Complete Structure of *trans*-1,2-Difluoroethylene from the Analysis of High-Resolution Infrared Spectra

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For comparison to the structure of the cis isomer with its puzzlingly lower energy, the complete structure of *trans*-1,2-difluoroethylene, a *nonpolar* molecule, has been determined. High-resolution infrared spectra have been recorded for three isotopomers, the $^{13}C_2$, d_2, and d_1 species. From the analysis of at least two band types for each isotopomer, a Watson-type Hamiltonian has been fit to ground state combination differences. Ground state rotational constants (in cm^{-1}) are $A = 1.8247501(32)$, $B = 0.13396608(66)$, and $C = 0.12473595$-(65) for the $^{13}C_2$ species, $A = 1.2634959(27)$, $B = 0.13403712(61)$, and $C = 0.12110234(59)$ for the d_2 species, and $A = 1.5198818(34)$, $B = 0.13429738(50)$, and $C = 0.12331713(54)$ for the d_1 species. From these constants and those previously published for the normal species, substitution coordinates have been found for the carbon and hydrogen atoms and effective coordinates have been found for the fluorine atoms. The resulting parameters are $r_{CH} = 1.080$ Å, $r_{CC} = 1.316$ Å, $r_{CF} = 1.352$ Å, $\alpha_{CCH} = 126.3°$, and $\alpha_{CCF} = 119.2°$. The most significant differences from the cis isomer are the 2.9° smaller CCF angle and the 2.4° larger CCH angle for the trans isomer. These differences correlate with a larger repulsion of CF bond dipoles in the cis isomer than in the trans isomer despite the lower energy of the cis isomer. In addition, the CF bond length is 0.015 Å longer and both the CC and CH bonds are somewhat shorter in the trans isomer. The synthesis of *trans*-1,2-difluoroethylene-$^{13}C_2$ is described, and various intermediates are identified.

Introduction

A complete structure for *trans*-1,2-difluoroethylene (*t*DFE) is of interest for comparison with its cis isomer because of the seemingly anomalous energy relationship between these two molecules. Despite the obviously greater repulsion of the C−F bond dipoles in the cis configuration than in the trans configuration, the cis isomer has the lower energy.[1] As summarized before,[2] a number of ab initio calculations have been done to explore this "cis effect." As a basis for assessing ab initio calculations and improving them, complete geometric parameters are needed for both isomers. Although a complete structure of the cis isomer has been known for some time from a microwave investigation,[3] only incomplete information about the structure of the trans isomer is available. Since the trans isomer lacks a dipole moment, its structure cannot be obtained by microwave methods. The trans isomer has been studied by electron diffraction,[4,5] but the results of these two studies are not in agreement. Also, the locations of the weakly scattering hydrogen atoms were poorly determined.

The cis effect occurs in other fluoro species with double bonds, as summarized previously.[2] It is also present in 1,2-dichloroethylene[2] and in 1,2-dimethoxyethylene.[6] An analogous "gauche effect" is found in 1,2-difluoroethane[7,8] and in 1,2-dimethoxyethane.[9] Thus, a better understanding of the energetic and structural consequences of this anomaly is needed. The most recent proposal for explaining the cis/gauche effect is from Wiberg and co-workers.[10,11] They have suggested that the effect is due to a destabilization of the trans or anti species rather than a stabilization of the cis or gauche species. They trace this destabilization to bent MOs formed from hybrid atomic orbitals on the carbon atoms. The AOs which contribute to the C−X σ MOs have enriched p character due to the highly electronegative substituent (X) and thus reduced bond angles with the AOs used in the CC σ bonds. Because of repulsions between nonbonded atoms, enhanced by the smaller angles, the hybrid AOs in the internuclear CC region are then tilted away from the CC axis. In the trans configuration the two hybrid σ AOs on the carbon atoms point somewhat away from each other, on opposite sides of the CC axis, to give reduced overlap. In the cis and gauche configurations the hybrid σ AOs point toward each other on the same side of the CC axis. Calculational evidence for this bond bending effect comes from a comparison of electron density maps for ab initio calculations at intermediate and higher levels of theory.[10,11]

In contrast to microwave spectroscopy, high-resolution FT-IR spectroscopy provides information about rotational transitions of polyatomic apolar molecules. In a previous paper we have applied this method to the normal isotopic species of *t*DFE and have obtained ground state values of the principal moments of inertia of this substance.[2] This molecule is a near-prolate symmetric top ($\kappa = -0.990$) and thus is a good candidate for this type of structural study. Three bands, an A-type band at 1274 cm^{-1}, a B-type band at 1657 cm^{-1}, and a C-type band at 874 cm^{-1}, were analyzed. From 1670 ground state combination difference (GSCD) frequencies obtained from the three bands, rotational constants were fitted to the ground state. From these rotational constants of the d_0 species it was apparent that the CCF bond angle was appreciably smaller in the trans isomer than in the cis isomer.

To obtain a complete structure of *t*DFE, spectra of at least two more isotopomers were required. A minimum of three sets of rotational constants is needed because a planar molecule has only two independent moments of inertia, and *t*DFE has five

Complete Structure of *trans*-Difluoroethylene

J. Phys. Chem., Vol. 100, No. 13, 1996 **5311**

structural parameters. Samples of the two deuterated species of this molecule were available from previous vibrational spectroscopy,[1] but they provide largely equivalent information. We have used, however, the moments of inertia of the d_1 and d_2 species as a check in our structural analysis.

The needed $^{13}C_2$ species had to be synthesized. It was made by reacting 1,2-dibromoethane-$^{13}C_2$ with silver difluoride and reacting the resulting 1,2-difluoroethane-$^{13}C_2$ with gaseous chlorine to make 1-chloro-1,2-difluoroethane-$^{13}C_2$, which was treated with strong base to give the isomers of DFE-$^{13}C_2$.

In this paper we report the high-resolution FT-IR spectra of the $^{13}C_2$, d_2, and d_1 modifications of *t*DFE and the analysis of the rotational structure of several bands for each isotopic species. From the resulting moments of inertia and those of the d_0 species a complete structure of the ground state of *t*DFE has been obtained. Since the goal of this work was the complete structure of the ground state of *t*DFE, little attention was paid to upper state rotational constants. Also, some fragmentary assignments were accepted.

Experimental Section

Synthesis. One g (5.3 mmol) of degassed 1,2-dibromoethane-$^{13}C_2$ (99% ^{13}C from Cambridge Isotope Laboratory, Woburn, MA) was distilled into a 100-mL flask equipped with a stopcock and a standard taper joint and containing 2.6 g (18 mmol) of silver difluoride (Aldrich Chemical Co., Milwaukee, WI) and some short pieces of Teflon tubing. The silver difluoride had been transferred into the flask under nitrogen and dried further in vacuo at heat-gun temperature. The mixture reacted for 2 h at room temperature with periodic shaking. During the first step in the treatment, some red-brown coloration (Br$_2$) appeared, and a yellowish deposit (AgBr) formed. The product was distilled through copper turnings to remove Br$_2$ and into a second flask containing another 2.6-g sample of dried silver difluoride for another round of reaction. This treatment was repeated a third time. Some noncondensible gas (CO?) was pumped away at liquid nitrogen temperature. Three mmol of reagent-grade chlorine gas (Matheson Co., East Rutherford, NJ) was condensed into the bottom of a stopcock-equipped 100-mL flask that contained a few pieces of Teflon tubing. Then, the crude 1,2-difluoroethane-$^{13}C_2$ was condensed higher up in the flask. The contents were carefully warmed in subdued light and kept mixed by shaking as the flask was slowly moved into room (fluorescent) lighting during a half hour. The mixture was then exposed to direct tungsten light for 2 h. The product hydrogen chloride and the byproduct silicon tetrafluoride were removed by evaporation at pentane-slush temperature. The crude product was dissolved in 12 mL of absolute ethanol and added dropwise through a water-cooled condenser into 25 mL of refluxing ethanol that was saturated with about 2.5 g of sodium hydroxide. The outflow at the top of the condenser went into a trap immersed in dry ice−acetone and terminated with a drying tube. This slow reaction was run for a total of about 15 h. Silicone stopcock grease was used except when chlorine was present. Then, Krytox grease was used.

The complex mixture of reaction products was separated by gas chromatography, and the components were identified by comparison with published gas-phase infrared spectra of normal isotopic species. The initial separation was done on a 5-m tricresylphosphate-on-Chromosorb column at 0 °C. In addition to the desired *cis*- and *t*DFE-$^{13}C_2$,[1] byproducts were carbon dioxide-^{13}C, 1-chloro-1-fluoroethylene-$^{13}C_2$,[12] *cis*- and *trans*-1-chloro-1,2-difluoroethylene-$^{13}C_2$,[13] 1,1-difluoroethylene-$^{13}C_2$,[14] and difluoromethane-^{13}C.[15] Some 1-fluoroethylene-$^{13}C_2$,[14] acetylene-$^{13}C_2$,[14] and chloroacetylene-$^{13}C_2$[16] were also formed. The

1-chloro-1-fluoroethylene arose from the alternative dehydrofluorination reaction. The 1-chloro-1,2-difluoroethylene isomers came from dehyrochlorination of 1,1-dichloro-1,2-difluoroethane, the result of some overchlorination.[17] 1-Fluoroethylene probably came from some residual 1-bromo-3-fluoroethane. Acetylene and chloroacetylene probably came from further dehydrohalogenation of haloethylenes. The source of the 1,1-difluoroethylene was puzzling as its presumed precursor 1-chloro-1,1-difluoroethane was not found in the practice experiments with the normal isotopic species. The sources of the difluoromethane and carbon dioxide were also puzzling. Difluorodimethylsilane was also found among the products of the first reaction, formed, no doubt, by the reaction of Silicone stopcock grease with silver difluoride. Separating the *t*DFE from difluoromethane by gas chromatography was difficult. Repeated use of the partial separation obtained on a 9-m triperfluorobutylamine-on-Chromosorb column at −50 °C succeeded.

cis-1,2-Difluoroethylene (*c*DFE) was formed in larger amounts than the trans isomer. To obtain enough of the trans isomer for high-resolution spectroscopy, the cis isomer was isomerized at 270 °C with iodine catalysis,[18] and the equilibrium mixture was passed through copper turnings and separated by gas chromatography on the tributylamine column at −30 °C. GC-pure *t*DFE-$^{13}C_2$ was dried by passing it through phosphorus pentoxide. From two preparations and two isomerizations, 0.27 mmol of *t*DFE-$^{13}C_2$ was harvested.

During the development of the synthetic method with normal isotopic species, two intermediates were identified by NMR. Survey infrared spectra were also recorded in the gas phase. 1-Bromo-2-fluoroethane was an intermediate in the first reaction. Its proton NMR spectrum consisted of a doublet ($J_{HF} = 20.2$ Hz) of triplets ($J_{HH} = 5.9$ Hz) at $\delta = 3.53$ ppm for the CBrH$_2$ end and a doublet ($J_{HF} = 46.7$ Hz) of triplets ($J_{HH} = 6.0$ Hz) at $\delta = 4.66$ ppm for the CFH$_2$ end. The ^{19}F spectrum was a triplet of triplets ($J_{HF} = 46.6$ and 20.2 Hz) at $\delta = -212.1$ ppm. The proton-decoupled ^{13}C spectrum had a doublet ($J_{CF} = 24.1$ Hz) at $\delta = 28.9$ ppm for the CBrH$_2$ end and a doublet ($J_{CF(bonded)} = 173.2$ Hz) at $\delta = 82.0$ ppm for the CFH$_2$ end. For 1-bromo-2-fluoroethane the principal IR bands with intensities and approximate band shape were 2980s, 2900m, 1455mB, 1425mA, 1385m, 1280mA, 1215mB, 1090sB, 1070s, 1025vs, 690sC, 585mB, and 445m.

For 1-chloro-1,2-difluoroethane the proton spectrum was a complex pattern at $\delta = 4.6$ ppm for the CFH$_2$ end. For the CFClH end the pattern was centered at 6.3 ppm and was a doublet ($J_{HF(gem)} = 51.9$ Hz) of doublets ($J_{HF} = 8.6$ Hz) of quartets that were spaced by 5.6 and 4.2 Hz on one side and 6.6 and 3.1 Hz on the other side. The ^{13}C spectrum contained a doublet of doublets ($J_{CF(bonded)} = 181.6$ Hz and $J_{CF} = 24.6$ Hz) at $\delta = 83.0$ ppm for the CFH$_2$ end and a doublet of doublets ($J_{CF(bonded)} = 245.4$ Hz and $J_{CF} = 25.8$ Hz) at $\delta = 98.6$ ppm for the CFClH end. For 1-chloro-1,2-difluoroethane the IR spectrum was 3000m, 2970m, 1120sB, 1090mB, 1050sA, 900mB, 810sA, and 480mC.

1,2-Difluoroethane was identified by its published IR[8,19] and NMR[20] spectra. The proton NMR spectrum of difluorodimethylsilane was a triplet ($J_{HF} = 6.2$ Hz) at $\delta = 0.33$ ppm, the ^{19}F spectrum was a septet ($J_{HF} = 6.2$ Hz) at $\delta = -131.5$ ppm, and the ^{13}C spectrum was a triplet ($J_{HF} = 16.7$ Hz) at $\delta = 3.1$ ppm. For difluorodimethylsilane the principal IR bands are 2980m, 1270sA, 1090mB, 950sC, 915s, and 820sC.

The samples of the d_2 and d_1 species were from a previous study.[1]

Spectroscopy. Survey infrared spectra were recorded on Perkin-Elmer 580B and 1760 spectrometers. NMR spectra were

obtained on a Bruker AC200 FT instrument for samples dissolved in $CDCl_3$ and referenced to external TMS and $CFCl_3$.

High-resolution infrared spectra were recorded on a Bomem DA3.002 Fourier transform spectrometer at NIST. The mercury cadmium telluride detector was cooled to liquid nitrogen temperature. Hamming apodization was applied except for the spectra of the d_1 species for which no apodization was used. The nominal resolution was 0.004 cm^{-1}. Gaseous samples were contained in a 17-cm cell with KBr windows for spectra of the ^{13}C species and in a 20-cm cell for the spectra of the deuterated species.

For the $^{13}C_2$ species the initial pressure was 1.3 kPa (10 Torr). This pressure was reduced to an estimated 0.7 kPa (5 Torr) and then to 0.096 kPa (0.72 Torr) by condensation in a stopcock-equipped side arm. For the A-type band at 1266 cm^{-1}, 144 scans were accumulated for the sample at the highest pressure. For the A-type band at 1139 cm^{-1}, 128 scans were accumulated at the lowest pressure. For the C-type band at 870 cm^{-1}, 120 scans were accumulated at the intermediate pressure. The actual resolution based on widths of isolated lines at half-heights was 0.007 cm^{-1} for the two A-type bands and 0.006 cm^{-1} for the C-type band. A calibration factor of 1.00000121, based on H_2O lines in the 1305–1350-cm^{-1} region,[21] was applied to the reported spectral lines.

Two bands of the d_2 species were investigated fully. For the A-type band at 1176 cm^{-1}, 114 scans were accumulated for a sample at 0.087 kPa (0.65 Torr). For the C-type band at 650 cm^{-1}, 459 scans were accumulated for a sample at 0.45 kPa (3.4 Torr). The widths of isolated lines at half-heights were 0.006 cm^{-1} for both bands. The calibration factors were 1.00000161 for the 1176-cm^{-1} band, on the basis of CO_2 lines from 2330 to 2380 cm^{-1},[22] and 1.00000182 for the 650-cm^{-1} band, on the basis of H_2O lines in the 500–580-cm^{-1} region.[23]

Four bands of the d_1 species were studied. For the A-type band at 1274 cm^{-1}, 61 scans were accumulated for a sample at 1.1 kPa (8.1 Torr). For a second A-type band at 940 cm^{-1}, 48 scans were accumulated at the same sample pressure. For the C-type bands at 828 cm^{-1} and at 673 cm^{-1}, 50 scans were accumulated for a sample at 0.39 kPa (2.9 Torr). The calibration factor was 1.00000237 on the basis of H_2O lines.[23]

Results

Both tDFE-$^{13}C_2$ and tDFE-d_2 are centrosymmetric molecules of C_{2h} symmetry. These molecules are also near-prolate symmetric tops with κ values of -0.989 and -0.977, respectively. The axis of the least moment of inertia, I_a, passes near the two carbon atoms and even closer to the two fluorine atoms. The axis for I_b also lies in the plane of the molecule, and the axis for I_c is perpendicular to this plane. Only modes of the a_u and b_u symmetry species are infrared active. For the fundamentals of a_u symmetry, which have dipole moment changes along the I_c principal axis, bands with C-type selection rules occur. For the fundamentals of b_u symmetry, hybrid A/B-type bands are expected.

With the only symmetry element being a plane of symmetry, the tDFE-d_1 molecule belongs to the C_s symmetry group. κ is -0.984. In-plane normal modes are of the a' symmetry species and give hybrid A/B-type bands in the gas-phase infrared spectrum. Out-of-plane normal modes are of the a'' symmetry species and give C-type bands.

In general, the strategy of assigning the lines in the high-resolution spectra of the isotopically substituted tDFE species was the same as that described in some detail in the paper on the analysis of the normal species.[2] Briefly, the near-prolate-symmetric-top character of these molecules permitted use of

symmetric top theory for higher K_a "quantum" numbers. A-type bands, for which the selection rules are $\Delta J = 0, \pm 1, \Delta K_a = 0$, and $\Delta K_c = \pm 1$, were analyzed first to obtain good values for the B'' and C'' rotational constants from GSCDs. The analysis proceeded to the C-type band, for which the selection rules are $\Delta J = 0, \pm 1, \Delta K_a = \pm 1$ and $\Delta K_c = 0, \pm 2$. Assignments of the higher-K_a subbands gave sufficient GSCDs to determine the A'' rotational constant and confirm $(B'' + C'')/2 = \bar{B}''$. Finally the analysis was pursued toward the center of the C-type band, where K_c splitting plays a large role due to the residual asymmetry in these molecular rotors. For unperturbed bands frequencies were predicted for unassigned series near the band center, one series at a time, while fitting all of the previously assigned lines. Such predictions were particularly useful in locating lines in subbands with large K_c splittings. Computed GSCDs were also used to predict lines for split series of K_a in the R branch from the assignments of the less strongly split lines of the related, $K_a + 2$ series in the P branch.

For the rotational contributions to the states of the molecules a Watson-type Hamiltonian was employed in the A-reduction and I^r representation

$$\mathbf{H} = 1/2(B + C)\mathbf{P}^2 + [A - 1/2(B + C)]\mathbf{P}_a^2 - \Delta_J\mathbf{P}^4 - \Delta_{JK}\mathbf{P}^2\mathbf{P}_a^2 - \Delta_K\mathbf{P}_a^4 + H_J\mathbf{P}^6 + H_{JK}\mathbf{P}^4\mathbf{P}_a^2 + H_{KJ}\mathbf{P}^2\mathbf{P}_a^4 + H_K\mathbf{P}_a^6 + [1/2(B - C) - 2\delta_J\mathbf{P}^2 + 2\phi_J\mathbf{P}^4](\mathbf{P}_b^2 - \mathbf{P}_c^2) - \delta_K\mathbf{P}_a^2(\mathbf{P}_b^2 - \mathbf{P}_c^2)$$

where $\mathbf{P}$, $\mathbf{P}_a$, $\mathbf{P}_b$, and $\mathbf{P}_c$ are the operators for the total angular momentum and its components; A, B, and C are the rotational constants; Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K are the quartic centrifugal distortion constants and H_J, H_{JK}, H_{KJ}, H_K, and ϕ_J are most of the sextic ones.[25] Fitting was done with a variant of Dr. Arthur Maki's ASYM7 computer program. Rotational constants for the ground state were fit to the GSCDs obtained from assignments for lines in all of the bands. Final fittings for upper state constants employed these best ground state constants.

t**DFE-$^{13}C_2$ Species.** The $^{13}C_2$ species has three pairs of spin-1/2 nuclei that are exchanged on rotation around the C_2 axis. Fermi–Dirac statistics apply. As a consequence, the weights of the eo and oo rotational states are 36, and the weights of the ee and oe rotational states are 28.[24] The intensity difference that is a consequence of these statistical weights is not large enough to be a reliable assignment guide for this molecule.

For the $^{13}C_2$ molecule two of the bands investigated were for modes of b_u symmetry: the band at 1266 cm^{-1} for ν_{10}, which is largely antisymmetric CH bending, and the band at 1139 cm^{-1} for ν_{11}, which is largely antisymmetric CF stretching. For both bands the A-type component was dominant. The third band investigated was a C-type band for ν_6, the out-of-plane CH flapping mode, at about 870 cm^{-1}. A surprising observation in the spectrum of the $^{13}C_2$ species was the decrease of more than 50% in the intensity of the band due to the antisymmetric CH bending mode in comparison with the corresponding band of the normal isotopomer. The frequency shift for this band between the isotopomers was only 8 cm^{-1}. Evidently for the normal species the CH bending fundamental must gain intensity by mixing with the antisymmetric CF stretching mode, which has a very intense absorption. This interpretation correlates with the smaller frequency difference of 115 cm^{-1} between the vibrational modes for CH bending and CF stretching in the normal species compared with the greater difference of 127 cm^{-1} for the $^{13}C_2$ species. Even after repulsion of the two modes due to mixing in the normal species the frequency difference is smaller. The decreased intensity in the band for

$t-HF^{13}C=^{13}CFH$

ν_{10} (b$_u$)   C–H bend
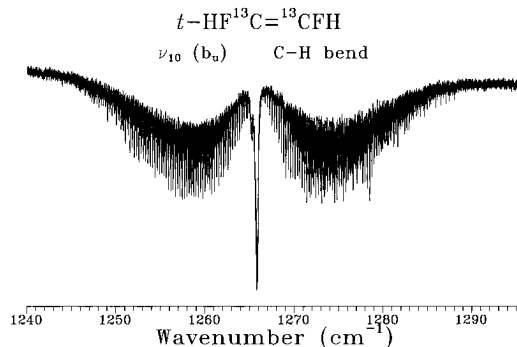
Figure 1. A-type band at 1266 cm^{-1} of tDFE-$^{13}C_2$. Pressure 1.3 kPa (10 Torr).

TABLE 1: Rotational Constants for *trans*-1,2-Difluoroethylene-$^{13}C_2$

| parameter/ cm^{-1}	ground state	ν_{10} state	ν_{11} state
A	1.8247501(32)	1.8234455(33)	1.8209357(44)
B	0.13396608(66)	0.13411919(28)	0.13346980(44)
C	0.12473595(65)	0.12468871(29)	0.12425611(41)
κ^a	−0.98914	−0.98890	−0.98914
$\Delta_K \times 10^5$	1.8405(13)	1.8622(53)	1.8540(59)
$\Delta_{JK} \times 10^7$	−3.491(25)	−3.554(21)	−3.345(20)
$\Delta_J \times 10^8$	2.487(15)	2.4910(43)	2.5446(87)
$\delta_K \times 10^7$	0.72(64)	0.72^b	0.72^b
$\delta_J \times 10^9$	1.29(10)	1.329(65)	1.34(11)
$H_K \times 10^{10}$	6.492(19)	15.7(23)	6.49^b
$H_{KJ} \times 10^{11}$	−1.69(40)	−1.69^b	−1.69^b
$H_{JK} \times 10^{12}$	1.38(51)	2.55(68)	1.38^b
$h_J \times 10^{13}$	−2.61^c	−2.61^c	−2.61^c
ν_0		1265.967039(72)	1139.002261(76)
std dev	0.000625	0.000573	0.000531
no. lines fit	1047	803	342

^{a} Unitless. ^{b} Ground state value. ^{c} Ground state value from d_0 species.

the CH bending mode of the $^{13}C_2$ species necessitated working at a higher sample pressure, where pressure broadening may have caused increased line widths. Intensities for the C-type bands of the two isotopomers were comparable.

Figure 1 is a beautiful A-type band at 1266 cm^{-1} for ν_{10}. This unperturbed, classically shaped band has a very narrow Q branch. Assignments were made for $K_a = 0-13$. Series were carried to J values in the range of 50. K_c splitting was observed from $K_a = 1-4$. 803 good lines were assigned. Blending, a particular problem for K_0 lines, prevented making more, useful assignments. Table 1 gives the rotational constants fitted to the upper state for this unperturbed band. $\Delta(A - B)$ is small in accord with the narrowness of the Q branch.

The intense A-type band at 1139 cm^{-1} for ν_{11} has prominent hot-band structure. Also, the Q branch is appreciably wider than for the band for ν_{10}. The hot-band structure impeded making a full analysis of this band. Nonetheless, 342 lines were assigned with K_a values ranging from 0 to 9 and J quantum numbers ranging up to 45. The upper state rotational constants fitted to the lines of this band are given in Table 1. $\Delta(A - B)$ for this band is over 2 times larger than for ν_{10}.

Figure 2 is the C-type band for ν_6(a$_u$), which is centered near 870 cm^{-1}. The frequency shift for this mode is about 4 cm^{-1} from the corresponding mode of the normal species. As a failed attempt to fit the Q branches to a polynomial confirmed, this band for the ^{13}C species is perturbed especially in the vicinity of the band center. A strong Q-branch-like feature occurs near 876 cm^{-1} that is probably related to the perturbation. In addition, this band shows considerable hot-band structure, which may also explain some of the clutter near the band center. Away

$t-HF^{13}C=^{13}CFH$

ν_6 (a$_u$)   C–H flap
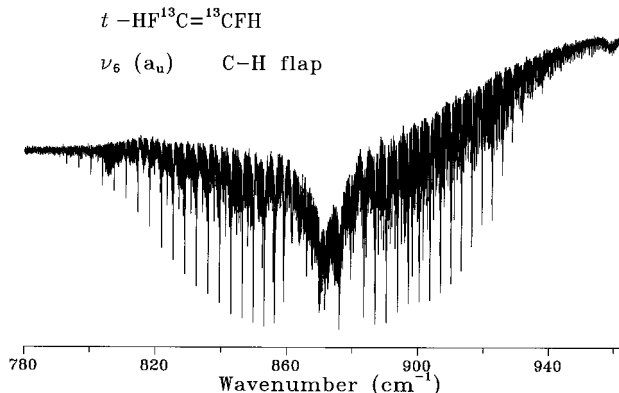
Figure 2. C-type band at 870 cm^{-1} of tDFE-$^{13}C_2$. Pressure 0.7 kPa (5 Torr).

t-HF^{13}C=^{13}CFH v_6
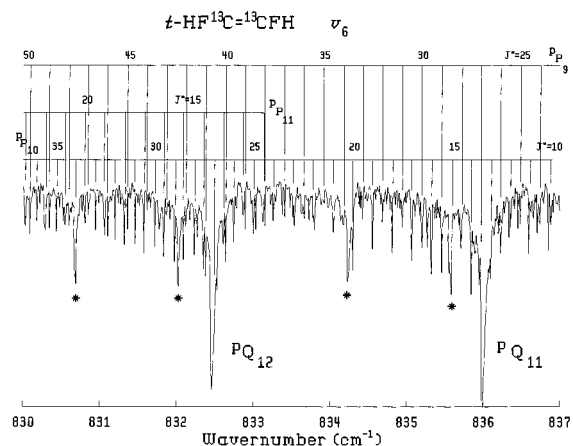
Figure 3. Detail of the C-type band of tDFE-$^{13}C_2$ in the region where the $^PP_{10}$ and $^PP_{11}$ series begin. Starred lines are Q-branches in two hot-band series.

from the band center a full analysis was done. Figure 3 shows, for example, the detailed assignment of lines in the region of the origins of the $^PP_{10}$ and $^PP_{11}$ series. A total of 2061 lines was assigned in the C-type band for $K_a = 4-21$ in the P branch and $K_a = 2-23$ in the R branch. In addition, many $^RQ_2$, $^RQ_3$, $^RQ_4$, $^PQ_4$, and $^PQ_5$ lines were assigned. It was not possible to assign the lines for the $^PP_3$ lines despite repeated attempts that included the use of subband simulations, predicted GSCDs, and possible assignments for the $^RR_1$ lines. The clutter of lines as well as the strong perturbation near the band center prevented the assignment of the remaining subband series in this region.

For the C-type band, the ^RR_K and ^PP_K subband series were subjected to an analysis using the relationship given before.[2] Figure 4 gives the B_{eff}' values obtained from this analysis for each subband in the two branches as a function of $(K_a')^2$. Where splitting occurs at lower K_a' values, the average B_{eff}' is plotted. From $K' = 8$ outward, the graph is linear, and the values from the two branches are coincident in accord with symmetric-top theory. These results support well the assignments in the two branches. The deviations from linearity as K' drops below 8 correlate with a perturbation near the band center.

In an attempt to identify the extra Q-type feature near the band center, a number of ^RR_K and ^PP_K series which related to weaker Q branches were investigated and, as a consequence, K_a values for Q branches were assigned. All of these assignments pointed, however, to band centers of presumed hot bands at frequencies below 870 cm^{-1}.

The cause of the perturbation in the C-type band can only be presumed since the vibrational spectrum of tDFE-$^{13}C_2$ has not been fully investigated. A perturbation of the corresponding
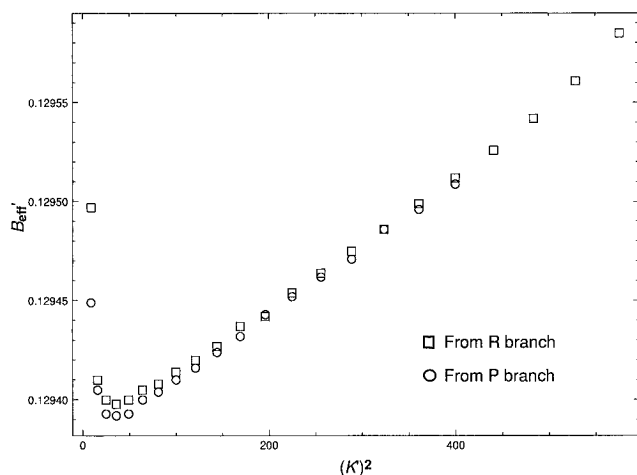
Figure 4. Subband analysis of the C-type band of tDFE-$^{13}C_2$. B_{eff}' values fitted to all lines in each subband in both branches and to ground state rotational constants.

C-type band occurred, morever, for the normal species.[2] This perturbation was due to interaction with the combination tones, $\nu_5(a_g) + \nu_7(a_u)$ and $\nu_5(a_g) + \nu_{12}(b_u)$, complicated by the strong Coriolis interaction between the ν_7 and ν_{12} fundamentals, which are almost degenerate. It is likely that these two fundamentals, which are skeletal modes, have large isotopic shifts with ^{13}C substitution. Thus, the same combination tones probably fall closer to the band center for the ^{13}C species and cause the observed perturbation for this species.

A total of 1047 GSCDs was fit to the Hamiltonian for the ground state. Of these GSCDs, 215 were obtained from the A-type band at 1266 cm^{-1}, 63 were obtained from the A-type band at 1139 cm^{-1}, and the remainder were from the C-type band. The paucity of GSCDs from the A-type bands, especially the second one, was a consequence of an imbalance in useful assignments between the R and P branches. Nonetheless, the absence of assignments for the middle of the C-type band was compensated by contributions from assignments all the way down to $K_a = 0$ for the two A-type bands as well as contributions from a number of split series in the C-type band. The first column in Table 1 gives the rotational constants fit to the ground state of the ^{13}C isotopomer. These ground state constants were used in fitting the upper state constants for ν_{10} and ν_{11} of this isotopomer. These rotational constants are also given in Table 1.

Available as supporting information are the assignments of the two A-type bands (Tables IS and IIS) and of the C-type band (Table IIIS) for the tDFE-$^{13}C_2$ species. Tables IS and IIS include the fitting of upper state constants, and Table IVS gives GSCDs and the fitting of the ground state constants.

***t*DFE-d_2 Species.** For tDFE-d_2, a consideration of spin statistics helped in the assignments for lines where K_c values were unique. Rotation around the C_2 axis in this molecule exchanges a pair of spin-1/2 nuclei and a pair of spin-1 nuclei.[24] Fermi−Dirac statistics apply. Thus, antisymmetric spin functions contribute a weight of 15, and symmetric spin functions contribute a weight of 21. Rotational states of *eo* and *oo* symmetry have an intensity of 21 compared with an intensity of 15 for rotational state of *ee* and *oe* symmetry. These intensity differences were used to reinforce assignments where lines corrsponded to single K_c values in the ground state.

An A-type band of the d_2 isotopomer was analyzed. This very intense band is due principally to the antisymmetric CF stretching mode, $\nu_{10}(b_u)$, and is centered at 1176 cm^{-1}. Despite the broad Q branch and the substantial hot-band structure

TABLE 2: Rotational Constants for *trans*-1,2-Difluoroethylene-d_2

parameter/ cm^{-1}	ground state	ν_6 state	ν_{10} state
A	1.2634959(27)	1.26016833(81)	1.2610808(67)
B	0.13403712(61)	0.13394428(23)	0.13347926(38)
C	0.12110234(59)	0.12121973(26)	0.12060870(38)
κ^a	−0.97735	−0.97766	−0.97743
$\Delta_K \times 10^5$	0.6195(13)	0.61243(54)	0.598(13)
$\Delta_{JK} \times 10^7$	−1.069(21)	−1.0227(89)	−1.264(63)
$\Delta_J \times 10^8$	2.412(24)	2.409(10)	2.374(14)
$\delta_K \times 10^7$	0.62(37)	0.23(31)	−0.78(30)
$\delta_J \times 10^9$	3.01(13)	2.49(11)	3.17(13)
$H_K \times 10^{10}$	1.28(20)	1.13(11)	−63.8(71)
$H_{KJ} \times 10^{11}$	−1.88^b	−2.00(16)	9.8(54)
$H_{JK} \times 10^{12}$	2.02(51)	1.77(14)	2.02^c
$h_J \times 10^{13}$	−2.61^b	−2.61^b	-2.61^b
ν_0		650.017678(34)	1176.408649(74)
std dev	0.000653	0.000489	0.000629
no. lines fit	1326	1929	679

^{a} Unitless. ^{b} Ground state value from d_0 species. ^{c} Ground state value.
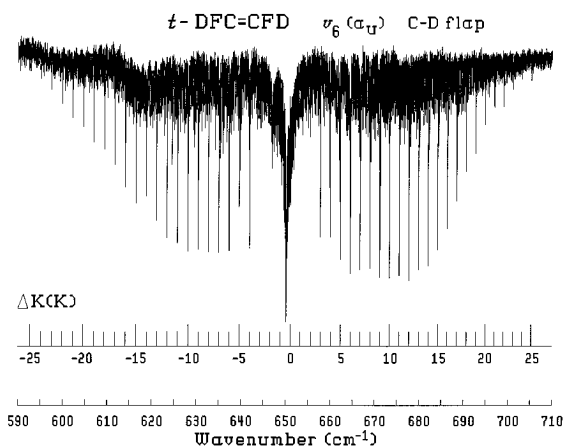
Figure 5. C-type band at 650 cm^{-1} of tDFE-d_2. Pressure 0.45 kPa (3.4 Torr).

associated with this band, 679 lines were assigned for $K_a = 0-11$ and for J ranging to about 45. The upper state rotational constants that were fitted to this band, which is unperturbed except for a local perturbation in the $K_a = 6-8$ region, are given in Table 2.

Figure 5 displays the C-type band that was analyzed for the d_2 isotopomer. Through manipulation on the computer a slowly changing background feature was largely removed from the P branch. This band, which is due to $\nu_6(a_u)$, the out-of-plane CD flapping mode, is centered at 650 cm^{-1}. In contrast to the band for the corresponding normal mode of the d_0 and $^{13}C_2$ species, this band is unperturbed. The upper states of combination tones that cause the perturbation of the corresponding band for the d_0 and $^{13}C_2$ species change little in frequency with deuteration, whereas the CD flapping mode is 220 cm^{-1} lower in frequency than the CH flapping mode of the d_0 species. Lines in the C-type band were assigned for $K_a = 0-19$ (R branch) and 0−20 (P branch) and for J values into the range 50−65. Seven Q branches were analyzed: $^RQ_0$, $^RQ_1$, $^PQ_1$, $^RQ_2$, $^PQ_2$, $^RQ_3$, and $^PQ_3$. 1929 lines were assigned. Table 2 gives the rotational constants that were fitted to the upper state.

Rotational constants for the ground state of the tDFE-d_2 species were fitted to GSCDs. For this purpose 259 GSCDs were obtained from the assignments for the A-type band and 1067 GSCDs were obtained from the C-type band. Because the C-type band was fully assigned, the relatively sparse assignment for the A-type band did not prevent a good fit of

Complete Structure of *trans*-Difluoroethylene

J. Phys. Chem., Vol. 100, No. 13, 1996 **5315**

TABLE 3: Rotational Constants for *trans*-1,2-Difluoroethylene-d_1

parameter/ cm^{-1}	ground state	ν_{10} state
A	1.5198818(34)	1.511689(19)
B	0.13429738(50)	0.13422238(17)
C	0.12331713(54)	0.12340181(19)
κ^a	−0.98428	−0.98441
$\Delta_K \times 10^5$	1.0887(27)	0.15(19)
$\Delta_{JK} \times 10^7$	−1.631(16)	−1.082(46)
$\Delta_J \times 10^8$	2.416(20)	2.4191(57)
$\delta_K \times 10^7$	1.69(22)	1.03(18)
$\delta_J \times 10^9$	2.633(55)	2.695(49)
$H_K \times 10^{10}$	3.80(65)	−7580.(510)
$H_{KJ} \times 10^{11}$	0.0	0.0
$H_{JK} \times 10^{12}$	0.0	0.0
ν_0		827.600119(53)
std dev	0.000580	0.000491
no. lines fit	1167	1022

^{a} Unitless.

TABLE 4: Principal Moments of Inertia for *trans*-1,2-Difluoroethylene and its Isotopomers (I's in u Å^2)

	I_a	I_b	I_c	Δ^a
HFC=CFH^b	8.9033194	125.30056	134.27728	0.0734(12)
HF^{13}C=^{13}CFH	9.2383233	125.83507	135.14653	0.0731(14)
HFC=CFD	11.091409	125.52465	136.70146	0.0854(11)
DFC=CFD	13.342055	125.76838	139.20153	0.0911(13)

^{a} Inertial defect, $I_c - I_a - I_b$. ^{b} From ref 2. All other values from the present work.

TABLE 5: Coordinates for *trans*-1,2-Difluoroethylene (in Å)

	a	b	c
r_s carbon ($^{13}C_2$)	±0.5153	±0.4094	0.0
r_s hydrogen (I's,d_1)^a	±0.4711	±1.4876	0.0
r_s hydrogen (P's,d_1)^b	±0.4774	±1.4901	0.0
r_s hydrogen (d_2)	±0.4773	±1.4897	0.0
r_0 fluorine (d_0,d_1)^c	1.7658	0.1051	0.0
r_0 fluorine (d_0,d_2)^d	1.7657	0.1034	0.0
r_0 carbon (all)	±0.5141	±0.4130	0.0
r_0 hydrogen (all)	±0.4750	±1.4897	0.0
r_0 fluorine (all)	1.7662	0.0972	0.0

^{a} Based on expressions in terms of moments of inertia (I's), eqs 13.64 and 13.65 in ref 26. ^{b} Based on expressions in terms of planar moments (P's), eqs 13.77 and 13.78 in ref 26. ^{c} Derived from the hydrogen coordinates from the I-based calculation with the d_1 species. ^{d} Derived from the hydrogen coordinates from the P-based calculation with the d_2 species.

ground state constants. The first column in Table 2 gives the ground state rotational constants. These ground state constants were used in fitting the upper state constants for the ν_{10} and ν_6 modes of this isotopomer.

The assignments and fittings of upper state constants for the A-type and C-type bands of the *t*DFE-d_2 species are available as supporting information in Tables VS and VIS. The fitting of ground state constants to GSCDs is in Table VIIS.

***t*DFE-d_1 Species.** Having lower symmetry than the $^{13}C_2$ and d_2 isotopic species, *t*DFE-d_1 has a greater probability of having perturbations in vibrational fundamentals. All four bands of the d_1 species that were investigated were perturbed. Only fragmentary assignments were made of three of the bands. One of these was the A-type band at 1274 cm^{-1} due to ν_4(a′), the CH bending mode. For K_a values of 0−7, 195 lines were assigned in this band. Another partly analyzed band was the A-type band at 940 cm^{-1} due to ν_7(a′), the CD bending mode. For K_a 3−8, 200 lines were assigned in this band. The third partly analyzed band was the C-type band at 672.6 cm^{-1} due to ν_{11}(a″), the CD flapping mode, for which 282 lines were assigned for K_a values of 6−13.

Though also perturbed, the C-type band at 828 cm^{-1} due to ν_{10}(a″), the CH flapping mode, was fully analyzed. Facilitating this analysis was the absence of a perturbation in the interior of the band from $K_a = 5$ inward. As a consequence, it was possible to fit the upper state of this band in its interior and thereby make useful, stepwise predictions of the subbands as the assignment progressed in this region. A total of 1829 lines was assigned for this C-type band, including the Q branches, $^RQ_0$, $^RQ_1$, $^PQ_1$, $^RQ_2$, $^PQ_2$, $^RQ_3$, $^PQ_3$, $^PQ_4$ and the offside subband series, $^RP_0$, $^RP_1$, $^RP_1$, $^PR_2$. The possibility that the perturbation was local was explored by attempting to include subbands with K_a about 11 and up in the upper state fitting. The result was unsatisfactory. Table 3 gives the upper state rotational constants for ν_{10} fit to 1026 lines in the interior of the band. The uncertainty for A' is about 10 times larger than customary due to the limited range of K_a values in this data set. Also the value for the sextic constant, H_K, is unreasonably large.

A total of 1167 GSCDs was obtained from the four bands that were investigated. 868 of these GSCDs were from the C-type band of the CH flapping mode. 110 were from the other C-type band. 92 were from the A-type band at 1274 cm^{-1}, and 97 were from the A-type band at 940 cm^{-1}. The rotational constants for the ground state obtained by fitting all the GSCDs are given in Table 3. Attemps to fit other sextic constants were unsuccessful.

Available as supporting information are tables of the assignments for the four bands of the d_1 species that were investigated. Tables VIIIS, IXS, and XS are the fragmentary assignments, respectively, for the A-type band at 1274 cm^{-1}, the A-type band at 940 cm^{-1}, and the C-type band at 673 cm^{-1}. Tables XIaS and XIbS give the full assignment of the C-type band 828 cm^{-1} along with the fitting of the upper state constants for the unperturbed, interior part of this band. Table XIIS is the fitting of ground state constants to the full set of GSCDs.

Structure of *trans*-1,2-Difluoroethylene. Table 4 gives the principal moments of inertia and the inertial defects of the ground states of the four isotopomers of *t*DFE that we have investigated. The small values of the inertial defects confirm beyond question that *t*DFE is a planar molecule. Table 5 gives the r_s coordinates found for the carbon and hydrogen atoms,[26] which have been isotopically substituted. Three sets of r_s values have been derived for the hydrogen atoms. Two sets come from single and double substitution and the use of expressions in terms of planar moments, P. These two sets agree closely. The other set comes from single substitution and the use of the expression in terms of I and is somewhat more divergent. Presumably, the distribution of the inertial defect affects the two formulations differently. By the two divergent methods the CH bond lengths are 1.079 and 1.081 Å, and the CCH bond angles are 126.1° and 126.2°. In each case the double substitution value is given second. We have used the values based on the two differing sets of hydrogen coordinates to compute the fluorine coordinates from the moments of inertia of the d_0 species. The two sets of fluorine coordinates, which do not differ greatly, are given in Table 5. The corresponding CF bond lengths are 1.3522 and 1.3515 Å, and the bond angles are 119.17° and 119.23°. The average parameters from this largely r_s analysis are designated r_s/r_0 and given on the last line of Table 6. A second set of coordinates was found for all of the atoms in a global fitting of the moments of inertia of all of the isotopic species along with the constraint, $\sum m_i a_i b_i = 0$. The results for the geometric parameters for this second treatment of *t*DFE are designated r_0 in the next-to-last line of Table 6. Agreement is close between the two treatments. The r_s/r_0 set in the last line is preferred.

TABLE 6: Geometric Parameters for *cis*- and *trans*-1,2-Difluoroethylene

	r_{CH}/Å	r_{CC}/Å	r_{CF}/Å	α_{CCH}/deg	α_{CCF}/deg	ref
MW, cis isomer	1.088	1.325	1.337	123.9	122.1	*a*
ED, cis isomer	1.084	1.331	1.335	121.6	123.7	*b*
ED, cis isomer	1.100	1.311	1.332	127	122.5	*c*
ab initio, cis isomer	1.080	1.326	1.343	122.5	122.7	*d*
ED, trans isomer	1.080	1.329	1.334	129.3	119.3	*b*
ED, trans isomer	1.088	1.320	1.338	125	119.8	*c*
ab initio, trans isomer	1.080	1.326	1.348	125.1	120.0	*d*
IR, trans isomer, r_0	1.077	1.319	1.352	126.7	119.1	*e*
IR, trans isomer, r_s/r_0	1.080	1.316	1.352	126.3	119.2	*e*

a MW = microwave. Reference 3. *b* ED = electron diffraction. Reference 4. *c* Reference 5. *d* Reference 27. *e* Present work.

A further estimate of the uncertainties in the parameters derived for the trans isomer comes from the critical estimates made for the cis isomer by Harmony et al.[3] For the uncertainties they give ±0.002 Å for bond lengths and ±0.2° for the bond angles. Furthermore, since the parameters for the trans isomer have been derived in the same way from spectroscopic data as those for the cis isomer, comparisons should be unusually reliable.

Comparison of the Structures of *cis*- and *trans*-1,2-Difluoroethylenes. The geometric parameters for the cis and trans isomers of difluoroethylene as found in various ways are compared in Table 6. Definitive microwave results are given on the first line for the cis isomer. The two electron diffraction studies of the cis isomer differ significantly between themselves and from the microwave study. The biggest differences are in the CH parameters, as would be expected, since the hydrogen atom is a weak scatterer of electrons. With the exception of the CH bond length, the ab initio result for the cis isomer is in reasonable agreement with the microwave results. For the trans isomer, the two electron diffraction studies show a significant difference, especially in the CH parameters. Fairly good agreement exists between the ab initio predictions and the results of the present infrared investigation.

Significant differences exist between the geometric parameters of the cis and trans isomers of DFE as found in the two spectroscopic investigations. The CCF bond angle is 2.9° smaller in the trans isomer, a change that is consistent with a significant CF bond dipole repulsion in the cis isomer, notwithstanding the lower electronic energy of the cis isomer compared with the trans isomer. Thus, the electronic effect that destabilizes the trans isomer must outweigh the greater CF bond moment repulsion in the cis isomer. In contrast to the change in the CCF bond angle, the CCH bond angle increases in going from the cis isomer to the trans isomer. This increase is 2.4°. Thus, it seems that the two CFH moieties rotate in concert in response to the configurational change. Changes in bond lengths also occur. Both the CC and CH bond lengths shrink somewhat in going from the cis to the trans isomer. In contrast, the CF bond length increases significantly. The most advanced ab initio calculation, as given in Table 6, shows no changes in the CH and CC bond lengths between the two isomers and only a small increase for the CF bond length in going from the cis to the trans isomer. The calculated bond angle changes are in the same sense as the experimental ones but smaller. Although the various adjustments in going from the cis to the trans isomer are consistent with the calculations of Wiberg et al.,[10,11] these adjustments do not seem to be qualitatively consistent with their bent bond argument. Since CC bonding is less favorable in the trans isomer, one would expect a longer CC bond in this isomer, the opposite of the experimental result. Also, greater repulsion between CF bond dipoles in the cis isomer might make the CF bond longer in the cis isomer, the opposite of the experimental result. The significant CF bond lengthening in the trans isomer is more consistent with Bingham's qualitative argument.[28] He attributed the cis effect to a less bent path of electron delocalization in the trans isomer and thus to a greater contribution of an energy-raising, antibonding orbital in this isomer.

The complete structure determination of "heavy," asymmetric-top molecules by analysis of the rotational structure in infrared bands is a significant new development made possible by high-resolution Fourier transform spectroscopy. Computerization of the handling of large data sets has also contributed. Through statistical averaging, rotational constants obtained this way rival those obtained from the inherently more accurate measurements in the microwave region. In addition, of course, we have been able to obtain the structure for a microwave-silent, nonpolar molecule.

Summary

The rotational structure of a number of bands in the high-resolution infrared spectra of three isotopomers of *trans*-1,2-difluoroethylene has been analyzed. From the moments of inertia of the ground states of the d_1 and d_2 species and of the $^{13}C_2$ species in comparison with those of the d_0 species, r_s parameters have been obtained, respectively, for the carbon and hydrogen atoms. Effective geometric parameters were then computed for the fluorine atoms. This new, complete structure of the trans isomer shows significant changes from the microwave-based structure of the cis isomer. These changes are larger than found in ab initio calculations. Principal differences are the 2.9° decrease in the CCF bond angle, the 2.4° increase in the CCH bond angle and the 0.015 Å increase in the CF bond length in going from the cis to the trans isomer. The larger CCF bond angle in the cis isomer correlates with a greater repulsion of CF bond dipoles in this isomer despite its lower energy, but the shorter CF bond length does not.

Supporting Information Available: Tables IS−XIIS of assignments for all of the bands and for the GSCDs reported in this paper (69 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Craig, N. C.; Overend, J. *J. Chem. Phys.* **1969**, *51*, 1127.

(2) Craig, N. C.; Brandon, D. W.; Stone, S. C.; Lafferty, W. J. *J. Phys. Chem.* **1992**, *96*, 1598.

(3) Harmony. M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

(4) Carlos, J. L.; Karl, R. R.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2* **1974**, *2*, 177.

(5) van Schaick, E. J. M.; Mijlhoff, F. C.; Renes, G.; Geise, H. J. *J. Mol. Struct.* **1974**, *21*, 17.

(6) Waldron, J. T.; Snyder, W. H. *J. Am. Chem. Soc.* **1973**, *95*, 5491.

(7) Huber-Wälchli, P.; Günthard, Hs. H. *Spectrochim. Acta* **1981**, *37A*, 285.

Complete Structure of *trans*-Difluoroethylene

J. Phys. Chem., Vol. 100, No. 13, 1996 **5317**

(8) Durig, J. R.; Liu, J.; Little, T. S.; Kalasinsky, V. F. *J. Phys. Chem.* **1992**, *96*, 8224.

(9) Connor, T. M.; McLauchlan, K. A. *J. Phys. Chem.* **1965**, *69*, 1888.

(10) Wiberg, K. B.; Murcko, M. A.; Laidig, K. E.; MacDougall, P. J. *J. Phys. Chem.* **1990**, *94*, 6956.

(11) Wiberg, K. B.; Hadad, C. M.; Breneman, C. M.; Laidig, K. E.; Murcko, M. A.; LePage, T. J. *Science* **1991**, *252*, 1266.

(12) Mann, D. E.; Aquista, N.; Plyler, E. K. *J. Chem. Phys.* **1955**, *23*, 2122.

(13) Craig, N. C.; Evans, D. A.; Piper, L. G.; Wheeler, V. L. *J. Chem. Phys.* **1970**, *74*, 4520.

(14) *Sadtler Standard Spectra, Gases and Vapors*; Sadtler Research Laboratories: Philadelphia, PA, 1972.

(15) Plyler, E. K.; Benedict, W. S. *J. Res. Natl. Bur. Stand.* **1951**, *47*, 202.

(16) Hunt, G. R.; Wilson, M. K. *J. Chem. Phys.* **1961**, *34*, 1301.

(17) Further chlorination, which occurred at a slower rate, gave 1,1-dichloro-1,2-difluoroethane, as identified by its NMR spectra. The proton spectrum was a doublet of doublets ($J_{HF(gem)}$ = 46.4 Hz and J_{HF} = 13.6 Hz) at δ = 4.68 ppm. The ^{19}F spectrum was a triplet of doublets ($J_{HF(gem)}$ = 47 Hz and J_{FF} = 23 Hz) at δ = −209.8 ppm for the CFH$_2$ group and a doublet of triplets (J_{FF} = 22.7 Hz and J_{HF} = 13.5 Hz) at −66.6 ppm for the CFCl$_2$ group, the latter multiplet having, in addition, unexplained doublets of 1 Hz spacing. The ^{13}C spectrum was a doublet of doublets ($J_{CF(bonded)}$ = 194.7 Hz and J_{CF} = 26.9 Hz) at δ = 85.9 ppm for the CFH$_2$ group and a doublet of doublets ($J_{CF(bonded)}$ = 300 Hz and J_{CF} = 23 Hz) at δ = 116 ppm for the CFCl$_2$ group, the latter values being less certain due to very low intensity. Principal bands in the gas-phase IR spectrum were 3000m, 2960m, 1175sC, 1100sC, 1070 sA, 940sC, 870s, 770 mC, 650s.

(18) Craig, N. C.; Entemann, E. A. *J. Am. Chem. Soc.* **1961**, *83*, 3047.

(19) Harris, W. C.; Holtzclaw, J. R.; Kalasinsky, V. F. *J. Chem. Phys.* **1977**, *67*, 3330.

(20) Abraham, R. J.; Kemp, R. H. *J. Chem. Soc. B* **1971**, 1240.

(21) Toth, R. A. *J. Opt. Soc. Am.* **1991**, *8B*, 2236.

(22) Guelachvili, G.; Rao, K. N. *Handbook of Infrared Standards*; Academic Press: Orlando, FL, 1986.

(23) Toth, R. A. Private communication.

(24) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; McGraw-Hill: New York, 1955; p 104.

(25) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1977; Vol. 6, pp 1−80.

(26) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; Wiley-Interscience: New York, 1984.

(27) Saebø, S.; Sellers, H. *J. Phys. Chem.* **1988**, *92*, 4266.

(28) Bingham, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 535.