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DEVELOPMENT OF ADVANCED TECHNOLOGIES
FOR PHOTOCHEMICAL TRITIUM RECOVERY

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Bi-quarterly Program Report for the
period April 1, 1980 through September
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DEVELOPMENT OF ADVANCED TECHNOLOGIES FOR PHOTOCHEMICAL TRITIUM RECOVERY

Bi-Quarterly Progress Report
For the Period April 1, 1980 through September 30, 1980

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ABSTRACT

The laboratory facility for photochemical tritium separation research has been completed. Methods for synthesizing the mono-tritiated halogenated methanes have been developed. Notably, CTF_3 has been synthesized and spectrally analyzed. The CTF_3 vibrational frequencies are found to be in quite good agreement with earlier calculations.

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Table of Contents

	Page
I. Introduction	3
II. Synthesis of the Mono-tritiated Halogenated Methane Working Molecules	4
III. Infrared Spectroscopy of CTF_3	7
IV. Concluding Remarks	8
V. Invention Disclosures and Patent Activity	9
VI. Appendix: "The Infrared Spectrum of CTF_3 and Implications Towards Tritium Isotope Separation By Infrared Laser Multiple- Photon Dissociation of Halogenated Methanes"	10

I. Introduction

During this reporting period the laboratory facilities for tritium recovery experiments were completed in the Lawrence Livermore National Laboratory Tritium Building. Included in this set-up is the recently-obtained Lumonics 103 CO_2 laser; this laser will be used either to directly photodissociate the mono-tritiated halogenated methane working molecule, or else to optically pump another molecular laser, such as the NH_3 laser, which instead will be the IR photolysis source. In addition, important progress was made in synthesizing these tritiated halogenated methanes. One of the halogenated methane molecules that was suggested in an earlier progress report as a possible working molecule for T/D separation, CTF_3 -tritiated trifluoromethane, was synthesized and its infrared spectrum was analyzed.

II. Synthesis of the Mono-tritiated Halogenated Methane Working Molecules

The various methods tested to synthesize mono-tritiated halogenated methanes employed tritiation by a gas-phase source of T_2 , rather than direct isotopic exchange with tritiated water. This was deemed necessary because of the much greater biological hazard of HTO , DTO and T_2O relative to T_2 . The safety operating procedures which are followed in the LLNL Tritium Facility, and also in other similar facilities, suggested that preliminary work should not involve the use of tritiated water.

The Wilzbach technique, in which T_2 and a halogenated methane are allowed to react (catalyzed solely by the tritium radiation field), was employed in Runs 1 — 5 listed in Table I; the intended products in these trials were $CTCl_3$ (Runs 1 — 2) or CTF_3 (Runs 3 — 5). In these experiments, the reagents were mixed in an infrared cell with KRS-5 windows. The extent of reaction was checked periodically *in situ* using an infrared spectrometer during the 8 — 22 day duration of the run. These experiments were characterized by a gradual disappearance of the organic reagent, accompanied by the appearance of a complex infrared spectrum. In Runs 3 — 5 there was evidence for some CTF_3 formation; however, there were many other observed spectral peaks that were not due to CTF_3 —and that remained unassigned.

The next method employed was UV catalysis. Ultraviolet photolysis of both CF_3I and $(CF_3)_2CO$ are well-known procedures to produce CF_3 radicals. Due to a reaction barrier of about 11 kcal/mole, CF_3 reacts fairly slowly with molecular hydrogen to form trifluoromethane, as in Reactions 1 and 2:

Fortunately, when CF_3I is used as the source of CF_3 , the most important reaction that competes with (2) is the relatively fast Reaction (4) which again produces the CF_3I reagent. Therefore, though the net quantum yield in forming CTF_3 may be small, the overall reaction yield may still approach unity.

Using 2527 Å radiation from an Hg lamp, the reaction of $CF_3 + D_2 \rightarrow CDF_3 + D$ —as monitored by gas chromatography— was tested in a quartz vessel near ambient temperature using either CF_3I or $(CF_3)_2CO$ as the source of trifluoromethyl

TABLE 1

Run No.	Intended Product	Reagents (t=torr)	Conditions	Results
1	$CTCl_3$	10t $CDCl_3$ /50t T_2	IR cell/8 days	No Carbon Products
2	$CTCl_3$	50t $CDCl_3$ /51t T_2	IR cell/15 days	No $CDCl_3$ / $CTCl_3$
3	CTF_3	40t CHF_3 /56t T_2	IR cell/18 days	Initial Organic
4	CTF_3	40t CF_3Br /61t T_2	IR cell/11 days	Consumed, Many Products
5	CTF_3	40t CF_3I /62t T_2	IR cell/22 days	Evidence for CTF_3
6	CTF_3	8t CF_3I /80t T_2	UV-2537Å/ 28 hours	See CTF_3 Complete Conversion (Some CHF_3 , CDF_3)
7	CTF_3	6t CF_3I /73t T_2	UV-1849Å/ 40 hours	See CTF_3 Complete Conversion (Some CHF_3 , CDF_3)
8	CTF_3	9t CF_3I /38t T_2	UV-1849Å/ 3.5 hours	See CTF_3 , CF_3I
9	CTF_3	8t CF_3I /24t T_2	UV-2537Å/ 23 hours	CTF_3
10	—	6t CF_3I		IR Scan
11	CTF_3	8t CF_3I /82t T_2	UV-2537Å/ 23 hours	CTF_3
12	CTF_3	8t CF_3I /75t T_2	Null in UV Cell	No Product
13	CTF_3	8t CF_3I / $\gtrsim$ 80t T_2	Pd Catalyst/5 days	80% Conv. to CTF_3
14	CTF_3	8t CHF_3 /83t T_2	Pd Catalyst	Pd Poisoned In Run No. 13
15	CTF_3	20t CF_3I /82t T_2	UV-1849Å, 2537Å/4 days	CTF_3

radicals. Only the route using CF_3I provided a clean method of CDF_3 production. Use of the 1849Å line from an Hg lamp apparently accelerated the CDF_3 production compared to the 2537Å line. Runs 6—9, 11 and 15, described in Table I, show that UV catalysis of the $CF_3I + T_2$ reaction proved to be quite successful in producing CTF_3 ; in fact, the trifluoromethane was produced at a much faster rate in runs with T_2 , rather than with D_2 .

CTF_3 was also produced using $CF_3I + T_2$ in the presence of palladium powder, a standard hydrogenation catalyst (Run 13 in Table I). However, this catalyst was poisoned by the organic reagent, and therefore alternate hydrogenation catalysts are preferred. (Recent tests show that platinum is a more suitable catalyst.)

The identity of the CTF_3 product was confirmed using infrared spectroscopy and mass spectrometry. As discussed in more detail in the following section, the observed peaks in the infrared spectrum of the product occurred at the vibrational frequencies predicted for CTF_3 , as described in an earlier reporting period report (Appendix I, Ref. 7). Most of the other observed peaks were small, and were readily identified as either CHF_3 , CDF_3 , CF_4 , C_2F_6 or SiF_4 . A medium-strength feature near 390 cm^{-1} , possessing quite pronounced PQR structure, appeared in some runs. However, since the strength of this peak in the various runs in which CTF_3 was produced, did not correlate with the six identified CTF_3 spectral features, it is an unidentified purity, and does not affect the identification of CTF_3 as the main product. CTF_3 was further confirmed to be the main product in mass spectrometric analysis.

Production of $CTCl_3$ may not be possible using a UV catalysis scheme similar to that described for CTF_3 . Using UV photolysis of CCl_3Br as a source of CCl_3 radicals and D_2 as the other reagent, no $CDCl_3$ product was observed as would be expected from Reactions (5) and (6).

CCl_4 appears to be produced using this technique. Apparently the ~ 15 kcal/mole barrier for Reaction (6) is too high to permit a reasonable yield at ambient temperature. Still $CTCl_3$ may be produced when T_2 is used as a reagent because of radiation catalysis. Also, use of a platinum catalyst may help produce $CTCl_3$. These techniques will be tested in the coming year.

III. Infrared Spectroscopy of CTF_3

The infrared spectrum of CTF_3 is shown in Figure 1 of the Appendix. This Appendix consists of a paper accepted for publication in the Journal of Physical Chemistry, that details the procedures followed in both the preparation and the infrared spectroscopy of CTF_3 . An expanded portion of the infrared spectrum near ν_2 ($\sim 1077\text{ cm}^{-1}$) is shown in Figure 2. The observed peak frequencies of the CTF_3 vibrational fundamentals are tabulated in Table II of this Appendix; they may be compared to calculations of the CTF_3 frequencies which were initially presented in an earlier quarterly report (Appendix; Ref. 7), and that are also reproduced in Table I (Appendix). Note that the vibrational fundamentals calculated using the force field of Kirk and Wilt (Ref. 9) are in very good agreement with observations.

Implications For Tritium-from-Deuterium Recovery

T/D separation using selective CO_2 laser multiple-photon dissociation of CTF_3 near 9.3μ (ν_2 mode) does not appear attractive, as the low fluence optical selectivity in absorption attains a maximum of only 30 in this region. Note, however, that the optical selectivity for T/H recovery is much higher, being ~ 700 , in this region. Use of two-wavelength IR photolysis and/or burning out the $^{13}CDF_3$ in the CDF_3 working molecule reservoir, will probably not sufficiently improve the optical selectivity, to make CO_2 laser photolysis of CDF_3/CTF_3 attractive for tritium recovery from heavy water nuclear power plants. Still, NH_3 laser MPD of the ν_5 mode in CTF_3 or CO laser MPD of ν_1 in CTF_3 may still be useful, and will be investigated further.

IV. Concluding Remarks

In the coming reporting period several other tritiated halogenated methanes will be synthesized and spectrally analyzed. IR laser photolysis experiments will soon begin. NH_3 laser photodissociation of $CTCl_3$ may be investigated after a more thorough analysis of CO_2 laser photolysis of $CDCl_3$ is performed.

V. Invention Disclosures and Patent Activity

Irving P. Herman and Jack B. Marling, "Laser Assisted Tritium Recovery from Trihalomethanes", Invention Case No. IL-6729, patent presently being drawn up.

VI. Appendix

The Infrared Spectrum of CTF_3 and Implications Towards
Tritium Isotope Separation By
Infrared Laser Multiple-Photon Dissociation of
Halogenated Methanes*

by

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ABSTRACT

The infrared absorption spectrum of nearly pure CTF_3 was measured, and compared with the fundamental absorption frequencies calculated using published CHF_3 and CDF_3 general harmonic force fields. The agreement between calculated and observed frequencies is found to be satisfactory. Based on calculated and measured absorption frequencies, photochemical separation of T from H is very attractive in trifluoromethane using CO_2 laser multiple-photon dissociation near the strong CTF_3 ν_2 band centered at 1077.0 cm^{-1} . Photochemical separation of both T from H and T from D is attractive using a CO laser near the strong CTF_3 ν_1 band centered at 1930.5 cm^{-1} .

I. Introduction

Trifluoromethane has recently been identified as the optimal working molecule for deuterium isotope separation by infrared laser multiple-photon dissociation (MPD)¹. Since such a separation process satisfies many requirements for commercial feasibility, several recent studies have focused on the photochemical and photophysical properties of CDF_3 and CHF_3 .¹⁻⁷ The past decade has also witnessed active investigation of the molecular force field of the trifluoromethane ground electronic state.⁸⁻¹¹ This paper reports the first published infrared spectrum of CTF_3 , tritiated trifluoromethane. These spectroscopic observations are analyzed in light of the predictions of the vibrational frequencies based on published force fields of CHF_3 and CDF_3 , and the possible application to photochemical tritium isotope separation.

Photochemical tritium separation from deuterium can be used to lower the high levels of tritium contamination (DFO in H_2O ; up to 6ppm T:D) found in heavy water fission reactors; similarly, tritium from protium recovery will be important in decontaminating the coolant water in fusion reactors. The recent success of D/H separation using pulsed CO_2 lasers in IR photolysis of $\text{CDF}_3/\text{CHF}_3$ ¹⁻⁴, suggests that infrared laser MPD of a halogenated methane, which can be tritiated by chemical exchange with water (DFO or HTO in T/D or T/H separation), may serve as the separative step in T/D or T/H recovery. A member of this attractive class of working molecules should have suitably high isotopic selectivity in absorption, near unity MPD dissociation probability at modest fluences, and a high enrichment factor

(isotopic dissociation selectivity) at the wavelength of an efficient pulsed infrared laser.¹ In particular, since halogenated methanes have relatively few vibrational modes, vis-a-vis most hydrogen-bearing molecules, there is a relatively enhanced probability that a suitable infrared feature in the tritiated molecule occurs at a wavelength where the deuterated or protonated analog is transparent. In addition, these small molecules dissociate within only a few nanoseconds once excited to only a few kcal/mole above the dissociation energy, thereby permitting decomposition that is unhindered by competitive vibrational quenching at pressures up to about 1 atm, when using a laser photodissociation pulse duration of a few nanoseconds¹.

II. Theoretical and Experimental Procedures

In a previous study⁷ the authors presented calculations of the fundamental vibrational frequencies of a number of tritiated halogenated methanes based on the published general harmonic force fields of the protonated and deuterated analogs. Based on the estimated high isotopic absorption selectivity ($>100:1$) at wavelengths at which efficient pulsed infrared lasers exist and other chemical and photochemical criteria (as previously described in detail for D/H separation¹), trifluoromethane, trichloromethane and dichloromethane were selected for further investigation.⁷ T/D recovery appeared promising using trifluoromethane near 9.4μ (CO_2 laser), 12.08μ (NH_3 laser) or 5.2μ (CO laser); using trichloromethane near 12.08μ (NH_3 laser); and using dichloromethane near 10.9μ (CO_2 laser). T/H separation showed very great promise employing trifluoromethane near 9.4μ (CO_2 laser) or 5.2μ (CO laser), and lesser promise in both this molecule and trichloromethane near 12.08μ (NH_3 laser).⁷ In this study the suitability of trifluoromethane is further considered based on the new spectroscopic observations.

The band center frequencies for $^{12}\text{CHF}_3$ were calculated using the Wilson F-G matrix method;¹² they are presented in Table I, columns 3-6, along with the observed frequencies for $^{12}\text{CHF}_3$ and $^{12}\text{CDF}_3$ in columns 1-2. The shift in frequency for the ^{13}C species ($^{13}\text{C}_v$ - $^{12}\text{C}_v$) for the ν_2 band in CHF_3 and CDF_3 is listed in parentheses to the right of the respective ^{12}C entry. General harmonic force fields from three studies were employed, assuming the trifluoromethane molecular geometry and the symmetry coordinates cited in reference 8. In column 3, the force field from the most recent and purportedly the most accurate study, that of Kirk and Wilt (KW)⁹, was employed. This field was determined using the harmonic frequencies¹³ of $^{12}\text{CHF}_3$, $^{13}\text{CHF}_3$, and $^{12}\text{CDF}_3$; in contrast, fundamental frequencies¹³ (observed frequencies) were employed to obtain the force fields utilized in columns 4-6. Since the standard F-G matrix technique is based on a multi-dimensional harmonic potential, it is preferable to use the anharmonicity-corrected harmonic frequencies to obtain the force field. (Anharmonic contributions are easily handled, as described below.) The KW force field was also corrected for the effects of Fermi-resonance perturbations on some of the observed fundamental frequencies, particularly for ν_1 . The calculated harmonic frequencies for $^{12}\text{CHF}_3$ are listed in brackets in column 3. The tabulated fundamental frequencies were derived from these values using known CHF_3 and CDF_3 anharmonic constants⁹, that were suitably isotope-shifted using the approximation to Dennison's rule cited by Kirk and Wilt⁹. The force field of D'Cuhna¹⁰ was used in column 4. In column 5, the 12 parameter general harmonic force field of Ruoff et al¹¹ was used; their 11 parameter hybrid orbital force field fit was employed in column 6.

General harmonic force fields fully reflect the symmetry of a molecule, and consequently they best describe intramolecular forces. Therefore, the general harmonic force field used here should predict the CTF_3 fundamentals more accurately than would any modified Urey-Bradley harmonic field; this is illustrated for CHF_3 and CHF_3 in Reference 10.

CTF_3 was successfully synthesized by catalysis of room temperature, gas-phase mixtures of $\text{CF}_3\text{I} + \text{T}_2$, using either ultraviolet light or a standard heterogeneous hydrogenation catalyst. Initial attempts at synthesis utilizing the Wilzbach technique¹⁴ of mixing T_2 with either CHF_3 , CF_3Br or CF_3I were unsuccessful. Despite the possibility of radiation-induced catalysis in this last technique, only small quantities of CTF_3 were produced along with greater amounts of other, unidentified compounds.

Employing UV catalysis, about 10 torr CF_3I and 80 torr T_2 (97.4% T_2 , 1.2% DT, 1.4% HT) were introduced into a quartz vessel and irradiated by either the 1849Å or 2537Å line from an array of low pressure Hg lamps for about a day. The effective irradiation flux was approximately 15 mw/cm^2 at either wavelength. In this process the CF_3I absorbs a UV photon, and then the C-I bond breaks to yield $\text{CF}_3 + \text{I}$. The measured thermal activation energy for the reaction $\text{CF}_3 + \text{H}_2 \rightarrow \text{CHF}_3 + \text{H}$ is about 11 kcal/mole¹⁵; unless the CF_3 is formed with sufficient internal energy the quantum yield in forming CTF_3 may be small because of competing reactions. Indeed, Kibby and Weston¹⁶ measured a quite small quantum yield $\approx 3 \times 10^{-5}$ for this reaction at $\lambda = 2537\text{Å}$. Fortunately, the only important competing reaction is the relatively fast $\text{CF}_3 + \text{I}_2 \rightarrow \text{CF}_3\text{I} + \text{I}$ (I_2 from $\text{I} + \text{I}$ recombination) which reforms the

starting material, and therefore does not decrease the branching ratio to form CTF_3 . C_2F_6 , from CF_3 recombination, and other products are observed only in trace amounts, and consequently, the branching ratio to CTF_3 is indeed found to be nearly unity. All starting CF_3I was consumed and the unexpectedly pure CTF_3 was, in fact, produced at a rate almost an order of magnitude faster than the studied $\text{CF}_3\text{I} + \text{D}_2 \rightarrow \text{CDF}_3 + \text{I} + \text{D}$ test case; this suggests that the radiation field of the tritium beta decay products may play a role in the catalysis.

In the second synthesis procedure, an equivalent molar mixture of $\text{CF}_3\text{I}/\text{T}_2$ was placed in a stainless steel vessel with a volume equal to that of the quartz cell (-30cc), also containing ~0.5g of activated palladium black powder. Essentially all the T_2 absorbed onto the palladium, and after five days, >80% of the initial CF_3I was converted to CTF_3 . Due to possible catalyst poisoning using palladium, platinum may prove to be a better choice of catalyst.

After performing either of the described procedures, the mixture was flowed through a liquid nitrogen cooled U-tube. The remaining T_2 was gettered by uranium powder, and other incondensables were pumped away. The remaining mixture in the U-tube was allowed to warm to room temperature, and was expanded into a 2 cm long double-walled stainless steel cell with KRS-5 windows, used to obtain infrared spectra. If a significant amount of CF_3I remained after synthesis, the U-tube was immersed in a pentane slush (-150°C) to selectively retain CF_3I while passing CTF_3 . Low resolution infrared absorption scans were made using a Perkin Elmer 538B. A representative scan is shown in Figure 1, where the CTF_3 fundamental modes are labeled. Figure 2 shows ν_2 on an expanded scale. For reference, the

position of the Q branch peaks of the D/H and $^{12}\text{C}/^{13}\text{C}$ varieties of trifluoromethane are also shown in Figure 2. The absorption peak frequencies were determined using standard infrared molecular reference lines: DCl and DBr (ν_1)¹⁷; NH_3 (ν_2, ν_4, ν_5)¹⁷; C_2H_2 (ν_3)¹⁷ or by using CHF_3 and CDF_3 (ν_3, ν_6)¹⁸, and are listed in Table II. Figure 1 shows that small amounts of the impurities CF_4 (1283 cm^{-1}), C_2F_6 ($\sim 1255\text{ cm}^{-1}$) and SiF_4 (1029 cm^{-1}) were formed. No SiF_4 was observed in runs using the palladium catalyst, and very little was produced with short UV photolysis times. No C_2F_4 , the carbon-bearing photoproduct of trifluoromethane IR MPD, was observed. In addition, small amounts of CHF_3 product ($<15\%$ CTF_3 partial pressure) were present as identified by the peaks of 1378 cm^{-1} (ν_4), 1150 cm^{-1} (ν_2, ν_5) and 700 cm^{-1} (ν_3); in some runs CDF_3 was also observed. Mass spectrometric analysis confirmed that CTF_3 was the major ($>80\%$) product, and the presence of the H and D isotopic variants.

III. Discussion

The fundamental peak frequencies listed in Table II are accurate to $\pm 0.3\text{ cm}^{-1}$, with ν_2 being accurate to $\pm 0.1\text{ cm}^{-1}$. The limitation in accurately measuring most peak frequencies was the actual determination of the peak location because of broad spectral features. For ν_5 the frequencies of the peak heights ("P" and "R" branches) are listed along with that of the central minimum. In Table II, band center frequencies for several modes are estimated from the observed values, based on published analyses of the rotational level contours and peak frequencies in CHF_3 and CDF_3 .^{8,18} In the last column of Table II, the estimated harmonic frequencies are listed. The KW force field seems to predict the observed fundamentals best for most

modes, with particularly good agreement for ν_2 , ν_5 , and ν_4 . Each calculation appears to be quite inaccurate for the ν_1 , C-T stretch; this is discussed in more detail below. Also each force field predicts a ν_5 fundamental frequency about 5 cm^{-1} too low. This is not surprising since these force fields, though derived from CHF_3 and CDF_3 spectroscopic data, do not predict an accurate frequency for ν_5 in either molecule.

Using the Teller-Redlich isotope product rule¹³, the ratio of the product of harmonic vibrational frequencies of A_1 symmetry (C_{3v} group) in CTF_3 vis-a-vis CDF_3 (CHF_3) should be 0.8229 (0.5863), compared to the ratio of 0.8318 (0.5920) using the experimentally determined harmonic frequencies. For the E symmetry vibrations the product ratio is calculated to be 0.8392 (0.6106), while experiment yields 0.8337 (0.6113). The agreement is satisfactory for the vibrations with E symmetry; however, the observed product ratio is significantly high for A_1 class. Since the observed ν_2 and ν_3 fundamental frequencies agree well with the calculated values in column 3 of Table I, it is likely that ν_1 is perturbed, and that the observed value has been raised by a Fermi resonance. Using the calculated product ratio and the experimentally obtained ν_2 and ν_3 harmonic frequencies, the unperturbed ν_1 harmonic frequency is estimated to be 1946.1 (1948.3) cm^{-1} or about 20 cm^{-1} lower than the observed value, in fair agreement with the harmonic frequency derived using the KW force field. Since Fermi resonance mixing apparently leads to larger positive frequency shifts in CHF_3 (44 cm^{-1}) and CDF_3 (43 cm^{-1})⁹ than in CTF_3 , the CTF_3 ν_1 eigenfrequency prediction based on the fundamental frequencies (Table I, columns 4-6) should, in fact, be too high by -10 - 20 cm^{-1} , in accord with observations.

The integrated absorption coefficients of the ν_2 , ν_3 , ν_4 and ν_6 fundamentals in CTF_3 are roughly equal to those in CDF_3 . However, the CTF_3 C-T stretch, ν_1 , is about three times stronger, while the C-T bend, ν_5 , is roughly four times weaker than the respective bands in CDF_3 . This can be explained by noticing that in CTF_3 , vis-a-vis CDF_3 , the ν_1 (ν_5) mode eigenfrequency is shifted towards (away from) the strong C-F stretching modes, and the mode eigenfunction contains a relatively larger (smaller) contribution from the C-F symmetry coordinates; this was shown in the above-referenced normal coordinate calculation.⁷

In the separation of light isotopes by MPD, it is the selectivity in absorption, and not the enrichment factor that is usually the limiting factor in determining the practical success of the separation, and therefore the absorption selectivity must be considered¹. The value of the isotopic optical selectivity, which is defined as the ratio of the absorption coefficients of CTF_3 to that of CHF_3 or CDF_3 at a given wavelength, for low fluences may now be estimated; it should be >100:1 for attractive tritium recovery. For T/D separation using MPD of the ν_2 mode, the optical selectivity appears to reach a maximum of about 30 near 9.3 μ ; whereas, for T/H separation the selectivity is much higher, approximately 700 near 9.3 μ . Reference to Fig. 2 suggests that burning out the ^{13}C isotope (1.1% natural abundance) may further increase the selectivity in $\text{CTF}_3/\text{CHF}_3$; however, this procedure will probably not improve the $\text{CTF}_3/\text{CDF}_3$ selectivity. Based on the ν_2 band strength, a CO_2 laser fluence of $\sim 30 \text{ J/cm}^2$ should lead to significant dissociation of CTF_3 at the Q branch peak

(for T/H recovery). T/D separation is favorable using an NH_3 laser at 12.08μ to pump the ν_5 mode, where the optical selectivity is >250 . However, since the ν_5 band strength in CTF_3 is much weaker than in CDF_3 , a much higher fluence of about 100 J/cm^2 will be required to dissociate CTF_3 , compared to the $\sim 20 \text{ J/cm}^2$ needed to decompose CDF_3 near $10.3\mu^{1,3}$. Since the ν_1 mode is fairly strong (absorption coefficient of $\sim 10^{-2}/\text{cm-torr}$) and the absorption spectrum near 1930 cm^{-1} is fairly clean in CHF_3 ($\alpha \approx 1 \times 10^{-5}/\text{cm-torr}$) and in CDF_3 ($\alpha \approx 6 \times 10^{-5}/\text{cm-torr}$), use of a CO laser may lead to successful tritium recovery.

Since the effective molecular absorption coefficient decreases with increasing fluence in multiple-photon absorption, the optical selectivity at the fluences of interest will be lower than those quoted here. Still, there appears to be some promise for photochemical T/H and T/D isotope separation using trifluoromethane.

It should be mentioned that at the conclusion of this study the authors learned of a parallel effort in tritium isotope separation involving MPD of halogenated methanes at The Institute of Physical and Chemical Research in Japan^{19,20}. In Reference 19 the fundamental vibrational frequencies of a number of tritiated halogenated methanes were calculated using a Urey-Bradley type force field. Reference 20 presents the results of preliminary experiments on CTF_3 ; no infrared spectrum of CTF_3 is reported in this work. The calculation of the CTF_3 spectrum reported here is in much better agreement with the observed spectrum (Figure 1 and Table II) than is the calculation of Reference 19. In addition, there are quite significant differences in the prediction of the vibrational frequencies of the other mono-tritiated halogenated methanes when Urey-Bradley fields are used (Ref. 19)

rather than general harmonic force fields (Ref. 7). These points emphasize the importance of using the more accurate general harmonic force field, preferably based on harmonic frequencies, in determining the halogenated methane fundamental frequencies.

Work is continuing on the spectroscopy and infrared laser photochemistry of the tritiated halogenated methanes.

Acknowledgment

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Table I
Fundamental Frequencies in Trifluoromethane^a

		$^{12}\text{CTF}_3(\text{calc.})$				
	$^{12}\text{CHF}_3^{(9)}(\text{obs})$	$^{12}\text{CDF}_3^{(9)}(\text{obs})$	KW ⁽⁹⁾ , c	D ⁽¹⁰⁾	RBB-12 ⁽¹¹⁾	RBB-11 ⁽¹¹⁾
<u>A₁ Symmetry</u>						
ν ₁	3035.4	2261.1	1903.5 [1940.4]	1941.4	1948.7	1946.4
ν ₂	1141.3 (-25.4) ^b	1111.2 (-21.4) ^b	1077.4 [1088.8]	1072.5	1067.7	1059.2
ν ₃	700.0	694.2	688.6 [698.8]	683.0	687.2	692.2
<u>E Symmetry</u>						
ν ₄	1377.7	1210.6	1200.2 [1227.0]	1193.9	1204.1	1203.6
ν ₅	1157.5	975.5	831.1 [842.3]	832.2	831.8	832.8
ν ₆	507.8	502.7	497.6 [508.2]	496.3	497.1	496.2

^aFrequencies are in cm⁻¹. ¹²CHF₃ and ¹²CF₃ are observed band center values⁽⁹⁾, while for ¹²CF₃ they are calculated from the respective, referenced force fields (KW: Kirk and Wilt⁽⁹⁾, D: D'Cunha⁽¹⁰⁾, RBB: Ruoff et al⁽¹¹⁾)(see text).

Note that the atomic displacements for the ν₄ and ν₅ modes in CHF₃ correspond to those in the ν₅ and ν₄ modes, respectively, in CDF₃ and CTF₃.

^bFor ν₂ the isotone shift for ¹³CHF₃(observed⁽⁹⁾) and ¹³CF₃(calculated from KW field⁽⁹⁾) are listed in parentheses as (¹³Cν₂ - 3¹²Cν₂).

^cThe fundamental frequencies were determined from the harmonic frequencies, listed in brackets, which were obtained using the KW force field.

Table II
Observed CTF₃ Vibrational Frequencies

	Observed Spectral Peak (cm ⁻¹)		Estimated Fundamental Band Center (cm ⁻¹)	Estimated Harmonic Frequency ^b (cm ⁻¹)
ν_1	1930.3		1930.5	1967.4
ν_2	1097.5	P	1077.4	1088.8
	1076.9	Q		
	1061.0	R		
ν_3	687.0		687.1	697.3
ν_4	1199.8		-1200.0	1226.6 ^c
ν_5	843.5	"P"	-837.6	849.1 ^c
	837.9	Valley		
	830.9	"R"		
ν_6	496.0 ^a		496.9 ^a	506.6

^a ν_6 estimated band center, determined by shifts from CHF₃ and CHF₃ spectra(16).

^bEstimated using isotope-shifted anharmonicity constants (see text) and the estimated band center frequency.

^cObserved frequency of ν_4 , Q-branch peak, or ν_5 , central valley, used to estimate harmonic frequency.

FIGURE CAPTIONS

Figure 1. The absorption spectrum of CTF_3 , showing the location of the six fundamental bands. The cell length is 2 cm and the CTF_3 pressure is -25 torr.

Figure 2. The absorption spectrum of CTF_3 , showing the ν_2 absorption band. The ν_2 Q branch peak frequencies of $^{12}\text{CHF}_3$, $^{13}\text{CHF}_3$, $^{12}\text{CDF}_3$, and $^{13}\text{CHF}_3$ are also indicated by the arrows.

Figure 1

Figure 2

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