Deuterium-induced ^{19}F isotope shifts in fluoroethenes

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Deuterium-induced ^{19}F isotope shifts in the NMR spectra of 17 fluoroethenes are reported here together with other NMR parameters (^{1}H and ^{19}F chemical shifts and FF, HF, DF, and DH coupling constants). The two-bond (*gem*) and three-bond (*trans*) isotope shifts exhibit correlations with nuclear spin–spin coupling constants $^2J_{gem}$(HF) and $^3J_{trans}$(HF). The isotope shifts are interpreted using derivatives of nuclear shielding with respect to bond extension derived from the ^{19}F temperature dependence at the zero-pressure limit, and the changes in the mean bond lengths due to isotopic substitution. The latter are calculated using the previously reported Urey–Bradley force fields for these molecules. The analysis of the isotope shifts lead to estimates of the change of ^{19}F nuclear shielding due to extension of a bond which is located at a *gem*, *cis*, or *trans* position relative to the resonant nucleus. These ^{19}F nuclear shielding derivatives correlate with the nuclear spin–spin coupling constants $^2J_{gem}$(HF), $^3J_{cis}$(HF), and $^3J_{trans}$(HF) which share the same pathway of electronic transmission.

INTRODUCTION

Chemical shifts in NMR spectra due to isotopic substitution of a neighboring atom have been widely observed and utilized in the determination of structure and reaction mechanisms.[1–4] The largest such isotope shifts are for substitution at a site one bond away from the resonant nucleus.

The measured isotope shift for nucleus A is defined in terms of the change in the nuclear resonance frequency upon replacement of an atom ^mX with a heavier isotope $^{m'}X$. In terms of the nuclear shielding, the one-bond isotope shift is

$$^1\Delta A(^{m'/m}X) = \sigma^A(A\text{–}^mX) - \sigma^A(A\text{–}^{m'}X). \tag{1}$$

The interpretation of one-bond isotope shifts is based on the same rovibrational averaging model that is used to explain the temperature dependent chemical shifts in the zero-pressure limit. In this model, the isotope shift is given by

$$^1\Delta A(^{m'/m}X) = (\partial\sigma^A/\partial\Delta r_{AX})_e\left[\langle\Delta r\rangle_{A^mX} - \langle\Delta r\rangle_{A^{m'}X}\right]$$

$$+ \tfrac{1}{2}(\partial^2\sigma^A/\partial\Delta r^2_{AX})_e\left[\langle(\Delta r)^2\rangle_{A^mX} - \langle(\Delta r)^2\rangle_{A^{m'}X}\right] + \cdots. \tag{2}$$

$(\partial\sigma^A/\partial\Delta r_{AX})_e$ is the derivative of nuclear shielding of A with respect to bond extension at the substitution site. This is a purely electronic factor, independent of mass. $\Delta_X = [\langle\Delta r\rangle_{A^mX} - \langle\Delta r\rangle_{A^{m'}X}]$ is the difference in the mean bond displacement between the light isotopomer with atom ^mX, and the heavy isotopomer with atom $^{m'}X$. For a complete analysis, the differences in mean bond angle deformations $\langle\Delta\alpha\rangle$ and also mean square amplitudes such as $\langle(\Delta\alpha)^2\rangle$, etc., and higher order terms, should be included in the above equation. It has been found that one-bond isotope shifts can be successfully interpreted with the leading term[5,6]

$$^1\Delta A(^{m'/m}X) \simeq (\partial\sigma^A/\partial\Delta r_{AX})_e\left[\langle\Delta r\rangle_{A^mX} - \langle\Delta r\rangle_{A^{m'}X}\right] \tag{3}$$

and that the dynamic factor is additive for multiple substitution at equivalent sites.[7] Furthermore, for a single substitution of an end atom, the dynamic factor may be approximated by[6,7]

$$\Delta_X = \left[\langle\Delta r\rangle_{A^mX} - \langle\Delta r\rangle_{A^{m'}X}\right]$$

$$\simeq \langle\Delta r\rangle_{A^mX}\left[(m'-m)/m'\right]\left[m_A/(m_A+m)\right]/2. \tag{4}$$

The mean bond displacement $\langle\Delta r\rangle$ varies with the pair of bonded atoms and can be estimated by assuming a Morse-type anharmonic stretching of the bond.[6] Thus, it is largely determined by the bond length and identity of the two atoms (i.e., knowing the rows of the Periodic Table to which the atoms belong allows one to estimate $\langle\Delta r\rangle$ from the bond length). For a given bond, e.g., C–F, $\langle\Delta r\rangle$ has been found to vary only slightly from molecule to molecule. The empirical trends in the dependence of the one-bond isotope shifts on electronic structure can thus be attributed directly to the dependence of $(\partial\sigma/\partial\Delta r)_e$ on various parameters of electronic structure such as bond order, hybridization, electronegativity of substituents, etc. The systematic trends in one-bond isotope shifts $^1\Delta$ are fairly well established and noted by several authors.[1,2,5–10] Studies of the dynamic factors have made it possible to associate with $(\partial\sigma/\partial\Delta r)_e$ the various trends observed in isotope shifts vs electronic structure.[11]

On the other hand, there has been no systematic study of two-bond and three-bond isotope shifts ($^2\Delta$ and $^3\Delta$). These shifts are generally smaller than one-bond isotope shifts and thus are only widely observed for deuterium substitution. Many of these long-range shifts have been reported in ring systems in which dynamic calculations are more difficult to carry out at the same level of sophistication as in small molecules. There is a need for a systematic study of $^2\Delta$ and $^3\Delta$ to discover correlations with electronic structure. Are they additive? Is there a stereochemical effect (e.g., are $^3\Delta_{cis}$ and $^3\Delta_{trans}$ different in magnitude)? What is the effect of electronegative substituents? Are pi-electron contributions important? There is some indication of this in that the truly long-range isotope shifts such as $^5\Delta$ and $^7\Delta$ have been observed only in conjugated systems.[12] The answers to these empirical questions will help in understanding $^2\Delta$ and $^3\Delta$ as well as in making practical use of their observation for diagnostic purposes.

There are further questions of fundamental importance. Substitution at a remote site from the observed nucleus necessitates a secondary effect. Although the greatest effect on the bond lengths due to isotopic substitution occurs at the bonds directed to the substituted atom, there are also secondary effects on the mean lengths of all the other bonds in the molecule. The greatest effect on the shielding is that of bond extension occurring at one of the bonds directed to the resonant nucleus. However, there are secondary changes in shielding due to extension of a remote bond. The two-bond isotope shift can be interpreted largely in terms of (i) the product of a primary shielding change with a secondary bond length change and (ii) the product of a secondary shielding change with a primary bond length change. There are fundamental questions such as which of these two general terms is more important? How do they depend on electronic structure? While the primary change in shielding upon bond extension is well documented from studies of temperature dependent chemical shifts in the isolated molecule as well as theoretical calculations in diatomic molecules, there is hardly anything known about changes in shielding due to a remote bond extension. This is an important fundamental question in itself, in addition to its relevance to the interpretation of isotope shifts. Are the secondary shielding changes characteristic of the transmission path between the extended bond and the resonant nucleus? In what way do the intervening bonds determine its magnitude? Only if we can understand two-bond and three-bond isotopic shifts can we begin to say anything at all about longer-range isotope shifts (e.g., over five or seven bonds).

In this paper we provide experimental measurements of $^2\Delta$ and $^3\Delta$ in several related molecules. These exhibit general trends including stereochemical effects. We perform dynamic calculations of the primary and secondary bond length changes in these molecules. By using primary shielding derivatives with respect to bond extension which have been obtained from the temperature-dependent chemical shifts in the zero-pressure limit, we make use of the experimental isotope shifts to obtain (secondary) shielding derivatives with respect to remote bond extension in these molecules. We do this for several related molecules so as to determine how variable these secondary derivatives are and how they are related to the primary derivatives in magnitude and sign.

EXPERIMENTAL RESULTS

Thirteen isotope shifts of ^{19}F due to D substitution are reported here for the first time. These two- and three-bond isotope shifts are shown in Table I and compared to four related molecules. We note several trends. (1) They are all the same sign as one-bond isotope shifts, i.e., substitution with a heavy atom at a remote site leads to increased shielding of the observed nucleus, just as for substitution of an atom bonded to the observed nucleus. (2) $|^2\Delta|$ are generally somewhat larger than $|^3\Delta|$ although the ranges of values form a continuum. (3) There is a definite stereochemical effect. We find $|^3\Delta(cis)|$ to be generally smaller than $|^3\Delta(trans)|$. Although the ranges of values overlap, the *cis* values are at the lower end and the *trans* values are at the higher end. (4) These isotope shifts are additive. Wherever $^2\Delta + {}^3\Delta$ are observed by double substitution, the calculated sum of single substitutions is indistinguishable, within experimental error, from the observed isotope shift. (5) There is a definite effect due to electronegative substituents; given a transmission path, the values are different depending on the atoms attached to the intervening bond or atom.

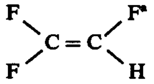
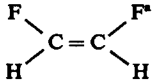
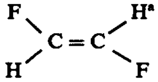
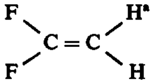
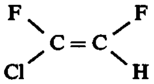
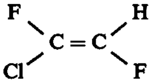
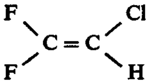
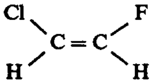
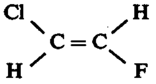
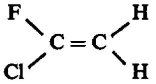
In addition to the isotope shifts which are of interest here, we also report the other NMR parameters (chemical shifts and coupling constants) observed in these molecules. The proton and ^{19}F spectra were taken at 60 MHz (Varian A-60) and 56.458 MHz (recorded on a Varian A56/60 at Case Western Reserve University) at room temperature in $CFCl_3$ solutions using $CFCl_3$ as the ^{19}F reference and TMS as the proton reference. The *trans* $HFC = CHCl$ and $FClC = CH_2$ ABX spectra were analyzed with the aid of a computer program. All the other spectra were analyzed as first order spectra. In each case the isotope shifts were measured in single samples where isotopic impurities were present so the isotope shifts, even the smallest ones, are believed to be reliable. A typical spectrum is shown in Fig. 1.

It is interesting to compare these values of $^2\Delta$ and $^3\Delta$ with those observed for the fluoroethanes. In ethyl fluoride $^2\Delta$ and $^3\Delta$ are -0.645 and -0.244, respectively,[13] which are of the same order of magnitude as the ones in Table I.

Two- and three-bond ^{1}H isotope shifts were also observed for the molecules in Table II. As expected these are very small. The values are -0.01 ppm for *gem* (i.e., D substitution at the position geminal to the observed ^{1}H nucleus), $+0.0025$, $+0.002$ ppm for *cis*, and -0.008, -0.005 ppm for *trans*. The relative magnitudes of *cis*, *trans*, and *gem* ^{1}H isotope shifts are in the same ordering as for ^{19}F isotope shifts, i.e., *cis* < *trans* < *gem*. The unusual sign of the *cis* three-bond ^{1}H isotope shift is consistent with the earlier results of Kanazawa *et al.* which also showed a positive isotope shift for *cis* $HFC = CFD$.[14]

The magnitudes of the two- and three-bond ^{19}F isotope shifts correlate with the two- and three-bond coupling constants in these molecules. In Fig. 2(b) we show the relationship between the ^{19}F isotope shifts due to D substitution of the H at a *gem* position and the coupling constant along the same path. In Fig. 2(a) we show the corresponding relationship between three-bond isotope shifts and the three-bond coupling constant for the *trans* pathway. The *cis* coupling constants are all small and do not provide a wide enough range for the correlation to be obvious, but even here the largest isotope shift is also observed (0.315 ppm) where the coupling is greatest (8.8 Hz).

TABLE I. Isotope shifts $^{2}\Delta^{19}\mathrm{F}(^{2/1}\mathrm{H})$ (*gem*) and $^{3}\Delta^{19}\mathrm{F}(^{2/1}\mathrm{H})$ (*cis* and *trans*) in fluoroethenes, in ppm.

Molecule	*gem*	*cis*	*trans*	Calc. Sum	Obs. Both
	-0.488	-0.162	-0.20		
	-0.504		-0.418	-0.923	-0.922
	-0.494	-0.289		-0.783	-0.782
		-0.208	-0.260	-0.468	-0.468
	-0.542		-0.303		
	-0.510	-0.236			
		-0.170	-0.209		
	-0.574		-0.460	-1.034	-1.04
	-0.586	-0.315		-0.901	-0.902
		-0.329	-0.393		

[a] Reference 23.

CALCULATIONS OF DYNAMICAL EFFECTS DUE TO DEUTERIUM SUBSTITUTION

The comparison of isotope effects in these molecules requires calculations using force fields of comparable quality and internal consistency within the set of compounds. This is possible with the use of Urey–Bradley force fields which have been systematically refined in the same way for the entire set of molecules for the quadratic part of the potential, and an anharmonic part which is modeled in the same way for the entire set of molecules. The quadratic force fields for most of these molecules have been determined by Craig *et al.*[15,16] and the vibrational frequencies have been determined for the rest.[17] The form of the potential function used is that for a general substituted ethylene by Mann *et al.*[18] which has been found to be quite successful in describing the vibrations of haloethenes.[19] The UB constants for H-containing ethenes are not exactly the same as for all-halogen substituted ethenes, however, the sets used here have been refined by an overlay procedure in the same fashion for the three sets of molecules: difluoro- , monofluorochloro- , and difluorochloroethenes. The method of calculation is described in the preceding paper[20] and will not be repeated here. The UB constants have been published for the difluoro- , and the

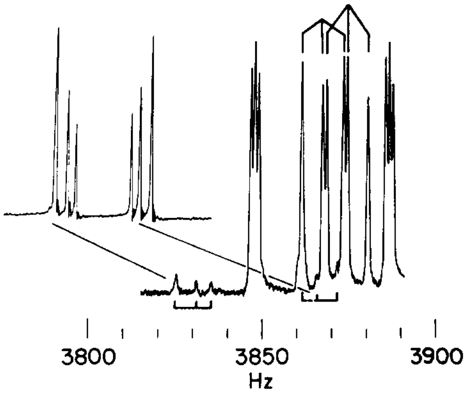


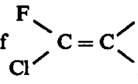
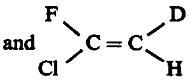
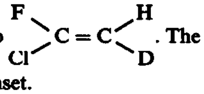
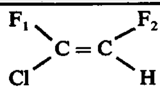
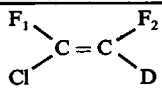
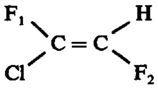
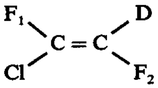
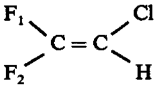
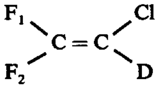
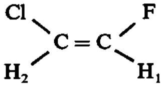
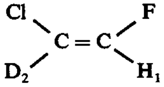
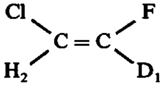
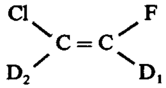
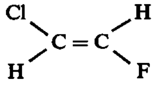
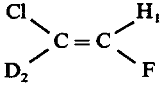
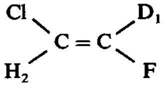
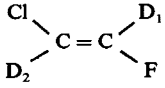
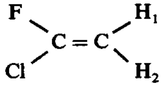
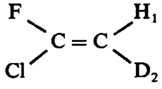
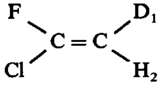
FIG. 1. ^{19}F spectrum of a mixture of  and  with FClC = CH$_2$ as an impurity, illustrating how the lines due to the undeuterated isotopomer serves to give accurate chemical shifts due to isotopic substitution. The interior sextet of lines is due to . The spectrum of FClC = CH$_2$ by itself is shown as an inset.

TABLE II. NMR parameters for some fluoroethenes, shifts are in ppm, coupling constants in Hz.

	 $\mathrm{F_1(Cl)C{=}C(F_2)H}$	 $\mathrm{F_1(Cl)C{=}C(F_2)D}$	 $\mathrm{F_1(Cl)C{=}C(H)F_2}$	 $\mathrm{F_1(Cl)C{=}C(D)F_2}$	 $\mathrm{F_1(F_2)C{=}C(Cl)H}$	 $\mathrm{F_1(F_2)C{=}C(Cl)D}$	 $\mathrm{Cl(H_2)C{=}C(F)H_1}$	 $\mathrm{Cl(D_2)C{=}C(F)H_1}$	 $\mathrm{Cl(H_2)C{=}C(F)D_1}$
$H_1\delta$[a]	6.39		7.26		5.18		6.79	6.79	
$H_2\delta$							5.51		5.51
$F_1\delta$[b]	− 104.5	− 104.9	− 130.3	− 130.6	− 86.8	− 87.1	− 127.9	− 128.3	− 128.5
$F_2\delta$	− 156.0	− 156.7	− 173.9	− 174.4	− 91.7	− 91.9			
$J(HF)_{gem}$[c]	72.9		74.3				78.0	78.0	
$J(DF)_{gem}$		11.4(11.2)[d]		11.5(11.4)					12.0(12.0)
$J(HF)_{trans}$	12.4				16.6		27.5		27.4
$J(DF)_{trans}$		1.9(1.9)				2.6(2.6)		4.2(4.2)	
$J(HF)_{cis}$			1.2		1.1				
$J(DF)_{cis}$				< 0.5(0.2)		< 0.5(0.15)			
$J(FF)_{gem}$					41.0	41.4			
$J(FF)_{trans}$			132.9	133.0					
$J(FF)_{cis}$	11.8	11.7							
$J(HH)_{gem}$									
$J(HD)_{gem}$									
$J(HH)_{trans}$									
$J(HD)_{trans}$									
$J(HH)_{cis}$							3.4		
$J(HD)_{cis}$								0.50(0.52)	0.50(0.52)

	 $\mathrm{Cl(D_2)C{=}C(F)D_1}$	 $\mathrm{Cl(H)C{=}C(H)F}$	 $\mathrm{Cl(D_2)C{=}C(H_1)F}$	 $\mathrm{Cl(H_2)C{=}C(D_1)F}$	 $\mathrm{Cl(D_2)C{=}C(D_1)F}$	 $\mathrm{F(Cl)C{=}C(H_1)H_2}$	 $\mathrm{F(Cl)C{=}C(H_1)D_2}$	 $\mathrm{F(Cl)C{=}C(D_1)H_2}$
$H_1\delta$		6.87	6.87			4.78	4.76	
$H_2\delta$		6.11		6.12		4.54		4.52
$F_1\delta$	− 128.8	− 131.4	− 131.6	− 131.9	− 132.3	− 68.1	− 68.6	− 68.5
$J(HF)_{gem}$		80.0	79.9					
$J(DF)_{gem}$	12.0(12.0)			12.4(12.3)	12.2(12.3)			
$J(HF)_{trans}$						38.7		38.6
$J(DF)_{trans}$	4.2(4.2)						5.9(5.9)	
$J(HF)_{cis}$		8.6		8.7		7.0	7.0	
$J(DF)_{cis}$			1.2(1.4)		1.4(1.4)			1.0(1.1)
$J(HH)_{gem}$						4.0		
$J(HD)_{gem}$							0.58(0.61)	0.60(0.61)
$J(HH)_{trans}$		10.6						
$J(HD)_{trans}$			1.6(1.6)	1.59(1.6)				

[a] ^{1}H shifts relative to TMS.

[b] ^{19}F shifts relative to $CFCl_3$. Add 188.7 ppm to get absolute shielding.

[c] Absolute signs cannot be measured in these experiments. However, by analogy with similar molecular systems, for which absolute sign assignments have been made [by relating relative signs obtained from multiple resonance experiments to an absolute positive sign for $^1J(CH)$], it can be assumed that $^2J(HF)_{gem}$ and $^3J(HF)_{trans}$ are positive while $^3J(HF)_{cis}$ is negative. Also, $^2J(FF)_{gem}$ and $^3J(FF)_{cis}$ are positive while $^3J(FF)_{trans}$ is negative (Ref. 27).

[d] Calculated from $J(HX)/6.514$.

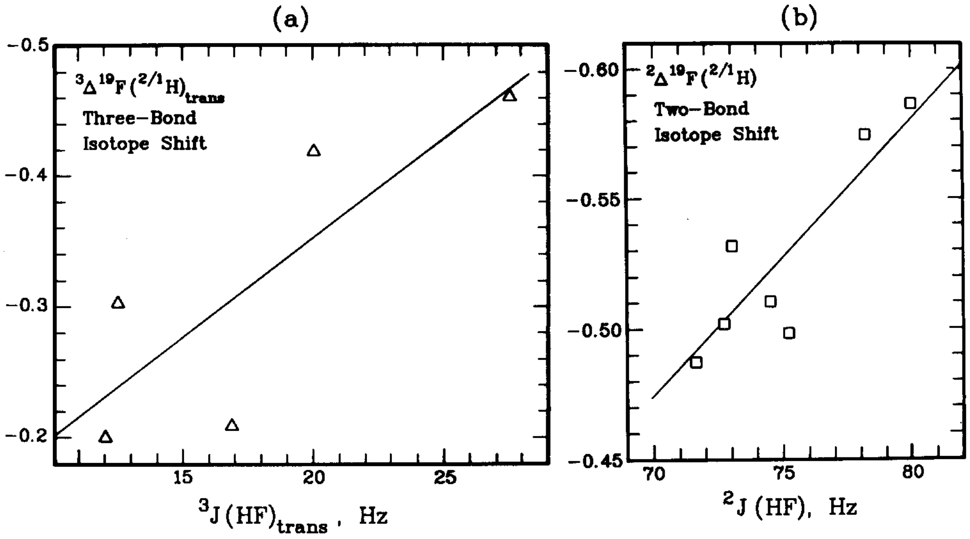


FIG. 2. Correlation of the ^{19}F isotope shift due to deuterium substitution of a proton at a *trans* (a) and *gem* (b) position with the ^{1}H–^{19}F spin–spin coupling constant $^2J(HF)_{trans}$ and $^2J(HF)_{gem}$ over the same electronic pathway in various fluoroethenes.

monofluorochloroethenes.[15,16] In Table III we give the set for difluorochloroethenes which reproduce the frequencies to the same degree of agreement with experiment as the other two sets. These UB constants are consistent with the sets obtained by Craig *et al.*[15,16] for the monofluoro- and difluorochloroethenes as well as with the trifluoroethenes; many of the constants have been transferred unchanged. Geometries used are those given by Craig *et al.*[15,16] except where recent data is available.[21]

The results of these dynamic calculations are shown in Table IV only for isotope effects. In addition we note several similarities with the results in the preceding paper for the trifluoroethenes and $CF_2 = CH_2$. In the mixed ethenes in this paper the mean bond displacements have the following ranges of values:

$$\langle \Delta r_{CF} \rangle = 5.3\text{–}5.6 \times 10^{-3}\ \text{Å} \quad \text{for difluorochloro-},$$

$$4.6\text{–}5.1 \times 10^{-3}\ \text{Å} \quad \text{for } CHF = CHF,$$

$$\text{and } 6.4\text{–}6.6 \times 10^{-3}\ \text{Å} \quad \text{for } CFH = CHCl,$$

$$\langle \Delta r_{CCl} \rangle = 7.1\text{–}8.3 \times 10^{-3}\ \text{Å} \quad \text{for Cl } gem \text{ to H},$$

$$5.5\text{–}5.8 \times 10^{-3}\ \text{Å} \quad \text{for Cl } gem \text{ to F},$$

$$\langle \Delta r_{CH} \rangle = 1.8\text{–}2.1 \times 10^{-2}\ \text{Å},$$

$$\langle \Delta r_{CD} \rangle = 1.3\text{–}1.5 \times 10^{-2}\ \text{Å}.$$

The temperature dependence, given by $\Delta_T \equiv \langle \Delta r \rangle^{400} - \langle \Delta r \rangle^{200}$ are

$$\Delta_T(r_{CF}) = 5.6\text{–}7.8 \times 10^{-4}\ \text{Å},$$

$$\Delta_T(r_{CCl}) = 1.4\text{–}1.7 \times 10^{-4}\ \text{Å},$$

$$\Delta_T(r_{CH}) = 2\text{–}4 \times 10^{-5}\ \text{Å}.$$

These values are comparable to the ones obtained for the trifluoroethene and $CF_2 = CH_2$.[20] We also find that the in-plane, out-of-plane vibrational and the rotational contributions are in the proportion 50%–60%, 15%, 25%–35% of $\langle \Delta r_{CF} \rangle$, 82%–89%, 6%–8%, 5%–11% of $\langle \Delta r_{CCl} \rangle$ and 97%, 3%, 0% of $\langle \Delta r_{CH} \rangle$. The contributions to the temperature dependence from the in-plane vibrations, out-of-plane vibrations and rotational contributions are typically 52%, 12%, 36% of $\Delta_T(r_{CF})$, and 64%, 7%, 29% of $\Delta_T(r_{CCl})$. We do not have temperature-dependent chemical shift experiments with which these may be compared, but the dominance of in-plane vibrations and rotational contributions are comparable to the ones obtained for trifluoroethene and $CF_2 = CH_2$.

Of particular importance to the calculation of isotope shifts which we have measured here are the primary and secondary effects on the mean bond displacements due to substitution of a hydrogen with a deuterium. We find that the primary isotope effects on mean bond displacements are large, $\Delta_D \langle \Delta r_{CH} \rangle = \langle \Delta r_{CH} \rangle - \langle \Delta r_{CD} \rangle = 4.9\text{–}5.3 \times 10^{-3}$ Å, as is usual for CH bonds. The secondary isotope effects on mean bond displacements are small, $\delta_D \langle \Delta r_{CF} \rangle = \langle \Delta r_{CF} \rangle_{light} - \langle \Delta r_{CF} \rangle_{heavy} = 4.2\text{–}6.8 \times 10^{-5}$ Å for *cis* substitution, 3.0–7.4 × 10^{-5} Å for *trans* substitution and 5–

TABLE III. Urey–Bradley force constants used for difluorochloroethenes, all in mdyn Å^{-1}.

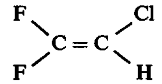
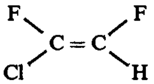
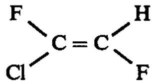
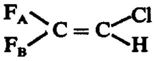
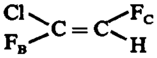
			
K_{CC}	7.9	7.9	7.9
K_{CF}	4.85	4.85	4.85
K_{CH}	4.75	4.75	4.75
K_{CCl}	2.66	2.66	2.66
F_{FF}	0.68		
F_{FH}		0.557	0.557
F_{FCl}		0.64	0.64
F_{ClH}	0.524		
F_{FC}	1.36	1.36	1.36
F_{HC}	0.394	0.394	0.394
F_{ClC}	0.77	0.77	0.77
C_{FF}		−0.16	
C_{FH}	−0.043		−0.043
C_{FCl}	0.03		0.03
C_{ClH}		−0.077	
H_{FCF}	0.41		
H_{FCCl}		0.273	0.273
H_{ClCH}	0.1466		
H_{FCH}		0.1196	0.1196
H_{FCC}	0.206	0.206	0.206
H_{HCC}	0.25	0.25	0.25
H_{ClCC}	0.0695	0.0695	0.0695

TABLE IV. Derivatives of ^{19}F nuclear shielding, ppm $Å^{-1}$.

Molecule	$(\partial\sigma^F/\partial\Delta r_{CF})_e$	$(\partial\sigma^F/\partial\Delta r_{CH})_{gem}$	$(\partial\sigma^F/\partial\Delta r_{CH})_{cis}$	$(\partial\sigma^F/\partial\Delta r_{CH})_{trans}$
$CF_2=CFH$ A	− 1250			− 30
B	− 1190		− 23	
C	− 2260	− 78		
$CF_2=CH_2$	− 990		− 33	− 47
$CHF=CHF$(*trans*)	− 1980	− 74	− 41	
$CHF=CHF$(*cis*)	− 1760	− 77		− 62
 B	− 1040		− 21	
A	− 990			− 32
 B	− 1160			− 53
C	− 1680	− 86		
$CHF=CHCl$(*trans*)	− 1430	− 90	− 41	
$CHF=CHCl$(*cis*)	− 1400	− 80		− 67

12×10^{-5} Å for substitution of D at a position *gem* from the fluorine. The effect of deuterium substitution on the $C=C$ bond is $\delta_D\langle\Delta r_{CC}\rangle\simeq1\times10^{-4}$ Å for all molecules. The relative contributions to these isotope effects on bond lengths by in-plane vibrations, out-of-plane vibrations, and rotation are as follows: The isotope effect on the CH bond by substitution of H with D, $\Delta_D\langle\Delta r_{CH}\rangle$, is essentially 100% due to the in-plane vibrations, the rotation and out-of-plane vibration contributions are extremely small and cancelling. The secondary isotope effect on the CF bond by deuterium substitution of a hydrogen has a minor rotational contribution, 3%–25%. The *gem* isotope effect is always dominated by the in-plane vibrations. On the other hand, the proportion of the in-plane and out-of-plane contributions to the *cis* and *trans* $\delta_D\langle\Delta r_{CF}\rangle$ varies from molecule to molecule, as should be expected, since the out-of-plane modes have an important role in modifying the bond lengths along the *cis* and *trans* pathways.

PRIMARY AND SECONDARY DERIVATIVES OF ^{19}F SHIELDING

The best source of the primary ^{19}F shielding derivatives which we need for interpretation of isotope shifts is the empirical fit to the observed temperature dependence of the ^{19}F shielding in the isolated molecule limit. However, of the molecules in Table I, these observations have only been made for the $CF_2=CFH$ and $CF_2=CH_2$ molecules (see preceding paper[20]). These derivatives for the four nuclear sites in these molecules cover a wide range of absolute shielding values and are found to form a straight line within the errors of determination of the empirical derivatives. All the ^{19}F sites in the other molecules being considered here have absolute shielding values within this range. Therefore, we use the four known derivatives and find the others by linear interpolation. The values so obtained are shown in Table IV.

We then assume that the two-bond and three-bond isotope shifts can be interpreted in the following way. For a single substitution of deuterium for an H atom located *gem* or *cis* from the observed ^{19}F nucleus,

$$^2\Delta\,^{19}F(^{2/1}H)=(\partial\sigma^F/\partial\Delta r_{CF})_e\cdot\delta_D\langle\Delta r_{CF}\rangle_{gem}+(\partial\sigma^F/\partial\Delta r_{CH})_{e\,gem}\cdot\Delta_D\langle\Delta r_{CH}\rangle, \tag{5}$$

$$^3\Delta_{cis}\,^{19}F(^{2/1}H)=(\partial\sigma^F/\partial\Delta r_{CF})_e\cdot\delta_D\langle\Delta r_{CF}\rangle_{cis}+(\partial\sigma^F/\partial\Delta r_{CH})_{e\,cis}\cdot\Delta_D\langle\Delta r_{CH}\rangle, \tag{6}$$

and a similar relation for *trans* isotopic substitution. The term $(\partial\sigma^F/\partial\Delta r_{CC})_e\cdot\delta_D\langle\Delta r_{CC}\rangle$ has been neglected in the above equations. Since it involves a secondary electronic factor multiplied by a secondary dynamic factor, it is expected to be at least an order of magnitude smaller than terms we do include in Eqs. (5) and (6). The terms involving the second derivatives have also been neglected, as we have consistently done, even for one-bond isotope shifts. At the present time, there is very little known about the magnitudes of secondary second derivatives. For ^1H in H_2O the magnitude of the secondary second derivative $(\partial^2\sigma^{H_a}/\partial\Delta r^2_{OH\,b})_e$ is one-fifth of the primary second derivative $(\partial^2\sigma^{H_a}/\partial\Delta r^2_{OH\,a})_e$.[22]

Since we have calculated all δ_D and Δ_D factors for the isotopic pairs and we have the primary derivatives $\partial\sigma^F/\partial\Delta r_{CF})_e$, we can therefore calculate the two contributions to the isotope shift and obtain $(\partial\sigma^F/\partial\Delta r_{CH})_e$ for *gem*, *cis*, and *trans* paths. The contributions to the isotope shifts from the $(\partial\sigma^F/\partial\Delta r_{CH})_e\cdot\Delta_D\langle\Delta r_{CH}\rangle$ term are 70%–80%, 67%–76%, and 75%–90% of the observed *gem*, *cis*, and *trans* isotope shifts, respectively. The secondary derivatives $(\partial\sigma^F/\partial\Delta r_{CH})_e$ so obtained are shown in Table IV. The force fields we are using are not sufficiently refined to give us accurate relative magnitudes of the secondary isotope effects on the bond length from molecule to molecule. Therefore the values given in Table IV should be considered only semiquantitative. Nevertheless, there are several interesting observations that can be made here.

(1) The values of the secondary derivatives are all one or two orders of magnitude smaller than the primary derivatives.

(2) They are all the same sign as the primary derivatives.

(3) Their magnitudes are in the order

$$|(\partial\sigma^F/\partial\Delta r_{CH})_e|: gem > trans > cis,$$

the average values being -80, -50, and -30 ppm $Å^{-1}$, respectively.

(4) The values have narrow ranges, changing by less than a factor of 2 for each of *gem*, *cis*, or *trans* pathways.

(5) We may compare these secondary derivatives with other *gem* pathways for which we have values:

$$(\partial\sigma^F/\partial\Delta r_{C=O})_e = -175 \text{ ppm } Å^{-1} \text{ in } O=CF_2,^{23}$$

$$(\partial\sigma^F/\partial\Delta r_{CCl})_e = -70 \text{ ppm } Å^{-1} \text{ in } CFCl_3.^{11}$$

It is reassuring that the ^{19}F secondary shielding derivatives we have found here are about the same magnitude as the ones for $O=CF_2$ and $CFCl_3$. We feel confident that these derivatives are of the correct sign and order of magnitude.

Another indication that these secondary derivatives are physically meaningful is the general correlation of their magnitudes with the magnitudes of *cis*, *trans*, and *gem* coupling constants, $^{2,3}J(HF)$. These coupling constants are reported in Table II for these molecules, and the others are given in the first paper of this series[24] and by Kanazawa *et al.*[14] The magnitudes of these coupling constants are in the relative order

$$|J(HF)|_{cis} < |J(HF)|_{trans} < |J(HF)|_{gem},$$

i.e., (0.5–8.8), (12–33.8), and (72–80) Hz, respectively. The magnitudes of the secondary derivatives are in the same relative order,

$$|(\partial\sigma^F/\partial\Delta r_{CH})_e|_{cis} < |(\partial\sigma^F/\partial\Delta r_{CH})_e|_{trans} < |(\partial\sigma^F/\partial\Delta r_{CH})_e|_{gem},$$

i.e., 20–40, 30–67, and 74–90 ppm $Å^{-1}$, respectively. This correlation is to be expected on a physical basis. Both the $J(HF)$ coupling and the secondary derivative of the shielding with respect to the remote bond extension involve the same through-bond electronic transmission pathway. This is also the same electronic transmission pathway through which a substituent X affects the shielding of a ^1H or ^{19}F nucleus in vinyl compounds or trifluorovinyl compounds, leading to the well-established *cis* < *trans* < *gem* substituent shifts.[25] Therefore, the observation of the general correlation supports the validity of the secondary derivatives found here. The relationship shown in Fig. 2(a) indicate correlations within the *trans* set of isotope shifts and coupling constants, and in Fig. 2(b) the same relationship within the *gem* set of data. These correlations have more scatter than the comparable correlation between the ^{13}C-induced ^{19}F isotope shifts and $^1J(CF)$ which have been noted earlier.[26] This may be due to the dynamic factors ($\delta_D\langle\Delta r_{CF}\rangle$ and $\Delta_D\langle\Delta r_{CH}\rangle$) being more variable in the different fluoroethene molecules than the corresponding $\Delta_C\langle\Delta r_{CF}\rangle$ in the fluoromethanes. Nevertheless, we find that these correlations become evident because the electronic factors in the isotope shift and the spin–spin coupling (a purely electronic quantity) varies with molecular electronic structure in the same way from one molecule to another within a related set such as halomethanes or fluoroethenes. This correlation provides support for our model of the isotope shift and also provides a convenient way of making empirical estimates of isotope shifts from the easily observed coupling constants, especially when the former are small and sometimes observable only in isotopically enriched compounds.

The correlations in Fig. 2 directly reflect the dominance of the term in $(\partial\sigma^F/\partial\Delta r_{CH})_e \cdot \Delta_D\langle\Delta r_{CH}\rangle$ in Eqs. (5) and (6), since the electronic part of this term carries the information about the transmission path. The force field calculations give reliable values of $\Delta_D\langle\Delta r_{CH}\rangle$, although the values of the secondary isotope effects $\delta_D\langle\Delta r_{CF}\rangle$ may be less accurate. We find that a major part of the observed isotope shift is due to the term $(\partial\sigma^F/\partial\Delta r_{CH})_e \cdot \Delta_D\langle\Delta r_{CH}\rangle$, with the term $(\partial\sigma^F/\partial\Delta r_{CF})_e \cdot \delta_D\langle\Delta r_{CF}\rangle$ playing a relatively minor role, the proportion being about 80%/20%. Thus, the secondary derivatives derived from the experimental isotope shifts measured here should be fairly reliable, assuming that the neglect of second and higher derivatives of shielding is valid.

One possible importance of the NMR isotope shift was thought to be in its use for evaluating the variation in molecular dimensions upon isotopic substitution,[1] i.e., that the NMR isotope shift might be used to predict the isotope effect on molecular dimensions, the shortening of the average length of the bond involving the isotope (primary isotope effect) as well as the remaining bonds (secondary isotope effect). From the evidence that is available, it appears that the isotope effects on mean bond lengths are more predictable (cover a narrower range of values) than the NMR isotope shifts, so that the magnitudes of NMR isotope shifts are much more indicative of the electronic distribution in the molecule, correlating with purely electronic quantities such as spin–spin coupling constants. In this respect, the NMR isotope shift is an important index of the chemical bond.

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