Variation of chemical shielding with internal coordinates. Applications to diatomic molecules

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The derivatives of ^{19}F and ^{13}C chemical shielding with respect to internuclear distance in the following diatomic molecules: F_2, ClF, and CO, have been obtained from experimentally observed variation of chemical shifts with temperature in the isolated molecules. A general theory for the temperature dependence of chemical shielding in isolated molecules is given. In all three diatomic molecules considered here, $(d\sigma/dR)_e$ was found to be negative.

The temperature dependent chemical shifts in the NMR spectra of gases arise from a combination of the intrinsic temperature dependence of chemical shielding in an isolated molecule and the temperature dependence of the effects of intermolecular interactions.[1] The first arises from the variation with temperature of the populations of the rotational and vibrations states (and low-lying electronic states, if any), the chemical shielding in the excited states being different from those in the ground state. Thus, the chemical shielding in a pure gas may be expanded in a virial expansion as follows:

$$\sigma(T) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \cdots .$$

The temperature dependent chemical shielding of an isolated molecule is $\sigma_0(T)$, and the remaining terms are the temperature dependent contributions to chemical shielding from binary and higher order interactions. For a structureless molecule such as Xe, the form of $\sigma_1(T)$ is a simple one,

$$\sigma_1(T) = 4\pi \int_0^\infty \sigma(R)\, e^{-V(R)/kT} R^2\, dR ,$$

in which $\sigma(R)$ is the shielding of Xe in a pair of interacting Xe atoms with internuclear separation R relative to that at infinite separation. $\sigma_0(T)$ is the thermal average of the shielding at infinite separation. Both the intermolecular and the intramolecular contribution to the temperature dependence of chemical shielding can be measured in low density samples. $\sigma_1(T)$ is obtained from the density dependence of the resonance signal, and $[\sigma_0(T) - \sigma_0(300)]$ is obtained from the extrapolation to zero density if the temperature dependence of the reference substance used is also known experimentally. The pressure must be high enough that collisional interactions cause a given molecule to pass through a representative number of thermally accessible vibrational states in a time which is short compared to the reciprocal of the NMR frequency difference between nuclei in different vibrational states. Otherwise, one cannot obtain a thermally averaged σ by averaging over vibrational states. Thus, mathematically speaking, one does not extrapolate the results to a true zero pressure, but to a pressure which is so low that collisional deformation of the molecules no longer contributes to σ; however, there are still enough collisions to provide the required rate to transitions between vibrational and rotational states. An extensive review of both contributions, with special attention to the intermolecular effects, has been given by Rummens.[2]

Values of $\sigma_0(T) - \sigma_0(300)$ have been reported recently by Jameson *et al.* for F_2, ClF, and CO molecules.[3] (See Table I.) The observed shifts are sufficiently large so that it is feasible to obtain derivatives of chemical shielding with respect to internuclear displacement. Proton shifts have also been reported previously; however, the attendant difficulties in making precise measurements of such small shifts as are observed in protons lead to unreliable results. The data on HBr are probably as good as can be expected.[4] While the precision appears to be better than other proton data previously reported, the too-sharp increase in the σ_1 for HBr at temperatures below room temperature is inconsistent with behavior of $\sigma_1(T)$ for other systems.[2]

In this paper, the empirical values of $[\sigma_0(T) - \sigma_0(300)]$ are used to determine the derivative $(d\sigma/dR)_e$ for ^{19}F in ClF and F_2 and for ^{13}C in CO. Some general observations are made about the relative contributions of anharmonic vibration and centrifugal distortion to $\sigma_0(T)$.

GENERAL FORMULATION

The observed isotropic chemical shielding of a nucleus in an isolated diatomic molecule is a statistical average of the chemical shielding tensor over all possible orientations of the molecule in the magnetic field. It is also an average over all possible rovibronic states of the molecule weighted according to the fraction of molecules occupying that state at that temperature. Thus, the value of the resonance frequency of a nucleus in a gas sample extrapolated to zero density at a given temperature is a weighted average of the values characteristic of each occupied state.

Alternatively, the chemical shielding can be considered as a function of the nuclear configuration of the

TABLE I. Experimental values of $[\sigma_0(T) - \sigma_0(300)]$ for F_2, ClF, and CO molcules in ppm, from Ref. 3. $\sigma_0(T) - \sigma_0(300) = a_1(T-300) + a_2(T-300)^2 + a_3(T-300)^3$.

	a_1	a_2	a_3
F_2	-0.033996	-0.10289×10^{-3}	$+0.4575\times 10^{-6}$
ClF	-0.010415	-0.187850×10^{-3}	$+0.846200\times 10^{-6}$
CO	-0.3133×10^{-3}		

molecule. The internuclear distances in a molecule are affected by the vibrational and rotational motions of the molecule. Since the vibration is in general anharmonic, the molecule is more or less deformed from the equilibrium configuration when the molecule vibrates. In addition, the centrifugal force due to the overall rotation acts on the component atoms to shift their average positions away from the center of gravity of the molecule. The observed chemical shielding is therefore a value characteristic of the thermal average of internuclear distances.

The quantum mechanical Hamiltonian for a vibrating rotor has been derived by Wilson and Howard[5] and is reviewed in detail by Nielsen[6]:

$$H = H^{(0)} + H^{(1)} + H^{(2)} + \cdots , \tag{1}$$

in which

$$H^{(0)} = (\hbar/2)\sum_{s\sigma} \lambda_s^{1/2}[(p_{s\sigma}^2/\hbar^2) + q_{s\sigma}^2] + \frac{1}{2}\sum_{\alpha} (P_\alpha^2/I_{\alpha\alpha}^{(e)}), \tag{2}$$

$$H^{(1)} = hc \sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''} k_{ss's''} q_{s\sigma} q_{s'\sigma'} q_{s''\sigma''} - \sum_{\alpha}\left(\frac{p'_\alpha P_\alpha}{I_{\alpha\alpha}^{(e)}}\right)$$
$$-\frac{1}{2}\sum_{s\sigma}\left(\frac{\hbar^2}{\lambda_s}\right)^{1/4}\left(\sum_{\alpha,\beta} a_{s\sigma}^{(\alpha\beta)} \frac{(P_\alpha - 2p_\alpha^*)P_\beta}{I_{\alpha\alpha}^{(e)} I_{\beta\beta}^{(e)}}\right) q_s . \tag{3}$$

The contributions to the energy due to $H^{(1)}$ and $H^{(2)}$ may be evaluated by the usual methods of perturbation theory. Only $H^{(1)}$ is shown here since wavefunctions to first order are required. In Nielsen's notation, k_{sss} is a cubic force constant in terms of the dimensionless normal coordinates, g_s is the degeneracy of the sth vibrational mode, and $a^{\alpha\alpha}$ are the coefficients in the expression of the moments of inertia in terms of the normal coordinates.[6] All of the other symbols have their usual meaning.

For the discussion of molecular structure in the vicinity of the equilibrium configuration, it is convenient to express any observable which is a function of nuclear configuration as a power series of the normal coordinates,

$$f = f_e + \sum_{s\sigma}\left(\frac{\partial f}{\partial q_{s\sigma}}\right)_e q_{s\sigma} + \frac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'}\left(\frac{\partial^2 f}{\partial q_{s\sigma}\partial q_{s'\sigma'}}\right)_e q_{s\sigma} q_{s'\sigma'} + \cdots , \tag{4}$$

where the subscript e designates the value at the equilibrium configuration; s denotes the sth vibrational mode, and σ classifies each of the degenerate vibrations. The dimensionless normal coordinates q are related to the normal coordinates $Q_{s\sigma}$ by $q_{s\sigma} = (2\pi c\omega_s/h)^{1/2} \times Q_{s\sigma}$. We will confine our calculations to terms of the second order, in which case it is necessary to use the wavefunctions of the first order designated by $|V_1, V_2, \ldots, R\rangle$ for obtaining the expectation values of $q_{s\sigma}$, whereas it is sufficient to use the zeroth order wavefunctions designated by $|v_1, v_2, \ldots, R\rangle$ for those of $q_{s\sigma}q_{s'\sigma'}$. The average value has been derived for a totally symmetric coordinate $q_{s\sigma}$, by Toyama, Oka, and Morino[7]:

$$\langle V_1, V_2, \ldots, R\,|\,q_s\,|\,V_1, V_2, \ldots, R\rangle$$
$$= -\frac{1}{\omega_s}\left[3k_{sss}(v_s + \tfrac{1}{2}) + {\sum_{s'}}' k_{ss's'}(v_{s'} + g_{s'}/2) - \frac{1}{4\pi c}\left(\frac{1}{hc\omega_s}\right)^{1/2} \sum_{\alpha} \frac{a_s^{(\alpha\alpha)}}{(I_{\alpha\alpha}^{(e)})^2}\langle v_1^*, v_2^*, \ldots, R\,|\,(P_\alpha - p_\alpha^*)^2\,|\,v_1^*, v_2^*, \ldots, R\rangle\right] . \tag{5}$$

For a non-totally-symmetric coordinate, the expectation value is zero. Thus, only the totally symmetric vibrations contribute in first order. In Eq. (5) the first two terms correspond to anharmonicity of the vibration and the last term comes from centrifugal distortion. The expectation value of $q_{s\sigma}q_{s'\sigma'}$ has been obtained by Toyama *et al.*[7]:

$$\langle v_1, v_2, \ldots, R\,|\,q_{s\sigma}q_{s'\sigma'}\,|\,v_1, v_2, \ldots, R\rangle = (1/g_s)(v_s + g_s/2)\delta_{ss'}\delta_{\sigma\sigma'} . \tag{6}$$

Here the zeroth order wavefunctions are sufficient to calculate the expectation value. Thus, a physical quantity which depends on nuclear configuration can be written in terms of these expectation values,

$$f = f_e + \sum_{s}\left(\frac{\partial f}{\partial q_s}\right)_e \left\{-\frac{1}{\omega_s}\left[3k_{sss}(v_s + \tfrac{1}{2}) + {\sum_{s'}}' k_{ss's'}(v_{s'} + g_{s'}/2)\right]\right.$$
$$\left. + \frac{1}{4\pi c\omega_s}\left(\frac{1}{hc\omega_s}\right)^{1/2} \sum_{\alpha} a_s^{(\alpha\alpha)} \frac{1}{(I_{\alpha\alpha}^{(e)})^2}\langle v_1^*, v_2^*, \ldots, R\,|\,(P_\alpha - p_\alpha^*)^2\,|\,v_1^*, v_2^*, \ldots, R\rangle\right\} + \frac{1}{2}\sum_{s\sigma}\left(\frac{\partial^2 f}{\partial q_s^2}\right)_e^2 \frac{1}{g_s}(v_s + g_s/2) . \tag{7}$$

To obtain the statistical average of this quantity in thermal equilibrium at temperature T, it is necessary to evaluate the statistical averages $\langle q_{s\sigma}\rangle^T$ and $\langle q_{s\sigma}q_{s'\sigma'}\rangle^T$. Using a classical average for the rotational portion and a quantum-mechanical average for the vibrational part, Toyama obtains[7]

$$\langle q_s\rangle^T = -\frac{1}{2\omega_s}\left[3k_{sss}\coth(hc\omega_s/2kT) + {\sum_{s'}}' g_{s'}k_{ss's'}\coth(hc\omega_{s'}/2kT) - \frac{kT}{2\pi c}\left(\frac{1}{hc\omega_s}\right)^{1/2}\sum_{\alpha}\frac{a_s^{(\alpha\alpha)}}{I_{\alpha\alpha}^{(e)}}\right] , \tag{8}$$

and

$$\langle q_{s\sigma}q_{s'\sigma'}\rangle^T = \tfrac{1}{2}\coth(hc\omega_s/2kT)\delta_{ss'}\delta_{\sigma\sigma'} . \tag{9}$$

Thus, the thermal average of the chemical shielding is given by

$$\langle\sigma\rangle^T = \sigma_e + \sum_{s}\left(\frac{\partial\sigma}{\partial q_s}\right)_e \langle q_s\rangle^T + \frac{1}{2}\sum_{s}\left(\frac{\partial^2\sigma}{\partial q_s^2}\right)_e \langle q_s^2\rangle^T + \cdots , \tag{10}$$

in which $\langle q_s\rangle^T$ and $\langle q_s^2\rangle^T$ are evaluated as above. These values depend on the fundamental vibration frequencies of the molecule, the moments of inertia, the cubic force constants, and the coefficients $a_s^{(xx)}$, $a_s^{(yy)}$, $a_s^{(zz)}$. The former are available from detailed analysis of vibrational–rotational spectra, and the latter are expressible for each molecular type, in terms of the Coriolis constants and other molecular constants.[6]

It should be noted that the linear term consists of two contributions: (a) the anharmonic vibration term, and (b) the centrifugal distortion term. Depending on the molecule, one or the other contribution may dominate the linear term. In most cases, both are expected to be significant in determining the temperature dependence of σ. The quadratic term can give a significant contribution to the temperature dependence if $kT/(hc\omega_s)$ is greater than 1.

Since most of the molecular constants for relatively simple molecules are available from spectroscopic data, then the derivatives $(\partial\sigma/\partial q_s)_e$ and $(\partial^2\sigma/\partial q_s^2)_e$ can be determined from a sufficiently precise experimental determination of the intrinsic temperature dependence of the resonance frequency of an isolated molecule. It is also possible to express σ in terms of the internal displacement coordinates of the molecule such as $R_1 = \Delta r_{12}$, $R_2 = \Delta\phi_{13}$, etc. The dimensionless normal coordinates $q_{s\sigma}$ and the true curvilinear internal displacement coordinates are related in a nonlinear manner.[8] However, approximate internal displacement coordinates which are related to the dimensionless normal coordinates in a linear transformation can be used. The significance of the distinction between approximate internal displacement coordinates and true curvilinear internal displacement coordinates is discussed in Ref. 8.

Using the linear transformation

$$\mathbf{R} = \bar{\mathbf{L}}\mathbf{q} , \tag{11}$$

the approximate internal displacement coordinate R_i is given by $\sum_i \bar{L}_{is} q_s$. R_i has the units of $\bar{L}_{is}$. A complete normal coordinate analysis yields the transformation matrix $\mathbf{L}$ as the normalized eigenvectors if the basis set used in the Wilson F and G matrices is the set of approximate internal displacement coordinates R_i.[9] $\bar{L}$ is then obtained by

$$\bar{L}_{is} = L_{is}\left(\frac{h}{4\pi^2 c\omega_s}\right)^{1/2} . \tag{12}$$

Using the transformation matrix $\bar{L}$, it is then possible to express the chemical shielding, or any other molecular quantity dependent on nuclear configuration, in the following way:

$$\left(\frac{\partial\sigma}{\partial q_s}\right)_e = \sum_i \left(\frac{\partial\sigma}{\partial R_i}\right)_e \bar{L}_{is} , \tag{13}$$

and

$$\left(\frac{\partial^2\sigma}{\partial q_s^2}\right)_e = \sum_{i,j} \left(\frac{\partial^2\sigma}{\partial R_i \partial R_j}\right)_e \bar{L}_{is}\bar{L}_{js} . \tag{14}$$

Therefore, the thermal average of the trace of the chemical shielding tensor is

$$\langle\sigma\rangle^T = \sigma_e + \sum_i \left(\frac{\partial\sigma}{\partial R_i}\right)_e \sum_s \bar{L}_{is}\langle q_s\rangle^T$$

$$+ \frac{1}{2}\sum_{i,j} \left(\frac{\partial^2\sigma}{\partial R_i \partial R_j}\right)_e \sum_s \bar{L}_{is}\bar{L}_{js}\langle q_s^2\rangle^T , \tag{15}$$

where $\langle q_s\rangle^T$ and $\langle q_s^2\rangle^T$ are evaluated according to Eqs. (8) and (9). In the simplest case, a diatomic molecule, there is only one normal coordinate. In this case,

$$\bar{L}_{11} = r_e(2B_e/\omega)^{1/2} = (h/4\pi^2\mu c\omega)^{1/2} , \tag{16}$$

$$k_{111} = K_{111}L_{11}^3/hc , \tag{17}$$

in which the cubic force constant in terms of $R_1 = \Delta r$, K_{111}, is expressible in terms of the vibrational–rotational interaction constant α and the two-particle force constant, $F = 4\pi^2\mu c^2\omega^2$:

$$K_{111} = -\frac{F}{2r_e}\left(1 + \frac{\alpha\omega}{6B_e^2}\right) . \tag{18}$$

For a diatomic molecule the constants $a^{(\alpha\alpha)}$ are related to one another in the following way[6]:

$$\begin{aligned} a_1^{(xx)} &= a_1^{(yy)} = 2I^{1/2} , \\ a_1^{(zz)} &= 0 . \end{aligned} \tag{19}$$

Therefore, the thermal average of the chemical shielding for a diatomic molecule is given by

$$\langle\sigma\rangle^T = \sigma_e + f(T)(d\sigma/dR)_e + g(T)(d^2\sigma/dR^2)_e , \tag{20}$$

where

$$f(T) = \frac{3h}{16\pi^2 r_e\mu c\omega}\left(1 + \frac{\alpha\omega}{6B_e^2}\right)\coth\left(\frac{hc\omega}{2kT}\right) + \frac{kT}{2\pi^2 r_e\mu c^2\omega^2}$$

and

$$g(T) = \frac{h}{16\pi^2\mu c\omega}\coth\left(\frac{hc\omega}{2kT}\right) .$$

This is essentially the same form which was used by Buckingham and Urland for a general molecular property of a diatomic molecule.[10] Knowing B_e, ω, and α for a diatomic molecule, it is possible to find the derivatives of the chemical shielding function at the equilibrium internuclear distance if the resonance frequency of the isolated molecule has been measured precisely over a wide temperature range. The relative contributions of the anharmonic vibration and the centrifugal distortion terms to the temperature dependence of the chemical shielding depends on the anharmonicity of the fundamental frequency. In the molecules studied here as examples, the magnitude of the centrifugal distortion contribution is less than 20% of the total linear term; however, its temperature dependence determines to a large extent the temperature dependence which is observed because of the somewhat less pronounced temperature dependence of $\coth(hc\omega/2kT)$ for these molecules at temperatures between 220 and 350 K.

The ratio of the anharmonic vibration term (occurring in first order) to the harmonic vibration term (occurring in second order) is, from Eq. (20),

$$\frac{\langle q_s\rangle^T_{\text{anh}}}{\langle q_s^2\rangle^T} = \frac{3}{r_e}\left(1 + \frac{\alpha\omega}{6B_e^2}\right) . \tag{21}$$

The term $\alpha\omega/(6B_e^2)$ will typically be greater than 1. Thus, the quadratic term will always be smaller than the linear term. The ratio $3[1 + \alpha\omega/(6B_e^2)]/r_e$ is calcu-

TABLE II. Molecular constants.

	$\omega(\mathrm{cm}^{-1})$	$B_e(\mathrm{cm}^{-1})$	$\alpha(\mathrm{cm}^{-1})$	μ(amu)	$\frac{3}{r_e}\left(1+\frac{\alpha\omega}{6B_e^2}\right)(\mathrm{cm}^{-1})$
F_2[a]	917.1	0.892	0.013	9.500	7.3768×10^8
^{35}ClF	786.15[b]	0.516508[c]	0.43584×10^{-2} [d]	12.3103	5.7379×10^8
$^{13}C^{16}O$[e]	2121.00	1.8464	0.016366	7.1724	7.1748×10^8

[a] W. Stricker and J. C. Hochenbleicher, Z. Naturforsch Teil A **28**, 27 (1973).

[b] A. Coxon, Chem. Phys. Lett. **33**, 136 (1975).

[c] A. H. Nielsen, J. Chem. Phys. **19**, 1117 (1951).

[d] D. A. Gilbert, A. Roberts, and P. A. Griswold, Phys. Rev. **76**, 1723 (1949).

[e] Calculated from $^{12}C^{16}O$ constants given by I. Suzuki, Bull. Chem. Soc. Jpn. **44**, 3277 (1971).

lated for several diatomic molecules in Table II. It can be seen that the quadratic term is indeed always much smaller than the anharmonic vibration contribution to the linear term. Both the centrifugal distortion and the anharmonic vibration contribution to the linear term are positive. Thus, when centrifugal distortion is included in the linear term, the ratio of the linear term to the quadratic term is even larger than the ratios given in Table II. For all practical purposes, the temperature dependence of chemical shielding in a diatomic molecule depends only on the linear term. The temperature dependence of the quadratic term is so small compared to the linear term as to prohibit the determination of $(d^2\sigma/dR^2)_e$. Thus, only two constants can be determined, $(d\sigma/dR)_e$ and $(\langle\sigma\rangle^{300}-\sigma_e)$.

RESULTS

The molecular constants used here are shown in Table II. The contributions to the linear term and the quadratic term are shown in Table III for F_2, ^{35}ClF, and $^{13}C^{16}O$. The quadratic term was dropped since it is at least 1 order of magnitude smaller than the linear term. The experimentally observed temperature dependence of the ^{19}F and ^{13}C resonance signal in F_2, ClF, and CO gas extrapolated to zero density from Ref. 3 gives $y(T)=\sigma_0(T)-\sigma_0(300)$, or, in the notation used in Eq. (10), $y(T)=(\langle\sigma\rangle^T-\langle\sigma\rangle^{300})$. The experimental function $y(T)$ is

TABLE III. The linear term $f(T)$ and its parts due to anharmonic vibration and centrifugal distortion, and the quadratic term $g(T)$, as defined in Eq. (20).

	T	Anharmonic (Å)	Centrifugal (Å)	$f(T)$ (Å)	$g(T)$ (Å^2)
F_2	220	0.723176E−02	0.914644E−03	0.814640E−02	0.972064E−03
	230	0.724247E−02	0.956218E−03	0.819868E−02	0.973503E−03
	240	0.725508E−02	0.997793E−03	0.825287E−02	0.975199E−03
	250	0.726970E−02	0.103937E−02	0.830907E−02	0.977163E−03
	260	0.728640E−02	0.108094E−02	0.836734E−02	0.979409E−03
	270	0.730525E−02	0.112252E−02	0.842777E−02	0.981942E−03
	280	0.732629E−02	0.116409E−02	0.849038E−02	0.984770E−03
	290	0.734953E−02	0.120567E−02	0.855519E−02	0.987895E−03
	300	0.737501E−02	0.124724E−02	0.862224E−02	0.991319E−03
	310	0.740270E−02	0.128882E−02	0.869151E−02	0.995040E−03
	320	0.743259E−02	0.133039E−02	0.876299E−02	0.999059E−03
	330	0.746468E−02	0.137197E−02	0.883665E−02	0.100337E−03
	340	0.749893E−02	0.141354E−02	0.891247E−02	0.100798E−03
	350	0.753531E−02	0.145512E−02	0.899042E−02	0.101298E−03
^{35}ClF	280	0.521954E−02	0.105899E−02	0.627853E−02	0.901957E−03
	290	0.524708E−02	0.109682E−02	0.634389E−02	0.906716E−03
	300	0.527664E−02	0.113464E−02	0.641127E−02	0.911824E−03
	310	0.530819E−02	0.117246E−02	0.648065E−02	0.917277E−03
	320	0.534168E−02	0.121028E−02	0.655195E−02	0.923063E−03
	330	0.537704E−02	0.124810E−02	0.662514E−02	0.929174E−03
	340	0.541423E−02	0.128592E−02	0.670015E−02	0.935601E−03
	350	0.545318E−02	0.132374E−02	0.677692E−02	0.942331E−03
$^{13}C^{16}O$	220	0.397298E−02	0.283148E−03	0.425613E−02	0.553955E−03
	230	0.397298E−02	0.296019E−03	0.426900E−02	0.553956E−03
	240	0.397300E−02	0.308889E−03	0.428188E−02	0.553958E−03
	250	0.397301E−02	0.321760E−03	0.429477E−02	0.553960E−03
	260	0.397303E−02	0.334630E−03	0.430766E−02	0.553963E−03
	270	0.397307E−02	0.347500E−03	0.432057E−02	0.553968E−03
	280	0.397312E−02	0.360371E−03	0.433348E−02	0.553975E−03
	290	0.397318E−02	0.373241E−03	0.434642E−02	0.553984E−03
	300	0.397328E−02	0.386111E−03	0.435939E−02	0.553997E−03
	310	0.397339E−02	0.398982E−03	0.437237E−02	0.554014E−03
	320	0.397354E−02	0.411852E−03	0.438539E−02	0.554035E−03
	330	0.397373E−02	0.424723E−03	0.439845E−02	0.554061E−03
	340	0.397397E−02	0.437593E−03	0.441156E−02	0.554094E−03
	350	0.397427E−02	0.450463E−03	0.442473E−02	0.554136E−03
	360	0.397462E−02	0.463334E−03	0.443796E−02	0.554185E−03
	370	0.397505E−02	0.476204E−03	0.445125E−02	0.554244E−03
	380	0.397555E−02	0.489075E−03	0.446462E−02	0.554315E−03

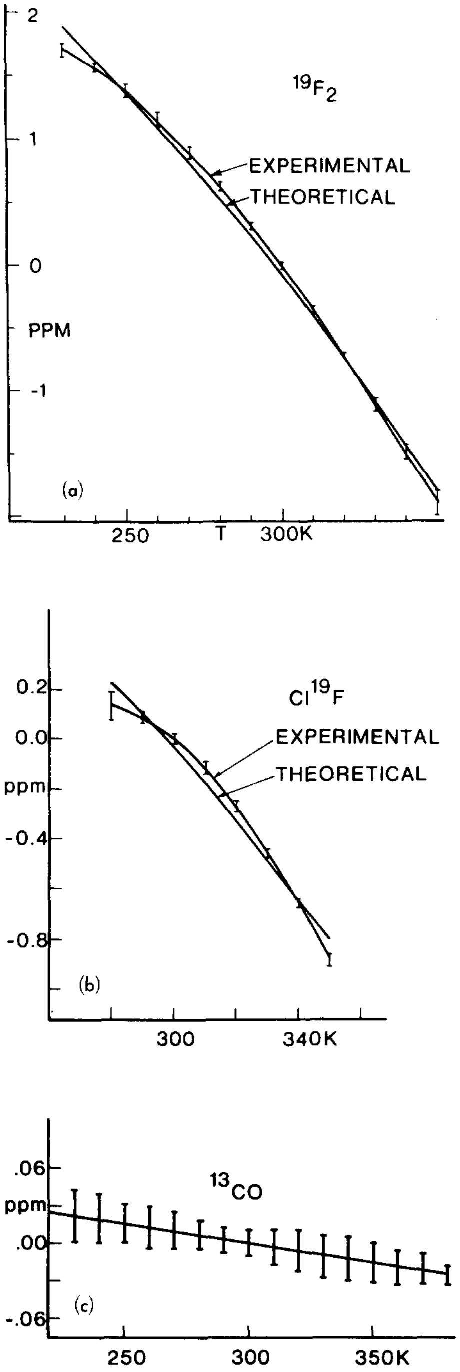

FIG. 1. (a)–(c): Comparison of the experimental and theoretical functions $[\sigma(T) - \sigma(300)]$ for an isolated F_2, ^{35}ClF, and ^{13}CO molecule. Note that the vertical scales are different for each molecule.

fitted to the two-parameter function $A + Bf(T)$, where $A = \sigma_e - \langle\sigma\rangle^{300}$, $B = (d\sigma/dR)_e$. Table III shows the total linear term $f(T)$ as well as its two parts due to the anharmonic vibration and centrifugal distortion. The fitting is done using a program in which the local minimum of a sum of squares of the residuals, $A + f(T)B - y(T)$, is found by an iterative process. The results are shown in Fig. 1 for F_2, ClF, and CO. The parameters which characterize the theoretical curves are given in Table IV. The first derivatives, $(d\sigma/dR)_e$, found for F_2, ClF, and CO are all negative, just as the values obtained for ^1H. There is reason to believe that this is the universal case, at least for ground state diatomic molecules.

For CO there exists a theoretical calculation of ^{13}C chemical shielding for various internuclear distances by Stevens and Karplus.[11] Subsequently, Raynes and Stanney calculated the temperature dependent chemical shifts for CO using their results.[12] Raynes and Stanney calculate $(\langle\sigma\rangle^{300} - \sigma_e)$ to be -0.10 ppm, and $\langle\sigma\rangle^T$ with a sizeable curvature with respect to temperature. Unlike the observed $(\langle\sigma\rangle^T - \langle\sigma\rangle^{300})$ for ClF and F_2, that for ^{13}CO is very small, just half of the temperature dependence of the reference substance. Therefore, in ^{13}CO the experimental data are not sufficiently accurate to distinguish between the value of $(d\sigma/dR)_e$ given by Stevens and Karplus (-413 ppm/Å) and our best fit value for this derivative. Neither is it possible to determine whether the sizeable curvature in the $\langle\sigma\rangle^T$ calculated by Raynes and Stanney is real.

CONCLUSIONS

The general treatment given here for polyatomic molecules expresses the chemical shielding temperature dependence in terms of the molecular constants obtained by vibrational–rotational spectroscopy, with the derivatives of the chemical shielding with respect to internal displacement coordinates such as bond stretches and angle displacements. For a diatomic molecule which has a large fundamental frequency, only the first derivative may be determined, since the coefficient of the second derivative is at least 1 order of magnitude smaller than that of the first derivative and its temperature dependence is essentially nil. The relative contributions to the temperature dependence of σ are shown in Fig. 2 for F_2. The curves shown are those of the anharmonicity and centrifugal distortion contributions at each temperature relative to that at 300 K. That is, the value at 300 K has been subtracted from each point, in order to exhibit the temperature dependence of the anharmonic and centrifugal distortion contribution. It can be seen that despite the smaller mag-

TABLE IV. ^{19}F and ^{13}C shielding parameters found by fitting experimental temperature dependence of σ in this work, compared with ^1H shielding.

	$\left(\frac{d\sigma}{dR}\right)_e$ (ppm/Å)	$\langle\sigma\rangle^{300} - \sigma_e$(ppm)
F_2	-4665	-40
^{35}ClF	-2073	-13
$^{13}C^{16}O$	-241	-1.05
HBr[a]	-398 ± 26	-7.11
$H^{35}Cl$[b]	-78.2 ± 19	-1.34
H_2[c]	-21.8	-0.38

[a] Reference 4.

[b] W. T. Raynes and B. P. Chadburn, Mol. Phys. **24**, 853 (1972).

[c] Theoretical values calculated by W. T. Raynes, A. M. Davies, and D. B. Cook, Mol. Phys. **21**, 123 (1971).

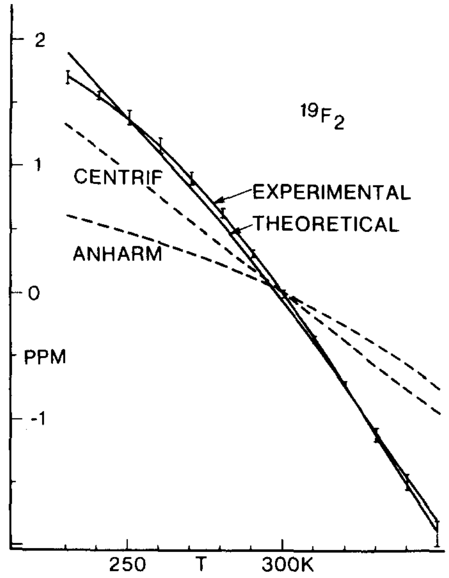

FIG. 2. Contributions to the temperature dependence of σ: the anharmonic vibration and the centrifugal distortion.

nitude of the centrifugal distortion contribution (less than 20% of the total linear term), its temperature dependence is larger than that of the anharmonic vibration contribution. Both are responsible for the temperature dependence of σ, with the centrifugal distortion being about twice as effective as the anharmonic vibration. This is typical for normal ground state diatomic molecules with modest fundamental frequencies of 1000 cm^{-1} or less. For CO, as for ClF and F_2, the anharmonic vibration contribution is seen in Table III to have a larger magnitude than the centrifugal distortion. However, the temperature dependence in CO comes entirely from the linear change in the centrifugal distortion with temperature. At temperatures easily accessible in NMR spectrometers, 100–450 K, $kT/hc\omega$ for CO, HBr, and HCl are of the order of 0.2 or less, in which case $\coth(hc\omega/2kT)$ is essentially constant. Thus, the temperature dependence of σ_0 in tightly bound diatomic molecules like CO, HBr, and HCl is nearly entirely due to centrifugal distortion.

We note in Table IV that $(\langle\sigma\rangle^{300} - \sigma_e)$ values are negative for all the diatomic molecules included. This means that the contributions to the shielding by the dynamic state of the molecule are negative. This is of course consistent with our findings that $(d\sigma/dR)_e$ is negative for these molecules. Another important point to note is that this difference between the thermal average of σ at 300 K and the σ value at the equilibrium configuration is not necessarily small, varying from 0.38 to 40 ppm. In the case of F_2, it is about 7% of the entire range of known ^{19}F chemical shifts! Thus, chemical shifts measured at room temperature should not be compared directly with differences in theoretical values of σ calculated at the equilibrium configuration of molecules.

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