

Observations on the Spectral Dependence and T/D Isotope Selectivity in the CO_2 Laser Multiple-Photon Dissociation of Trifluoromethane

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Abstract. Pulsed CO_2 laser multiple-photon dissociation of CTF_3 (ν_2 mode) bathed in argon and CDF_3 , CHF_3 or CCl_4 is examined as a function of laser wavelength (9.2–9.6 μm) and fluence. The dependence of the dissociation profile on wavelength is analyzed and comparisons are made to prior work. The single-step T/D enrichment factor for infrared photolysis of trifluoromethane is measured; potential practical isotope separation is discussed. Pulsed infrared laser photolysis of CTF_3 (ν_5 mode) using a 12 μm NH_3 laser is also attempted.

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During the past several years, the use of pulsed infrared laser multiple-photon dissociation (MPD) to separate gas-phase molecules containing different hydrogen isotopes has been reported by various laboratories [1–22]. Successful D/H separation was initially demonstrated using MPD of CF_3CDCl_2 at 10.6–10.8 μm [1] and CDF_3 at 10.2–10.3 μm [2–4]. Further work addressed several aspects of the photophysics and photochemistry of CDF_3 and CHF_3 [2–10]; this included measuring a single step D/H enrichment factor of $\beta > 20,000$ [2]. The use of laser MPD of fluoroform for tritium-from-protium separation was suggested by the calculated [23, 24] and measured [24] infrared spectra of CTF_3 near 9.2 μm , and T/H separation was concomitantly demonstrated in the laboratory ($\beta > 1000$) [11–14]. Separation of deuterium from a ternary H/D/T mixture was also achieved by MPD of CDF_3 at 10.3 μm [15]. Though the relative spectral features of CTF_3 and CDF_3 did not suggest successful T/D separation based on the necessary though not sufficient condition of $\beta \gg 1000$, the absorption features of the chlorinated analog (CTCl_3 and CDCl_3) [16, 24] did. The first successful laser T/D separation was achieved using 12.08 μm MPD of tritiated chloroform [16] and in further

studies [17] $\beta > 15,000$ was measured for this process at room temperature. Tritium separation by infrared laser MPD has also been studied using C_2TF_5 (T/H [19] $\beta \sim 500$ at 10.6 μm ; T/D [20], $\beta \sim 3000$ at 10.7 μm , -78°C), CF_3CTCIF [21] (T/H, $\beta \sim 23$ at 10.3 μm) and CDTCl_2 [22] (T/D, $\beta \sim 30$ at 11.0 μm).

This paper describes an investigation of the wavelength and fluence dependence of isotopically selective MPD of CTF_3 , bathed in either CDF_3 , CHF_3 or CCl_4 , using a pulsed CO_2 laser to excite the ν_2 mode. Four factors motivated this study. First, the spectral profiles of the CTF_3 MPD probability measured by Makide et al. [11] and by Nève de Mévergnies et al. [14] in recent studies of T/H separation are in striking disagreement with each other. An attempt was made here to reconcile these two findings. Second, in an earlier, unpublished experimental study performed by the authors [18] on the spectral dependence of CTF_3 and CDF_3 MPD, some observed spectral features were not easily explained by standard spectroscopic models of collision-free MPD; this was considered worthy of further investigation. Third, though the low-fluence infrared spectra of isotopically-substituted fluoroform suggests that T/D separation by ν_2 mode excitation (9.2 μm) of this molecule should be inferior to separa-

tion by the $12\text{ }\mu\text{m}$ $\text{CTCl}_3/\text{CDCl}_3$ process [16, 17, 24], measurement of the enrichment factor in $\text{CTF}_3/\text{CDF}_3$ was still of interest. Finally, there was the additional motivation to extend the examination of the MPD of CTF_3 (in CDF_3) to the optically "cleaner" ν_5 region [24] (at 828 cm^{-1}), using a CO_2 laser pumped NH_3 laser for CTF_3 excitation.

1. Experimental Procedure

Trifluoromethane-*t* (CTF_3) was synthesized by ultraviolet irradiation of gas-phase mixtures of CF_3I in excess T_2 , using low pressure mercury lamps, as described previously [24]. This process results in an extremely clean preparation in which all of the CF_3I is consumed, and the CTF_3 is easily isolated from T_2 and the by-products, TI and I_2 . Subsequent dilutions were made using either CDF_3 , CHF_3 or CCl_4 to either 20 or 200 ppm of CTF_3 . In typical runs 200 mtorr of this diluted mixture was used and buffered by 50 torr of argon. The experimental apparatus and procedure were similar to that used in previously reported work [16, 17] and is only briefly described here.

A TEA CO_2 laser (Lumonics 103-2) was focused in the center of a metal photolysis cell (8 cm long, 1.2 cm ID) using a 50 cm focal length KCl lens. The laser pulse consisted of an 80 ns spike, followed by a $1\text{ }\mu\text{s}$ tail each containing roughly equal energy. CaF_2 plates were utilized as laser beam attenuators, and laser pulse energy was continuously monitored and averaged using a joulemeter and a voltage-to-frequency converter/counter. Following irradiation, the sample was frozen out and the argon removed. The sample was rewarmed and then cryogenically transferred to a gas sampling loop of a thermal conductivity gas chromatograph/ionization chamber detection system. Cell-averaged dissociation probabilities were deduced from the depletion in reactant concentrations. To correct for slightly different average pulse energies at different laser wavelengths, small linear corrections were made to extrapolate measured dissociation probabilities to the average pulse energy in a series of runs. The expected fluoroform MPD products are: CF_2 , leading to C_2F_4 , and hydrogen fluoride [2]. In experiments with sufficient fluoroform decomposition to permit detection of the C_2F_4 product, one C_2F_4 was observed for each two decomposing fluoroform molecules, as expected. Product hydrogen fluoride reacted with the cell walls before transfer to the gas chromatograph [9] in this apparatus. Run-to-run reproducibility was 5%, and in null runs the non-tritiated reactant component detection precision was 0.2%, while that of the tritiated component was 2%. Experiments were performed over a several month period with little variation in measured system response.

In several experiments the CO_2 laser was operated with minimal N_2 , eliminating most of the $1\text{ }\mu\text{s}$ tail while preserving enough pulse energy for an attempt to duplicate conditions in one of the above-cited $\text{CTF}_3/\text{CHF}_3$ studies [14]. For these particular experiments, pressures of 10 torr of the 20 ppm $\text{CTF}_3/\text{CDF}_3$ (or CHF_3) mixture were used in 100 Torr of argon buffer, and the 50 cm f.l. lens was replaced by a lens with 75 cm focal length. Attempts to photolyze CTF_3 near the ν_5 absorption transition utilized a CO_2 laser optically pumped NH_3 laser at 828 cm^{-1} , described previously [16, 17], as the excitation source.

2. Results

The dependence of the cell-averaged CTF_3 (CDF_3 , CHF_3) dissociation probability per pulse ($d_{\text{T,D,H}}$) on laser frequency was measured in the vicinity of the ν_2 absorption band of CTF_3 . Figure 1a shows that low-fluence CTF_3 absorption in this region consists of a sharp *Q*-branch maximum at 1076.9 cm^{-1} , a *P*-branch maximum at 1061.0 cm^{-1} and an *R*-branch centered at 1097.5 cm^{-1} (not shown). Figures 1b, c, and 2a display the results of CTF_3 infrared laser MPD in CDF_3 at three laser pulse energies (188, 377 and 880 mJ/pulse). Each run was performed using 200 mTorr of 207 ppm CTF_3 in CDF_3 plus 50 Torr of argon buffer gas (to facilitate rotational hole filling) [2, 3, 6]. Note that the left hand ordinate scale increases two orders of magnitude in going from the 188 to 880 mJ/pulse experiment. Figures 2b and c are "high" fluence (880 mJ/pulse) runs but using 200 mTorr of 207 ppm of CTF_3 in CHF_3 and CCl_4 , respectively, (plus 50 Torr of argon) instead of CDF_3 , as further described below. In each case the dissociation probability of both CTF_3 and the background gas are plotted. The right hand ordinate in Figures 1b and c and 2a and b is the T/D (or T/H) enrichment factor, $\beta \equiv d_{\text{T}}/d_{\text{D}}$ (or $d_{\text{T}}/d_{\text{H}}$). No data was taken in the region between 1056 to 1072 cm^{-1} due to the lack of suitably strong CO_2 laser lines in this gap; the curves connecting data points are interpolated in this region.

For CTF_3 dissociation, there are two local MPD maxima in the vicinity of the *Q*-branch. The first one is observed near 1083 cm^{-1} and appears to track the CDF_3 dissociation curve in both shape and absolute magnitude (Figs. 1b, c, and 2a). It is tempting to speculate that the CTF_3 dissociation in this region is due to vibrational energy transfer from excited CDF_3 , since CDF_3 absorption is rising in this region, reaching a *P*-branch maximum at 1088 cm^{-1} and a *Q*-branch peak located at 1110 cm^{-1} (not shown).

To further investigate the influence of energy transfer in CTF_3 dissociation, a duplicate set of runs was conducted, resulting in the data plotted in Fig. 2b with

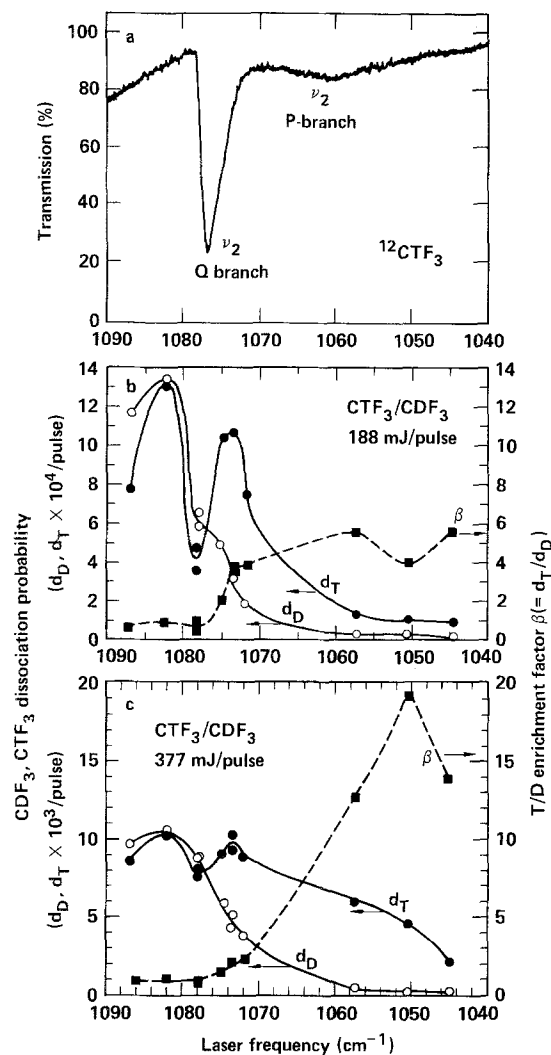


Fig. 1. (a) The low-fluence infrared spectrum of $^{12}\text{CTF}_3$. (b) The cell-averaged, per-pulse MPD dissociation probability of CTF_3 (d_T) and CDF_3 (d_D) (left hand ordinate) as a function of laser photon frequency. The laser, with pulse energy of 180 mJ/pulse ($\sim 7.5 \text{ J/cm}^2$ peak fluence), was focused by a 50 cm f.l. lens into a cell containing 200 mTorr of a 207 ppm $\text{CTF}_3/\text{CDF}_3$ mixture buffered by 50 Torr argon. The right hand ordinate plots the single-step enrichment factor defined as $\beta \equiv d_T/d_D$. (c) Same as in (b) except the laser pulse energy is 377 mJ/pulse ($\sim 15 \text{ J/cm}^2$ peak fluence)

880 mJ/pulse, but using 200 mTorr CTF_3 (21 ppm) in CHF_3 , again with 50 Torr of argon. (The CHF_3 bath contained 170 ppm of CDF_3 since it was made by diluting a 50:50 $\text{CTF}_3/\text{CDF}_3$ sample with CHF_3 which included 150 ppm of CDF_3 from natural abundance. These levels of deuterated fluoroform are inconsequential to the experiment.) Figure 2b shows a CTF_3 MPD spectral profile similar to that using CTF_3 in a bath of CDF_3 . The two maxima and the local minimum all occur at the same CO_2 laser line frequencies. The first d_T maximum at 1083 cm^{-1} is

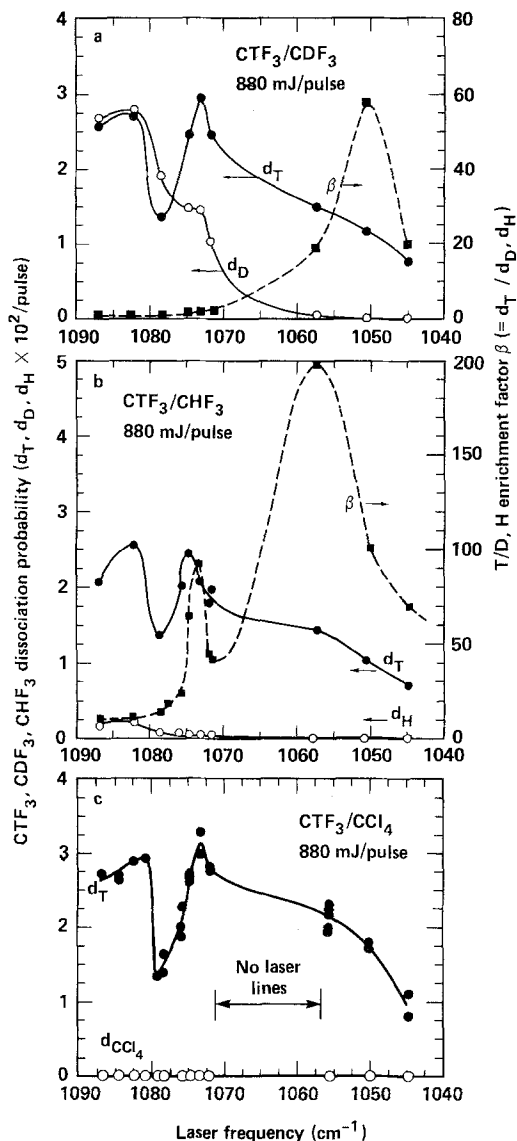


Fig. 2a-c. The cell-averaged, per-pulse MPD probability plotted vs. laser frequency with 880 mJ laser pulses (peak fluence $\sim 35 \text{ J/cm}^2$). Further details are given in the Fig. 1 caption and the text. (a) $\text{CTF}_3/\text{CDF}_3$, $\beta \equiv d_T/d_D$. (b) $\text{CTF}_3/\text{CHF}_3$, $\beta \equiv d_T/d_H$. (c) $\text{CTF}_3/\text{CCl}_4$

unchanged from that in Fig. 2a even though the dissociation yield of CHF_3 in this region is an order of magnitude lower than that for CDF_3 . This experiment does not conclusively discount the importance of collisions since there is still some residual absorption and a small amount of dissociation in CHF_3 . In order to more stringently test the hypothesis of the energy transfer mechanism, it was necessary to dissociate CTF_3 in a background gas which has no absorption (including overtones, combination bands and hot bands) in this spectral region, but which could

efficiently vibrationally relax CTF_3 . (Simply diluting CTF_3 in argon proved to be unfeasible due to vapor pressure considerations in sample preparation and transfer.) Such a molecule is CCl_4 , which has only one significant absorption peak, at 790 cm^{-1} , and is essentially transparent ($<1\%$ absorption for 600 Torr-cm) in the $1045\text{--}1090\text{ cm}^{-1}$ region. Figure 2c shows the results of the CTF_3 dissociation experiment using 200 mTorr of $200\text{ ppm } \text{CTF}_3/\text{CCl}_4$, also in 50 Torr of argon. Again there is a strong rise in the CTF_3 MPD probability to the high frequency side of 1080 cm^{-1} , while there is no detectable loss of CCl_4 . Clearly, this MPD resonance at 1083 cm^{-1} is not due to collisional energy transfer from a secondary absorbing species.

A second CTF_3 MPD maximum occurs near the $9\text{ }\mu\text{m}$ $R(12)\text{ CO}_2$ laser transition at 1073 cm^{-1} and is similar in magnitude to the first maximum at 1083 cm^{-1} . In between these two peaks, a local minimum occurs near the $R(20)\text{ CO}_2$ laser line at 1079 cm^{-1} . These local extrema appear to be independent of the laser energy range used in these experiments. As the laser pulse energy is increased from 188 mJ to 880 mJ/pulse (corresponding to an increase in the peak fluence from ~ 7.5 to $\sim 35\text{ J/cm}^2$), a possible third maximum is suggested, located near the shoulder at 1056 cm^{-1} . However, its precise location cannot be ascertained due to the lack of laser lines between 1056 and 1072 cm^{-1} .

Each of the fluoroform dissociation probabilities, d_T , d_D , and d_H falls off to the low frequency side of the second d_T maximum at 1073 cm^{-1} , with d_H decreasing the most rapidly. Consequently, the best enrichment factor is obtained for T/H separation with $\beta=200$ peaking near 1050 cm^{-1} . As shown in [11–14], even higher single-step enrichment factors can be obtained by optimizing conditions. In the three runs using CTF_3 in CDF_3 , the T/D enrichment factor increases with increasing laser energy due to the appearance of the third CTF_3 MPD “maximum” attaining a peak value of $\beta=60$ (Fig. 2a). Even with optimizing conditions at room temperature, this enrichment factor would still be much smaller than the $\beta>15,000$ measured in $12\text{ }\mu\text{m}$ MPD of $\text{CTCl}_3/\text{CDCl}_3$ [17].

Using a CO_2 laser pumped NH_3 laser (300 mJ/pulse , $\sim 12\text{ J/cm}^2$ peak fluence, at 828 cm^{-1}) to excite the ν_5 CTF_3 transition “R”-branch ($\Delta K=+1$) maximum at 831 cm^{-1} in a $\text{CTF}_3/\text{CDF}_3$ /argon mixture, led to no observable CTF_3 reactant depletion ($d_T<2\times 10^{-5}$), apparently due to the weak absorption strength of this band ([24] and below) and the lower laser pulse energy available at $12\text{ }\mu\text{m}$ vis-a-vis $9\text{ }\mu\text{m}$. This excitation wavelength should promote the maximum dissociation probability, as was found for CDF_3 $\nu_5\leftarrow 0$ excitation in [9] where photolysis directly on and

several cm^{-1} below the lower frequency doublet (“R”-branch) peak displayed maximum MPD yield. These experiments were conducted to minimize d_D or d_H and consequently to maximize the enrichment factor since neither CDF_3 nor CHF_3 has appreciable absorption in this region.

The estimates of the relative strength of fundamental band features in CTF_3 and CDF_3 first given in [24] have been somewhat refined here. New estimates for the ratio of the strength of the CDF_3 feature to its CTF_3 analog are: 0.6 for the ν_1 Q-branch peak, 1.2 for the ν_2 Q-branch peak, 5.2 ± 1 for the ν_5 P and R peaks heights, and 5.5 ± 1 for the ν_5 integrated band intensity.

3. Discussion

Fluoroform is an oblate symmetric top of C_{3v} symmetry. The ν_2 band is a parallel transition of type a_1 symmetry and represents a C–F symmetric stretch. The ν_5 band is a perpendicular transition (e) and corresponds to an H–C–F bend. The ν_2 transition exhibits a cleanly resolved PQR band structure with unequal P and R-branch intensities weighted heavily to the R-branch, due to the different P and R-branch transition matrix elements and Coriolis coupling [25]; the ν_5 band is an RP doublet representing $\Delta K=\pm 1$ transitions, respectively.

The aims of this study were to compare the present observations with those reported previously as well as to call attention to several new features. One observation is that the CDF_3 , $\nu_2\leftarrow 0$ MPD spectrum measured here matches that of Gauthier et al. [5] who reported a local dissociation probability maximum near 1083 cm^{-1} . Similarly, the CHF_3 , $\nu_2\leftarrow 0$ MPD spectrum observed here matches that reported by both Makide et al. [11] and by Nève de Mévergnies et al. [14].

Furthermore, the rise in CTF_3 MPD probability (d_T) to the high frequency side of 1080 cm^{-1} (and the Q-branch at 1077 cm^{-1}) observed in each case here, was also noted by both Makide et al. [11] and Nève de Mévergnies et al. [14] in experiments using $\text{CTF}_3/\text{CHF}_3$ mixtures. Neither of the two groups presented data to the high frequency side of 1082 cm^{-1} (the first CTF_3 MPD peak) where d_T again decreases. Both groups attributed the rise to the increase of d_H resulting from the absorption tails of either the ν_2 band of $^{13}\text{CHF}_3$ (Q-branch at 1116 cm^{-1}) and/or the ν_2 band of $^{12}\text{CHF}_3$ (at 1141 cm^{-1}). The present study, in which CTF_3 was also photolyzed in optically transparent CCl_4 /argon, has proven that this CTF_3 MPD resonance is not influenced by collisional energy transfer from a co-absorbing species.

The spectral location and relative magnitude of the second observed MPD peak of CTF_3 is in excellent

agreement with the work reported by Makide et al. [11] in which they found a CTF₃ dissociation local minimum near 1079 cm⁻¹, a maximum near 1075 cm⁻¹, and monotonically decreasing d_T for lower laser frequencies. Their experiment was performed using 5 Torr of 0.2 ppm CTF₃/CHF₃ and no argon buffer gas. Also, in their study CO₂ laser pulse energies of 600 mJ were focused with a 7.5 cm f.l. lens, and no nitrogen was used in the CO₂ lasing medium (i.e., no temporal 1 μs tail). While Nève de Mévergnies et al. [14] also found a local minimum near 1079 cm⁻¹, their CTF₃ dissociation maximum occurs at 1057 cm⁻¹, close to the center of the $\nu_2 \leftarrow 0$ *P*-branch at 1061 cm⁻¹ and 12 cm⁻¹ to the low frequency side of that found here and in [11]. These experiments were performed at even higher pressures, 15 Torr of 0.03 ppm CTF₃/CHF₃ plus 100 Torr of argon. Laser pulses of 90–100 ns FWHM (and no tail) and pulse energies of 1.8 J were used, focused with a 76 cm f.l. lens. Several careful attempts to duplicate these experimental conditions were unsuccessful due to dielectric breakdown in the sample medium at these very high pressure and fluence conditions. Apparently, the cell-averaged MPD probabilities are weighted to higher fluences in [14] than in [11] and here. Note, however, that as the laser pulse energy is increased in the present study, there is some evidence that a third MPD feature is beginning to grow in the region of the MPD maximum found by Nève de Mévergnies et al. [14].

Attempts to explain coarse features in MPD spectral profiles often rely on vibrational anharmonicity and/or rotational compensation arguments [26–28], while explanations of the finer details, obtained using pump lasers that are continuously tunable in frequency (which are not used here), sometimes in addition consider the effect of multiquantum overtone/combination/hot band resonance transitions [29, 30]. Few molecular resonances examined in MPD studies have the cleanly resolved, relatively unperturbed PQR structure of the CTF₃ (and CDF₃) $\nu_2 \leftarrow 0$ ground state transition. The MPD spectrum of the less cleanly resolved PQR structure in the chloroethane ν_8 , C–C stretching mode has two resonances, lying midway between the *P* and *Q* and also between the *Q* and *R*-branch peaks [31]. There is some evidence for similar MPD structure in the ν_9 , CH₂ rocking mode of gauche chloroethane-2-*d*₁ [32].

The *R*, *Q* and *P* peaks in the low fluence $\nu_2 \leftarrow 0$ spectrum of CTF₃ are at 1097.5, 1076.9 and 1061.0 cm⁻¹, respectively, while the peaks in the MPD spectrum are at 1083 (peak 1), 1073 (peak 2) and 1056 cm⁻¹ (peak/shoulder 3). The two sharp MPD peaks lie on either side of the *Q*-branch by ~ 6 cm⁻¹. Alternately, the MPD peaks 1, 2 and “3” lie 14, 4 and 4 cm⁻¹, respectively, to the low frequency side of the *R*,

Q and *P* spectral peaks. Furthermore, the CDF₃ MPD peak at 1083 cm⁻¹, which coincides with MPD peak 1 in CTF₃ and is not collisionally coupled to this CTF₃ feature, lies 45, 28, and 5 cm⁻¹ to the low frequency side of the CDF₃ $\nu_2 \leftarrow 0$ *R*, *Q* and *P* peaks, respectively. Therefore, with a corresponding 5 cm⁻¹ frequency downshift from the *P* peak the analogous MPD peak in CTF₃ should be at 1056 cm⁻¹, near the observed CTF₃ MPD peak/shoulder 3, and the broad peak observed at 1057 cm⁻¹ by Nève de Mévergnies et al. [14]. This correlation is uncertain since the CDF₃ MPD peak appears sharper than the corresponding CTF₃ peak. The low-fluence infrared absorption profile of ν_2 in CDF₃ is slightly stronger than in CTF₃, while both have similar degrees of *R*/*P*-branch strength asymmetry (with the integrated absorption strength of the *R*-branch much larger than that of the *P*-branch for reasons mentioned above). This difference in MPD probability in CTF₃ and CDF₃ at the same laser fluence may be due to the slightly different transition strengths or due to fine details in multiple-photon excitation. Attempts to correlate the CTF₃ MPD peaks with multiquantum resonances in the ν_2 vibrational ladder, including the effects of anharmonicity ($X_{22} \simeq -0.6$ cm⁻¹ in CTF₃) [33, 34], rotational level compensation, and averaging over the rotational partition function have proven unsuccessful.

The technique of 12 μm MPD of chloroform still seems to be the best photochemical route for tritium-from-deuterium recovery [16, 17]. The relative merits of 10.2 μm fluoroform separation, including cheaper molecules, direct use of a CO₂ laser instead of a CO₂ laser pumped NH₃ laser, simpler post-photolysis chemistry and slower *V*–*T* transfer (which influences intrapulse gas dynamics in the reaction cell), are outweighed by the relative disadvantages of this method. Both the enrichment factor $\beta \sim 60$, which is a figure of merit for the single-step upgrade of the tritium fraction and reagent consumption, and T/D absorption selectivity (CTF₃ absorption cross-section at 10.2 μm divided by that in CDF₃, ~ 30 at low fluence), which is a figure of merit for the fraction of photons absorbed by the tritium species, are far too small in fluoroform for practical isotope separation. Though T/D selectivity will improve with lower temperature operation, this improvement will probably not significantly help overall process economics.

4. Concluding Remarks

Evidence presented in this study suggests that differences in the published spectral MPD profiles of CTF₃ may be due to use of different laser fluences. Respective features of the CTF₃ and CDF₃ MPD

spectra, as well as their similarities and differences, have been discussed. Vibrational-energy collisional transfer from either a CDF_3 or CHF_3 bath gas to CTF_3 does not influence MPD in this molecule in the experimental regimes studied. Based on the fairly low T/D absorption selectivity near the ν_2 band in trifluoromethane (~ 30), the relatively low enrichment factors measured here (i.e., low by chloroform MPD standards) are not surprising. Though higher T/D dissociation and absorption selectivities are expected for ν_5 band excitation near 828 cm^{-1} , no CTF_3 dissociation was observed here using resonant laser pulses with 12 J/cm^2 fluence, probably because of the weak strength of this transition.

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