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Infrared Spectrum of CTF_3 and Implications toward Tritium Isotope Separation by Infrared Laser Multiple-Photon Dissociation of Halogenated Methanes

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The infrared absorption spectrum of nearly pure CTF_3 was measured and compared with the fundamental absorption frequencies calculated by using published CHF_3 and CDF_3 general harmonic force fields. The agreement between calculated and observed frequencies is found to be satisfactory. On the basis of calculated and measured absorption frequencies, photochemical separation of T from H is very attractive in trifluoromethane when 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 when using a CO laser near the strong CTF_3 ν_1 band centered at 1930.3 cm^{-1}.

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 (DTO in D_2O; up to 6 ppm 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 CDF_3/CHF_3[1-4] suggests that infrared laser MPD of a halogenated methane, which can be tritiated by chemical exchange with water (DTO 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-â-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 analogue is transparent. In addition, these small molecules dissociate within only a few nanoseconds once excited to only a few kcal/mol above the dissociation energy, thereby permitting decomposition that is unhindered by competitive vibrational quenching at pressures up to ~1 atm, when using a laser photodissociation pulse duration of a few nanoseconds.[1]

Theoretical and Experimental Procedures

In a previous study[7] we 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 analogues. 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 separation[1]), trifluoromethane, trichloromethane, and dichloromethane were selected for further investigation.[7] T/D recovery appeared promising with trifluoromethane near 9.4 (CO_2 laser), 12.08 (NH_3 laser), or 5.2 μm (CO laser); with trichloromethane near 12.08 μm (NH_3 laser); and with dichloromethane near 10.9 μm (CO_2 laser). T/H separation showed very great promise when employing trifluoromethane near 9.4 (CO_2 laser) or 5.2 μm (CO laser), and lesser promise in both this molecule and trichloromethane near 12.08 μm (NH_3 laser).[7] In this study the suitability of trifluoromethane is further considered on the basis of the new spectroscopic observations.

The band center frequencies for $^{12}CTF_3$ were calculated by using the Wilson F-G matrix method;[12] they are presented in Table I, columns 3–6, along with the observed frequencies for $^{12}CHF_3$ and $^{12}CDF_3$ in columns 1–2. The shift in frequency for the ^{13}C species ($^{13C}\nu-{}^{12C}\nu$) 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 ref 8. In column 3, the force field from the most recent and purportedly the most accurate study,

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TABLE I: Fundamental Frequencies in Trifluoromethane[a]

			^{12}CTF$_3$(calcd)			
	^{12}CHF$_3$(obsd)[a]	^{12}CDF$_3$(obsd)[a]	KW[9,c]	D[10]	RBB-12[11]	RBB-11[11]
			A$_1$ Symmetry			
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
			E Symmetry			
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

[a] Frequencies are in cm^{-1}. ^{12}CHF$_3$ and ^{12}CDF$_3$ are observed band center values,[9] while for ^{12}CTF$_3$ 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 ν_4 and ν_5 modes in CHF$_3$ correspond to those in the ν_5 and ν_4 modes, respectively, in CDF$_3$ and CTF$_3$. [b] For ν_2 the isotope shift for ^{13}CHF$_3$(observed)[9] and ^{13}CDF$_3$(calculated from KW field)[9] are listed in parentheses as (^{13}C$_\nu$ − ^{12}C$_\nu$). [c] The fundamental frequencies were determined from the harmonic frequencies, listed in brackets, which were obtained by using the KW force field.

that of Kirk and Wilt (KW),[9] was employed. This field was determined by using the harmonic frequencies[13] of ^{12}CHF$_3$, ^{13}CHF$_3$, and ^{12}CDF$_3$; in contrast, fundamental frequencies[13] (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 multidimensional 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}CTF$_3$ are listed in brackets in column 3. The tabulated fundamental frequencies were derived from these values by using known CHF$_3$ and CDF$_3$ anharmonic constants,[9] which were suitably isotope-shifted by using the approximation to Dennison's rule cited by Kirk and Wilt.[9] The force field of D'Cuhna[10] was used in column 4. In column 5, the 12-parameter general harmonic force field of Ruoff et al.[11] 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 CDF$_3$ in ref 10.

CTF$_3$ was successfully synthesized by catalysis of room-temperature, gas-phase mixtures of CF$_3$I + T$_2$, using either ultraviolet light or a standard heterogeneous hydrogenation catalyst. Initial attempts at synthesis utilizing the Wilzbach technique[14] of mixing T$_2$ with CHF$_3$, CF$_3$Br, or CF$_3$I 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, we introduced ~10 torr of CF$_3$I and 80 torr T$_2$ (97.4% T$_2$, 1.2% DT, 1.4% HT) into a quartz vessel and irradiated the mixture by either the 1849- or 2537-Å line from an array of low-pressure Hg lamps for ~1 day. The effective irradiation flux was ~13 mW/cm^2 at either wavelength. In this process the CF$_3$I absorbs a UV photon, and then the C–I bond breaks to yield CF$_3$ + I. The measured thermal activation energy for the reaction CF$_3$ + H$_2$ → CHF$_3$ + H is ~11 kcal/mol;[15] 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 Weston[16] measured a quite small quantum yield ($\simeq 3 \times 10^{-5}$) for this reaction at λ = 2537 Å. Fortunately, the only important competing reaction is the relatively fast CF$_3$ + I$_2$ → CF$_3$I + I (I$_2$ from I + I recombination) which reforms the starting material and therefore does not decrease the branching ratio to form CTF$_3$. C$_2$F$_6$, 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$_3$I was consumed, and the unexpectedly pure CTF$_3$ was, in fact, produced at a rate almost an order of magnitude faster than the studied CF$_3$I + D$_2$ → CDF$_3$ + I + D test case; this suggests that the radiation field of the tritium β decay products may play a role in the catalysis.

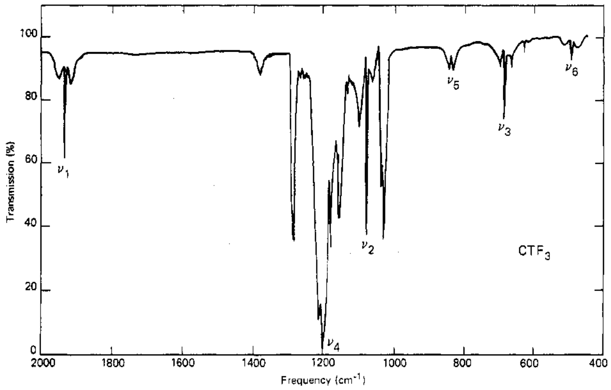

Figure 1. Absorption spectrum of CTF$_3$, showing the location of the six fundamental bands. The cell length is 2 cm and CTF$_3$ pressure is ~25 torr.

In the second synthesis procedure, an equivalent molar mixture of CF$_3$I/T$_2$ was placed in a stainless-steel vessel with a volume equal to that of the quartz cell (~30 cm^3), also containing ~0.5 g of activated palladium black powder. Essentially all of the T$_2$ adsorbed onto the palladium and, after 5 days, >80% of the initial CF$_3$I was converted to CTF$_3$. Because of 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,

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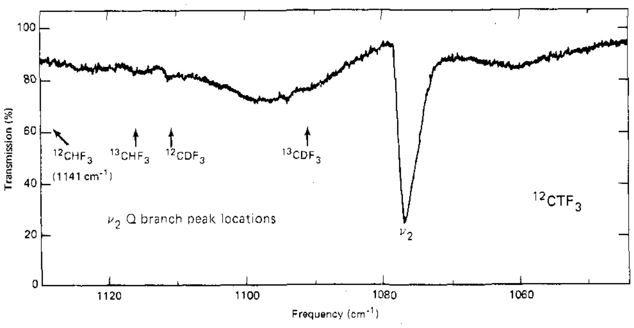

Figure 2. Absorption spectrum of CTF_3, showing the ν_2 absorption band. The ν_2 Q branch peak frequencies of $^{12}CHF_3$, $^{13}CHF_3$, $^{12}CDF_3$, and $^{13}CHF_3$ are also indicated by the arrows.

TABLE II: Observed CTF_3 Vibrational Frequencies

	obsd 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[6] 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]	496.0[a]	506.6

[a] ν_6 estimated band center, determined by shifts from CHF_3 and CDF_3 spectra.[8,18] [b] Estimated by using isotope-shifted anharmonicity constants (see text) and the estimated band center frequency. [c] Observed frequency of ν_4, Q-branch peak, or ν_5, central valley, used to estimate harmonic frequency.

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 (-130 °C) to selectively retain CF_3I while passing CTF_3. Low-resolution infrared absorption scans were made with 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 $^{12}C/^{13}C$ varieties of trifluoromethane are also shown in Figure 2. The absorption peak frequencies were determined by 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 (~1255 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 at 1378 (ν_4), 1150 (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, along with smaller amounts of the H and D isotopic variants.

Discussion

The fundamental peak frequencies listed in Table II are accurate to $\lesssim 0.3$ cm^{-1}, with ν_2 being accurate to ± 0.1 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_3, 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 ~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.

When the Teller–Redlich isotope product rule[13] is used, the ratio of the product of harmonic vibrational frequencies of A_1 symmetry (C_{3v} group) in CTF_3 vis-á-vis CDF_3 (CHF_3) should be 0.8229 (0.5863), compared to the ratio of 0.8318 (0.5920) when the experimentally determined harmonic frequencies are used. For the E symmetry vibrations the product ratio is calculated to be 0.8392 (0.6106), while experiment yields 0.8387 (0.6113). The agreement is satisfactory for the vibrations with E symmetry; however, the observed product ratio is significantly high for the 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. When the calculated product ratio and the experimentally obtained ν_2 and ν_3 harmonic frequencies are used, the unperturbed ν_1 harmonic frequency is estimated to be 1946.1 (1948.3) cm^{-1} or ~20 cm^{-1} lower than the observed value, in fair agreement with the harmonic frequency derived by 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 ~3 times stronger, while the C–T bend, ν_5, is roughly 4 times weaker than the respective bands in CDF_3. This can be explained by noticing that in CTF_3, vis-á-vis CDF_3, the ν_1 (ν_5) mode *eigenfrequency is shifted toward (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 considered.[1] 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

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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 ~30 near 9.3 μm, whereas for T/H separation the selectivity is much higher, ~700 near 9.3 μm. Reference to Figure 2 suggests that burning out the ^{13}C isotope (1.1% natural abundance) may further increase the selectivity in CTF_3/CHF_3; however, this procedure will probably not improve the CTF_3/CDF_3 selectivity. Based on the ν_2 band strength, a CO_2 laser fluence of ~30 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 with an NH_3 laser at 12.08 μm 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 ~100 J/cm^2 will be required to dissociate CTF_3, compared to the ~20 J/cm^2 needed to decompose CDF_3 near 10.3 μm.[1,3] Since the ν_1 mode is fairly strong (absorption coefficient of ~10^{-2}/(cm torr)) and the absorption spectrum near 1930 cm^{-1} is fairly clean in CHF_3 ($\alpha \simeq 1 \times 10^{-5}$/(cm torr)) and in CDF_3 ($\alpha \simeq 6 \times 10^{-5}$/(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, we 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 ref 19 the fundamental vibrational frequencies of a number of tritiated halogenated methanes were calculated by 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 that 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 ref 19. In addition, there are quite significant differences in the prediction of the vibrational frequencies of the other monotritiated 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.

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A Strong Metal–Support Interaction between Mononuclear and Polynuclear Transition Metal Complexes and Oxide Supports Which Dramatically Affects Catalytic Activity

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The interaction of carbonyl complexes with catalyst supports, primarily γ-alumina, has been studied by temperature-programmed decomposition. In all cases, including cluster complexes and complexes of noble metals, after heating to 600 °C in flowing He the catalysts are significantly oxidized due to a redox reaction between surface hydroxyl groups and the initially zero-valent metal. Contrary reports are probably incorrect and likely reflect the insensitivity of the experimental techniques used. For all but the most thermally unstable complexes, the oxidation occurs during the latter stages of decarbonylation indicating that there is no significant accumulation of bare zero-valent metal. Hence, decomposition does not in general provide a direct route to supported metals and, contrary to some claims, molecular cluster complexes cannot necessarily be used as precursors to supported metal clusters. Further, knowledge of this redox reaction is critical for understanding patterns of activity and for the development of improved catalysts.

Introduction

Transition metal complexes *directly* deposited on high surface area refractory supports (as alumina, silica, and molecular sieves) have been receiving wide attention in the last few years as a new class of catalysts. These materials physically lie at the frontier between traditional homogeneous and heterogeneous catalysts (note the metal is not insulated from the support by a chain of ligands and these are not immobilized homogeneous catalysts) and in fact have the potential of combining the better features of both types of catalysts: the wide gamut of catalyst precursors, better characterization, and possible improved selectivity of homogeneous catalysts and the enhanced stability of heterogeneous catalysts. Particular attention has been focused on supported carbonyl complexes, both mononuclear and polynuclear.[1-3] It has also recently been demonstrated that in some cases carbonyl-derived catalysts can

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