Effect of centrifugal distortion and anharmonic vibration on the ^{19}F chemical shielding in CH_3F

Cynthia J. Jameson

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

A. Keith Jameson

Department of Chemistry, Loyola University, Chicago, Illinois 60626

(Received 5 January, 1978)

The temperature and density dependence of the ^{19}F NMR frequency has been measured for CH_3F gas. The NMR chemical shielding for ^{19}F nucleus in the isolated CH_3F molecule was obtained from 280 to 380 K by extrapolating the frequencies to zero density. This temperature dependence is interpreted in terms of the thermal average of powers of the normal coordinates. The linear term in this expansion is due to centrifugal distortion and anharmonic vibration. Using the cubic force constants and other molecular constants which have been reported for CH_3F, an estimate of the dependence of the ^{19}F shielding on the CF bond extension has been obtained.

The chemical shielding of a magnetically active nucleus in a gas phase molecular species is affected by intermolecular and intramolecular interactions. Experimentally these effects are measured by finding the coefficients in the virial expansion[1]

$$\sigma(\rho, T) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \cdots \quad . \tag{1}$$

The $\sigma_0(T)$ function contains the intramolecular effects characteristic of the isolated molecule. Operationally it is separated from the intermolecular effects by extrapolation of the NMR frequencies observed for samples of various densities to zero density.

The temperature dependence of the chemical shielding of a nucleus in an isolated molecule has been interpreted in terms of anharmonic vibration and centrifugal distortion contributions.[2,3] In the simplest case, in which only bond extensions have a nonzero thermal average, the chemical shielding function $\sigma_0(T)$ may be written as[2]:

$$\sigma_0(T) = \sigma_e + (\partial\sigma/\partial\Delta r)_{\rm eq}\langle\Delta r\rangle^T + (\partial^2\sigma/\partial\Delta r^2)_{\rm eq}\langle(\Delta r)^2\rangle^T + \cdots \quad . \tag{2}$$

The anharmonic vibration contribution to $\langle\Delta r\rangle^T$ depends on the normal coordinates and cubic force constants of the molecule.[4] Only for a few of the simplest polyatomic systems have the anharmonic contributions to the spectrum been determined accurately and calculations of the potential constants carried out.[5] The large number of additional terms which arise in the potential energy when cubic and quartic constants are taken into account has made the empirical determination of such constants from available spectroscopic data a formidable problem. The relationship between the cubic and quartic potential constants and the experimentally observed quantities (the anharmonicity constants x_{ij} and the vibration–rotation interaction constants α_s) are well known.[6] However, even for very small molecules, the number of parameters to be determined is sometimes greater than the number of independent experimental quantities available from the vibrational–rotational spectra of a molecule. A way in which the number of parameters may be reduced is by using closed-form expressions for the potential and thereby relating the potential constants of various orders.[7] The assumption is made that valence bonds behave like diatomic molecules so that closed-form anharmonic potential energy expressions which have been used for diatomic molecules, such as the Morse potential, can be transferred to represent the the anharmonic terms in the polyatomic potential energy due to the bonding stretching coordinates. Other potential forms are used for nonbonded interactions and angle deformations. This method has been used in the determination of the cubic force constants of CH_4, PH_3, and CH_3F.[8–10]

Since CH_3F is one of the very few molecules for which anharmonic force constants have been reported, it is a logical choice for the experimental determination of the $\sigma_0(T)$ function. In this paper we report the experimental results for $\sigma_0(T)$ and $\sigma_1(T)$ of ^{19}F in CH_3F. We choose to observe ^{19}F nuclei rather than ^1H due to the larger temperature shifts of ^{19}F nuclei compared to ^1H. On the basis of our previous results for ^1H in HCl and HBr,[11] the temperature dependence of ^1H in the limit of zero density is expected to be too small to be observed above the errors in the temperature dependence of the reference substance. We calculated the anharmonic vibration and centrifugal distortion contributions to the bond extensions $\langle\Delta r_{\rm CH}\rangle^T$, $\langle\Delta r_{\rm CF}\rangle^T$ and the angle deformations $\langle\Delta\alpha_{\rm HCH}\rangle^T$ and $\langle\Delta\beta_{\rm HCF}\rangle$. ^{T}. Using an equation similar to Eq. (2), we can compare the experimental $\sigma_0(T)$ function with that calculated from the dynamic quantities $\langle\Delta r\rangle^T$, $\langle\Delta\alpha\rangle^T$ in order to find an estimate of $(\partial\sigma_{\rm F}/\partial\Delta r_{\rm CF})_{\rm eq}$.

EXPERIMENTAL RESULTS

The ^{19}F NMR spectra of CH_3F gas in samples with densities up to 42 amagat were observed at 21.1 kG with a Bruker spectrometer operating in the FT mode. The $^2J_{\rm HF}$ coupling constant was found to be constant within statistical error, 46.4 Hz. Since temperature and density dependent information is contained in all four components of the quartet, the average value of the coupling constant was used to bring all four peaks to the center of the spectrum. In this way each spectrum yields four

0021-9606/78/6904-1655$01.00

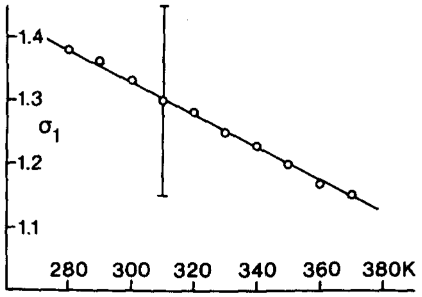

FIG. 1. $\sigma_1(T)$ function for ^{19}F in CH_3F gas, in Hz/amagat at 84.68 MHz. The bar indicates the estimated error associated with the magnitude of σ_1 at a given temperature.

data points instead of one. The resonance frequencies are found to behave linearly with density at a given temperature in the temperature range covered (280–380 K). The slopes are plotted in Fig. 1. They are the values of the $\sigma_1(T)$ function. When both the temperature dependence of the reference (toluene-*d*8) and $\sigma_1(T)\rho$ are removed from each frequency, the remaining temperature dependence gives the $\sigma_0(T)$ function shown in Fig. 2. This is the least pronounced temperature dependence which we have observed for ^{19}F nuclei in an isolated molecule, a total change of about 15 Hz in 100 deg. The scatter of the points shown in Fig. 2 reflect all the random errors which accompany the measurements; errors in determining the densities of the samples, the statistical errors in collecting a 5000 Hz spectral range as 2048 discrete points, errors associated with temperature regulation and long term (several days) instabilities of the spectrometer.

In an unpublished doctoral thesis, R. A. Meinzer reported both the temperature and density dependence of ^{19}F NMR shifts in CH_3F gas in the form of an empirical equation[12]:

$$\sigma(T,\rho)=aT+(b+cT)\rho+e\ .$$

The values of the parameters *a*, *b*, *c*, and *e* were given as

$$a=15.31\times10^{-3}\ \text{ppm/deg}\ ,$$
$$b=43.60\ \text{ppm}\,\text{cm}^3/\text{g}\ ,$$
$$c=-9.7\times10^{-2}\ \text{ppm}\,\text{cm}^3\,\text{deg}^{-1}\,\text{g}^{-1},$$
$$e=-221.41\ \text{ppm}\ .$$

By comparing his equation to

$$\sigma(T,\rho)=\sigma_0(T)+\sigma_1(T)\rho+\cdots\ ,$$

we find that his $\sigma_0(T)$ is $221.41-15.31\times10^{-3}\,T$ ppm and his $\sigma_1(T)$ is $(-0.0662+1.47\times10^{-4}\,T)$ ppm/amagat. The temperature dependence of his σ_0 appears to be very large compared to our (Table I). The large discrepancy is not a real one. The value of *a* is in fact a factor of about 10 too large because of the incorrect adjustment of his observed shifts by addition of the temperature shift of the reference. The correction should have been of the opposite sign, giving $a=1.65\times10^{-3}$ ppm/deg which is not too different from our 1.76×10^{-3} ppm/deg. This value of *a* is surprisingly good considering the fact that only 20% of the measured shift with temperature in Meinzer's experiment was due to CH_3F itself, the rest was due to the temperature dependence of his reference substance, benzotrifluoride.[13] His $\sigma_1(T)$ function gives a value at 300 K of -0.0221 ppm/amagat (with no error estimate) whereas ours is -0.0157 ± 0.0018 ppm/amagat. His value is outside our estimated experimental errors.

TABLE I. The $\sigma_0(T)$ and $\sigma_1(T)$ functions for the ^{19}F nucleus in CH_3F.

T (K)	$\Delta\nu$ (Hz)[a,b]	σ_1 (Hz/amagat)[b]
280	-3.0 ± 1.9[c]	1.38 ± 0.152[c]
290	-1.5	1.36
300	0	1.33
310	1.5	1.30
320	3.0	1.28
330	4.5	1.25
340	6.0	1.23
350	7.4	1.20
360	8.9	1.17
370	10.4	1.15

[a] Observed at 84.68 MHz. $\sigma_0(T)-\sigma_0(300)=-\Delta\nu/(84.68\times10^6)$.

[b] These data can be represented within experimental error by the functions

$$\sigma_0(T)-\sigma_0(300)=-0.00176(T-300)\ \text{ppm},$$

$$\sigma_1(T)=-0.015702+3.04\times10^{-5}(T-300)\ \text{ppm/amagat}.$$

[c] Average standard deviation for the temperature range covered.

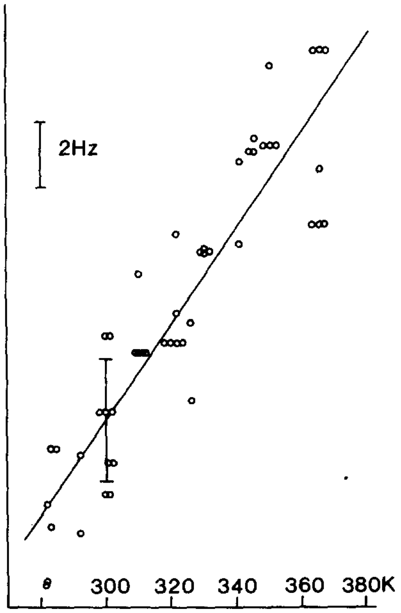

FIG. 2. Observed frequencies minus reference shift minus $\sigma_1\cdot\rho$. This should show the temperature dependence of the ^{19}F NMR resonance signal of the isolated CH_3F molecule at 84.68 MHz.

CALCULATION OF $\langle \Delta r_{CF} \rangle$

There are six normal modes for CH_3F, three are totally symmetric and three are of E symmetry. In order to calculate the thermal average of Δr_{CF}, Δr_{CH}, and $\Delta\alpha$ (α is the HCH bond angle), we will use the method of Toyama, Oka, and Morino.[4] First we will determine the thermal average of the dimensionless normal coordinates of CH_3F and by the use of appropriate transformations obtain the thermal averages of the desired internal coordinates. The thermal average of the dimensionless normal coordinates have been derived by Toyama *et al.* from the solution of the vibration–rotation problem by perturbation theory. The anharmonic vibration and centrifugal distortion contributions are[4]:

$$\langle q_i \rangle^T_{\text{anh}} = -\left[3k_{iii}\coth(hc\omega_i/2kT) + \sum_{s=1}^{6}{}' g_s k_{iss}\coth(hc\omega_s/2kT)\right]\Big/ 2\omega_i\ , \quad i=1,\,2,\,3 \in A_1 \tag{3}$$

$$\langle q_i \rangle^T_{\text{centr}} = \frac{kT}{4\pi c\omega_i}\left(\frac{1}{hc\omega_i}\right)^{1/2} \sum_{\alpha} \frac{a_i^{\alpha\alpha}}{I^{(e)}_{\alpha\alpha}}\ . \tag{4}$$

In the above equations, the important molecular constants which are required are the harmonic frequencies ω_i and the cubic force constants k_{iss}. Only the symmetry coordinates belonging to A_1 have to be included since the normal coordinates which are nontotally symmetric have a zero thermal average and therefore do not contribute to first order. They do have a nonzero second-order contribution, $\langle q^2 \rangle^T$.

The inertial constants $a_i^{\alpha\alpha}$ which appear in the centrifugal distortion contributions have to be determined. Alternatively, $\langle q \rangle^T_{\text{centr}}$ may be determined from Eq. (58) of Toyama *et al.*[4]

$$\langle \mathbf{Q} \rangle^T_{\text{centr}} = kT\,\mathbf{L}^{-1}\,\mathbf{F}_S^{-1}\mathbf{G}_S^{-1}\,\mathbf{UB}\Omega\mathbf{X}\ , \tag{5}$$

or else, the thermal average of the internal coordinates can be obtained directly as

$$\langle \mathbf{R} \rangle^T_{\text{centr}} = kT\mathbf{U}^T\,\mathbf{F}_S^{-1}\mathbf{G}_S^{-1}\,\mathbf{UB}\Omega\mathbf{X}\ . \tag{6}$$

The matrices in the above equations are the usual ones involved in a normal coordinate analysis by the Wilson F and G matrix method.[14] $\mathbf{U}$ is the transformation matrix which relates the internal coordinates $\mathbf{R}$ (which has elements Δr_1, $\Delta\alpha_i$, and $\Delta\beta_i$) to the symmetry coordinates $\mathbf{S}$:

$$\mathbf{S} = \mathbf{UR}\ . \tag{7}$$

The following set of symmetry coordinates is used here:

$$\begin{aligned}
S_1 &= (\Delta r_1 + \Delta r_2 + \Delta r_3)/\sqrt{3}\ ,\\
S_2 &= a(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - b(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)\ ,\\
S_3 &= \Delta r_4\ ,\\
S_{4a} &= (2\Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{6}\ ,\\
S_{4b} &= (\Delta r_2 - \Delta r_3)/\sqrt{2}\ ,\\
S_{5a} &= (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)/\sqrt{6}\ ,\\
S_{5b} &= (\Delta\alpha_2 - \Delta\alpha_3)/\sqrt{2}\ ,\\
S_{6a} &= (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)/\sqrt{6}\ ,\\
S_{6b} &= (\Delta\beta_2 - \Delta\beta_3)/\sqrt{2}\ ,
\end{aligned} \tag{8}$$

where $\Delta r_1 = \Delta r(C-H_i)$, $\Delta r_4 = \Delta r(C-F)$, $\Delta\alpha_i = \Delta\alpha(H_j-C-H_k)$, and $\Delta\beta_i = \Delta\beta(H_i-C-F)$. $a = \kappa/[3(1+\kappa^2)]^{1/2}$, $b = 1/[3(1+\kappa^2)]^{1/2}$, $\kappa = -3\sin\beta_e\cos\beta_e/\sin\alpha_e$.

$\mathbf{F}_S$ is the matrix of force constants in terms of the symmetry coordinates above. Elements of $\mathbf{F}_S$ are given for CH_3F by Russell, Needham, and Overend.[15] The $\mathbf{G}_S$ matrix for the totally symmetric coordinates is[16]:

$$\mathbf{G}_{A_1} = \begin{bmatrix} \mu_H + 3\mu_C\cos^2\beta_e & \dfrac{3\mu_C\sqrt{\kappa^2+1}\,\sin\beta_e\cos\beta_e}{r_{CH}} & \sqrt{3}\mu_C\cos\beta_e \\ & \dfrac{(\kappa^2+1)(\mu_H + 3\mu_C\sin^2\beta_e)}{r^2_{CH}} & \dfrac{\mu_C\sqrt{3}\sqrt{\kappa^2+1}\,\sin\beta_e}{r_{CH}} \\ & & \mu_C + \mu_F \end{bmatrix}, \tag{9}$$

where $\mu_H = 1/m_H$, with similar definitions for μ_C and μ_F. α_e and β_e are the equilibrium values of the HCH and HCF angles. The $\mathbf{B}$ matrix relates the internal coordinates to the Cartesian displacement coordinates

$$\mathbf{R} = \mathbf{Bx}\ . \tag{10}$$

$\mathbf{x}$ has elements Δx_i, Δy_i, Δz_i. The matrix $\mathbf{B}$ can be determined by choosing the molecule fixed axes, through the center of mass of the molecule (We used the same axes as in Fig. 1 of Russell, Needham, and Overend.[15]), finding the unit vectors directed from one atom to another along the bond (Wilson's vectors e_{ij})[14] and expressing the internal coordinates (Δr_1, $\Delta\alpha_1$, $\Delta\beta_1$, etc.) in terms of these unit vectors by the method given in Chap. 4 Wilson, Decius, and Cross.[14] Ω is a diagonal matrix with the elements

$$\Omega_{ii}^{(\alpha\alpha)} = 1/I^{(e)}_{\beta\beta} + 1/I^{(e)}_{\gamma\gamma}\ , \tag{11}$$

from Eq. (62) of Ref. 4. $\mathbf{X}$ are the coordinates of the atoms with respect to the chosen molecule-fixed axes.

For CH$_3$F, we find the following expression for **UBΩX** for the totally symmetric coordinates

$$\mathbf{UB\Omega X}_{A_1}=\begin{bmatrix} \sqrt{3}r_{\mathrm{CH}}\sin^2\beta_e & \sqrt{3}r_{\mathrm{CH}}\cos^2\beta_e \\ \dfrac{\sqrt{3}\sin\beta_e}{\sqrt{1+\kappa^2}}\left(\dfrac{r_{\mathrm{CH}}}{r_{\mathrm{CF}}}-\kappa^2\cos\beta_e\right) & \dfrac{\sqrt{3}\sin\beta_e}{\sqrt{1+\kappa^2}}\left(\dfrac{r_{\mathrm{CH}}}{r_{\mathrm{CF}}}+\kappa^2\cos\beta_e\right) \\ 0 & r_{\mathrm{CF}} \end{bmatrix}\begin{bmatrix}\Omega_x \\ \Omega_z\end{bmatrix}. \tag{12}$$

While this expression was derived for CH$_3$F specifically, it applies in general to any molecule of the type CX$_3$Y. Simply replace r_{CH} by r_{CX}, r_{CF} by r_{CY} and define β_e as the XCY bond angle. Thus, the thermal averages of the internal coordinates are

$$\begin{bmatrix}\langle\Delta r_{\mathrm{CH}}\rangle^T_{\mathrm{centr}} \\ \langle\Delta\alpha\rangle^T_{\mathrm{centr}} \\ \langle\Delta\beta\rangle^T_{\mathrm{centr}} \\ \langle\Delta r_{\mathrm{CF}}\rangle^T_{\mathrm{centr}}\end{bmatrix}=kT\begin{bmatrix}\frac{1}{\sqrt{3}} & 0 & 0 \\ 0 & a & 0 \\ 0 & -b & 0 \\ 0 & 0 & 1\end{bmatrix}\mathbf{F}^{-1}_{A_1}\mathbf{G}^{-1}_{A_1}(\mathbf{UB\Omega X})_{A_1}, \tag{13}$$

where $\mathbf{F}^{-1}_{A_1}$ and $\mathbf{G}^{-1}_{A_1}$ are the inverse of the F and G matrices for the A_1 symmetry coordinates.

The anharmonic contributions to the thermal average of the internal coordinates are calculated as follows:

$$\langle\Delta r_1\rangle^T_{\mathrm{anh}}=\frac{1}{\sqrt{3}}\sum_{i\in A_1}^{3}\bar{L}_{1i}\langle q_i\rangle^T_{\mathrm{anh}}, \tag{14}$$

where $\bar{L}_{ti}=(h/4\pi^2c\omega_i)^{1/2}L_{ti}$, in which L_{ti} are the elements of the eigenvectors in Wilson's method of normal coordinate analysis, which have been calculated for CH$_3$F by Russell, Needham, and Overend.[15] The $\langle q_i\rangle^T_{\mathrm{anh}}$ are calculated by Eq. (3), using the harmonic frequencies and cubic force constants from LaBoda and Overend.[10] The relative signs of the L_{ti} for a given normal coordinate q_i are determined in the normal coordinate analysis. However, the absolute signs depend only on the choice of phase of q. The normal coordinate force constant $k_{ss's''}$ depend on the phase of q_s if s enters with an odd power, i.e., the sign of $k_{sss'}$ depends on the phase of $q_{s'}$, but not on the phase of q_s. The signs of LaBoda and Overend's force constants are based on the phases of the normal coordinates being defined such that the positive phase of q_1 corresponds to the extension of the CH bonds, the positive phase of q_2 to the opening of the HCH angle and the positive phase of q_3 to compression of the CF bond. The signs of L_{t3} given in Table VII of Russell, Needham, and Overend have to be reversed in order to be consistent with the k_{3ss} of LaBoda and Overend. A summary of the constants used in this paper are given in Table II. The results are shown in Figs. 3 and 4 and Table III. We note that the centrifugal distortion contribution has a much smaller magnitude

TABLE II. Molecular constants for CH$_3$F.

s	1	2	3	4	5	6	Ref.
ω_s, cm^{-1}	3045.7	1495.5	1076.7	3164.8	1514.4	1207.4	10
k_{1ss}, cm^{-1}	−175.70	116.98	21.36	−552.05	89.30	140.19	10
k_{2ss}	−29.96	2.49	2.64	−6.56	79.00	26.08	10
k_{3ss}	19.68	2.64	63.58	13.36	−6.78	−0.38	10
$L_{1s}^{-1/2}$(amu)	1.008333	0.017930	−0.016630[a]	0	0	0	15
L_{2s}	−0.122329	1.387491	−0.151458[a]	0	0	0	15
L_{3s}	−0.052948	0.081728	−0.355588[a]	0	0	0	15
F_{11}	5.354 mdyn/Å		($F_{12}=F_{13}=0$)				15
F_{22}	0.739 mdyn Å/rad^2						15
F_{23}	−0.644 mdyn/rad						15
F_{33}	5.803 mdyn/Å						15
I_{zz}	3.309 amu Å^2						b
I_{xx}	19.79488 amu Å^2						b
$r_{\mathrm{CH}}^{(e)}$	1.095 Å						16
$r_{\mathrm{CF}}^{(e)}$	1.386 Å						16
α_e	110°20′						16
β_e	108°36′						16

[a] These signs are opposite to those given in Ref. 15 for reasons discussed in the text.

[b] F. A. Andersen, B. Bak, and S. Brodersen, J. Chem. Phys. 24, 989 (1956).

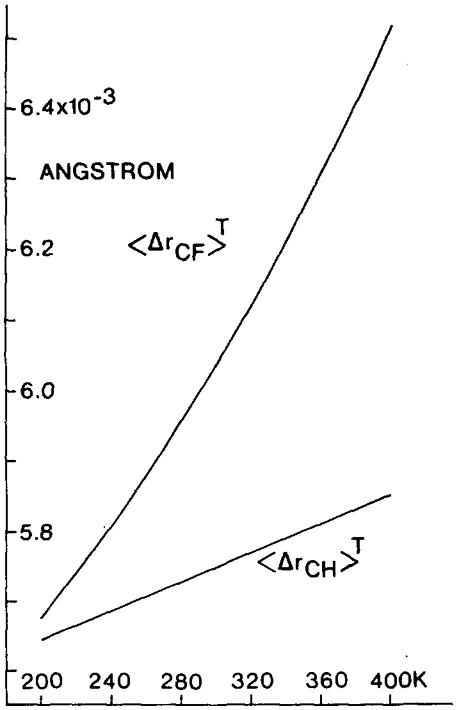

FIG. 3. Thermal average of the CH and CF bond extensions.

than the anharmonic vibration contribution to $\langle \Delta r_{\mathrm{CH}} \rangle^T$ and $\langle \Delta r_{\mathrm{CF}} \rangle^T$. There is very little curvature in the thermal averages of the internal coordinates. They are linear within the errors of the molecular constants for CH$_3$F. It should also be noted that 75% and 97% of the change with temperature of $\langle \Delta r_{\mathrm{CF}} \rangle^T$ and $\langle \Delta r_{\mathrm{CH}} \rangle^T$, respectively, are due to the centrifugal distortion contribution.

CALCULATION OF THE THERMAL AVERAGE OF CHEMICAL SHIELDING

The chemical shielding or any other electronic property of a molecule can be expressed as a Taylor series in the nuclear coordinates[4]

$$\langle \sigma \rangle^T = \sigma_e + \sum_i (\partial \sigma / \partial q_i)_{\mathrm{eq}} \langle q_i \rangle^T + \frac{1}{2} \sum_{i,j} (\partial^2 \sigma / \partial q_i \, \partial q_j)_{\mathrm{eq}} \langle q_i q_j \rangle^T + \cdots \, . \tag{15}$$

Because of molecular symmetry, $\langle \Delta r_1 \rangle^T = \langle \Delta r_2 \rangle^T = \langle \Delta r_3 \rangle^T$. Expressed in the internal coordinates, the leading terms in $\langle \sigma \rangle^T$ for the CH$_3$F molecule are as follows:

$$\begin{aligned} \langle \sigma \rangle^T = \sigma_e &+ \langle \Delta r_1 \rangle^T \left\{ \left(\frac{\partial \sigma}{\partial \Delta r_1} \right)_{\mathrm{eq}} + \left(\frac{\partial \sigma}{\partial \Delta r_2} \right)_{\mathrm{eq}} + \left(\frac{\partial \sigma}{\partial \Delta r_3} \right)_{\mathrm{eq}} \right\} + \langle \Delta r_{\mathrm{CF}} \rangle^T \left(\frac{\partial \sigma}{\partial \Delta r_{\mathrm{CF}}} \right)_{\mathrm{eq}} \\ &+ \langle \Delta \alpha_1 \rangle^T \left\{ \left(\frac{\partial \sigma}{\partial \Delta \alpha_1} \right)_{\mathrm{eq}} + \left(\frac{\partial \sigma}{\partial \Delta \alpha_2} \right)_{\mathrm{eq}} + \left(\frac{\partial \sigma}{\partial \Delta \alpha_3} \right)_{\mathrm{eq}} \right\} + \langle \Delta \beta_1 \rangle^T \left\{ \left(\frac{\partial \sigma}{\partial \Delta \beta_1} \right)_{\mathrm{eq}} + \left(\frac{\partial \sigma}{\partial \Delta \beta_2} \right)_{\mathrm{eq}} + \left(\frac{\partial \sigma}{\partial \Delta \beta_3} \right)_{\mathrm{eq}} \right\} + \cdots \, . \end{aligned} \tag{16}$$

If $\langle \sigma \rangle^T$ is to be determined for either of the nuclei which are located at the three-fold axis of the CH$_3$F molecule (^{13}C or ^{19}F), then the following relationship holds:

$$(\partial \sigma / \partial \Delta r_1)_{\mathrm{eq}} = (\partial \sigma / \partial \Delta r_2)_{\mathrm{eq}} = (\partial \sigma / \partial \Delta r_3)_{\mathrm{eq}} \, .$$

Similar relations hold for the derivatives with respect to $\Delta \alpha_i$ and $\Delta \beta_i$. The quadratic terms in the above equation will not be considered here. We have shown that in the diatomic molecule case the quadratic terms contribute negligibly to the temperature dependence of $\langle \Delta r \rangle^T$ though there is a significant contribution to the magnitude of $\langle \Delta r \rangle^T$ at a given temperature.[2]

Even if only the linear terms in the Taylor series are included, there will still be four parameters to be determined. Since $\langle \Delta \alpha \rangle^T$ and $\langle \Delta \beta \rangle^T$ are opposite in sign and changing with temperature in opposite directions, as a first approximation we could assume that these terms largely cancel out each other. (In a tetrahedral molecule like CH$_4$ they do exactly cancel out, there is no linear term in the angle.) There will then be two parameters left to be determined: $(\partial \sigma_{\mathrm{F}} / \partial \Delta r_{\mathrm{CH}})_{\mathrm{eq}}$ and $(\partial \sigma_{\mathrm{F}} / \partial \Delta r_{\mathrm{CF}})_{\mathrm{eq}}$. Since both the observed $\sigma_0(T)$ and the $\langle \Delta r \rangle^T$ functions are linear, only one adjustable parameter can be obtained by comparison of the calculated $\langle \sigma \rangle^T$ with the experimental $\sigma_0(T)$ in Fig. 2. It is reasonable to assume that the term in Δr_{CH} is small compared to that in Δr_{CF}. The change in Δr_{CF} with temperature is four times as large as the change in Δr_{CH}. Moreover, $\partial \sigma_{\mathrm{F}} / \partial \Delta r_{\mathrm{CF}}$ is expected to be larger than $\partial \sigma_{\mathrm{F}} / \partial \Delta r_{\mathrm{CH}}$ since the latter expresses the change in the environment of a ^{19}F

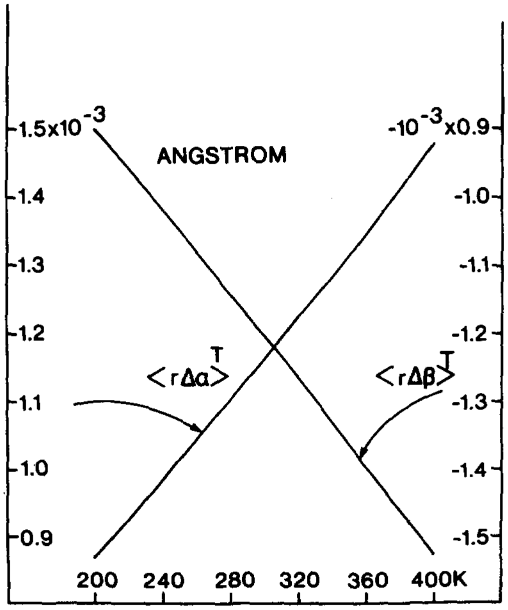

FIG. 4. Thermal average of $r\Delta\alpha$ and $r\Delta\beta$, where α is the HCH angle and β the HCF angle.

TABLE III. Thermal average of Δr_{CH}, Δr_{CF}, $r\Delta\alpha$, and $r\Delta\beta$ in CH_3F, calculated according to Eqs. (13) and (14), in units of 10^3 Å.

T (K)		200	240	280	320	360	400
$\langle\Delta r_{CH}\rangle^T$	centr	0.201	0.241	0.281	0.322	0.362	0.402
	anh	5.446	5.447	5.447	5.449	5.450	5.453
	tot	5.647	5.688	5.729	5.770	5.812	5.855
$\langle\Delta r_{CF}\rangle^T$	centr	0.612	0.734	0.857	0.979	1.101	1.224
	anh	5.065	5.078	5.104	5.149	5.213	5.297
	tot	5.677	5.812	5.961	6.128	6.314	6.520
$\langle r\Delta\alpha\rangle^T$	centr	0.571	0.685	0.799	0.913	1.027	1.142
	anh	0.298	0.300	0.304	0.312	0.322	0.335
	tot	0.869	0.985	1.103	1.225	1.349	1.477
$\langle r\Delta\beta\rangle^T$	centr	−0.590	−0.708	−0.826	−0.944	−1.062	−1.180
	anh	−0.308	−0.310	−0.315	−0.322	−0.333	−0.347
	tot	−0.898	−1.018	−1.141	−1.266	−1.395	−1.527

nucleus due to the extension of a remote bond. Thus, if we can neglect the Δr_{CH} term in comparison to the Δr_{CF} term, we can get an estimate for $(\partial\sigma_F/\partial\Delta r_{CF})_{eq}$ in CH_3F. The value obtained is −420 ppm/Å. This is surprisingly small, only about a third of the analogous value in CF_4.[3] The $(\partial\sigma_F/\partial\Delta r_{CF})$ is smaller for CH_3F than for CF_4. This may be due to the higher ionic character of the C–F bond in CH_3F than in CF_4. As the ionic character of a C–F bond is increased, σ_F approaches the value for F^- ion and would be less dependent on bond distance. (We wish to thank a referee for bringing this point to our attention.)

We have found that the estimate for $(\partial\sigma_F/\partial\Delta r_{CF})_{eq}$ in CH_3F is largely dependent on the temperature dependence of $\langle\Delta r_{CF}\rangle^T$. While the magnitude of $\langle\Delta r_{CF}\rangle^T$ is largely due to the anharmonic vibration contribution (as seen in Table III), most of the temperature dependence is due to centrifugal distortion. For the 200 deg change in temperature the change in $\langle\Delta r_{CF}\rangle^T$ is 6.1191×10^{-4} Å due to anharmonic vibration and 2.3146×10^{-4} Å due to anharmonic vibration. The 25% due to anharmonic vibration comes largely from the $\langle q_3\rangle^T$ term which in turn derives most of its temperature dependence from the terms in k_{3ss}. The centrifugal distortion contribution depends on molecular quantities that are fairly accurately known. On the other hand, since there is some degree of uncertainty in the determination of k_{3ss}, the anharmonic contribution is probably not very accurate. This uncertainty will be reflected in the estimated value of $(\partial\sigma_F/\partial\Delta r_{CF})_{eq}$. Moreover, there is not enough information about the chemical shielding function to allow an educated guess about the relative signs and magnitudes of $(\partial\sigma_F/\partial\Delta r_{CH})_{eq}$ and $(\partial\sigma_F/\partial\Delta r_{CF})_{eq}$. A nonnegligible contribution from the $\langle\Delta r_{CH}\rangle^T$ term will cause some error in our estimate of $(\partial\sigma_F/\partial\Delta r_{CF})_{eq}$.

The support of this work by the National Science Foundation in grants to the University of Illinois at Chicago Circle (CHE77-09133) and Loyola University (CHE77-09197) is gratefully acknowledged.

[1] W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, J. Chem. Phys. **36**, 3481 (1962).

[2] C. J. Jameson, J. Chem. Phys. **66**, 4977 (1977).

[3] C. J. Jameson, J. Chem. Phys. **67**, 2814 (1977).

[4] M. Toyama, T. Oka, and Y. Morino, J. Mol. Spectrosc. **13**, 193 (1964).

[5] I. Suzuki, Appl. Spectrosc. Rev. **9**, 249 (1975).

[6] H. H. Nielsen in *Handbuch der Physik* (Springer, Berlin, 1959), Vol. 37, Part 1.

[7] K. Kuchitsu and L. S. Bartell, J. Chem. Phys. **36**, 2460 (1962).

[8] K. Kuchitsu and L. S. Bartell, J. Chem. Phys. **36**, 2470 (1962).

[9] K. Kuchitsu, J. Mol. Spectrosc. **7**, 399 (1961).

[10] M. L. LaBoda and J. Overend, Spectrochim. Acta A **32**, 1033 (1976).

[11] A. K. Jameson, K. Schuett, C. J. Jameson, S. M. Cohen, and H. Parker, J. Chem. Phys. **67**, 2821 (1977).

[12] R. A. Meinzer, Ph.D. thesis, University of Illinois, 1965 (University Microfilm Inc., Ann Arbor, No. 66-4238).

[13] The same corrections applied to his CHF_3 and CF_4 data brings them from his -17.31×10^{-3} and -18.30×10^{-3} ppm/deg to -3.65×10^{-3} and -4.64×10^{-3} ppm/deg. The latter values are in agreement with our observations (Refs. 17 and 18) whereas the former are too large by a factor of 4–5, a discrepancy of 110–120 Hz over a 100 degree temperature change, easily observable under our conditions of observation.

[14] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[15] J. W. Russell, C. D. Needham, and J. Overend, J. Chem. Phys. **45**, 3383 (1966).

[16] J. Aldous and I. M. Mills, Spectrochim. Acta **18**, 1073 (1962).

[17] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **67**, 2771 (1977).

[18] C. J. Jameson, A. K. Jameson, and H. Parker (to be published).