup>CF<sub>3</sub> from  $t = 0$  to  $t = t_0$ . The result gives an expression for  $\alpha$  which simplifies to

$$\alpha = \left( \frac{k_9}{k_{10}P} \right) \left( \frac{n_{12} + n_{13}}{n_{12}} \right) + 1, \quad (16)$$

under the assumptions that  $k_9$  is large compared to  $t_0^{-1}$  and that no scrambling occurs after the dissociation.

Consequently, the simple model presented by Reactions (8)–(10) explains why  $\alpha$  increases as  $P$  decreases. More explicitly, substitution of Eq. (16) into Eq. (5) predicts that  $\ln\beta_r$  should increase as  $P^{-1}$ :

$$\ln\beta_r = \ln(1/f) \left[ 1 + P \frac{k_{10}n_{12}}{k_9n_{12} + n_{13}} \right]^{-1}. \quad (17)$$

Although it is not clear that the fractional dissociation,  $f$ , was constant in their experiments, an increase in  $\ln\beta_r$  with  $P^{-1}$  was observed by Ambartzumian *et al.*<sup>29(a)</sup>

For CF<sub>3</sub>I the dependence of  $\alpha$  on pressure is somewhat stronger than the  $P^{-1}$  dependence of Eq. (16). This may be due to the fact that collisional scrambling following dissociation, Reaction (15), also depends on pressure.

Dever and Grunwald<sup>7</sup> have suggested in their study of CCl<sub>3</sub>F and CF<sub>3</sub>Cl that the energy provided by the laser stays predominantly in one vibrational mode prior to dissociation. Their operating pressures exceeded 60 torr. While the question of *intramolecular* energy transfer prior to dissociation remains unanswered, our data strongly suggest that, at one torr, *intermolecular* energy transfer occurs sufficiently often to scramble the isotopic selectivity before dissociation. At 60 torr we would expect a large degree of collisional redistribution of the energy among the vibrational modes prior to dissociation.

#### D. Optimization of the selectivity

As the products of the multiphoton dissociation of CF<sub>3</sub>I become enriched in <sup>12</sup>C, the remaining reactants become

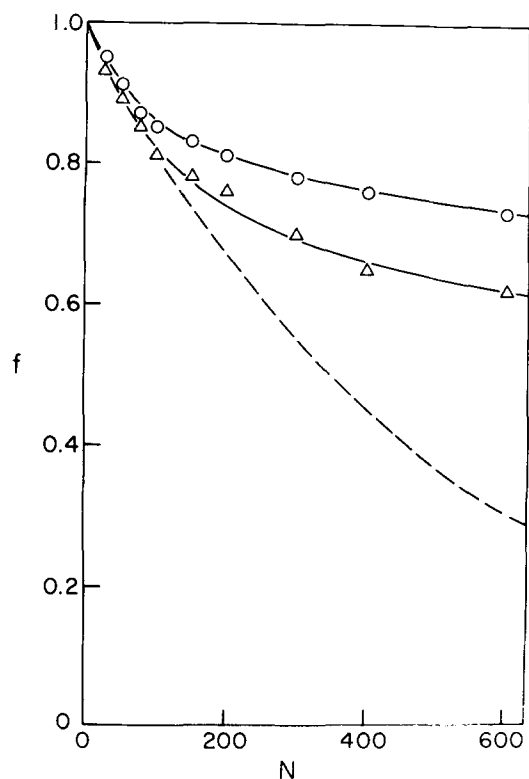


FIG. 2. Plot of remaining fraction of  $\text{CF}_3\text{I}$  as a function of number of laser pulses and cell temperature:  $T = 298^\circ\text{K}$  (circles) and  $T = -80^\circ\text{C}$  (triangles). The dashed line is the prediction of Eq. (7) of the text.

enriched in  $^{13}\text{C}$ . For a given value of  $\alpha$  the limit of enrichment in the reactants depends through Eq. (5) on their remaining fraction,  $f$ . In order to obtain an efficient separation we would like  $f$  to fall as rapidly as possible with the number of pulses,  $N$ .

Figure 2 shows the dependence of  $f$  on  $N$ . The upper line (circles) is a fit to the experimental data for a cell temperature of  $298^\circ\text{K}$ , while the dashed line is the prediction of Eq. (7), where  $\Delta f$  has been chosen to fit the region of low  $N$ . The middle line (triangles) shows the effect of cooling the cell to  $-80^\circ\text{C}$ . It is evident that cooling increases the rate of decomposition with  $N$ . This increase may be due to at least two effects: 1) Cooling may place more population in the absorbing levels and, therefore, increase the fractional dissociation. 2) Cooling may also affect the fractional dissociation through inhibition of the Reaction (14), which would otherwise cause a decrease in  $\Delta f$  with  $N$  as  $\text{I}_2$  accumulated in the cell. The rate of Reaction (14) has been reported<sup>30</sup> to be  $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . At  $-80^\circ\text{C}$  the vapor pressure of  $\text{I}_2$  is below  $10^{-6}$  torr,<sup>31</sup> whereas the vapor pressures of  $\text{CF}_3\text{I}$  and  $\text{C}_2\text{F}_6$  are both larger than our operating pressures. Thus, at this temperature Reaction (14) should be effectively eliminated;  $\text{I}_2$  will condense at the cell walls between laser pulses (0.5 Hz). Since it is unlikely that radicals will reach the cell walls (radius = 2 cm) before recombining, other effects of cooling must be attributable to the temperature variation of the recombination rates. The source of residual deviation between the  $-80^\circ\text{C}$  curve and the predicted curve of Fig. 2 is still under investigation.

By cooling the cell to  $-80^\circ\text{C}$  we have achieved a 590-fold enrichment of  $^{13}\text{CF}_3\text{I}$ . Naturally occurring  $\text{CF}_3\text{I}$  ( $^{13}\text{C}/^{12}\text{C} \approx 1/99$ ) at 0.10 torr was irradiated with 2000 pulses on the  $R(14)$  line of the  $9.6 \mu\text{m}$   $\text{CO}_2$  laser band. The peak intensity was  $25 \text{ MW/cm}^2$  corresponding to an energy fluence of  $3 \text{ J/cm}^2$ . Mass spectral analysis showed that 86% of the residual reactant was  $^{13}\text{CF}_3\text{I}$ . These data are summarized in Table I, Runs 13–15.

### E. Efficiency of the multiphoton process

By measuring both the amount of energy absorbed by the sample and the number of product molecules, it is possible to determine the quantum efficiency of the multiphoton dissociation. We have examined the efficiency as a function of incident intensity over the range  $1\text{--}10 \text{ MW/cm}^2$ .

A substantial uncertainty in the efficiency arises from the kinetics. If Reaction (12) and (14) occur faster than Reaction (11), then the net number of products created or reactants consumed will be substantially less than the number of dissociations. This will result in a lower apparent efficiency for dissociation than that which would be obtained in the absence of these reactions. Of the set of Reactions (11)–(14), Reaction (13) is known to be slow<sup>32</sup> under our experimental conditions. The rate for Reaction (11) has been reported<sup>33–36</sup> to be in the range  $5 \times 10^{-12}$ – $3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , while that for Reaction (12) has been reported<sup>37–39</sup> to be in the range  $(1.5\text{--}6.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . Based on the value of  $5 \times 10^{-12}$  for Reaction (11), Andreeva *et al.*<sup>39</sup> have found that Reaction (12) has a rate of  $(1.5\text{--}2.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . It would thus appear that roughly 80% of the  $\text{CF}_3$  radicals recombine with  $\text{I}$  to form  $\text{CF}_3\text{I}$ . The remainder form  $\text{C}_2\text{F}_6$  unless the pressure of  $\text{I}_2$  is high enough to allow Reaction (14) to occur ( $k_{14} = 5 \times 10^{-12}$ ).<sup>30</sup> Consequently, the fractional dissociation will actually be five times larger than the apparent value we measure. The fractional dissociation per shot and the efficiency reported below have not been corrected by this factor since there is still some uncertainty in the relative rates of Reactions (12) and (13).

The first step in determining the efficiency of the multiphoton dissociation process is to determine the fraction of molecules dissociated in the beam per pulse,  $\Delta f$ . If we ignore the effect of Reaction (14),  $\Delta f$  may be determined from  $N$  and the measured value of  $f$  using Eq. (7). In Table I, Runs 16–24 give the results for 0.5 torr of  $\text{CF}_3\text{I}$  and a range of incident intensities. These are plotted in Fig. 3. The fractional dissociation exhibits a threshold below  $2 \text{ MW/cm}^2$  ( $0.24 \text{ J/cm}^2$ ) and then increases with intensity. At an intensity of  $10 \text{ MW/cm}^2$  ( $1.2 \text{ J/cm}^2$ ), roughly 8.4% of the molecules in the beam are dissociated per pulse, while at  $16 \text{ MW/cm}^2$  ( $1.9 \text{ J/cm}^2$ ) the fraction increases to 15%.

The fractional dissociation in the beam per pulse may be converted to an efficiency if the amount of energy absorbed by the sample is measured. For 0.5 torr of  $\text{CF}_3\text{I}$  absorption could conveniently be measured in the intensity range below  $11 \text{ MW/cm}^2$ . The resulting curve was interpolated to yield the values listed in the column of Table I headed " $E_{\text{abs}}$ ". Since the  $\text{CF}_3\text{--I}$  bond strength

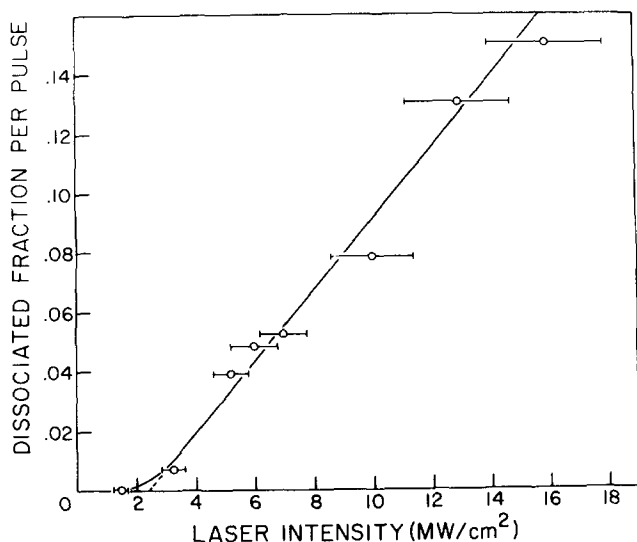


FIG. 3. Fractional dissociation in the beam per pulse,  $\Delta f$ , as a function of laser intensity. The pressure of CF<sub>3</sub>I was 0.5 torr. Intensity may be converted to energy fluence in J/cm<sup>2</sup> by multiplication by 0.12.

is 55 kcal/mole and roughly equal to the energy of 18 laser photons, we define an efficiency of 1.0 to correspond to one dissociation for every 18 photons absorbed. Division of  $\Delta f$  by  $E_{\text{abs}}$  (in photons/molecule in the beam) and multiplication by 18 yields the efficiencies listed in Table I. At 10 MW/cm<sup>2</sup> (1.2 J/cm<sup>2</sup>) the efficiency is found to be 9.1%. Thus, one in every 11 photons absorbed contributes its energy to the dissociation process at this intensity. The actual efficiency may be much higher, considering the relative rates of Reactions (12) and (13).

#### IV. CONCLUSION

Multiphoton dissociation of CF<sub>3</sub>I has been shown to be an isotopically selective and efficient process. Enrichment of carbon-13 by a factor of nearly 600 has been achieved. At 10 MW/cm<sup>2</sup> (1.2 J/cm<sup>2</sup>) the observation that at least 8.4% of the molecules in the beam are dissociated leads to the conclusion that at this intensity at least one in every 11 absorbed photons contributes its energy to the breaking of the CF<sub>3</sub>-I bond. These values may be as much as five times higher, considering the relative rates and Reactions (12) and (13). We are currently investigating the dependence of the selectivity and efficiency on wavelength and pressure of added gases.

#### ACKNOWLEDGMENTS

We would like to thank Dr. Robert Swofford for technical assistance during the early part of this investigation. We gratefully acknowledge support for this project through a grant from the Standard Oil Company of Ohio.

<sup>1</sup>N. Bloembergen, Opt. Commun. 15, 416 (1975).

<sup>2</sup>D. M. Larsen and N. Bloembergen, Opt. Commun. 17, 254 (1976).

<sup>3</sup>R. V. Ambartsumian, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puzetskii, Sov. Phys. JETP Lett. 23, 22 (1976).

- <sup>4</sup>S. Mukamel and J. Jortner, Chem. Phys. Lett. 40, 150 (1976).  
<sup>5</sup>S. Mukamel and J. Jortner, J. Chem. Phys. 65, 5204 (1976).  
<sup>6</sup>N. R. Isenor, V. Merchant, R. S. Hallsworth, and M. C. Richardson, Can. J. Phys. 51, 1281 (1973).  
<sup>7</sup>D. F. Dever and E. Grunwald, J. Am. Chem. Soc. 98, 5505 (1976).  
<sup>8</sup>M. J. Coggiola, P. A. Schulz, Y. T. Lee, and Y. R. Shen, Phys. Rev. Lett. 38, 17 (1977).  
<sup>9</sup>J. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, Phys. Rev. Lett. 38, 1131 (1977).  
<sup>10</sup>N. R. Isenor and M. C. Richardson, Appl. Phys. Lett. 18, 225 (1971).  
<sup>11</sup>H. Walther, "Atomic and Molecular Spectroscopy with Lasers," Topics in Applied Physics, Vol. 2, Laser Spectroscopy, edited by H. Walther, (Springer, Berlin, 1976).  
<sup>12</sup>Laser Spectroscopy, Proceedings of the Second International Conference, Megeve, June 23-27, 1975, edited by S. Haroche, J. C. Pebay-Peyroula, T. W. Hansch, S. E. Harris, (Springer, Berlin, 1975).  
<sup>13</sup>V. S. Letokhov and C. B. Moore, Sov. J. Quantum Electron. 6, 129, 259 (1976).  
<sup>14</sup>J. P. Aldridge III, J. H. Birely, C. D. Cantrell III, and D. C. Cartwright, "Experimental and Theoretical Studies of Laser Isotope Separation," Physics of Quantum Electronics, Vol. 4, Laser Photochemistry, Tunable Lasers, and Other Topics, edited by S. F. Jacobs, M. Sargent III, M. O. Scully, and C. T. Walker (Addison-Wesley, Reading, Mass., 1976).  
<sup>15</sup>A. Yegorov and R. M. J. Benmair, J. Am. Chem. Soc. 97, 4430 (1975).  
<sup>16</sup>G. Koren, U. P. Oppenheim, D. Tal, M. Okon, and R. Weil, Appl. Phys. Lett. 28, 40 (1976).  
<sup>17</sup>R. V. Ambartsumian, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Sov. Phys. JETP Lett. 20, 273 (1974).  
<sup>18</sup>S. M. Freund and J. J. Ritter, Chem. Phys. Lett. 32, 255 (1975).  
<sup>19</sup>R. V. Ambartsumian, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, E. A. Ryabov, and N. V. Chekalin, Sov. J. Quantum Electron. 5, 1196 (1975).  
<sup>20</sup>J. L. Lyman and S. D. Rockwood, J. Appl. Phys. 47, 595 (1976).  
<sup>21</sup>R. A. Ambartsumian, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puzetskii, Sov. Phys. JETP Lett. 22, 177 (1975).  
<sup>22</sup>R. V. Ambartsumian, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, Sov. Phys. JETP Lett. 21, 171 (1975).  
<sup>23</sup>J. L. Lyman, R. J. Jensen, J. Rink, C. P. Robinson, and S. D. Rockwood, Appl. Phys. Lett. 27, 87 (1977).  
<sup>24</sup>R. V. Ambartsumian, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, Sov. Phys. JETP Lett. 22, 96 (1975).  
<sup>25</sup>A preliminary report of this work has been presented at the Fifth Conference on Chemical and Molecular Lasers, Paper TAI7, April 18-20, St. Louis, Mo.  
<sup>26</sup>H. Jones and F. Kohler, J. Mol. Spectrosc. 58, 125 (1975).  
<sup>27</sup>A. B. Petersen, J. Tiee, and C. Wittig, Opt. Commun. 17, 259 (1976).  
<sup>28</sup>M. Benedict and T. H. Pigford, Nuclear Chemical Engineering (McGraw-Hill, New York, 1957) pp. 380, 381.  
<sup>29</sup>(a) R. V. Ambartsumian, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, Sov. Phys. JETP 42, 993 (1976); (b) 44, 231 (1976).  
<sup>30</sup>J. G. Amphlett and E. Whittle, Trans. Faraday Soc. 62, 1662 (1966).  
<sup>31</sup>R. Honig and H. Hook, RCA Rev. 21, 360 (1960).  
<sup>32</sup>J. A. Blake and G. Burns, J. Chem. Phys. 54, 1480 (1971).  
<sup>33</sup>P. Ayscough, J. Chem. Phys. 24, 944 (1956).  
<sup>34</sup>T. Ogawa, G. A. Carlson, and G. C. Pimentel, J. Phys. Chem. 74, 2090 (1970).  
<sup>35</sup>N. Basco and F. G. M. Hathorn, Chem. Phys. Lett. 8, 291 (1971).  
<sup>36</sup>R. Hiatt and S. W. Benson, Int. J. Chem. Kinet. 4, 479

- (1972).
- <sup>37</sup>T. L. Andreeva, S. V. Kuznetsova, A. I. Maslov, I. I. Sobel'man, and V. N. Sorokin, *Sov. Phys. JETP Lett.* **13**, 449 (1971).
- <sup>38</sup>I. M. Belousova, N. G. Gorshov, O. B. Danilov, V. Yu. Zaleskii, and I. L. Yachnev, *Sov. Phys. JETP* **38**, 254 (1974).
- <sup>39</sup>T. L. Andreeva, S. V. Kuznetsova, A. I. Maslov, I. I. Sobel'man, and V. N. Sorokin, *High Energy Chem. (USSR)* **6**, 368 (1972).