Dependence of ^{19}F chemical shielding on internal coordinates in CF_4, SiF_4, and BF_3

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The thermal average of chemical shielding for CF_4-, BF_3-, SF_6-, HCN-, CO_2-, and NH_3-type molecules is explicitly expressed in terms of molecular constants such as fundamental frequencies and elements of the L matrix for the totally symmetric vibration, Coriolis constants, moments of inertia, and cubic force constants $k_{ss's'}$. Expressions for the k_{lss} cubic force constants for a BF_3-type molecule are derived and values of k_{lss} are calculated for CF_4, SiF_4, and BF_3. The thermal average of chemical shielding calculated using these cubic force constants is compared with the experimental temperature dependence of the ^{19}F NMR signal, yielding values of $(\partial\sigma/\partial R)$ for CF_4, SiF_4, and BF_3. Despite the large differences in chemical shifts the values of $(\partial\sigma/\partial R)$ obtained are nearly identical: 1115, 1170, and 1115 ppm/Å, respectively.

INTRODUCTION

The temperature dependence of the NMR signal of a nucleus in a molecule can be measured in the limit of zero pressure.[1,2] The temperature dependence so obtained, $\sigma_0(T)$, is an intrinsic property of the molecule and can be interpreted in terms of the dependence of chemical shielding σ on the internal coordinates of the molecule. For diatomic molecules

$$\langle \sigma\rangle^T = \sigma_e + (\partial\sigma/\partial R)_e \langle R\rangle^T + (\partial^2\sigma/\partial R^2)_e \langle R^2\rangle^T + \cdots ,$$

where $R = r - r_e$. In diatomic molecules the first derivative of σ with respect to the displacement from the equilibrium internuclear distance, $(d\sigma/dR)_e$, has been determined for ^1H in H_2,[3] HCl,[4] and HBr,[5] and for ^{13}C in CO and ^{19}F in F_2 and ClF.[6] It has also been shown for F_2 and ClF that the terms in the second derivative are negligible in contributing to the temperature dependence.[6] The interpretation of the diatomic molecule chemical shifts with temperature appears to be satisfactory and sufficient to explain the general empirical trends in isotope shifts.[7]

While there is a single first and second derivative of σ in the diatomic molecule, in a polyatomic molecule with three or more internal coordinates there are several first derivatives and an even larger number of second derivatives. At first glance the analysis of $\sigma_0(T)$ in polyatomic molecules appears to be hopeless. However, the isotope shifts in polyatomic molecules show the same general trends which in diatomic molecules were easily explained in terms of the single first derivative $(d\sigma/dR)_e$.[7] This indicates that perhaps not all of the linear and quadratic terms are important. With the great variety of molecules for which isotope shifts are available, one would expect that the magnitudes and the signs of the second derivatives of chemical shielding with respect to bond stretches and angle deformations are likely to be very different. There are a great variety of mixed second derivatives possible: a stretch combined with another stretch, a stretch with an adjacent angle, a stretch with an opposite angle, and so on. For example, in the NH_3 molecule there are six and in SF_6 there are 11 unique second derivatives of σ with respect to internal coordinates. If the terms involving the second derivatives were important then the sign of the isotope shift with heavy isotope substitution is not expected to be so universally uniform.[7] Thus, we are inclined to believe that the terms in the second derivatives are no more important for polyatomic molecules than they were for diatomic molecules.[6]

In a polyatomic molecule the thermal average of chemical shielding may be expressed in terms of the thermal average of powers of the dimensionless normal coordinates, q_t[8]:

$$\langle \sigma\rangle^T = \sigma_e + \sum_{t\subset A_1} (\partial\sigma/\partial q_t)\langle q_t\rangle^T + \cdots \mathcal{O}(\partial^2\sigma/\partial q^2) , \quad (1)$$

where $\mathcal{O}(\;)$ indicates terms of this order or higher. The dimensionless normal coordinates q are related to the internal coordinates R by way of the symmetry coordinates S[9]:

$$S = LQ = \bar{L}q , \quad (2)$$

$$S = UR , \quad (3)$$

$$R = U^T S , \quad (4)$$

$$R = U^T \bar{L} q . \quad (5)$$

L is the usual L matrix defined by Wilson, Decius, and Cross, and $\bar{L}$ is the counterpart of L when dimensionless normal coordinates rather than the usual normal coordinates Q are used. $\bar{L}_{tt} = (h/4\pi^2 c\omega_t)^{1/2} L_{tt}$. R_m stands for internal coordinates Δr_m or $r_0\Delta\phi_{mn}$. Using Eqs. (2)–(5) the derivatives $\partial\sigma/\partial q_t$ can be expressed in terms of the derivatives $(\partial\sigma/\partial R_m)$:

$$\partial\sigma/\partial q_t = \sum_t \sum_m (\partial\sigma/\partial R_m) \cdot U_{tm} \cdot \bar{L}_{tt} . \quad (6)$$

Thus, the thermal average of chemical shielding in a polyatomic molecule may be written as follows:

$$\langle\sigma\rangle^T = \sigma_e + \sum_m \partial\sigma/\partial R_m \times \left[\sum_t U_{tm}\left(\sum_{t\subset A_1} \bar{L}_{tt}\langle q_t\rangle^T\right)\right] + \mathcal{O}(\partial^2\sigma/\partial R^2) . \quad (7)$$

In specific cases the linear terms take a relatively simple form.

For T_d AX_4, D_{3h} AX_3, and O_h AX_6 molecules, there is only one totally symmetric normal mode of vibration, q_1:

$$S_1 = n^{-1/2}(R_1 + R_2 + \cdots + R_n) \; n = 3, \; 4, \text{ or } 6 \; , \tag{8}$$

$$S_1 = \bar{L}_{11} q_1 \; , \tag{9}$$

$$\partial\sigma/\partial q_i = n^{-1/2} \bar{L}_{11} \sum_m \partial\sigma/\partial R_m \; , \tag{10}$$

$$\langle\sigma\rangle^T = \sigma_e + n^{-1/2} \bar{L}_{11} \langle q_1 \rangle^T \cdot [\partial\sigma/\partial R_1 + \partial\sigma/\partial R_2 + \cdots + \partial\sigma/\partial R_n] + \mathcal{O}(\partial^2\sigma/\partial R^2) \tag{11}$$

Since $L_{11} = G_{11}^{1/2} = m_X^{-1/2}$ for these cases, then

$$\bar{L}_{11} = (h/4\pi^2 \omega_1 c m_X)^{1/2} \tag{12}$$

The thermal average of σ for a $T_d\,AX_4$, $D_{3h}\,AX_3$, or $O_h\,AX_6$ molecule is:

$$\langle\sigma\rangle^T = \sigma_e + (h/4\pi^2 \omega_1 c n m_X)^{1/2} \langle q_1\rangle^T \cdot p_1 \tag{13}$$

where $p_1 = (\partial\sigma/\partial R_1 + \partial\sigma/R_2 + \cdots + \partial\sigma/\partial R_n)$ is a parameter to be determined. Note that in this sum some terms may be more important than others. For example, for the ^{19}F chemical shielding of fluorine nucleus in CF_4, $(\partial\sigma_{F_1}/\partial R_1)$ is surely much greater than $(\partial\sigma_{F_1}/\partial R_2)$, etc. In this paper we will simply call the sum $(\partial\sigma/\partial R)$.

For $C_{\infty v}$ ABC molecules, the linear terms are

$$S_1 = 2^{-1/2}(R_1 + R_3) \qquad S_3 = 2^{-1/2}(R_1 - R_3) \; , \tag{14}$$

where $R_1 = \Delta r_{AB}$ and $R_3 = \Delta r_{BC}$, $R_2 = r_0 \Delta\phi$,

$$R_1 = 2^{-1/2}(\bar{L}_{11} + \bar{L}_{31}) q_1 + 2^{-1/2}(\bar{L}_{13} + \bar{L}_{33}) q_3 \; , \tag{15}$$

$$R_3 = 2^{-1/2}(\bar{L}_{11} - \bar{L}_{31}) q_1 + 2^{-1/2}(\bar{L}_{13} - \bar{L}_{33}) q_3 \; , \tag{16}$$

$$\langle\sigma\rangle^T = \sigma_e + (\partial\sigma/\partial R_1)\,[2^{-1/2}(\bar{L}_{11} + \bar{L}_{31})\langle q_1\rangle^T + 2^{-1/2}(\bar{L}_{13} + \bar{L}_{33})\langle q_3\rangle^T] + (\partial\sigma/\partial R_3)\,[2^{-1/2}(\bar{L}_{11} - \bar{L}_{31})\langle q_1\rangle^T + 2^{-1/2}(\bar{L}_{13} - \bar{L}_{33})\langle q_3\rangle^T] + \mathcal{O}(\partial^2\sigma/\partial R_2^2) \tag{17}$$

The thermal average of σ for a linear ABC molecule is:

$$\langle\sigma\rangle^T = \sigma_e + \langle q_1\rangle^T p_1 + \langle q_3\rangle^T p_3 + \langle q_2^2\rangle^T p_2 + \cdots \; , \tag{18}$$

where

$$p_1 = 2^{-1/2}(\bar{L}_{11} + \bar{L}_{31})(\partial\sigma/\partial R_1) + 2^{-1/2}(\bar{L}_{11} - \bar{L}_{31})(\partial\sigma/\partial R_3) \; , \tag{19}$$

$$p_3 = 2^{-1/2}(\bar{L}_{13} + \bar{L}_{33})(\partial\sigma/\partial R_1) + 2^{-1/2}(\bar{L}_{13} - \bar{L}_{33})(\partial\sigma/\partial R_3) \; , \tag{20}$$

$$p_2 = \bar{L}_{22}^2 (\partial^2\sigma/\partial R_2^2) \; . \tag{21}$$

There are two parameters to be determined, p_1 and p_3, from which $\partial\sigma/\partial R_1$ and $\partial\sigma/\partial R_3$ may be obtained. In addition, the most significant quadratic term may be included, with a third parameter to be determined, $\partial^2\sigma/\partial R_2^2$.

For $D_{\infty h}$ AX_2 molecules, the terms are the same as above, except that by symmetry,

$$\langle q_3\rangle^T = 0, \; L_{13} = L_{31} = 0. \tag{22}$$

The thermal average of σ for a linear XAX molecule is:

$$\langle\sigma\rangle^T = \sigma_e + 2^{-1/2} \bar{L}_{11} \langle q_1\rangle^T (\partial\sigma/\partial R_1 + \partial\sigma/\partial R_3) + \bar{L}_{22}^2 \langle q_2^2\rangle^T (\partial^2\sigma/\partial R_2^2) \tag{23}$$

in which $\bar{L}_{11} = (h/4\pi^2\omega_1 c m_X)^{1/2}$.

For $C_{3v}\,AX_3$ molecules, there are two totally symmetric modes:

$$S_1 = \bar{L}_{11} q_1 + \bar{L}_{12} q_2 \qquad S_2 = \bar{L}_{21} q_1 + \bar{L}_{22} q_2 \; , \tag{24}$$

$$S_1 = 3^{-1/2}(R_1 + R_2 + R_3) \qquad S_2 = 3^{-1/2} r_0 (\alpha_1 + \alpha_2 + \alpha_3) \; , \tag{25}$$

$$\text{where } R_1 = \Delta r_1, \; \alpha_1 = \Delta\phi_{23} \tag{26}$$

The thermal average of σ for a $C_{3v}\,AX_3$ molecule is:

$$\langle\sigma\rangle^T = \sigma_e + 3^{-1/2}(\bar{L}_{11}\langle q_1\rangle^T + \bar{L}_{12}\langle q_2\rangle^T) \cdot (\partial\sigma/\partial R_1 + \partial\sigma/\partial R_2 + \partial\sigma/\partial R_3) + 3^{-1/2}(\bar{L}_{21}\langle q_1\rangle^T + \bar{L}_{22}\langle q_2\rangle^T) \cdot (\partial\sigma/\partial\alpha_1 + \partial\sigma/\partial\alpha_2 + \partial\sigma/\partial\alpha_3) \tag{27}$$

or

$$\langle\sigma\rangle^T = \sigma_e + p_1\langle q_1\rangle^T + p_2\langle q_2\rangle^T \; , \tag{28}$$

where p_1 and p_2 are parameters made up of the constants in Eq. (27).

THE THERMAL AVERAGE OF THE NORMAL COORDINATES

A general formula for the thermal average of the normal coordinate has been obtained by Toyama *et al.*, including the effects of anharmonic vibration as well as centrifugal distortion[10]:

$$\langle q_1\rangle^T_{\text{anh}} = -\left[3k_{111}\coth(hc\omega_1/2kT) + \sum_s g_s k_{1ss}\coth(hc\omega_s/2kT)\right]\Big/2\omega_1 \; , \tag{31}$$

$$\langle q_1\rangle^T_{\text{cent}} = (kT/4\pi c\omega_1)(hc\omega_1)^{-1/2} \sum_{\alpha=1}^{3} (a_1^{\alpha\alpha}/I^e_{\alpha\alpha} \; , \tag{32}$$

$$\langle q_1\rangle^T = \langle q_1\rangle^T_{\text{anh}} + \langle q_1\rangle^T_{\text{cent}} \; , \tag{33}$$

$$\langle q_2^2\rangle^T = \tfrac{1}{2}\coth(hc\omega_2/2kT) \; . \tag{34}$$

The molecular quantities which are needed for the calculation of $\langle q\rangle^T$ are the cubic force constants $k_{ss's'}$ and $\Sigma_{\alpha=1}^3 a_s^{\alpha\alpha}/I^e_{\alpha\alpha}$. The constants $a_s^{\alpha\alpha}$ are the coefficients of q_s in the normal coordinate expansion of the principal moments of inertia. They can be found in terms of the elements of the transformation of mass-weighted Cartesian displacement coordinates into normal coordinates.[11] For the specific molecular types which we are considering here, the sum $\Sigma_{\alpha=1}^3 a_s^{\alpha\alpha}/I^e_{\alpha\alpha}$ is given by

(a) For $T_d\,AX_4$, $D_{3h}\,AX_3$, and $O_h\,AX_6$ molecules:

$$\sum_{\alpha=1}^{3} a_1^{\alpha\alpha}/I^e_{\alpha\alpha} = 6/(nm_X r^2)^{1/2} \; ; \tag{35}$$

(b) For $C_{\infty v}$ ABC molecules:

$$\sum_{\alpha=1}^{3} a_1^{\alpha\alpha}/I^e_{\alpha\alpha} = 4\zeta_{23}(I^e)^{-1/2} \text{ for } q_1 \text{ and } 4\zeta_{21}(I^e)^{-1/2} \text{ for } q_3 \; , \tag{36}$$

such that $\zeta_{23}^2 + \zeta_{21}^2 = 1$. ζ_{23} is close to 1.0;

(c) For $D_{\infty h}\,AX_2$ molecules:

$$\sum_{\alpha=1}^{3} a_1^{\alpha\alpha}/I^e_{\alpha\alpha} = 4\zeta_{23}(I^e)^{-1/2} \simeq 4(2m_X r^2)^{-1/2} \; , \tag{37}$$

since ζ_{23} is close to 1.0.

(d) For C_{3v} AX_3 molecules: $a_1^{\alpha\alpha}$ and $a_2^{\alpha\alpha}$ are given by H. H. Nielsen for an NH_3-type molecule.[11]

$$\sum_{\alpha=1}^{3} a_1^{\alpha\alpha}/I_{\alpha\alpha}^e = 4[(I_{xx}^e - \tfrac{1}{2}I_{zz}^e)^{1/2}\beta_1 + \tfrac{1}{2}\beta_3(I_{zz}^e)^{1/2}]/I_{xx}^e + 2\beta_3/(I_{zz}^e)^{1/2} , \tag{38}$$

$$\sum_{\alpha=1}^{3} a_2^{\alpha\alpha}/I_{\alpha\alpha}^e = 4[(I_{xx}^e - \tfrac{1}{2}I_{zz}^e)^{1/2}\beta_3 - \tfrac{1}{2}\beta_1(I_{zz}^e)^{1/2}]/I_{xx}^e - 2\beta_1/(I_{zz}^e)^{1/2} , \tag{39}$$

in which β_1 and β_3 are molecular constants of AX_3 which involve the masses of A and X and the quadratic force constants.

For the specific cases of interest here, Eq. (7) may be rewritten as:

$$\langle\sigma\rangle^T = \sigma_e + (\partial\sigma/\partial R)[\langle R\rangle_{\text{cent}}^T + \langle R\rangle_{\text{anh}}^T] + \cdots .$$

The centrifugal distortion for symmetrical molecules (T_d AX_4, D_{3h} AX_3, O_h AX_6) reduces to a simple form by using Eqs. (12), (32), and (35):

$$\langle R\rangle_{\text{cent}}^T = \sum_t U_{tm}\left[\sum_{i\in A_1} \bar{L}_{ti}\langle q_i\rangle_{\text{cent}}^T\right] = 3kT/nr_e F_{11} , \tag{40}$$

where F_{11} is the totally symmetric force constant which is $F_{11} = 4\pi^2 mc^2\omega_1^2$. m is the mass of the fluorine atom in CF_4, SiF_4, and BF_3, and ω_1 is the harmonic frequency of the totally symmetric mode of the molecule.

DETERMINATION OF ANHARMONIC FORCE CONSTANTS, $k_{ss's'}$

The direct determination of cubic force constants from ir and Raman data for molecules with more than three atoms is practically impossible.[12] For example, the number of nonvanishing force constants up to quartic in a bent XYZ molecules is 31, that in a linear XY_2 is 12. So far only five molecules have been treated in the most general way. They are CO_2, CS_2, HCN, OCS, and N_2O. The force constants for these five molecules have been obtained without constraints or assumptions on their values. They probably constitute the best sets so far obtained. However, even in these molecules the values of certain force constants must still be regarded with some reservations since the independent adjustment of 12 to 21 separate parameters is an extremely difficult problem. For example in N_2O the vibration–rotation constants depend mainly on the normal coordinate force constants k_{111}, k_{122}, and k_{133} and the remaining constants are ill-determined.[12]

Fortunately, for several of the molecules of interest here, (CF_4, SiF_4, SF_6, BF_3), in which there is only one totally symmetric mode, only the k_{1ss} are required for the calculation of the terms involving the first derivatives of σ since $\langle q\rangle^T$ is zero for the nontotally symmetric modes. Even so, values of k_{1ss} are available in the literature for only a very few molecules with four or more atoms (NH_3, PH_3, C_2H_2, C_2H_4).[13-16] They are not available for CF_4, SiF_4, SF_6, or BF_3, for which we have measured $\sigma_0(T)$.[2] Therefore, we have to calculate k_{1ss} first.

The problem of the general quartic force field for molecules with four or more atoms is formidable. One cannot expect to obtain sufficient experimental data to determine all the k constants uniquely. For example, while the six independent cubic k constants can be determined uniquely from six independently measured α constants in bent XY_2 molecules, for pyramidal XY_3 molecules the 14 cubic k constants cannot be uniquely determined from 8 α constants and two l-type doubling constants currently available.[12] Nor is it likely that the use of isotopic data will be sufficiently effective to overcome this difficulty. Hence, the experimental information has to be supplemented by model functions.

There are two basic types of contributions to the cubic force constants.[17] One arises from quadratic force constants in internal coordinates through the nonlinear transformation from internal to normal coordinates. This transformation is nonlinear because the basic assumption of infinitesimal amplitudes in harmonic calculations is no longer valid in anharmonic calculations. Since not only linear terms need to be evaluated in the latter, the instantaneous values of these coordinates rather than their projections on the equilibrium positions must be noted. Thus a force field which includes only quadratic terms when expressed in the true curvilinear coordinates may involve all anharmonic terms (cubic, quartic, etc.) when transformed into normal coordinates.[18] The second contribution arises from cubic force constants in internal coordinates which may be included by the adoption of model functions. For example, a Morse function may be used for the valence bond-stretching potential and a Buckingham or Lennard-Jones potential may be used for nonbonded interactions. The adoption of a model function V implicitly defines a cubic force constant ($\partial^3V/\partial r^3$).

A modified Urey–Bradley force field for polyatomic molecules was proposed by Kuchitsu and Bartell in which the cubic potential constants may be estimated from the quadratic force constants and the elements of the L matrices.[17] In their model, the two types of contributions to cubic force constants are included. The stretching and nonbonded potentials are assumed to have the Morse and Buckingham forms. The latter has been found to work well for the H–H interaction such as in the H_2O and CH_4 molecules considered by Kuchitsu and Bartell. They found that their method gave satisfactory agreement in the test case, H_2O, for which reliable cubic force constants were available.

k_{1ss} FOR T_d AX_4 MOLECULES

Kuchitsu and Bartell give a matrix equation for the calculation of k_{1ss} for a CH_4-type molecule from the Urey–Bradley force constants and from the parameters of the Morse and the Buckingham potentials.[17] In applying Kuchitsu and Bartell's model to CF_4 and SiF_4 we used the Lennard-Jones instead of the Buckingham function since Shimanouchi has shown that the former works well for F–F nonbonded interactions.[19] The Urey–Bradley force constants κ, K, F, G, and H were obtained from the data of Chalmers and McKean for CF_4 and of McKean for SiF_4.[20,21] F' and F_3 were obtained as first and third derivatives of the Lennard-Jones repulsive function for F–F interactions (with $\sigma = 2.70$ Å and $a = 31.1 \times 10^{-4}$ mdyn Å, values taken from Shimanouchi).[19] The anharmonic force constants k_{1ss} are calculated from these Urey–Bradley force constants using Eq. (23) of Kuchitsu and Bartell, reproduced below.[17]

$$\begin{bmatrix} k_{111} \\ k_{122} \\ k_{133} \\ k_{144} \end{bmatrix} = \begin{bmatrix} 0 & \frac{1}{2}\alpha^3 & 0 & 0 & 0 & 0 & 0 & 0 & 4t\alpha^3 \\ \frac{1}{2}\alpha^3 & 0 & \frac{3}{2}\alpha^3 & -\frac{1}{2}\alpha^3 & 3\alpha^3 & 0 & 6\alpha^3 & 3t\alpha^3 & 3t\alpha^3 \\ \frac{1}{4}\alpha\delta^2 & \frac{3}{2}\alpha\beta^2 & \frac{3}{4}\alpha\delta^2 & -\frac{1}{4}\alpha\delta^2 & \alpha\delta^2 & 0 & 0 & -\frac{4}{3}t\alpha\sigma^2 & 4t\alpha\sigma^2 \\ \frac{1}{4}\alpha\epsilon^2 & \frac{3}{2}\alpha\gamma^2 & \frac{3}{4}\alpha\epsilon^2 & -\frac{1}{4}\alpha\epsilon^2 & \alpha\epsilon^2 & 0 & 0 & -\frac{4}{3}t\alpha\tau^2 & 4t\alpha\tau^2 \end{bmatrix} \begin{bmatrix} (K+4F')/2r_e \\ -\frac{1}{2}aK \\ G/2r_e \\ -F'/r_e \\ -(H+\kappa/2\sqrt{2}r_e^2)/2r_e \\ H_3/6r_e \\ -\kappa/2\sqrt{2}r_e^3 \\ (F-F')/2q_e \\ F_3/6q_e \end{bmatrix} .$$

The calculated cubic force constants k_{1ss} as well as the other molecular constants used for CF_4 and SiF_4 are shown in Table I. Precise estimates of the normal coordinates and quadratic force constants require the harmonic frequencies ω_s rather than the observed fundamental frequencies. The frequencies ω_s used in calculating the F matrices are harmonic frequencies obtained from observed frequencies ν_s by applying the empirical Dennison's rule to polyatomic molecules.[20]

k_{1ss} FOR D_{3h} AX_3 MOLECULES

The formalism of Kuchitsu and Bartell can be extended to molecules of the BF_3-type and the matrix equation for the calculation of k_{1ss} derived. For BF_3 the form of V in terms of Δr_i and $\Delta\alpha_{ij}$ is given below:

$$\begin{aligned} V_{BF_3} = {} & r_e K' \sum_{i=1}^{3} \Delta r_i + \tfrac{1}{2}K \sum_{i=1}^{3} (\Delta r_i)^2 - \tfrac{1}{2}aK \sum_{i=1}^{3} (\Delta r_i)^3 + G \sum_{i<j}^{3} (\Delta r_i)(\Delta r_j) + r_e H' \sum_{i<j}^{3} r_e(\Delta\alpha_{ij}) \\ & + \tfrac{1}{2}H \sum_{i<j}^{3} r_e^2 (\Delta\alpha_{ij})^2 + \left(\frac{H_3}{6r_e}\right) \sum_{i<j}^{3} r_e^3 (\Delta\alpha_{ij})^3 + q_e F' \sum_{i<j}^{3} \Delta q_{ij} + \tfrac{1}{2}F \sum_{i<j}^{3} (\Delta q_{ij})^2 + \left(\frac{F_3}{6q_e}\right) \sum_{i<j}^{3} (\Delta q_{ij})^3 . \end{aligned} \tag{41}$$

For a molecule such as BF_3, there is no need to introduce an intramolecular tension κ since the redundancy condition is a linear one: i.e., the three FBF angles in BF_3 are subject to the condition $\Sigma_i \alpha_i - 2\pi = 0$.[22] That part V' of the potential function comprising cubic terms of the Cartesian displacement coordinates is:

$$\begin{aligned} V' &= V_1' + \cdots + V_8' , \\ V_1' &= (K-K')/2r_e) \sum_{i}^{3} \Delta z_i [(\Delta x_i)^2 + (\Delta y_i)^2] , \\ V_2' &= -\tfrac{1}{2}aK \sum_{i}^{3} (\Delta z_i)^3 , \\ V_3' &= (G/2r_e) \sum_{i<j}^{3} \Big[(\Delta z_i)[(\Delta x_j)^2 + (\Delta y_j)^2] + (\Delta z_j)[(\Delta x_i)^2 + (\Delta y_i)^2]\Big] , \\ V_4' &= (H'/r_e) \sum_{i<j}^{3} \Big[\Delta x_i (\Delta z_i)^2 + \Delta x_j (\Delta z_j)^2 - \tfrac{1}{2}(\Delta x_i + \Delta x_j)[(\Delta x_i)^2 + (\Delta x_j)^2 + (\Delta y_i)^2 + (\Delta y_j)^2] - \cot\alpha [(\Delta y_i)^2 (\Delta z_i) \\ &\quad + (\Delta y_j)^2 (\Delta z_j)] - \tfrac{1}{2}\cot^2\alpha (\Delta x_i + \Delta x_j) [(\Delta y_i)^2 + (\Delta y_j)^2 + 2\Delta y_i \Delta y_j \sec\alpha] - \operatorname{cosec}\alpha (\Delta y_i)(\Delta y_j)(\Delta z_i + \Delta z_j)\Big] , \\ V_5' &= (-H/r_e) \sum_{i<j}^{3} (\Delta x_i + \Delta x_j) \Big[(\Delta x_i)(\Delta z_i) + (\Delta x_j)(\Delta z_j) + (1/2\sqrt{3})[(\Delta y_i)^2 + (\Delta y_j)^2 - 4(\Delta y_i)(\Delta y_j)]\Big] , \\ V_6' &= (H_3/6r_e) \sum_{i<j}^{3} (\Delta x_i + \Delta x_j)^3 , \\ V_7' &= (F-F')/2q_e \sum_{i<j}^{3} (\Delta\zeta_{ij}) [(\Delta\xi_{ij})^2 + (\Delta\eta_{ij})^2] , \\ V_8' &= (F_3/6q_e) \sum_{i<j}^{3} (\Delta\zeta_{ij})^3 . \end{aligned} \tag{42}$$

TABLE I. Molecular constants for CF_4, SiF_4, and BF_3.[19,a]

	$^{12}CF_4$	$^{28}SiF_4$	$^{11}BF_3$
ν_1 cm^{-1}	908	801	888
ν_2	435	264	691.3
ν_3	1282.6	1031.8	1454.
ν_4	631.3	389.3	477.8
F_{11} mdyn/Å	9.238	7.181	8.827
F_{22}	0.71	0.27	
F_{33}	6.489	6.406	6.561
F_{34}	−0.827	−0.291	−0.317
F_{44}	1.010	0.438	0.512
K	4.642	5.81	6.168
H	0.297	0.16775	0.280
F	1.294	0.34	0.782
G	−0.193	−0.00325	0.157
κ mdyn Å	0.370	0.3011	
F'/F ratio	−0.066	−0.0366	−0.631
F_3/F ratio	−15.0	−17.67	−15.25
L_{11} amu$^{-1/2}$	0.229	0.229	0.229
L_{22}	0.397	0.397	0.4988
L_{33}	0.40043	0.34670	0.4340
L_{34}	0.057325	−0.02121	−0.0289
L_{43}	−0.61393	−0.35983	0.57729
L_{44}	0.41513	−0.47590	0.4849
r_0 Å	1.32	1.56	1.29
q_0	2.16	2.547	2.23
a Å^{-1}	2.37	1.925	2.44
k_{111} cm^{-1}	−32.91	−21.27	−31.32
k_{122}	−26.77	−4.20	+52.34
k_{133}	−73.47	−76.73	−338.62
k_{144}	−37.06	0.03	−9.97

[a] Values of ν and F matrix for CF_4 from Ref. 19, for SiF_4 from Ref. 21, for BF_3 from Ref. 23.

When the Cartesian coordinates are expanded in terms of the dimensionless normal coordinates the above equations are expressed as a cubic function of normal coordinates:

$$V' = k_{111} q_1^3 + k_{122} q_1 q_2^2 + k_{133} q_1 (q_{3a} + q_{3b})^2 + \cdots . \tag{43}$$

Collecting corresponding coefficients gives k_{1ss} in terms of the constants K, G, etc. The results are shown in Table II. Here, as in the CF_4 case, K', K, and K_3 are the stretching force constants, H', H, and H_3 are the bending force constants and F', F, and F_3 are the repulsive force constants. The values of K, G, H, F given by Shimanouchi *et al.* (set I) for BF_3 was used.[23] The ratios F'/F and F_3/F were calculated from the Lennard-Jones function describing F–F interactions. K' and H' are both obtained from F' with the equilibrium conditions that

$$K' + 4F' \sin^2(\phi_e/2) = 0$$

and (44)

$$H' + F' \sin\phi_e = 0$$

so that $K' = -3F'$ and $H' = -\sqrt{3}/2\, F'$. H_3 was neglected since it is expected to be very small. These Urey-Bradley force constants and the L matrix elements for BF_3 calculated from the F matrix given by Shimanouchi *et al.* were substituted in Table II and the k_{1ss} for $^{11}BF_3$ were calculated. These values of k_{1ss} are shown in Table I.

COMPARISON OF $\langle\sigma\rangle^T$ WITH EXPERIMENT

From the harmonic frequencies ω_s and these k_{1ss} values, the anharmonic vibration and the rotational (centrifugal disdistortion) contribution to $\langle q\rangle^T$ can be calculated using Eqs. (31) and (32). Tables III–V show the temperature dependence of the anharmonic vibration and centrifugal distortion contributions to $\langle q\rangle^T$ for CF_4, SiF_4, and BF_3. As in diatomic molecules, the magnitude of the anharmonic vibration contribution to $\langle q_1\rangle^T$ is greater than the rotational contribution.[6] However, unlike diatomic molecules, the change with temperature is greater for anharmonic vibration than for centrifugal distortion. With increasing complexity of the molecule, a larger fraction of the chemical shift with temperature is due to vibration, as shown in Table VI. The second order terms are not included here. Note that the per-

TABLE II. Matrix equation for cubic force constants of BF_3-type molecules in same notation as Kuchitsu and Bartell.[17]

$$\begin{bmatrix} k_{111} \\ k_{122} \\ k_{133} \\ k_{144} \end{bmatrix} = \begin{bmatrix} 0 & \frac{\alpha^3}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 3\alpha^3 \\ \frac{\alpha\phi^2}{\sqrt{3}} & 0 & \frac{2\alpha\phi^2}{\sqrt{3}} & \frac{4\alpha\phi^2}{\sqrt{3}} & 0 & 0 & \frac{4\alpha\phi^2}{\sqrt{3}} & 0 \\ \frac{\alpha\delta^2}{\sqrt{3}} & \sqrt{3}\,\alpha\beta^2 & \frac{2\alpha\delta^2}{\sqrt{3}} & \frac{4\alpha\beta\delta}{\sqrt{3}} & \sqrt{3}\,\alpha\delta^2 & 0 & \frac{3}{4}\alpha\delta^2 & 3\alpha\sigma^2 \\ \frac{\alpha\epsilon^2}{\sqrt{3}} & \sqrt{3}\,\alpha\gamma^2 & \frac{2\alpha\epsilon^2}{\sqrt{3}} & \frac{4\alpha\gamma\epsilon}{\sqrt{3}} & \sqrt{3}\,\alpha\epsilon^2 & 0 & \frac{3}{4}\alpha\epsilon^2 & 3\alpha\tau^2 \end{bmatrix} \begin{bmatrix} \frac{K-K'}{2r_e} \\ -\frac{1}{2}aK \\ \frac{G}{2r_e} \\ \frac{H'}{r_e} \\ \frac{-H}{r_e} \\ \frac{H_3}{6r_e} \\ \frac{F-F'}{2q_e} \\ \frac{F_3}{6q_e} \end{bmatrix},$$

where $\sigma = \sqrt{3}\beta + \delta$, $\tau = \sqrt{3}\gamma + \epsilon$, $\phi = L_{22}$.

TABLE III. Temperature dependence of the anharmonic vibration and centrifugal distortion contributions to $\langle q_1\rangle^T$ and chemical shielding of ^{19}F in $^{12}CF_4$.

T, K	anh, 10^3 Å	centrif, 10^3 Å	$\langle q_1\rangle^T$, 10^3 Å	$\langle\sigma\rangle^T - \langle\sigma\rangle^{300}$, ppm	
				exptl	calc
270	6.1393	0.2293	6.3686	0.1433	0.1405
280	6.1710	0.2378	6.4087	0.0971	0.0958
290	6.2043	0.2463	6.4506	0.0493	0.0491
300	6.2393	0.2548	6.4941	0.0	0.0006
310	6.2760	0.2632	6.5393	−0.0509	−0.0498
320	6.3144	0.2717	6.5861	−0.1033	−0.1019
330	6.3543	0.2802	6.6345	−0.1573	−0.1559
340	6.3957	0.2887	6.6844	−0.2127	−0.2115
350	6.4386	0.2972	6.7359	−0.2698	−0.2689
360	6.4830	0.3057	6.7887	−0.3284	−0.3278
370	6.5288	0.3142	6.8431	−0.3885	−0.3884
380	6.5760	0.3227	6.8987	−0.4502	−0.4505
390	6.6246	0.3312	6.9558	−0.5134	−0.5141
400	6.6744	0.3397	7.0141	−0.5782	−0.5791
410	6.7256	0.3482	7.0737	−0.6445	−0.6456

TABLE IV. Temperature dependence of the anharmonic vibration and centrifugal distortion contributions to $\langle q_1\rangle^T$ and chemical shielding of ^{19}F in $^{12}SiF_4$.

T, K	anh, 10^3 Å	centrif, 10^3 Å	$\langle q_1\rangle^T$, 10^3 Å	$\langle\sigma\rangle^T - \langle\sigma\rangle^{300}$, ppm	
				exptl	calc
270	4.5651	0.2493	4.8144	0.1158	0.0965
280	4.5811	0.2585	4.8397	0.0769	0.0670
290	4.5983	0.2678	4.8661	0.0383	0.0361
300	4.6167	0.2770	4.8937	0.0	0.0037
310	4.6363	0.2862	4.9226	−0.0381	−0.0300
320	4.6572	0.2955	4.9527	−0.0759	−0.0652
330	4.6792	0.3047	4.9839	−0.1134	−0.1018
340	4.7025	0.3139	5.0164	−0.1506	−0.1398
350	4.7269	0.3232	5.0500	−0.1876	−0.1791
360	4.7524	0.3324	5.0849	−0.2244	−0.2198
370	4.7792	0.3416	5.1208	−0.2608	−0.2619
380	4.8070	0.3509	5.1579	−0.2970	−0.3052
390	4.8359	0.3601	5.1960	−0.3329	−0.3499

TABLE V. Temperature dependence of the anharmonic vibration and centrifugal distortion contributions to $\langle q_1\rangle^T$ and chemical shielding of ^{19}F in $^{11}BF_3$.

T, K	anh, 10^3 Å	centrif, 10^3 Å	$\langle q_1\rangle^T$, 10^3 Å	$\langle\sigma\rangle^T - \langle\sigma\rangle^{300}$, ppm	
				exptl	calc
290	9.3270	0.3513	9.6783	0.0119	0.0315
300	9.3343	0.3634	9.6977	0.0	0.0099
310	9.3474	0.3755	9.7180	−0.0147	−0.0126
320	9.3514	0.3876	9.7391	−0.0323	−0.0361
330	9.3613	0.3997	9.7611	−0.0526	−0.0607
340	9.3723	0.4190	9.7841	−0.0758	−0.0864
350	9.3842	0.4240	9.8082	−0.1018	−0.1132
360	9.3972	0.4361	9.8333	−0.1305	−0.1411
370	9.4112	0.4482	9.8594	−0.1620	−0.1703
380	9.4264	0.4603	9.8868	−0.1964	−0.2008
390	9.4428	0.4724	9.9152	−0.2336	−0.2325
400	9.4602	0.4845	9.9448	−0.2735	−0.2655
410	9.4789	0.4967	9.9756	−0.3162	−0.2998

TABLE VI. Summary of vibrational contributions to chemical shift.

Molecule	Temperature range, K	Total chemical shift (calc), ppm	Anharmonic vibration, %[a]
$^{12}CF_4$	270–410	0.786	83
$^{28}SiF_4$	270–390	0.446	67
$^{11}BF_3$	290–410	0.341	51
^{35}ClF	280–350	1.033	47
F_2	220–350	3.937	36
^{13}CO	220–380	0.050	1

[a] Since only linear terms are being considered here, the centrifugal distortion contribution is the remaining fraction.

TABLE VII. ^{19}F shielding parameters found by fitting experimental temperature dependence of σ in this work, compared with ^{19}F shielding in diatomic molecules.[6]

Molecule	$(\partial\sigma/\partial R)_e$ ppm/Å	$\langle\sigma\rangle^{300} - \sigma_e$, ppm
F_2	−4665	−40
^{35}ClF	−2073	−13
$^{12}CF_4$	−1115	−7.24
$^{28}SiF_4$	−1170	−5.73
$^{11}BF_3$	−1115	−10.82

centage of the total chemical shift (over the range of temperature given) which is due to anharmonic vibration varies from 1% in ^{13}CO to 83% in CF_4.

From the anharmonic vibration and the centrifugal distortion contributions, we are able to calculate $(\langle\sigma\rangle^T - \langle\sigma\rangle^{300})$ in terms of the unknown parameter $(\partial\sigma/\partial R)_e$. When compared with the experimentally measured $\sigma_0(T)$ in a least squares fitting procedure, this yields the $(\partial\sigma/\partial R)_e$ values shown in Table VII. Figure 1(a)–(c) shows the comparison of the theoretical and calculated temperature dependence of chemical shielding in isolated CF_4, SiF_4, and BF_3. We note that the curvature of the theoretical curves reproduces fairly well that of the experimental curves despite the use of only one parameter. The best agreement is in the case of CF_4, where the experimental and theoretical curves virtually concide. For SiF_4 and BF_3 there is complete agreement within the experimental error.

In summary, it appears to be sufficient to use terms in the first derivatives for polyatomic molecules and still be able to obtain satisfactory agreement with the experimental temperature dependence of chemical shielding in the isolated molecules. The values of $(\partial\sigma/\partial R)_e$ obtained for ^{19}F in CF_4, SiF_4, and BF_3 appear to be comparable (−1115, −1170, and −1115 ppm/Å) despite the rather large differences in the observed temperature dependence of σ.[2] This implies that such differences are at-

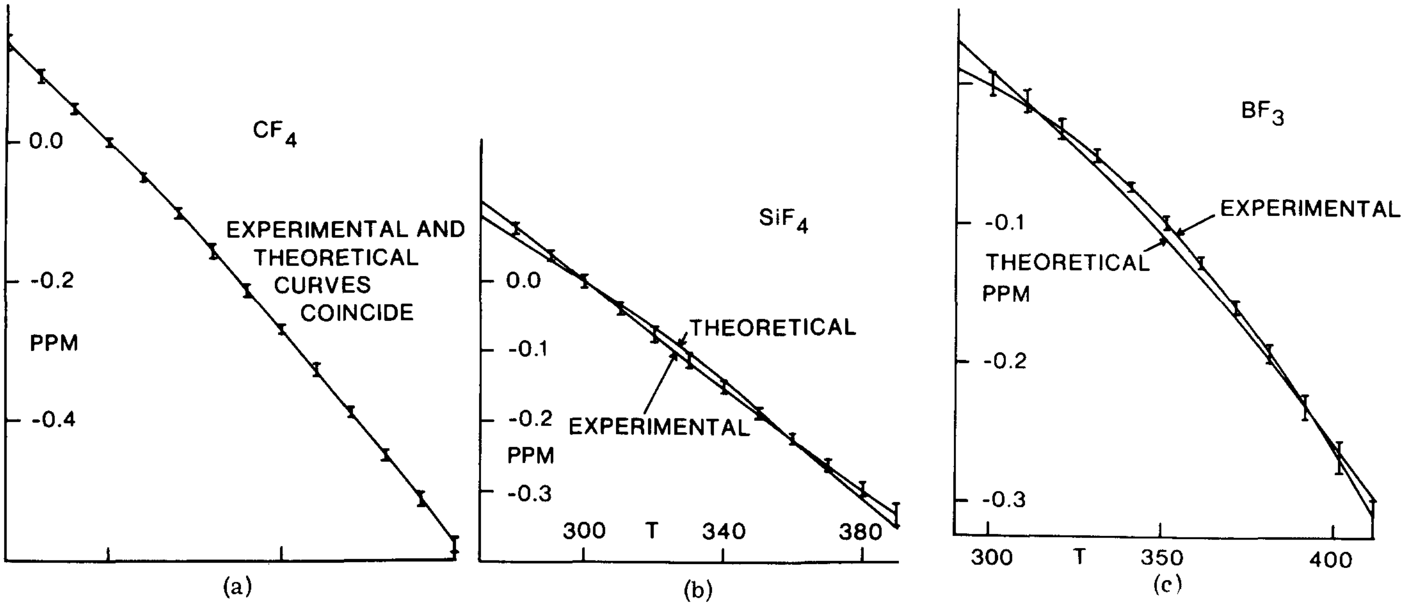

FIG. 1. Comparison of the experimental and theoretical functions $\langle\sigma\rangle^T - \langle\sigma\rangle^{300}$ for an isolated (a) $^{12}CF_4$, (b) $^{28}SiF_4$, and (c) BF_3 molecule. Note that the vertical scales are different for each molecule.

tributable mainly to differences in the dynamic states of these molecules rather than differences in $(\partial\sigma/\partial R)$. If this is the case, then perhaps some simple rules may be found for the prediction of $(\partial\sigma/\partial R)_e$ for ^{19}F in molecules of the type AF_n. With the determination of experimental $(\langle\sigma\rangle^T - \langle\sigma\rangle^{300})$ curves for other ^{19}F-containing molecules such as NF_3 and PF_3, some general trends in $\partial\sigma/\partial R$ may emerge.

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