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# The vibrational spectrum of tetrafluoropropyne

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**Abstract**—The i.r. spectrum of gaseous tetrafluoropropyne has been measured from 4000 to 100 $cm^{-1}$, and all of the observed bands have been assigned. The *e* mode frequencies of the $CF_3$ group are similar to those of other $CF_3CCX$ species, and even though the $a_1$ modes are less regular, the variations can be explained without changes in force constants other than those involving the C–X bond. Several bands, particularly $\nu_1$ and combinations with $\nu_1$, show pronounced sequence structure due to excited levels of $\nu_{10}$, the C–C–C skeletal bend.

## INTRODUCTION

Although the vibrational spectra $CF_3CCH$ [1, 2] and $CF_3CCX$ (X = Cl, Br or I) [3, 4] have been analyzed, no detailed studies of the i.r. spectrum of tetrafluoropropyne (TFPY) [5, 6] have been reported. Given the assumptions of $C_{3v}$ symmetry and the harmonic oscillator approximation, there should be five $a_1$ and five *e* fundamental modes for each of these species, and the spectra may be assigned with this model. Those $CF_3CCX$ *e* modes that involve primarily $-CF_3$ motion have nearly the same frequencies throughout the series, but the $a_1$ modes show marked variations, so these species provide an interesting example of extended internal mode coupling.

More recent interest in the $CF_3CCX$ spectra [7–9] has been related to potential applications in studies of mechanisms of multiple photon excitation and intramolecular vibrational relaxation. The very low frequency skeletal bending mode along with several other low frequency modes results in a high population in excited vibrational states at 25°C (less than 10% of TFPY is in the ground vibrational state), and several bands, particularly the "C≡C stretch", show well separated sequence structure or "hot bands". The spectrum of TFPY has, of course, many similarities to the spectra of the other $CF_3CCX$ species, but there are also some interesting differences in both the frequency patterns and in the sequence structure.

## EXPERIMENTAL

Tetrafluoropropyne was prepared by deiodination of 1,3,3,3-tetrafluoro-1,2-diiodopropene isomers with acid-washed zinc in dioxane at 70°C. The TFPY was purified by trap-to-trap distillation on a vacuum line. The only impurity identified in the i.r. spectrum was ethylene which was probably formed from dioxane in the deiodination reaction.

Infrared spectra in the 7000–100 $cm^{-1}$ range were obtained using an IBM Model 98A FT-i.r. spectrometer with unapodized resolution from 1.0 to 0.03 $cm^{-1}$. The gas cells (2.5, 10 or 12 cm path length) had KCl, CsI, or polyethylene windows; the pressure of TFPY in the cells was measured by means of a MKS Baratron (222BHS) capacitance manometer.

## RESULTS AND DISCUSSION

The spectrum of TFPY at several pressures is shown in Fig. 1, and our assignments are listed in Table 1. We also obtained spectra in the 7000–4000 $cm^{-1}$ range with sample pressures up to 210 Torr in a 10 cm cell, but no additional features were identified in those spectra.

Simulations of the band shapes were performed with prolate symmetric rotor line strengths and energy levels [10], triangular line shapes for individual transitions, and all levels for which the Boltzmann factor was greater than 0.0005 at 25°C (up to $J = 188$ for $K = 0$ and $J = 92$ for $K = 90$). The calculated spectrum for a parallel band with $A' = 0.19225$, $A'' = 0.19230$, $B' = 0.04445$, and $B'' = 0.04460$, for example, had *P* and *R* branch maxima separated by 10.4 $cm^{-1}$; the experimental value for $\nu_3$ was 10.2 $cm^{-1}$.

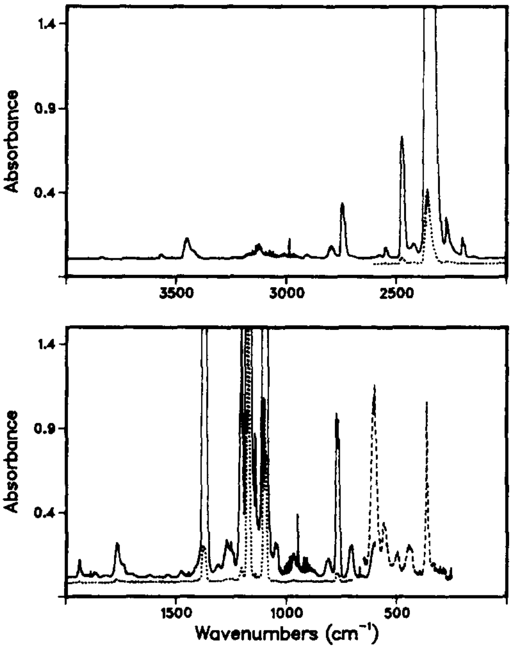

Fig. 1. Infrared spectrum of tetrafluoropropyne. Absorbance scale is 0 to 1.5. (· · · ·) 9 Torr, 2.5 cm path length; (——) 48 Torr, 2.5 cm; (– – –) 135 Torr, 12 cm.

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Table 1. Infrared spectrum and assignments for $CF_3CCF$

| Band centre ($cm^{-1}$) | Relative intensity | Assignment |
|---|---|---|
| 3840 | | $2\nu_2+\nu_3=3852$ |
| 3568 | | $\nu_2+2\nu_3=3576$ |
| 3465 | 1.2 | $\nu_1+\nu_3=3470$ |
| 3129 | | $\nu_1+\nu_4=3136$ |
| 2907 | 0.1 | $\nu_1+\nu_5+\nu_{10}=2918$ |
| 2807 | 0.5 | $\nu_1+\nu_5=2815$ |
| 2747 | 2.0 | $2\nu_2=2752$ |
| 2576 | | $\nu_2+\nu_3+\nu_{10}=2579$ |
| 2550 | | $\nu_2+\nu_6=2553$ |
| 2477 | | $\nu_2+\nu_3=2476$ |
| 2424 | | |
| 2370 | 77 | $\nu_1$ |
| 2274 | 0.6 | $\nu_3+\nu_6=2277$ |
| 2195 | 0.4 | $2\nu_3=2200$ |
| 1939 | 0.3 | $\nu_4+\nu_6=1943$ |
| 1867 | | $\nu_3+\nu_4=1866$ |
| 1820 | | $\nu_2+\nu_5=1821$ |
| 1770 | | $\nu_6+\nu_7=1778$ |
| 1739 sh | | $\nu_2+\nu_9=1739$ |
| 1700 | | $\nu_3+\nu_7=1701$ |
| 1620 | | $\nu_5+\nu_6=1622$ |
| 1540 | | $\nu_3+\nu_5=1545$ |
| 1477 | | $\nu_2+\nu_{10}=1479$ |
| 1376 | 26 | $\nu_2$ |
| 1273 | | $\nu_6+\nu_{10}=1280$ |
| 1204 | 4.6 | $\nu_3+\nu_{10}=1203$ |
| 1177 | 143 | $\nu_6$ |
| 1143 | | $\nu_6$ ($^{13}C$) |
| 1100 | 100 | $\nu_3$ |
| 817 | 0.6 | $\nu_8+\nu_9=818$ |
| 810 | | $\nu_7+2\nu_{10}=807$ |
| 766 | 5.4 | $\nu_4$ |
| 704 | 1.3 | $\nu_7+\nu_{10}=704$ |
| 601 | 1.6 | $\nu_7$ |
| 558 | | $\nu_8+\nu_{10}=558$ |
| 496 | | $\nu_7-\nu_{10}=498$ |
| (455) | | $\nu_8$ |
| 445 | | $\nu_5$ |
| 363 | 0.3 | $\nu_9$ |
| (103) | | $\nu_{10}$ |

Spectra taken at 0.03 $cm^{-1}$ resolution (before apodization) showed poorly resolved rotational fine structure, particularly on $\nu_3$ which had less pronounced hot band structure than most of the other bands. The average separation of the *P* and *R* branch lines, 0.097 $\pm 0.008$ $cm^{-1}$ and $0.082 \pm 0.008$ $cm^{-1}$ respectively, allowed crude estimates of $B' + B''$ ($0.089 \pm 0.008$) and $B' - B''$ $(-1.6 \pm 1.2) \times 10^{-4}$ $cm^{-1}$.

### Fundamentals

The parallel bands at 1100, 766 and 445 $cm^{-1}$ are easily assigned as the $a_1$ modes $\nu_3$, $\nu_4$ and $\nu_5$ respectively. The high frequency side of $\nu_2$ at 1376 $cm^{-1}$ has the same shape as the 1100 $cm^{-1}$ band, but the low frequency side of the band is more complex because of hot bands. The frequency of $\nu_2$ is at least 100 $cm^{-1}$ higher than that for the $-CF_3$ symmetric stretch in any of the other $CF_3CCX$ species, and the integrated absorption intensity is only about 20% of that of $\nu_6$; the $a_1$ and *e* $CF_3$ stretching modes in the other $CF_3CCX$ species have nearly equal intensities [1, 3]. The $C \equiv C$ stretch ($\nu_1$) shows a series of well resolved *Q* branches due to hot bands of $\nu_{10}$ and will be discussed in more detail later; the frequency listed in Table 1 for $\nu_1$ is that of the highest frequency *Q* branch. Spectra in the vicinity of each of the $a_1$ modes are shown in Fig. 2.

The most intense band in the spectrum is a perpendicular band at 1177 $cm^{-1}$, which is nearly the same frequency as that found for $\nu_6$ in the other $CF_3CCX$ species. The band at 601 $cm^{-1}$ is also at nearly the same frequency as that of the $CF_3$ deformation in the other species; the band is broader than $\nu_6$ and shows two overlapping structures most likely due to hot bands of $\nu_5$, $\nu_8$, $\nu_9$ and $\nu_{10}$. A band at 363 $cm^{-1}$ is clearly a perpendicular band due to the C–C–F bending mode; the corresponding band for HCCF is at 367 $cm^{-1}$ [11]. The other two *e* modes ($CF_3$ rock and C–C–C skeletal bend) were not identified directly even though pressures up to 275 Torr in a 12 cm path length cell were used. These two bands also were not

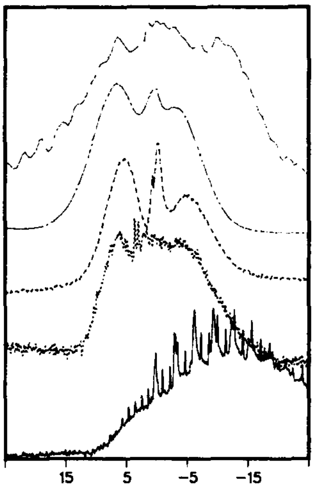

Fig. 2. Band shapes of the spectra of the $a_1$ fundamentals. The wavenumber scale is relative to the band origin for each (see Table 2). (——) $\nu_1$ (with $CO_2$ in background), (· · · · ·) $\nu_2$, (– – –) $\nu_3$, (—·—) $\nu_4$, (—-—) $\nu_5$.

found in the i.r. spectrum of $CF_3CCCl$ although several combination bands were identified [3].

*Combinations and overtones*

Several of the combination bands with $\nu_1$ are easily identified by the series of $Q$ branches arising from excited levels of $\nu_{10}$, and these are discussed in more detail later. The band at 558 cm$^{-1}$ was assigned to $\nu_8 + \nu_{10}$; this combination was also observed in the $CF_3CCCl$ spectrum [3] even though both of the fundamentals had lower intensities. The band at 704 cm$^{-1}$ has a band shape similar to that of the $\nu_7$ fundamental at 601 cm$^{-1}$ and was assigned as $\nu_7 + \nu_{10}$. For each of the $CF_3CCX$ cases this band is of comparable or even greater intensity than $\nu_7$. The assignments of most of the other bands in the spectrum are unambiguous and are listed in Table 1.

*Force constants*

The fundamental frequencies for TFPY along with those of several related compounds are summarized in Table 2 where the mode numbering is appropriate only for TFPY. The most striking result is the similarity of the frequencies of the $-CF_3$ $e$ modes as compared to the considerable variation among the corresponding $a_1$ modes. The trace of the $GF$ matrix [12, 13], i.e.

$$\lambda_s = \sum \lambda_i = \sum G_{ii} F_{ii} + 2 \sum \sum G_{ij} F_{ij}, \qquad (1)$$

may be used to aid in the selection of estimates of some of the force constants. The values of $\lambda_s$ for each of the symmetry classes are given in Table 2. If the $-CF_3$ geometry is assumed to be invariant for the molecules listed, then the $G$ matrix for the $a_1$ modes is the same for each except for the diagonal term for the C–X stretch. The small differences among the frequencies of the $e$ modes involving the $-CF_3$ group suggests that the diagonal force constants for the $-CF_3$ $a_1$ modes must also be nearly the same for this group of molecules. For the case of isotopic variations of X, $F_{CX}$ may be obtained directly from the values of $\lambda_s$, and for $CF_3CCH$ and $CF_3CCD$ the value of $F_{C-H}$ is calculated to be 5.76 mdyne/Å. If $G_{11}$ and $F_{11}$ were the only variables for the other cases, then the values of $F_{C-X}$ would be 8.10, 3.64, 2.16 and 0.73 mdyne/Å for X = F, Cl, Br and I respectively.

There is no possibility of obtaining a unique set of force constants for TFPY with isotopic variations, so we have performed a normal coordinate analysis for

Table 2. Fundamentals of $CF_3CCX$*

| | X = H† | D† | F§ | Cl‖ | Br‖ | I‖ | Approx. motion |
|---|---|---|---|---|---|---|---|
| $A_1$ modes | | | | | | | |
| $\nu_1$ | 2165 | 2014 | 2370 | 2270 | 2243 | 2218 | C≡C stretch |
| $\nu_2$ | 1253 | 1250 | 1376 | 1276 | 1275 | 1263 | $CF_3$ stretch |
| $\nu_3$ | 3327 | 2626 | 1100 | 723 | 686 | 661 | C–X stretch |
| $\nu_4$ | 812 | 808 | 766 | 937 | 883 | 857 | $CF_3$ deform. |
| $\nu_5$ | 536 | 529 | 445 | 377 | 285 | 253 | C–C stretch |
| $\lambda_s$ | 10.180 | 7.926 | 5.600 | 4.904 | 4.706 | 4.566 | |
| $E$ modes | | | | | | | |
| $\nu_6$ | 1179 | 1179 | 1177 | 1174 | 1177 | 1174 | $CF_3$ stretch |
| $\nu_7$ | 612 | 611 | 601 | 606 | 607 | 608 | $CF_3$ deform. |
| $\nu_8$ | 453 | 456 | 455 | 448 | 455 | 450 | $CF_3$ rock |
| $\nu_9$ | 686 | 539 | 363 | 311 | 278 | 263 | C–C–X bend |
| $\nu_{10}$ | 171 | 163 | 103 | 97 | 90 | 85 | C–C–C bend |
| $\lambda_s$ | 1.455 | 1.348 | 1.236 | 1.209 | 1.206 | 1.194 | |

*Wavenumbers in cm$^{-1}$. The mode numbering is appropriate for TFPY only. $\lambda_s$ is the sum of the eigenvalues (mdyne/Å/a.m.u.) within a class.

†Refs [1, 2].

§This work.

‖Ref. [3].

Table 3. $A_1$ symmetry force constants for $CF_3CCX$ (mdyne/Å)*

| | | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| X=H | 1 | 5.80 | −0.04 | −0.45 | −0.03 | −0.65 |
| X=F | 1 | 8.85 | −0.22 | 0.31 | −0.36 | 0.09 |
| X=Cl | 1 | 5.27 | −0.38 | 0.79 | −0.13 | 0.23 |
| X=Br | 1 | 3.92 | −0.27 | 0.69 | −0.04 | −0.09 |
| X=I | 1 | 3.29 | −0.24 | 1.00 | −0.03 | 0.10 |
| | 2 | | 8.02 | −0.01 | 0.52 | 0.74 |
| | 3 | | | 16.62 | −0.04 | 0.41 |
| | 4 | | | | 0.94 | −0.33 |
| | 5 | | | | | 4.96 |

*See Ref. [14] for explicit definitions of symmetry coordinates. $S_1 = CX$ stretch, $S_2 = CF_3$ symmetric stretch, $S_3 = C{\equiv}C$ stretch, $S_4 = CF_3$ symmetric deformation, and $S_5 =$ C–C stretch.

the $CF_3CCX$ species with all $F_{ij}$ values except those involving C–X assumed to be the same for all species. The symmetry coordinates were the same as those used for propyne [14] in order to illustrate more easily changes due to the variation of X; the definitions are given in Table 3. The initial set of constants for all $F_{ij}$ other than $i, j = 1$ were those calculated previously for $CF_3CCCl$ [4]; a set of force constants which yields frequencies within 1 cm$^{-1}$ of the observed for all cases (except $\nu_1$ of $CF_3CCH$ and $CF_3CCD$) is shown in Table 3.

From the $L$ matrix for TFPY,

$$\partial\mu/\partial Q_2 = -0.18\mu_1 - 0.17\mu_2 - 0.03\mu_3 + 0.54\mu_4 + 0.33\mu_5$$

and

$$\partial\mu/\partial Q_3 = -0.18\mu_1 + 0.20\,\mu_2 - 0.05\,\mu_3 - 0.40\,\mu_4 - 0.03\,\mu_5$$

where $\mu_i = \partial\mu/\partial S_i$; $\mu$ is the dipole moment, $Q_i$ a normal coordinate, and $S_i$ a symmetry coordinate. Because $\mu_1$ and $\mu_2$ should have opposite signs, the intensity of $\nu_2$ is predicted to be less than that of $\nu_3$ as observed; other force constants set with $F_{11}$ ranging from 5.5 to 9.0 mdyne/Å gave similar results. These two modes have major contributions from both the $CF_3$ stretch and CF stretch symmetry coordinates; $\nu_2$ has a somewhat greater contribution from $S_1$ and $\nu_3$ from $S_2$. Even though the "C–F stretch" in monofluoroacetylene is at 1055 cm$^{-1}$ [11], the 1100 cm$^{-1}$ band in TFPY cannot be clearly identified as a similar mode. For the Cl, Br and I cases, $\nu_2$ is more clearly assigned as the $CF_3$ symmetric stretch. Although $\nu_4$ and $\nu_5$ are usually assigned (for X = halogen) as the C–C stretch and $CF_3$ symmetric deformation modes, respectively, the normal coordinates suggest the reverse assignment; both symmetry coordinates are major contributors to these modes. If all bonds except C–C were rigid and $F_{CC}$ were the same as in TFPY for each of the others, then the C–C stretch frequencies would be 535 (H), 527 (D), 405 (Cl), 356 (Br) and 333 cm$^{-1}$ (I). Even though it is impossible to obtain a unique set of force constants for these molecules, it is clear that the rather marked variation in the frequencies of the $a_1$ modes can be explained by variations only in the $F_{1j}$ force constants.

Fig. 3. Hot band structure (1 cm$^{-1}$ resolution) of (——) $\nu_1$, (· · · · ·) $\nu_1 + \nu_5$, and (– – –) $\nu_1 + \nu_3$. The wavenumber scale is relative to 2370, 2807 and 3465 cm$^{-1}$ respectively.

### *Sequence structure*

In the absence of Fermi resonances, vibrational energy levels may be approximated by [13, 15]

$$E = E_0 + \sum \omega_i^0 n_i + \sum\sum x_{ij}^0 n_i n_j + \sum\sum g_{ij} l_i l_j. \quad (3)$$

The inhomogeneous or "hot band" structure on $\nu_1$ and combination bands involving $\nu_1$ is particularly pronounced as shown in Fig. 3; $Q$ branch maxima for these transitions are given in Table 4. The value of $x_{1,10}$ calculated with Eqn (3) is $-3.2 \pm 0.2$ cm$^{-1}$; for $CF_3CCH$ [2] and $CF_3CN$ [16] the corresponding values are −3.3 and −3.2 cm$^{-1}$, respectively. The separations of the $\nu_{10}$ hot band $Q$ branches in the $\nu_1$ combination bands are $-3.0 \pm 0.2$, $-2.3 \pm 0.4$, and $-2.8 \pm 0.2$ cm$^{-1}$ for $\nu_1 + \nu_3$, $\nu_1 + \nu_4$ and $\nu_1 + \nu_5$, respectively. No clear indication of sequence structure due to $\nu_1 + n\nu_9 - n\nu_9$ was found.

Table 4. $Q$ branch maxima for $\nu_1$ and combinations with $\nu_1$

| $n_{10}$ | $\nu_1$ | $\nu_1+\nu_5$ | $\nu_1+\nu_4$ | $\nu_1+\nu_3$ |
|---|---|---|---|---|
| 0 | 2370.4 | 2807.0 | 3129.1 | 3464.7 |
| 1 | 2367.1 | 2804.1 | 3127.2 | 3461.3 |
| 2 | 2363.9 | 2801.2 | 3124.8 | 3458.4 |
| 3 | 2360.7 | 2798.8 | 3122.8 | 3455.5 |
| 4 | 2357.7 | 2795.9 | 3120.4 | 3452.6 |
| 5 | 2354.7 | 2793.0 | 3117.5 | 3449.7 |
| 6 | 2351.3 | | | |

A 0.03 $cm^{-1}$ resolution spectrum of $\nu_2$ showed a complex structure shaded to the low frequency side of the band. A simulation of the band shape with $x_{2,10} = -0.6\ cm^{-1}$ gave general agreement with the observed spectrum. The spectrum of $\nu_3$ showed a series of overlapped $Q$ branches beginning at 1099.52 $cm^{-1}$ and higher with an average separation of 0.08 $cm^{-1}$, i.e. $x_{3,10} = +0.08\ cm^{-1}$. In $CF_3CCH$ the C–H stretch sequences with $\nu_{10}(\nu_1+n\nu_{10}-n\nu_{10})$ are separated by 0.84 $cm^{-1}$, and the $\nu_1+n\nu_9-n\nu_9$ separations are 0.45 $cm^{-1}$, but the C–H stretch is strongly coupled to the C–C–H bend ($x_{17} = -19.5\ cm^{-1}$) [8, 9]. If there were strong coupling of the C–F stretch ($\nu_2$ or $\nu_3$) with the CCF bend ($\nu_9$) in TFPY, the $\nu_2(\nu_3)+\nu_9-\nu_9$ transition should be observed with an intensity of about 35% of that of the fundamental; we found no candidate features on the low frequency side of the $\nu_2$ or $\nu_3 Q$ branches, but there is a feature on the high frequency side of $\nu_3$ at 1100.71 $cm^{-1}$ with an appropriate intensity; if this assignment is correct, then $x_{3,9} = +1.2\ cm^{-1}$.

The large separations of the $\nu_{10}$ hot band transitions with $\nu_1$, $\nu_1+\nu_3$, $\nu_1+\nu_4$, and $\nu_1+\nu_5$ should prove useful for future vibrational relaxation studies.

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