The mean bond displacements and the derivatives of ^{19}F shielding in $CF_2 = CFX$ and $CF_2 = CH_2$

Cynthia J. Jameson
Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680
H. Jörg Osten
Academy of Sciences of the GDR, Central Institute of Physical Chemistry, 1199 Berlin, Rudower Chaussee 6, German Democratic Republic

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The mean bond displacements $\langle \Delta r \rangle$ for molecules $CF_2 = CFX$ (X = H, F, Cl, Br, I) and $CF_2 = CH_2$ have been calculated as a function of temperature using a Urey–Bradley force field augmented by stretching anharmonic terms and cubic nonbonded interactions. The temperature dependence of the ^{19}F nuclear shielding in the isolated molecule limit is interpreted in terms of $\langle \Delta r_{CF} \rangle^T$ and an electronic factor $(\partial \sigma^F / \partial \Delta r_{CF})_e$ which is found by fitting the experimental data with $\sigma_0(T) - \sigma_0(300\text{ K}) = (\partial \sigma^F / \partial \Delta r_{CF})_e [\langle \Delta r_{CF} \rangle^T - \langle \Delta r_{CF} \rangle^{300}]$. The derivatives for each of the three F sites in the $CF_2 = CFX$ molecules vary systematically with the absolute shielding of the F site. The ^{19}F nucleus *gem* to the X substituent exhibits the greatest change of shielding with bond displacement. For X = Cl, Br, I, the derivatives $(\partial \sigma^F / \partial \Delta r_{CF})_e$ are (-1940, -2000, -1950 ppm Å^{-1}) for the F nucleus *trans* to X; (-2190, -2290, -2300 ppm Å^{-1}) for the F nucleus *cis* to X; and (-2550, -2890, -3160 ppm Å^{-1}) for the F nucleus *gem* to X. In $CF_2 = CF_2$ and $CF_2 = CH_2$ the derivatives are -2080 and -990 ppm Å^{-1}, respectively. For $CF_2 = CFH$ they are -1250, -1190, and -2260 ppm Å^{-1} for the F nucleus *trans*, *cis*, and *gem*, respectively, to the H substituent.

I. INTRODUCTION

Our studies of the temperature dependence of ^{19}F nuclear shielding have been motivated by the possibility of using an experimental observable, the temperature coefficient of the ^{19}F nuclear shielding in the isolated molecule, to provide information about the nuclear shielding function for the F nucleus in a variety of electronic environments in addition to that which can be obtained from the absolute shielding at room temperature. We have found in the halomethanes that the most shielded ^{19}F nuclei exhibit the smallest dependence on temperature in the limit of the isolated molecule in the CF_3X (X = F, Cl, Br, I) and the CF_nCl_{4-n} series.[1] These observed temperature dependences of F shielding are interpreted in terms of a rovibrational averaging model,

$$\sigma_0(T) = \sigma_e + (\partial \sigma^F / \partial \Delta r_{CF})_e \langle \Delta r_{CF} \rangle^T + \cdots .$$

We found that the dynamic factor $\langle \Delta r_{CF} \rangle^T$ varied with temperature in a qualitatively similar way in all the halomethanes and that the derivatives $(\partial \sigma^F / \partial \Delta r_{CF})_e$, which are a measure of the sensitivity of the F shielding to bond extension, correlated with the absolute shielding σ_e in a smooth curve which roughly reflected the correlation between the observed temperature coefficients $(d\sigma_0^F/dT)$ and the absolute shielding at room temperature, σ_0 (300 K).

In the previous paper we measured the temperature dependence of ^{19}F in the series $CF_2 = CFX$ (X = H, F, Cl, Br, I).[2] In the fluoroethenes the most shielded ^{19}F nuclei exhibit the greatest dependence on temperature. The trends in the temperature coefficient $(d\sigma_0/dT)$ with absolute shielding σ_0 for ^{19}F in the fluoroethenes are qualitatively different from those in the fluoromethanes. The comparison is made in Fig. 1. The reverse correlation in the ethenes could be inherent in the electronic structure of the molecules, i.e., the $(\partial \sigma^F / \partial \Delta r_{CF})_e$ could vary with σ_e in a different way than in the methanes, or the reverse correlation could be due to the differences in the dynamic averaging of the fluorines in the three nuclear sites in the $CF_2 = CFX$ molecule. In order to answer this question, it is necessary to carry out dynamic calculations on the family of molecules $CF_2 = CFX$. One can expect that the comparison of dynamic and electronic factors for a related group of molecules will be specially revealing concerning several questions of fundamental interest: Are derivatives $(\partial \sigma^F / \partial \Delta r_{CF})_e$ in analogous nuclear sites relatively invariant for groups of related molecules? Are the dynamic factors $[\langle \Delta r \rangle^T - \langle \Delta r \rangle^{300}]$ relatively predictable for a given bond, e.g., C–F, in similar electronic environments?

II. THE FORCE FIELD FOR A GENERAL TYPE OF SUBSTITUTED ETHENE

The potential function used here is the general potential function given by Mann *et al.*[3] for a general type of substituted ethene in terms of the Urey–Bradley constants. The advantage of the UBFF is that it is readily adapted to the treatment of large families of related molecules such as the substituted ethenes of this paper and the following paper, with the use of only a small number of force constants all of which are physically reasonable. Some of these are directly transferable from one molecule to another and the remaining others can be obtained by linear interpolation. Thus all UB

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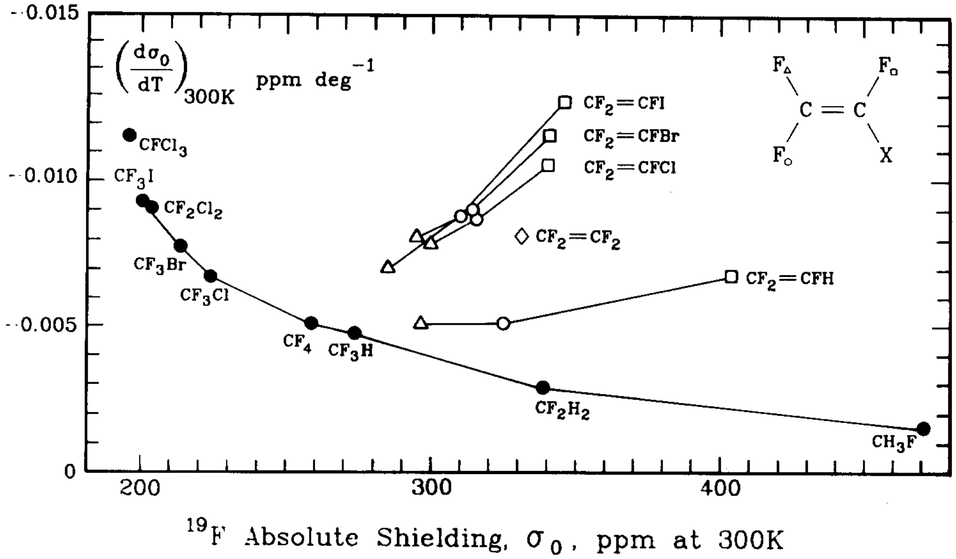
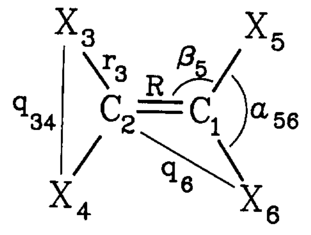


FIG. 1. Correlation between absolute ^{19}F shielding in the isolated molecule and the temperature coefficients of the shielding at 300 K.

constants for haloethenes are directly descended from fits to frequencies of C_2F_4, C_2Cl_4, C_2Br_4, and C_2I_4 only. With these constants all mixed haloethene frequencies can be reproduced to within a few percent. Furthermore, no better force fields are available for any of the molecules which we are considering here or in the following paper except for $CF_2 = CH_2$, and CFH = CHF *cis* and *trans*, for which modified valence force fields are also available.[4] The additional advantage of the UB field used here is that it allows the calculation of mean bond displacements $\langle \Delta r \rangle$ in the series of related molecules with comparable force fields for the entire set of $CF_2 = CFX$ (X = H, F, Cl, Br, I), and $CF_2 = CH_2$ molecules considered here, as well as the wide variety of difluoro-, monofluorochloro-, and difluorochloroethenes considered in the following paper. By using the same quality of potential function, the calculated $\langle \Delta r \rangle$ values should be directly comparable for all these molecules.

The numbering system is adopted from Mann *et al.*[3] as follows:



The in-plane internal coordinates ΔR, Δr_i, $\Delta\beta_i$, and $\Delta\alpha_{ij}$, Δq_i, and Δq_{ij} are self-explanatory. The potential function in terms of these coordinates is given by

$$2V = K_{CC}(\Delta R)^2 + 2K'_{CC}(R\Delta R) + \sum_{i=3}^{6} K_{CX_i}(\Delta r_i)^2$$
$$+ 2\sum_{i=3}^{6} K'_{CX_i}(r_i\Delta r_i) + \sum_{i=3}^{6} H_{CX_i}(r_i^2)(\Delta\beta_i)^2$$
$$+ H_{X_3X_4}(r_3r_4)(\Delta\alpha_{34})^2 + H_{X_5X_6}(r_5r_6)(\Delta\alpha_{56})^2$$
$$+ \sum_{i=3}^{6} F_{CX_i}(\Delta q_i)^2 + 2\sum_{i=3}^{6} F'_{CX_i}(q_i\Delta q_i)$$
$$+ F_{X_3X_4}(\Delta q_{34})^2 + F_{X_5X_6}(\Delta q_{56})^2 + 2F'_{X_3X_4}(q_{34}\Delta q_{34})$$
$$+ 2F'_{X_5X_6}(q_{56}\Delta q_{56}) + C_{X_3X_5}(\Delta q_{35})^2 + C_{X_4X_6}(\Delta q_{46})^2$$
$$+ 2C'_{X_3X_5}(q_{35}\Delta q_{35}) + 2C'_{X_4X_6}(q_{46}\Delta q_{46}). \quad (1)$$

Δq's can be further expressed in terms of valence coordinates

$$\Delta q_{ij} = s_{ij}\Delta r_i + s_{ji}\Delta r_j + (t_{ij}t_{ji})^{1/2}(r_ir_j)^{1/2}\Delta\alpha_{ij}$$
$$+ [t_{ij}^2(\Delta r_i)^2 + t_{ji}^2(\Delta r_j)^2 - s_{ij}s_{ji}(r_ir_j)(\Delta\alpha_{ij})^2 - 2t_{ij}t_{ji}\Delta r_i\Delta r_j$$
$$+ 2t_{ij}s_{ji}\Delta r_i(r_j\Delta\alpha_{ij}) + 2t_{ji}s_{ij}\Delta r_j(r_i\Delta\alpha_{ij})]/2q_{ij}, \quad (2)$$

where

$$s_{ij} = (r_i - r_j\cos\alpha_{ij})/q_{ij}, \quad s_{ji} = (r_j - r_i\cos\alpha_{ij})/q_{ij},$$
$$t_{ij} = r_j\sin\alpha_{ij}/q_{ij}, \quad t_{ji} = r_i\sin\alpha_{ij}/q_{ij}. \quad (3)$$

Expressions involving K' drop out and each of the constants F' and C' is set equal to -0.1 times the corresponding F and C.

The out-of-plane coordinates are γ_1, γ_2, and τ, where γ_1 is the change in the angle between the plane defined by atoms 516 and the C_1C_2 bond, γ_2 is the change in the angle between the plane defined by atoms 324 and the C_1C_2 bond. The torsional coordinate τ is the change in the dihedral angle between the planes of the 321 and the 512 atoms.

A. $CF_2 = CF_2$, $CF_2 = CFCl$, and $CF_2 = CFBr$

The perhalogenated ethenes have been studied systematically by Mann *et al.*[5] A force field model of the Urey–Bradley type was used for the planar vibrations and a simple valence potential for the nonplanar modes. Using the three molecules C_2F_4, C_2Cl_4, and C_2Br_4, UB constants were obtained by a least squares process. The best set obtained for these molecules were transferred unchanged or were linearly interpolated and applied to the mixed haloethenes. The agreement btween calculated and observed frequencies in 24 mixed haloethenes was quite good. We use the set of UB force constants resulting from this process from Mann *et al.* for $CF_2 = CFX$ for X = F, Cl, Br.

TABLE I. Observed infrared bands of $CF_2 = CFI$.

Frequency	Assignment	Calculated
1756 cm^{-1}	a'	1756 cm^{-1}
1310	a'	1326
1172	a'	1221
999	a'	1006
650	a'	648
508	a'	504
321	a'	324
289	a'	304
191	a'	178
538	a''	(538)
349	a''	(349)
146	a''	(146)
935	650 + 289	
883	538 + 349	
694	2×349	
486	349 + 146	
386	2×191	

B. $CF_2 = CFI$

The vibrational frequencies of $CF_2 = CFI$ have not been previously reported. Therefore, we measured the infrared spectrum of this molecule. In the range 50 to 500 cm^{-1} the IR spectrum was taken in the liquid phase in a 0.2 mm polyethylene holder with an IBM Fourier transform spectrometer, model IR-90. In the mid-IR range 500 to 3000 cm^{-1}, the spectrum was taken of the liquid in a 0.2 mm NaCl cell in a conventional IR spectrometer (Perkin–Elmer 457). The observed frequencies are given in Table I. The assignments of the out-of-plane vibrations were made by analogy with $CF_2 = CFCl$ and $CF_2 = CFBr$. $a'' = 538, 369, 166\ cm^{-1}$ for the chloro-[6] and 538, 355, 150 cm^{-1} for the bromotrifluoroethene.[7] Thus, we assigned 538, 349, 146 cm^{-1} to a'' in $CF_2 = CFI$. These assignments are supported by the excellent agreement between the observed and calculated frequencies for the in-plane vibrations. The presence of overtones of the wagging (538, 349 cm^{-1}) frequencies, as well as the binary sum band (538 + 349 cm^{-1}) with appreciable intensity in the infrared spectrum has been noted as characteristic of a number of haloethenes[6] and further supports these assignments.

In the same manner as Mann *et al.* we find the Urey–Bradley force constants for the planar vibrations of $CF_2 = CFI$, by including the best set of UB constants obtained by Flourie and Jones for C_2I_4.[8] The K_{CC} constant for $CF_2 = CFI$ was obtained from $[3K_{CC}(C_2F_4) + K_{CC}(C_2I_4)]/4$. The other constants are obtained as follows:

$$\begin{aligned} C_{FI} &= [C_{FF}(C_2F_4) + C_{II}(C_2I_4)]/2\,, \\ F_{FI} &= [F_{FF}(C_2F_4) + F_{II}(C_2I_4)]/2\,, \\ H_{FCI} &= [H_{FCF}(C_2F_4) + F_{ICI}(C_2I_4)]/2\,. \end{aligned} \tag{4}$$

K_{CI}, H_{ICC}, F_{CI} were taken unchanged from Flourie and Jones. All other constants involving only F atoms were taken directly from Mann *et al.*[5] With this nonadjusted set we calculated the frequencies shown in Table I. The agreement between observed and calculated frequencies is excellent although constants were obtained entirely from C_2F_4 and C_2I_4 data, once again demonstrating the applicability of the Urey–Bradley field to haloethenes. Frequencies of all mixed haloethenes including the I substituent can be calculated just as Mann *et al.* had done for ethenes with F, Cl, Br substituents.

C. $CF_2 = CFH$ and $CF_2 = CH_2$

The experimental frequencies used for these molecules were taken from the 1982 paper by Kagel *et al.*[9] Although UB constants had been reported previously for $CF_2 = CH_2$, the earlier vibrational assignments had not been consistent and earlier force constant calculations proceeded from wrong vibrational assignments. For $CF_2 = CFH$ and $CF_2 = CH_2$ we used a set of UB force constants which is consistent with the ones obtained by Craig *et al.* for *cis* and *trans* CHF = CHF[10] as well as for monofluorochloro- and difluorochloroethenes,[11,12] and which also reproduces the observed fundamental frequencies for $CF_2 = CFH$, $CF_2 = CH_2$, and all their deuterated modifications within 1%.

The UB constants in Table III show less transferability than those in Mann *et al.*[5] and in Table II. This is typical of hydrogen-containing compounds. Although Ngai and Mann found that one set of UB constants could be used to reproduce the frequencies of all the mixed halomethanes within 1%–2%,[13] no single set of UB constants could be used for the fluoromethanes such as CH_nF_{4-n} CH_nCl_{4-n}, or the CH_nBr_{4-n} or the mixed ones such as CH_2FCl, CHF_2Cl, etc.[14] The set shown in Table III is consistent with the ones found by Craig *et al.*[10–12] for mixed H, F, and Cl-substituted ethenes. They also found some small differences in UB constants for difluoro-, compared with either monofluorochloro- or difluorochloroethenes. Nevertheless, the differences are small and some constants are the same for all these molecules (such as $F_{FC} = 1.36$, $F_{FF} = 0.68$, $C_{FH} = -0.045$ mdyn $Å^{-1}$ and $H_{HCC} = 0.25$ mdyn Å rad^{-1}).

TABLE II. Urey–Bradley force constants for $CF_2 = CFX$ molecules, all in mdyn $Å^{-1}$.

X =	F[a]	Cl[a]	Br[a]	I[b]
K_{CC}	8.89	8.41	8.42	8.38
K_{CF}	5.2	5.2	5.2	5.2
K_{CX}	5.2	2.66	2.11	1.6
F_{FC}	1.36	1.36	1.36	1.36
F_{XC}	1.36	0.92	0.71	0.60
F_{FF}	0.68	0.68	0.68	0.68
F_{FX}	0.68	0.64	0.59	0.52
C_{FF}	−0.09	−0.09	−0.09	−0.09
C_{FX}	−0.09	0.03	0.06	0.18
H_{FCF}	0.41	0.41	0.41	0.41
H_{FCX}	0.41	0.27	0.235	0.25
H_{FCC}	0.1	0.1	0.1	0.1
H_{XCC}	0.1	0.09	0.05	0.05

[a] Reference 5.

[b] Obtained from Urey–Bradley force constants for $CF_2 = CF_2$ and $CI_2 = CI_2$ by linear interpolation method of Mann *et al.* (Ref. 5) as described in the text. Urey–Bradley constants for $CI_2 = CI_2$ were taken from Ref. 8.

TABLE III. Urey–Bradley force constants for $CF_2=CFH$ and $CF_2=CH_2$, all in mdyn Å^{-1}.

	$CF_2=CFH$	$CF_2=CH_2$
K_{CC}	8.4	7.95
K_{CF}	4.85	5.15
K_{CH}	4.7	4.95
F_{FF}	0.68	0.68
F_{FH}	0.80	
F_{HH}		0.20
F_{FC}	1.36	1.36
F_{HC}	0.394	0.394
C_{FF}	− 0.2	
C_{FH}	− 0.045	− 0.045
H_{FCF}	0.41	0.65
H_{FCH}	0.12	
H_{HCH}		0.22
H_{FCC}	0.206	0.05
H_{HCC}	0.25	0.25

D. Out-of-plane vibrations

The out-of-plane vibrations were treated in a similar manner. Since the potential constants are not known for all of these molecules, we used a method for the computation of approximate force constants by Herranz and Castano.[15] This method is based on a generalization of the concept of characteristic vibrations and assumes that the interaction force constants are small. We used the standard symmetry coordinates as defined by Mann *et al.*: $S_1=(\gamma_1+\gamma_2)/\sqrt{2}$, $S_2=(\gamma_2-\gamma_1)/\sqrt{2}$, and $S_3=\tau$ (where γ_1 and γ_2 are the wagging coordinates and τ the torsion coordinate defined earlier) as a characteristic set. This approximate method depends on being able to assign the fundamental frequencies to the appropriate characteristic coordinate. Fortunately, for the out-of-plane vibrations a unique assignment of the three frequencies is possible. The lowest out-of-plane frequency is assigned to the torsion, the highest one to S_1, and the middle frequency to S_2. The small extent of mixing of S_1, S_2, and S_3 obtained by Oskam and Elst[4] supports our assumption that the interaction force constants between these coordinates are small. In special cases, of course, these characteristic coordinates correspond to normal coordinates, e.g., in $CF_2=CH_2$, S_3 is a normal coordinate by symmetry (A_2), it does not mix with S_1 or S_2. On the other hand, for *cis* and *trans* $CHF=CHF$, S_2 is a normal coordinate (B_g). Given the proper choice of the characteristic set and proper frequency assignments, the mixing of supposed characteristic coordinates leads to only small errors in the $\langle\Delta r\rangle$ due to out-of-plane modes. Since $\langle\Delta r\rangle$ depends on the products of F matrix elements with mean square amplitudes calculated according to Eq. (11), thus the errors in F and L which arise due to the use of the approximate force constants partially compensate each other in the calculation of $\langle\Delta r\rangle$. In any case it will be found that the out-of-plane vibrations have a relatively minor role to play in the temperature dependence of $\langle\Delta r\rangle$.

E. Anharmonic terms

The anharmonic force field is available for ethene itself but not for the halosubstituted ethenes. Therefore, we use the usual approach suggested by Bartell, which has been found adequate in the interpretation of electron diffraction intensities.[16] The quadratic potential function is augmented with the anharmonic terms in the stretch and nonbonded displacements with appropriate parameters a (Morse constant) and F^3, respectively.

$$V_{\mathrm{anh}}=\sum_{i=1}^{5}-a_iK_i(\Delta r_i)^3+\sum_i\sum_{j\neq i}(1/6q_{ij})\,F^3_{ij}\,(\Delta q_{ij})^3\,. \tag{5}$$

In order to be able to directly compare the $\langle\Delta r\rangle$ results in the ethenes with those from our previous calculations on the halomethanes, the same basis for calculating F^3 was used. This is the nonbonded halogen–halogen interaction potential of a Lennard-Jones form using r_0 and ϵ constants from the internally consistent set by Kestin *et al.* for the rare gas atom pairs.[17] The additional nonbonded interactions which arise in the ethenes between nonbonded hydrogen-halogen, hydrogen–carbon, and carbon–halogen atoms were represented by the set optimized for fitting internal rotational barriers in 15 haloethanes by Boyd and Kesner.[18] F^3 is obtained from the third derivative of their potential

$$F^3=q_e\,[\partial^3V(q)/\partial q^3]e\,, \tag{6}$$

$$V(\mathrm{nonbonded})=A_{ij}\exp(-B_{ij}q_{ij})-C_{ij}\,q_{ij}^{-6} \tag{7}$$

evaluated at the appropriate nonbonded distance in each molecule. The parameters appropriate to the various atom pairs are taken from Boyd and Kesner's tables. The Morse parameter a is obtained for each bond according to the method of Herschbach and Laurie.[19]

F. *G* Matrix

The inverse kinetic energy matrices G are obtained from the elements of the matrices D, representing the transformation from mass-weighted Cartesian coordinates to internal coordinates, (given in the Appendix of Mann *et al.*) by $G=DD^T$. The structural data for $CF_2=CF_2$, $CF_2=CFCl$, $CF_2=CFH$, and $CF_2=CH_2$ were taken from electron diffraction and microwave spectra reported by Carlos *et al.*,[20] Stone and Flygare,[21] Mom *et al.*,[22] and Mijlhoff *et al.*,[23] respectively. There are no $CF_2=CFBr$ and $CF_2=CFI$ structural data of comparable quality to those recently available for the other molecules. For these we used average bond lengths and angles obtained from analogous molecules: 1.31 Å for C = C, 1.31 Å for C–F, 2.11 Å for C–Br, 2.092 Å for C–I, and the same bond angles as in $CF_2=CF_2$. The frequencies and L matrices are obtained by solving the $(GF)L=L\Lambda$ matrix equation by standard techniques.

III. CALCULATION OF MEAN BOND DISPLACEMENTS

Calculation of $\langle\Delta r\rangle$ values follows the method due to Bartell[24] used previously for $O=CF_2$.[25] Mean bond angle deformations $\langle\Delta\alpha\rangle$ are neglected and only the five $\langle\Delta r\rangle$ unknowns are expressed in simultaneous coupled equations in terms of the mean square amplitudes. These coupled equations are obtained by taking the potential of Mann *et al.*[3] and setting

$$\langle \partial V/\partial z_k \rangle = 0 \tag{8}$$

for each atom k. The derivatives $\partial V/\partial z_k$ coming from the in-plane coordinates can be expressed in terms of the following[25]:

$$\frac{\partial \Delta r_i}{\partial z_k} = \delta_{ik} + \cdots ,$$
$$\frac{\partial \Delta \alpha_{ij}}{\partial z_k} = -\frac{\Delta \alpha_{kj}}{2r_k}\delta_{ik} + \cdots = -\frac{\Delta \alpha_{ik}}{2r_k}\delta_{jk} , \tag{9}$$
$$\frac{\partial \Delta q_{ij}}{\partial z_k} = s_{kj}\,\delta_{ik} + \cdots = s_{ik}\delta_{jk} + \cdots .$$

For the out-of-plane coordinates,

$$(\partial \gamma_2/\partial z_3) = -\frac{\gamma_2}{2r_3}\cos(\alpha_{34}/2) + \cdots , \tag{10}$$
$$(\partial \tau/\partial z_k) = -\tau/4r_k , \quad k = 3,4,5,6 .$$

The five coupled equations in the five mean bond displacements $\langle \Delta r \rangle$ involve the various elements of the mean square amplitude matrix, $\langle \Delta r \Delta \alpha \rangle$, $\langle \Delta r^2 \rangle$ $\langle (\Delta \alpha)^2 \rangle$, etc. The mean square amplitudes are calculated from the observed fundamental frequencies in the usual way:

$$\langle R_i R_j \rangle = (L \langle Q^2 \rangle L^T)_{ij} , \tag{11}$$

in which $\langle Q^2 \rangle_{ii} = (h/4\pi^2 c\omega_i)(v_i + 1/2)$. As usual, we compute the thermal average of $(v_i + 1/2)$ using a harmonic oscillator partition function with the observed fundamental frequencies.

$$\langle v_i + 1/2 \rangle^T = (1/2)\coth(hc\omega_i/2kT) . \tag{12}$$

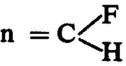
The rotational contribution to $\langle \Delta r \rangle^T$ was calculated by the usual method due to Toyama *et al.*,[26]

$$\langle R \rangle_{\rm rot} = kT\,U^T F_S^{-1} G_S^{-1}\,{\rm U B \Omega} X \tag{13}$$

from the equilibrium Cartesian positions of the atoms X and $\Omega^{\alpha\alpha} = (I_{\beta\beta})^{-1} + (I_{\gamma\gamma})^{-1}$ in terms of the equilibrium moments of inertia. Only the in-plane vibrations contribute to this centrifugal stretching. The out-of-plane modes do not have the proper symmetry.[27]

IV. RESULTS

The $\langle \Delta r \rangle^T$ values were obtained for $T = 200$ to 400 K at 20° intervals. Representative results are shown in Tables IV and V. The contributions to the mean CF bond displacement from the in-plane vibrations dominate over those from out-of-plane vibrations and rotation. The latter two contributions together account for less than about 10% of the mean bond displacement. The contributions to the temperature dependence from the in-plane vibrations, the out-of-plane vibrations, and rotation are around 70%, 15%, and 15%, respectively, in $CF_2 = CFX$, X = Cl, Br, I. For $CF_2 = CFH$ and $CF_2 = CH_2$ the out-of-plane vibrations and the rotational contributions are 10%–15% and 20%–30%, respectively. We see that the small errors associated with the approximation involved in the out-of-plane vibrations have a proportionately small effect on the overall results.

The mean bond displacements of the CF bonds in the ethenes are comparable to those of the CF bonds in the halomethanes: $5.5–6.2 \times 10^{-3}$ Å for F bonded to carbons with halogens. (The small $\langle \Delta r_{CF} \rangle$ in  $=C\langle^{F}_{H}$ is unusual, however see the following paper for other similar values.) This supports our previous contention that the magnitude of $\langle \Delta r \rangle$ at room temperature is fairly typical for a given bond between two atoms with a given bond length, varying over a small range of values with differing molecular structure.[28]

There appears to be no site effect on $\langle \Delta r \rangle$; the CF mean bond displacements in sites A, B, and C which are, respectively, *trans*, *cis*, and *gem* positions relative to the substituent X in $CF_2 = CFX$, do not show any systematic ordering.

The sensitivity of $\langle \Delta r \rangle$ to temperature is indicated by $\Delta_T \equiv \langle \Delta r \rangle^{400} - \langle \Delta r \rangle^{200}$. In Table V we note that the temperature dependence of the mean bond displacements for the CX bonds (X = Cl, Br, I) are much greater than those for the CF bonds. On the other hand, while the mean bond displacements are very large for the CH bonds (Table IV) the temperature dependence is small. Whereas $\langle \Delta r_{CH} \rangle$ suffers a 1% change over a 200° change in temperature, the $\langle \Delta r \rangle$ for the

TABLE IV. Mean bond displacements in $CF_2 = CFX$ and $CF_2 = CH_2$ molecules at 300 K.

		$\Delta r_{CF}/10^{-3}$ Å				$\Delta r_{CC}/10^{-3}$ Å				$\Delta r_{CX}/10^{-3}$ Å			
Molecule		in-plane	out-of-plane	rot.	total	in-plane	out-of-plane	rot.	total	in-plane	out-of-plane	rot.	total
$CF_2 = CF_2$		5.276	0.299	0.226	5.800	2.125	−0.096	0.115	2.143				
$CF_2 = CFCl$	A	5.194	0.300	0.182	5.676	2.237	−0.103	0.105	2.239	4.884	0.389	0.455	5.728
	B	5.094	0.298	0.172	5.564								
	C	5.176	0.298	0.218	5.693								
$CF_2 = CFBr$	A	5.235	0.295	0.155	5.684	2.391	−0.099	0.102	2.394	4.667	0.411	0.620	5.698
	B	5.141	0.292	0.134	5.568								
	C	5.146	0.298	0.229	5.667								
$CF_2 = CFI$	A	5.227	0.294	0.130	5.652	2.385	−0.102	0.095	2.373	4.691	0.455	0.765	5.911
	B	5.092	0.289	0.127	5.508								
	C	5.194	0.302	0.205	5.701								
$CF_2 = CFH$	A	5.416	0.374	0.325	6.115	2.364	−0.106	0.123	2.381	17.342	0.482	0.076	17.900
	B	5.343	0.371	0.372	6.086								
	C	4.461	0.334	0.181	4.976								
$CF_2 = CH_2$		5.371	0.429	0.409	6.205	2.507	−0.118	0.191	2.580	18.868	0.581	0.034	19.483

TABLE V. Temperature dependence of the mean bond displacements in $CF_2 = CFX$ and $CF_2 = CH_2$ molecules.

Molecule		$[\langle \Delta r_{CF} \rangle^{400} - \langle \Delta r_{CF} \rangle^{200}]/10^{-4}$ Å				$[\langle \Delta r_{CC} \rangle^{400} - \langle \Delta r_{CC} \rangle^{200}]/10^{-4}$ Å				$[\langle \Delta r_{CX} \rangle^{400} - \langle \Delta r_{CX} \rangle^{200}]/10^{-4}$ Å			
		in-plane	out-of-plane	rot.	total	in-plane	out-of-plane	rot.	total	in-plane	out-of-plane	rot.	total
$CF_2 = CF_2$		5.173	1.504	1.278	7.956	− 0.360	− 0.413	0.766	0.317				
$CF_2 = CFCl$	A	5.054	1.305	1.214	7.574	− 0.472	− 0.447	0.703	− 0.216	11.680	1.684	3.032	16.396
	B	5.000	1.298	1.149	7.447								
	C	5.104	1.287	1.457	7.848								
$CF_2 = CFBr$	A	4.934	1.317	1.032	7.286	− 0.345	− 0.440	0.682	− 0.103	15.217	1.813	4.132	21.16
	B	4.945	1.303	0.896	7.144								
	C	4.532	1.316	1.486	7.334								
$CF_2 = CFI$	A	4.856	1.325	0.870	7.052	− 0.508	− 0.456	0.604	− 0.361	19.102	2.013	5.099	26.214
	B	4.750	1.301	0.846	6.898								
	C	4.311	1.337	1.366	7.014								
$CF_2 = CFH$	A	5.138	1.120	2.165	8.424	+ 0.117	− 0.316	0.819	0.620	0.654	1.432	0.509	2.596
	B	5.425	1.111	2.481	9.017								
	C	3.854	0.992	1.210	6.055								
$CF_2 = CH_2$		4.769	0.778	2.724	8.271	+ 0.193	− 0.218	1.275	1.250	0.615	1.121	0.226	1.962

C–Cl, Br, I bonds change by 29%, 37%, and 44%, respectively. The reason for these differences lies in the lower vibrational frequencies associated with bonds to heavy atoms. Within the temperature range commonly accessible in NMR experiments (200–400 K), the $\coth(hc\omega_i/2kT)$ function changes relatively slightly for the high vibrational frequency associated with a C–H bond. Although all the vibrational frequencies affect Δ_T, the extent of mixing in the coupled equations which relate $\langle \Delta r \rangle$ values to $\langle Q^2 \rangle$ values is determined by the derivatives $(\partial V/\partial z_k)$ which favor contributions from normal modes which involve the stretch of the bond in question.

The lesson in this is that the ^1H nucleus is a poor probe of dynamic averaging of shielding and a heavy nucleus is a very good probe. The latter already has the advantage of greater shielding sensitivity (large chemical shifts). In addition, we note here that there is the advantage of larger dynamic factors (Δ_T) leading to much larger observable changes in chemical shifts with temperature.

Δ_T for CF bonds in haloethenes are $7.0–8.0 \times 10^{-4}$ Å, and slightly more variable for $CF_2 = CFH$ and $CF_2 = CH_2$ $(6–9 \times 10^{-4}$ Å), to be compared with $8.1–8.4 \times 10^{-4}$ Å for halomethanes[1] and $7.5–9.0 \times 10^{-4}$ for $CH_n F_{4-n}$.[29] There is a site effect on Δ_T in that $\Delta_T(B) < \Delta_T(A) < \Delta_T(C)$ for $CF_2 = CFX$ (X = F, Cl, Br, I) and the reverse order in $CF_2 = CFH$. This is due to the rotational contribution being more pronounced for the C (*gem*) site than the A (*trans*) or B (*cis*) site for X heavier than F (X = Cl, Br, I) and in the reverse order for X = H. Vibrational effects do not show this systematic trend except in $CH_2 = CFH$. Thus, a small part of the observed differences in $(d\sigma_0/dT)$ for the three sites comes from the dynamic factors. However, the electronic factors are largely responsible, as we shall see in Table VI.

The 11 values of $\langle \Delta r \rangle$ obtained between 200 and 400 K are represented adequately by a polynomial function and the latter is fitted to the experimental ^{19}F resonance frequencies $\nu_0(T)$ with one parameter as follows:

$$\nu_0(T) = A + (\partial\sigma^F/\partial\Delta r)_e \langle \Delta r \rangle^T(-84.67) + \epsilon(T) \quad (14)$$

within statistical experimental error $\epsilon(T)$. A is not an adjustable constant, its value depends on $(\partial\sigma^F/\partial\Delta r)_e \langle \Delta r \rangle^{300\,K}$. The numerical factor converts the calculated shielding temperature dependence to frequencies at the ^{19}F NMR observation frequency = 84.67 MHz. Thus, $(\partial\sigma^F/\partial\Delta r)_e$ values are obtained for fluorine nuclei at the sites A, B, and C in $CF_2 = CFX$. The goodness of the fit of the equation above to the observed data can be seen in Fig. 2. The least squares best parameters $(\partial\sigma^F/\partial\Delta r)_e$ are given in Table VI. As is usual, all the derivatives are negative and generally reflect the observed temperature coefficient $(d\sigma_0/dT)$ for the fluorine site.

The rovibrational corrections to absolute shielding at room temperature are calculated as $(\partial\sigma^F/\partial\Delta r)_e \langle \Delta r \rangle^{300}$. (This is not the entire correction, as the second and higher derivatives have not been included.) These rovibrational corrections range from − 9.5 to − 18.0 ppm for the haloethenes. As is usual they are deshielding and are in the same order of magnitude as those found for the halomethanes

TABLE VI. Derivatives of fluorine shielding in $CF_2 = CFX$ and $CF_2 = CH_2$ $(\partial\sigma^F/\partial\Delta r_{CF})_e$/ppm $Å^{-1}$. Also shown in parentheses are the absolute shielding at 300 K, $\sigma_0(300\ K)$/ppm from Ref. 30 and the rovibrational corrections to the absolute shielding at 300 K $[\sigma_0(300\ K) - \sigma_e]$/ppm.

X	F_A	F_B	F_C
H	− 1250 (297.5, − 7.6)	− 1190 (325.3, − 7.2)	− 2260 (404.2, − 11.2)
F	− 2080 (330.7, − 12.0)	− 2080 (330.7, − 12.0)	− 2080 (330.7, − 12.0)
Cl	− 1940 (300.1, − 11.0)	− 2190 (316.7, − 12.2)	− 2550 (340.6, − 14.5)
Br	− 2000 (295.4, − 11.4)	− 2290 (314.2, − 12.8)	− 2890 (341.4, − 16.4)
I	− 1690 or − 1950 (286.3, − 9.5)	− 2160 or − 2300 (310.5, − 11.9)	− 3160 (346.3, − 18.0)
$F_2C = CH_2$	− 990 (279.0, − 6.1)		

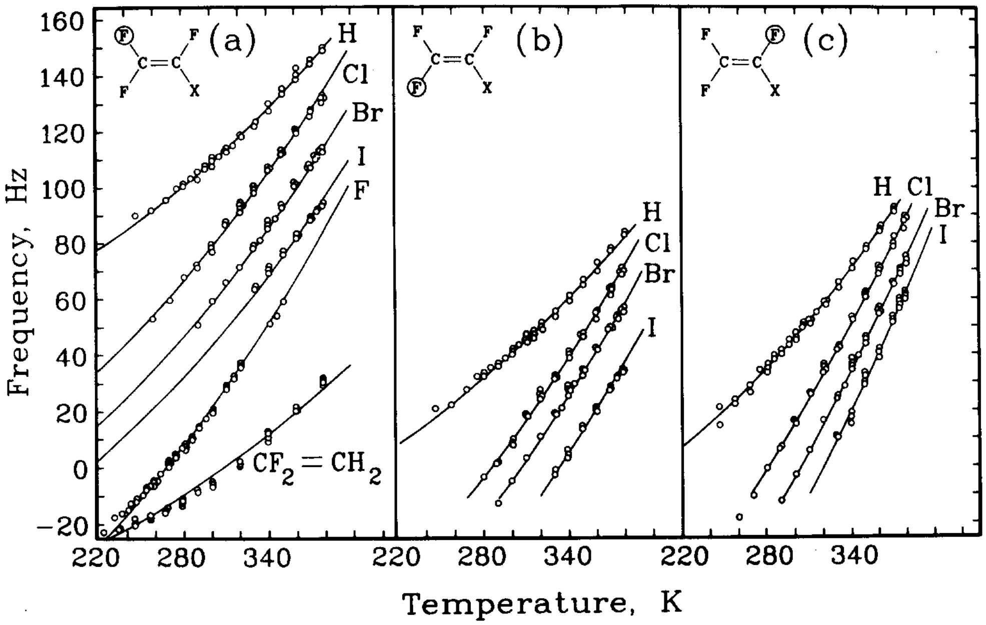


FIG. 2. Comparison of $(\partial\sigma^F/\partial\Delta r)_e\langle\Delta r\rangle^T$ with experimental resonance frequencies in the isolated molecule. The parameter $(\partial\sigma^F/\partial\Delta r)_e$ is obtained by a least squares fit to the experimental data.

($-$6.8 to $-$15.4 ppm).[1] For the H-containing ethenes they are somewhat smaller ($-$6.1 to $-$11.2 ppm). This is not unexpected, in CH_nF_{4-n} these values are likewise smaller ($-$2.1 to $-$8.3 ppm).[29] The higher vibrational frequencies associated with H-containing compounds leads to smaller rovibrational corrections to shielding.

V. DISCUSSION

We find that the variation in $\langle\Delta r\rangle^T$ is insufficient to account for the differences in temperature coefficients of shielding at the A, B, and C sites in the ethenes. Thus, such differences have to be attributed primarily to the electronic factors $(\partial\sigma^F/\partial\Delta r)_e$. A smooth correlation of these derivatives with σ_e has been found in the halomethanes.[1,29] For the ethenes, the results of this correlation are shown in Fig. 3. σ_e values have been obtained from the absolute shielding at 300 K, σ_0(300 K),[30] by using the rovibrational corrections which are shown in Table VI.

First we note in Fig. 2 that the $CF_2=CFI$ experimental chemical shifts in the zero-pressure limit are available for only a narrow range of temperatures. While the derivatives shown in Table VI were obtained by a least squares fit, the values shown in parentheses are also consistent with experiment within the experimental errors in the chemical shift measurements.

Second, we note that the $CH_2=CF_2$ derivative ($-$990 ppm Å^{-1} is close to the $O=CF_2$ derivative ($-$1146 ppm Å^{-1}). We had compared the experimental $\sigma_0(T)$ functions for these ^{19}F sites and noted that the two curves are nearly parallel.[31] The similar values of the derivatives accounts for this parallel behavior.

Thirdly we note the systematic trends for each nuclear site. For F_C (*gem* to X) the derivatives fall on a straight line in X = F, Cl, Br, I order. Likewise for F_B (*cis* to X). For F_C the trend is very clear since the derivatives cover a wide range of values. This is an indication that the results are internally consistent and comparison between molecules are meaningful. As expected, the derivatives of the A site which is farthest away from X (the *trans* position) are essentially insensitive to X substitution.

Fourth, we note that the derivatives associated with H-containing ethenes are smaller than those for haloethenes. This is found also in halomethanes[1] and CH_nF_{4-n},[29] although in the latter case the H-containing compounds can be fitted within the same systematic trend as the halomethanes.

The correlation observed in Fig. 3 for $(\partial\sigma^F/\partial\Delta r_{CF})_e$ vs σ_e in haloethenes is opposite to the trend obtained in halomethanes. $|(\partial\sigma^F/\partial\Delta r)_e|$ increases with absolute shielding σ_e in the ethenes. The opposite trend in ethenes compared to

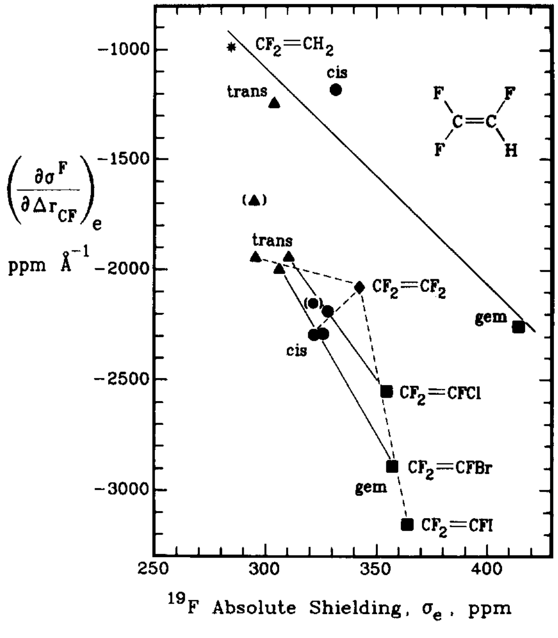


FIG. 3. Correlation between the derivatives of ^{19}F shielding and the absolute shielding in $CF_2=CFX$ and $CF_2=CH_2$.

TABLE VII. Comparison of the components of the absolute shielding tensor of ^{19}F in $CF_2 = CH_2$ and other molecules (ppm).

	Along the CF bond	In-plane	⊥ to plane	Reference
CF_4	351	213	213	32
CF_3H	344	201	277	33
CF_3Cl	262	262	142	32
CF_3Br	242	258	128	32
CF_3I	217	260	104	32
CF_2H_2[a]	395	391	225	24
CFH_3	426	493	493	35
$CF_2 = CH_2$[a]	291	281	242	36
ϕF	356.5	312.5	247.5	37
1,3,5 $C_6H_3F_3$	366.5	305.5	224.5	37

[a] The shielding tensor in the principal axis system has been rotated into the axis system of the fluoromethanes, using the known molecular geometry, for comparisons of components along the CF bond.

halomethanes requires an interpretation in terms of the individual shielding tensor components. Only the derivative of the isotropic average is obtained here and compared with the isotropic absolute shielding. It has already been pointed out that these derivatives correlate linearly with shielding tensor components σ_{33} along the C–F bond and σ_{11} perpendicular to the CFX plane in CF_3X.[1] That is, the three components of the ^{19}F shielding tensor do not have the same derivatives with respect to bond extension. It may be expected that the components perpendicular to the CF bond change more drastically upon bond extension than the parallel component does. A comparison of the methanes and $CF_2 = CH_2$ is given in Table VII. Here the shielding tensor in the principal (also the inertial) axis system has been rotated into the $\alpha\beta\gamma$ axis system of the halomethane using the known molecular geometries. The γ axis is parallel to the CF bond, the α axis is in the XCF plane and perpendicular to the CF bond, the β axis is perpendicular to the XCF plane. This allows us to compare directly the shielding components parallel to the CF bond in the tetrahedral and planar molecules.

It will be noted that the (β) component *perpendicular to the plane* of the ethene ($CF_2 = CH_2$) is the least shielded, this means that this component has the largest negative paramagnetic contribution. In halomethanes the components parallel to the CF bond and perpendicular to the FCX plane correlate in the *same* way with the derivative $(\partial\sigma^F/\partial\Delta r_{CF})_e$ upon X substitution with Cl, Br, I, thus reinforcing the trend of $|(\partial\sigma^F/\partial\Delta r_{CF})_e|$ decreasing with increasing isotropic shielding.[1] In the fluoromethanes CH_nF_{4-n} the components parallel to the CF bond in the FCF plane correlate in the same way with $(\partial\sigma^F/\partial\Delta r_{CF})_e$.[29] In the fluoroethenes the differences between the absolute shielding in A, B, and C sites in the same molecule are more pronounced than the differences between A sites in different molecules, for example. The correlation observed in the ethenes is primarily with the change in site A, B, and C, since the average shielding changes only slightly for a given site upon X substitution. This may indicate that the shielding component which is most sensitive to the F position relative to the X atom is not necessarily the same one(s) which suffers the greatest change upon C–F bond extension in the ethenes. In order to explain the observed trends in ethenes, the derivatives must correlate in an opposite way with at least one of the components of the shielding tensor (i.e., $|(\partial\sigma^F/\partial\Delta r_{CF})_e|$ must increase with increasing $\sigma^F_{\alpha\alpha}$ for at least one $\alpha\alpha$ component) as the site is varied from A to B to C. It would therefore be enlightening to compare the shielding tensor components in $CF_2 = CFX$. Experimental measurements of the ^{19}F shielding tensors in the $CF_2 = CFX$ (X = H, F, Cl, Br, I) are essential to the complete understanding of the trends discovered here.

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