IR PHOTOLYSIS OF CDF_3: A STUDY IN KINETICS OF MULTIPLE-PHOTON DISSOCIATION WITH APPLICATIONS TO DEUTERIUM SEPARATION *

Irving P. HERMAN and Jack B. MARLING
Lawrence Livermore Laboratory, University of California, Livermore, California, USA

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CO_2 laser multiple-photon dissociation (MPD) of CDF_3 is examined as a function of fluence and collisions, providing new understanding of MPD. Notably, the dissociation yield is increased 100-fold due to collisions with argon. Photochemically, this molecule is ideally suited for deuterium separation.

1. Introduction

Outstanding questions remain concerning the kinetics of the multiple-photon absorption (MPA) process which contributes to collision-free and collision-assisted multiple-photon dissociation (MPD). This letter reports an experimental study of CO_2 laser MPD in deuterated trifluoromethane, CDF_3 (fluoroform-*d*), in which some of these questions are addressed. Specifically, the MPD of fluoroform has been studied as a function of laser fluence as well as of collision partner and pressure. These results shed additional understanding on the MPA process. In addition, because of the isotopically-selective dissociation of CDF_3, trifluoromethane is found to be nearly ideal from a photochemical viewpoint for viable large-scale deuterium separation.

The infrared absorption spectrum of CDF_3 [1] is shown in fig. 1; it exhibits strong, selective peaks at 10.21 μ and 10.31 μ, corresponding to the P and R branch peaks of the ν_5 mode (C–D wag). The low intensity, low resolution absorption coefficient at 10.2 μ is 1.0×10^{-2}/cm Torr at room temperature and the isotopic optical selectivity, based on the ratio of CDF_3 to CHF_3 absorption coefficients, is >2000 from 10.2–10.3 μ. (Note that in fig. 1 the CHF_3 pressure is one hundred times the CDF_3 pressure.)

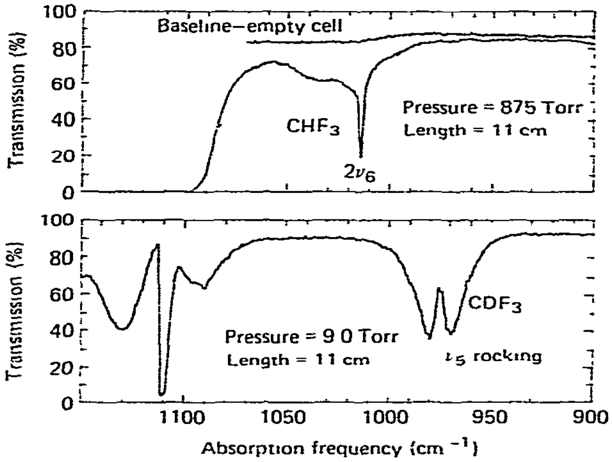

Fig. 1. Low intensity, low resolution infrared spectrum of fluoroform near 10 μ. Upper trace: 875 Torr CHF_3 in 11 cm long cell. Lower trace: 9 Torr CDF_3 in 11 cm cell.

The primary step in thermal decomposition of CHF_3 is: $CHF_3 \rightarrow :CF_2 + HF$ ($E_{act} = 69.0 \pm 1.6$ kcal/mole), followed by $:CF_2$ recombination to form C_2F_4 [2]. An analogous mechanism is expected in the MPD of CDF_3.

2. Experimental procedure

The output from a commercial TEA CO_2 laser (5 J, 0.5 Hz, 90 ns fwhm pulses with ≈ 500 ns tail, 20–700 pulses) was focused into a 3.5 cm i.d. cell with KCl win-

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dows, which contained the desired mixture of trifluoromethane and other gases. To achieve focal fluences of $\leqslant 30$ J/cm^2, the laser was focused into the center of a 60 cm long cell by a 100 cm f.ℓ. BaF$_2$ lens; for 30–180 J/cm^2 fluences, a 30 cm long cell and a 40 cm f.ℓ. lens were employed. The incident laser fluence was varied by inserting suitable attenuating flats after the laser.

After irradiation the products were transferred by cryogenic condensation from the cell to another, smaller volume from which a sample was extracted with a syringe for gas chromatographic analysis. A Poropak T column (60°C) cleanly separated the main carbon-bearing product, C_2F_4, from CDF_3. The flame ionization detector sensitivity to C_2F_4 was measured to be 7.94 ± 0.10 times its sensitivity to fluoroform.

CDF_3 was obtained from Merck Ltd. ($\geqslant 98\%$ D) and was used without any further purification, aside from pumping away any volatiles remaining at 77 K. It contained an $\approx 1\%$ C_2F_4 impurity which could not be removed by distillation without significant loss of CDF_3 (CHF_3 b.p. = −82.1°C; C_2F_4 b.p. = −76.3°C) [3]. Since C_2F_4 was the expected carbon-containing product, this approximately 1% C_2F_4 background contribution was subtracted from the total amount appearing in the laser-irradiated samples of CDF_3. CHF_3 (Matheson, $> 98.0\%$) was found to contain $\lesssim 0.01\%$ C_2F_4 and was used without further purification, as was the argon (Airco, 99.998%). A reference sample of C_2F_4 was obtained by low pressure thermal decomposition of teflon chips.

3. Experimental results

The only main carbon-containing product observed in IR photolysis of CDF_3 was C_2F_4. Under certain conditions other products were formed, but their yield was always $< 5\%$ times that of the C_2F_4 product. The product yield at high fluence (150 J/cm^2; 75 mTorr CDF_3) was insensitive to the CO_2 laser line employed between 10.2 and 10.3 μ, the ν_5 P and R branch peaks. Unless otherwise specified below, the laser was tuned to 10.2 μ [R(26) + R(28)], the CDF_3 P branch peak, in all the experiments described.

The dependence of CDF_3 decomposition on laser fluence for (near-) collision-free conditions (66 mTorr) is indicated by the lower curve in fig. 2. The mechanism proposed by Pelitanskii and Shevchuk [2] was employed to relate the amount of C_2F_4 produced to the amount of the reagent decomposed. The fraction of reagent which dissociated per pulse was normalized by dividing by the volume of molecules within the Rayleigh range of the focus, i.e., the volume in which the fluence exceeded half the peak focal fluence; this is hereafter referred to as the yield.

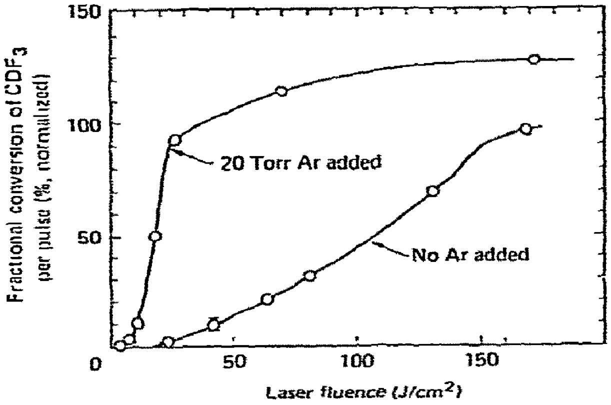

Fig. 2. Fluence dependence of CDF_3 dissociation probability in pure CDF_3 (66 mTorr) and with 20 Torr argon added (λ = 10.2 μ).

The effect on the dissociation yield of CDF_3 at 25 J/cm^2 fluence due to adding varying pressures of an argon buffer gas to a fixed partial pressure of CDF_3 (65 mTorr) is shown in fig. 3. In the range of 0–10 Torr pressure of added argon, the yield increases linearly from the value of 2% in pure CDF_3, saturates near 100% with approximately 15–50 Torr of argon, and then decreases at higher pressure. Therefore the addition of about 20 Torr argon increases the yield by a factor of 50 at a fluence of 25 J/cm^2. At lower fluences ($\approx$ 10 J/cm^2) this increase is *100-fold*, as is seen in fig.

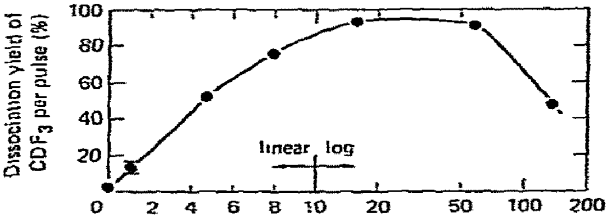

Fig. 3. Dependence of yield of MPD in CDF_3 (65 mTorr) as a function of added argon pressure (10 2 μ, 25 J/cm^2).

4. Equally large yield enhancements with added argon have also been observed with the laser tuned to the R branch peak [10.3 μ, R(10) + R(12)]. Use of the other inert gases as buffers should lead to qualitatively the same results [4].

Reference to fig. 2 shows that the fluence dependence of the dissociation probability of CDF_3 is very different for a neat, collision-free sample of CDF_3 compared to one with 20 Torr of argon added. This latter decomposition probability (upper curve, fig. 2) increases rapidly with fluence near 15 J/cm^2 and saturates near 100% above 30 J/cm^2. Since at high fluence levels the effective dissociation volume far exceeded the Rayleigh range volume, these data were normalized by use of either the focal volume in which the incident fluence was $\geqslant$ 12.6 J/cm^2 or the Rayleigh range volume, whichever was larger. This specified fluence cut-off corresponds to a 20% dissociation probability; the exhibited results are insensitive to the exact choice of this cut-off.

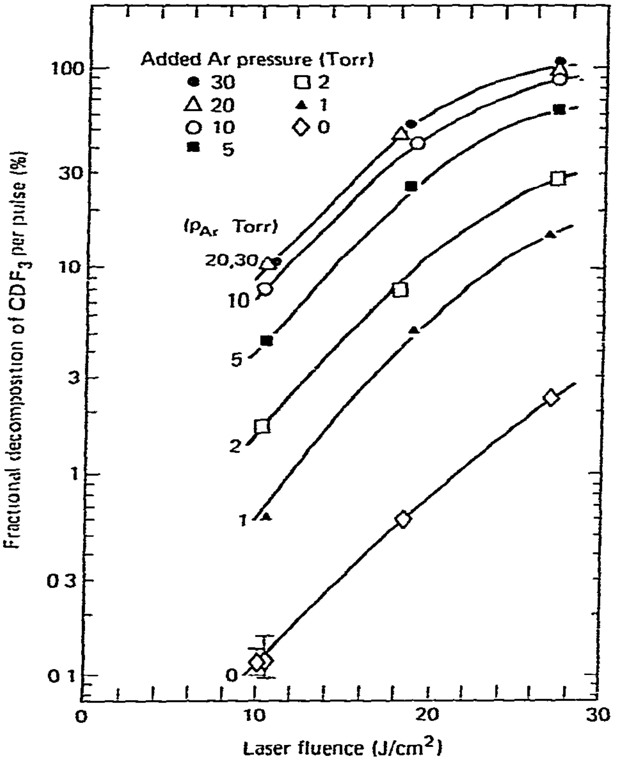

Fig. 4. Fluence dependence of fractional CDF_3 dissociation for various pressures of added argon (65 mTorr CDF_3, 10.2 μ).

Still, at high fluences this normalization procedure is only approximate.

The detailed fluence dependence of argon collision-assisted MPD in CDF_3 was investigated and the results are exhibited in fig. 4, in which a family of yield versus fluence curves for various argon buffer gas pressures is plotted. Since each pair of curves in this plot are parallel in regions where saturation is unimportant, the addition of a fixed partial pressure of argon simply increases the fraction of dissociating molecules by a constant factor. Each curve exhibits a yield which is proportional to fluence to the 3.0 ± 0.5 power in regimes where saturation plays no role.

Of particular interest from the viewpoint of deuterium separation is the effect of collisions with CHF_3. This is shown in fig. 5 under conditions otherwise similar to those in fig. 3. It is assumed that CHF_3 does not undergo MPD itself to form C_2F_4; this is substantiated below. With small amounts of added CHF_3, the yield increases linearly with CHF_3 pressure, at approximately the same slope as with Ar, indicated in fig. 3. However, in this case the yield peaks at 4.6% with $\approx \frac{1}{2}$ Torr CHF_3 (corresponding to 250 ns between hard sphere CHF_3–CDF_3 collisions [5]), and rapidly decreases at higher pressure.

The possibility of MPD of CHF_3 was then studied using CO_2 laser pulses with 170 J/cm^2 fluence (λ = 10.2 μ) incident on 65 mTorr of neat CHF_3. Only one dominant, though quite small, product peak appeared in the gas chromatographic analysis of the laser-irradiated sample and it had a retention time almost, though not exactly, equal to that of C_2F_4; however, in mass spectrometric analysis no C_2F_4 was observed. Addition of

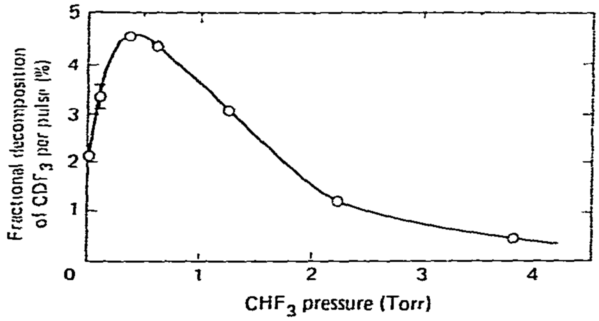

Fig. 5. Dependence of yield of CDF_3 dissociation in presence of CHF_3 (62 mTorr CDF_3, 10.2 μ, 27 J/cm^2).

several hundred mTorr more CHF_3 or, alternatively, 20 Torr of argon decreased the observed yield. The yield monotonically increased with laser fluence but was insensitive to the wavelength of the laser line chosen and whether or not it was on or off either a CDF_3 or CHF_3 resonance. Evidently, the unidentified product was due to heterogeneous reactions. Assuming the calibration for C_2F_4 relative to CHF_3, the normalized yield per pulse for this product was $\approx 6 \times 10^{-3}\%$ for 65 mTorr CHF_3 in 20 Torr of argon (30 J/cm^2: $\lambda = 10.2\ \mu$ [R(26) + R(28)]), or 2×10^4 times smaller than for C_2F_4 produced from CDF_3 under similar conditions.

4. Discussion

4.1. *Kinetics of the multiple-photon process*

Since tetrafluoroethene is the dominant product in CDF_3 IR photolysis, DF elimination is most probably the initial chemical step, followed by $:CF_2$ recombination

$$CDF_3 + nh\nu \rightarrow :CF_2 + DF, \qquad (1)$$

$$:CF_2 + :CF_2 \rightarrow C_2F_4. \qquad (2)$$

A third possible step in the mechanism [6]:

$$:CF_2 + CHF_3 \rightarrow HF + C_2F_4 \qquad (3)$$

was proven to be unimportant by Politanskii and Shevchuk [2], who showed that added $:CF_2$ does not accelerate fluoroform thermal decomposition. Since the yield versus fluence curves of fig. 4 are proportional to one another, and since collisions increase the yield, it may be concluded that rotational relaxation of ground state molecules is the principal effect of CDF_3–Ar collisions in MPA and MPD. After collisional rotational transfer, molecules which formerly were not resonant with the laser can then absorb photons and undergo MPD. The decrease in yield for $p_{Ar} > 100$ Torr shown in fig. 3 can be attributed to V–T relaxation of vibrationally excited CDF_3 in the "quasi-continuum" with internal energy near the dissociation energy. Conceivably, collisions may also enhance MPD by promoting V–V intramolecular transfer; this would then enable moderately excited molecules to absorb more photons, and would also allow a molecule excited above the dissociation barrier to transfer to dissociating vibrational levels. The plot of the yield with no added gas in fig. 4 would fall much faster with decreasing fluence than would the other curves if these MPA and MPD rotational level bottleneck-removing collisions were not the dominant collisional influence on MPD in CDF_3. Equivalently, the fluence threshold for MPD would then appear to decrease with increased buffer gas pressure. Evidently, this is not true in CDF_3, which has a threshold (as defined in ref. [7]) independent of buffer pressure. Quick and Wittig [7] have made similar observations for MPD of C_2H_3F, and have also attributed the increase in dissociation yield with added buffer (He) to rotational relaxation.

These observations can shed new light on the multiple-photon absorption process. Kolodner et al. [8] and Lyman et al. [9] showed that as the CO_2 laser pulse width decreased from 100 to $\approx$ 1 ns, with fluence held constant, the MPD rate in SF_6 increased by only a small amount ($\approx$ 10–30%). It has been conventional wisdom since these experiments were performed, that it is the fluence of the laser pulse, and not the peak intensity, that is the determining factor in MPD. However, the relative importance of fluence and intensity in fact specifically depend on the details of examined molecule, such as: (a) the complexity of ground-state rotational structure; (b) the $V = 1 \leftarrow 0$ absorption coefficient; (c) the internal energy onset of the quasi-continuum; (d) the effective absorption coefficient in the quasi-continuum, etc.

In experiments with sufficient buffer gas, 100% of all CDF_3 molecules residing in the laser focus decompose when subjected to an incident laser fluence of 30 J/cm^2; whereas, without added beneficial buffer gas, only 2% dissociate. Approximately 180 J/cm^2 fluence is required for 100% yield in collision-free MPD of CDF_3. Since at lower fluences the dominant effect of CDF_3–Ar collisions appears to be ground-state rotational relaxation, apparently a fluence of 30 J/cm^2 is sufficient to permit absorption of the $\approx$ 30 photons required for MPD once the molecule is in the quasi-continuum. Without the assistance of collisions, a much higher fluence (180 J/cm^2) is required (with the same pulse shape). Evidently, the higher fluence laser pulse is required to allow all molecules, initially in any rotational state, to undergo MPD. It is most likely the increase in laser intensity, rather than the accompanying increase in fluence, that is responsible for removing this ground-state-rotational level "bottleneck".

Though smaller than in CDF_3, noticeable enhancement in MPD due to added inert gas has been observed in other molecules: methyl acetylene-d_1 ($\approx$ 15-fold-enhancement in isomerization to allene-d_1) [10], CF_2HCl ($\approx$ 10) [11], $H_3C{-}CHF_2$ ($\approx$ 2) [7], C_2H_3F ($\approx$ 3–6) [7], $H_2C{=}CF_2$ ($\approx$ 5) [7], and SF_6 ($\approx$ 5 in absorption at 1 mJ/cm^2 fluence, no enhancement at 1 J/cm^2) [4]. In addition, Quick and Wittig [7] observed a fluence-dependent decrease in the enhancement of MPD in C_2H_3F due to the addition of 11 Torr He, from 6.5 to 3.2-fold as the fluence was increased from 3 to 45 J/cm^2, though the absolute yield, with and without added buffer, increased with fluence. Perhaps this increase in fluence partially removed the ground-state-rotational level bottleneck, in addition to increasing photon absorption for molecules already in the quasi-continuum.

It may be concluded that in molecules such as CDF_3 which are lighter and smaller than, for example, SF_6, the intensity-dependent rotational-level bottleneck is removed at higher fluences (using standard TEA CO_2 lasers) than that required for MPD of molecules placed in the quasi-continuum. The dynamics of rotational-level mixing in a strong infrared field, resonant with a vibrational transition, is presently under examination [12].

4.2. Deuterium separation

The authors [13] originally suggested use of trifluoromethane for viable laser separation of deuterium based on its attractive spectroscopic features. The present study verifies that its photochemistry is nearly ideal as well. The essential requirement of efficient photon utilization [14] is satisfied for trifluoromethane, provided its low intensity deuterium isotopic selectivity in absorption of $> 2000:1$ (10.3 μ) is maintained at high fluence. CDF_3 dissociates to DF with a near-unity probability at a laser fluence of 180 J/cm^2 (10.2 μ), which is reduced six-fold to only 30 J/cm^2 when sufficient inert buffer gas is added. Homogeneous MPD in CHF_3 (yielding HF) is at least 10^{+4} times less probable than in CDF_3 under identical conditions. This ensures very high single-step deuterium enrichment factors, conservatively $\gtrsim 1000$, since isotopic scrambling according to eq. (3) is not important. Note that single-step deuterium enrichment factors of 1400 have been obtained in MPD of CF_3CHCl_2 (Freon 123) [14]. For a given laser pulse width, the maximum operating pressure of trifluoromethane in a deuterium separation process is limited by the relaxation of laser-excited CDF_3 by CHF_3; this is evident from fig. 5 in which the CDF_3 decomposition yield is quenched with added CHF_3 at higher pressures. In addition, at high pressures the collisionally-excited CHF_3 may itself undergo MPD. thus decreasing enrichment.

Redeuteration of trifluoromethane by H/D exchange tied to natural gas or water is essential for large-scale deuterium separation [14]. Trifluoromethane undergoes D/H exchange in methanol at a rather slow rate of 3.4×10^{-6} liter/mole s at 70°C, proportional to added base (sodium methoxide) as catalyst [15]. D/H exchange in water with added OH^- (base-catalyst) is expected to occur at a rate about five fimes faster [16]; however, hydrolysis may occur at a comparable rate [17]. This H/D exchange rate is much slower than for CF_3CHCl_2, another very attractive candidate molecule for laser separation of deuterium [14]. If the H/D exchange rate of trifluoromethane can be significantly increased by proper choice of exchange medium and catalyst, then trifluoromethane will possess all the properties required for viable large-scale laser separation of deuterium.

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