Effects of Intermolecular Interactions and Intramolecular Dynamics on Nuclear Resonance in NF_3, PF_3, POF_3, and PF_5

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The temperature-dependent chemical shifts in 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. Both contributions have been measured for the ^{31}P and ^{19}F nuclei in NF_3, PF_3, POF_3, and PF_5. The intramolecular contribution can be interpreted in terms of the derivatives of nuclear shielding with respect to bond extension and angular displacement.

Introduction

The magnetic shielding observed for a nucleus in a molecule in the gas phase is an average affected by intermolecular interactions as well as the intramolecular dynamics which occurs even in the isolated molecule. As a consequence, the observed average exhibits a density and a temperature dependence. The magnetic shielding can then be expressed as an expansion in powers of density:[1]

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \ldots \qquad (1)$$

where ρ is the density of the pure gas, $\sigma_1(T)$ is the second virial coefficient of nuclear magnetic shielding, and $\sigma_0(T)$ is the temperature-dependent shielding in the isolated molecule. When observing a given nucleus in a molecule X in a gaseous mixture, there will be as many terms $\sigma_1(X,A)\rho_A$ as there are molecular species A interacting with X, including X itself. Because the intermolecular effects exhibit a density dependence, it is possible to separate the intermolecular effects and their T dependence, $\sigma_1(T)\rho + \sigma_2(T)\rho^2$, from the temperature dependence of the shielding in the isolated molecule. One merely prepares several samples of various densities and observes the nuclear resonance as a function of T for each sample. By limiting the sample densities to values sufficiently low so that terms quadratic and higher order in density are not observed, one can determine the functions $\sigma_1(T)$ and $\sigma_0(T)$ separately. Of course the latter cannot be determined in an absolute sense, but only relative to the shielding value in the isolated molecule at some fixed temperature, which we have chosen to be 300 K.

In our studies of $\sigma_1(T)$ for various molecular pairs, we have found that while the form of $\sigma_1(T)$ is fairly simple for an interacting pair of rare gas atoms, in which case $\sigma_1(T)$ is given by

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

the situation is not nearly so simple for polyatomic molecules. In polyatomic molecules, one would expect some dependence of σ_1 on the location of the nucleus in the observed molecules (one might call this a site effect) in addition to the more complicated multidimensional nature of the potential surface of interaction. Even in the case of two interacting rare gas atoms, the pair shielding function $\sigma(R)$ is not necessarily a simple monotonic function of R.[2] Until such time as models for the $\sigma(R)$ function are found to be valid in reproducing the magnitudes and the temperature dependence of σ_1, there will be little success in using NMR gas phase studies for determination of intermolecular potential functions $V(R,\theta,\phi)$. This is unfortunate in that NMR does have the advantage of providing a number of probes in an interacting pair of molecules (given by the number of nonequivalent magnetic nuclei in the pair) all probing the same single intermolecular potential surface. At this stage in the development of models for $\sigma(R)$, we can do little more, experimentally, than determine $\sigma_1(T)$ functions as accurately as possible for some pairs of very simple molecules for comparison with theory in some future time.[3]

On the other hand, the effect of intramolecular dynamics on the nuclear magnetic shielding in an isolated molecule is at a more favorable interpretive level. Since there are very successful models for intramolecular potential functions which are probed by very accurate vibrational–rotational–electronic spectroscopic measurements, these surfaces are much more well known.[4] The derivatives of these surfaces are observed as quadratic, cubic, and quartic force constants which derive from an interpretation of spectroscopic constants which are subject to very accurate measurements.[5] Since the relationship between the potential function derivatives and these spectroscopic constants has been very well established for simple molecular types,[6] success is more likely in the interpretation of $\sigma_0(T)$ than $\sigma_1(T)$. Thus, we have investigated $\sigma_0(T)$ for molecules ranging from diatomics[7] to linear AX_2 types,[8] tetrahedral AX_4,[9,10] planar and pyramidal AX_3,[10,11] octahedral AX_6,[9] as well as symmetric tops such as AYX_3.[12,13] For the most part we have observed ^{19}F nuclei due to their high sensitivity and wide range of chemical shifts which allow the $\sigma_0(T)$ function to be defined with high relative precision. Other nuclei we have observed are ^{15}N, ^{13}C, ^{11}B, and ^{31}P. We found that, except for one case,[14] $d\sigma_0/dT$ is negative, that is, a downfield shift is usually observed as the temperature increases when the observed frequencies are extrapolated to zero density. The $\sigma_0(T)$s we have previously observed for ^{19}F in various molecules are shown in Figure 1 together with the new results reported below. The $\sigma_0(T)$s previously observed for other nuclei are shown in Figure 2 together with a selected few ^{19}F data for comparison, and the new ^{31}P results reported herein.

It will be noted that the ^{31}P in PH_3 shows a $\sigma_0(T)$ function which has a $d\sigma_0(T)/dT$ sign opposite all the others. This was the first instance of a positive $d\sigma_0(T)/dT$ ever found.[13] In order to determine whether this is an

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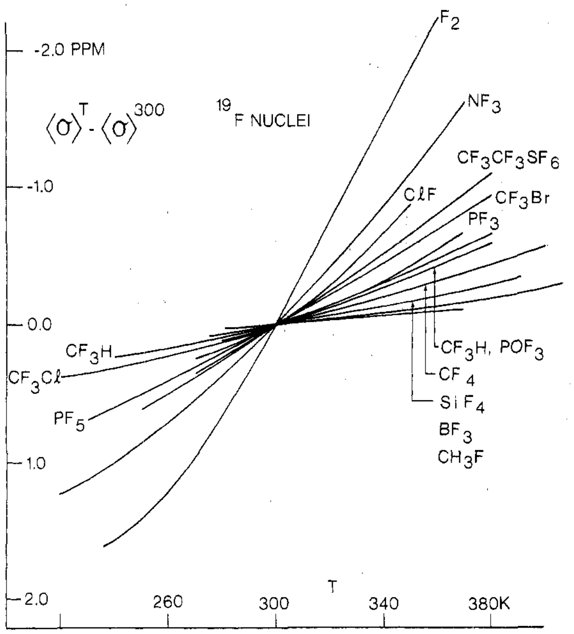

Figure 1. Temperature dependence of the ^{19}F chemical shielding in various isolated molecules. The new results for NF_3, PF_3, POF_3, and PF_5 are also included.

isolated unusual case or whether this is typical of ^{31}P or typical of the apical nucleus in a pyramidal AX_3 molecule, we decided to investigate $\sigma_0(T)$ of nuclei in similar environments. This program of study includes (a) a study of ^{31}P nuclei in other molecules and (b) a study of other pyramidal AX_3 compounds. PF_3, POF_3, and PF_5 were chosen as typical of the symmetrically substituted phosphines, a symmetrically substituted phosphoryl, and a pentacoordinate phosphorus, respectively. The pyramidal molecules to be investigated for comparison with PH_3 are PF_3, NH_3, ND_3, and NF_3. This paper deals with the entire program of study with the exception of the ^{15}N in NH_3, ND_3, and NF_3, which will be reported later.[15]

Of additional interest in these specific molecules is the possibility of observing some unusual effects in $\sigma_0(T)$ in systems in which there could be important contributions to the chemical shielding average from geometries other than the local minima. In AX_3 molecules interconversion between pyramidal forms is possible. In PF_5 the ^{31}P is the central nucleus in a fluxional molecule (PF_5 is undergoing pseudorotation). In both cases the averaging over displacements from equilibrium which are larger than the small vibration limit previously considered may lead to some unusual behavior of σ_0.

Results

The procedures used here are the same as those reported earlier.[16] All gases were from commercially available sources and were degassed before sample preparation. The samples were made in standard borosilicate sample tubes. To the sample tubes containing PF_5 a small amount of solid NaF was added as an HF getter to minimize reaction of PF_5 with the tubes. These samples were kept at liquid nitrogen temperatures until the spectra were taken. Samples of NF_3, PF_3, POF_3, and PF_5 were prepared in sealed sample tubes of approximately 0.25 mL volume, sufficiently small so as to have a negligible temperature gradient over the length of the tube. The Fourier transform NMR spectra were taken with a 90-MHz Bruker spectrometer with a Nicolet data acquisition system. The lock solvent used was toluene-d_8 (the CD_3 nuclei) whose temperature dependence relative to a Xe atom has been measured.[17] The temperature range was limited by condensation at the lower end and the boiling point of the reference toluene-d_8 near 370 K. PF_5 was found to decompose if the temperature was raised above 300 K. ^{19}F spectra were taken with a sweep width of 1000–2000 Hz, 64 to 2K scans in 1K of memory, zero-filling to 8K prior to data transformation. Typical repetition rates were 0.3 s for these lines with line widths of 5–50 Hz. ^{31}P spectra were taken with a sweep width of 2000–5000 Hz, 128 to 8K scans in 1K of memory, again zero-filling to 8K. Repetition rates were 0.2–0.5 s. Line widths of individual peaks ranged from 15 to 80 Hz. The coupling constants observed in gases of density ranging from 8 to 40 *A* (amagat unit) were $J^{PF} = 1400 \pm 1$ Hz in PF_3, 1052 ± 2 Hz in POF_3, and 929 ± 1 Hz in PF_5 which are in essential agreement with literature values for the liquids.[18-20] J^{NF} in $^{14}NF_3$ was not measured because the triplet was incompletely resolved.[21] The five fluorines in PF_5 were found to be magnetically equivalent on the NMR time scale as has been previously observed in the liquid.[20] Any density or temperature dependence of these coupling constants were within experimental error. In the ^{31}P spectra of POF_3, PF_3, and PF_5 each of the largest four members of the multiplets were treated as independent measures of the resonance frequency by using a temperature independent $^{1}J^{PF}$ to correct to the multiplet center. Within our experimental error this appeared to be adequate.

TABLE I: Second Virial Coefficient of ^{19}F Shielding in ppm/amagat[a]

$\sigma_1(T) = a_0 + a_1(T - 300) + a_2(T - 300)^2$

	a_0	a_1	a_2
NF_3	-0.006810 ± 0.0033	1.99×10^{-5}	-5.98×10^{-7}
PF_3	-0.0116 ± 0.0009	2.1×10^{-5}	
POF_3	-0.0229 ± 0.0016		
PF_5	-0.0190 ± 0.0075	7.16×10^{-5}	$-5.00\ 10^{-10}$

[a] Temperature range same as in Table III.

TABLE II: Second Virial Coefficient of ^{31}P Shielding in ppm/amagat[a]

$\sigma_1(T) = a_0 + a_1(T - 300)$

	a_0	a_1
PF_3	-0.00639	
POF_3	-0.0125	4.56×10^{-6}
PF_5	-0.0023	

[a] Temperature range same as in Table III.

The density dependences of the ^{19}F in NF_3, PF_3, POF_3, and PF_5 are shown in Table I where the σ_1 values and their temperature coefficients are reported in cases where they are sufficiently large. The σ_1 for ^{31}P in PF_3, POF_3, and PF_5 are shown in Table II. They are very small and nearly independent of temperature. The gas-to-liquid shifts are also found to be small, and within experimental error they can be entirely accounted for with a $\sigma_1\Delta\rho$ term where $\Delta\rho$ is the density difference between gas and liquid in equilibrium. The temperature coefficients of the density of the liquid were obtained from Landolt-Bornstein tables.[22]

The $\sigma_0(T)$ functions were obtained by the usual procedures.[10] $\sigma_1(T)\rho$ and the known temperature dependence of the reference were removed from the raw data for several samples. The remainders are shown in Figure 3 for ^{19}F in NF_3, PF_3, POF_3, and PF_5 and in Figure 4 for ^{31}P in PF_3, POF_3, and PF_5. We see in Figure 3 that the relative precision is sufficiently good to define the ^{19}F $\sigma_0(T)$ functions reasonably well. In Figure 4 the ^{31}P results are

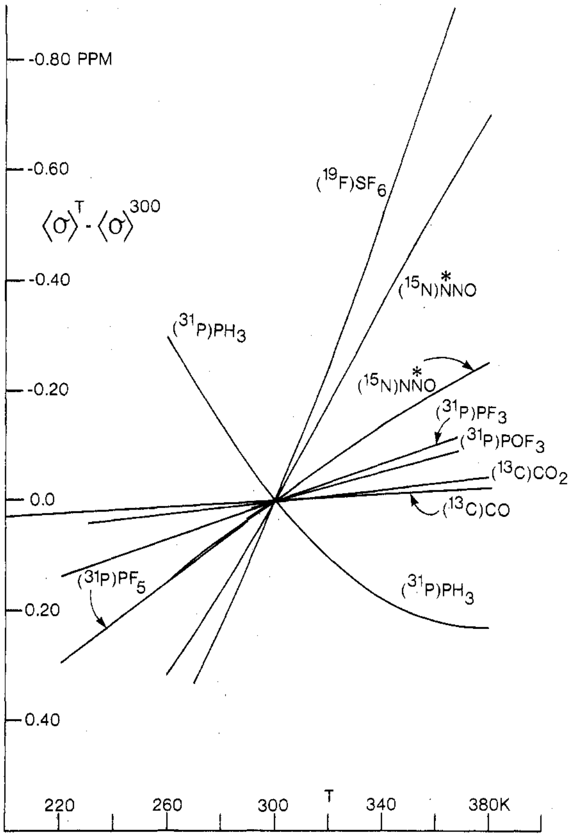

Figure 2. Temperature dependence of the chemical shielding of ^{11}B, ^{13}C, ^{15}N, and ^{31}P nuclei in various isolated molecules. The new results for ^{31}P in PF_3, POF_3, and PF_5 are also included.

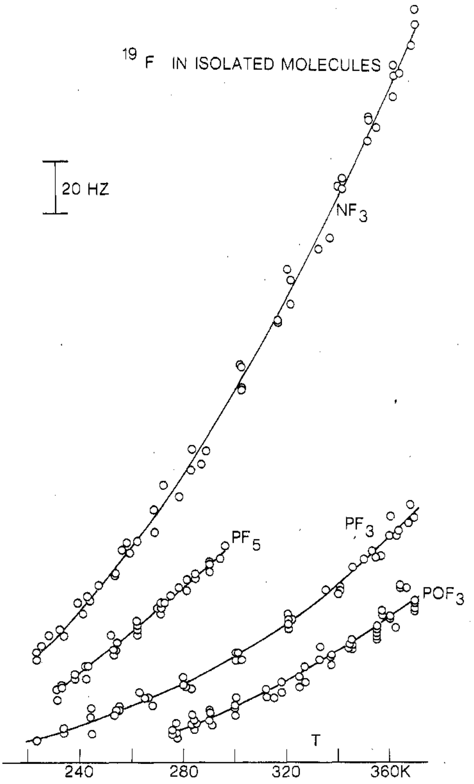

Figure 3. Temperature dependence of the ^{19}F NMR frequency in isolated NF_3, PF_3, POF_3, and PF_5 molecules.

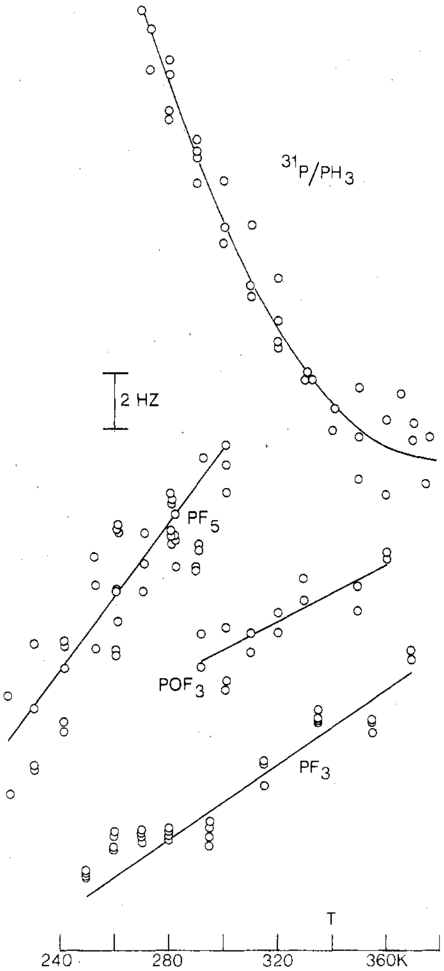

Figure 4. Temperature dependence of the ^{31}P NMR frequency in isolated PF_3, POF_3, and PF_5 molecules.

TABLE III: Temperature Dependence of ^{19}F Shielding in Isolated Molecules, in ppm

$$\sigma_0(T) - \sigma_0(300) = a_1(T - 300) + a_2(T - 300)^2 + a_3(T - 300)^3$$

	T, K	10^3a_1	10^5a_2	10^8a_3
NF_3	220-370	−19.96	−5.23	5.87
PF_3	220-370	−6.73	−3.26	−11.95
POF_3	290-370	−5.65	−2.97	8.29
PF_5	220-300	−9.79	0.798	8.46

TABLE IV: Temperature Dependence of ^{31}P Shielding in Isolated Molecules

$$\sigma_0(T) - \sigma_0(300) = a_1(T - 300)$$

	T, K	10^3a_1, ppm/deg
PF_3	220-370	−1.70
POF_3	290-370	−1.41
PF_5	220-300	−3.70

compared with the ^{31}P in PH_3 which had been previously reported. The ^{31}P $\sigma_0(T)$ function in PF_3, POF_3, and PF_5 all have the usual sign of the temperature coefficients as can be seen in Figure 2. Only ^{31}P in PH_3 remains the exception. The temperature coefficients of these $\sigma_0(T)$ functions are given in Tables III and IV for ^{19}F and ^{31}P, respectively. It is interesting that the $d\sigma_0(T)/dT$ for ^{31}P in PF_3 has the same sign as all the other molecules, not like PH_3. The remaining test cases, those of ^{15}N in NH_3, ND_3, and NF_3, will be investigated.[15] There is some possibility that ^{15}N in NH_3/ND_3 behaves unusually like the ^{31}P in the PH_3/PD_3 system.

Effect of Intermolecular Interactions

The magnitudes of σ obtained here for ^{19}F are in the same order as those previously reported.[9,12,13] The σ_1 found for ^{31}P are somewhat smaller than in P_4[23] or PH_3.[11] Unlike

TABLE V: Range of σ_1 Values for Various Nuclei in ppm/amagat

nuclei	$\lvert\sigma_1\rvert$
^{1}H	0-0.008
^{11}B	0.0085 in BF_3
^{13}C	0.0022-0.0105
^{15}N	0.0026-0.02
^{19}F	0.006-0.07
^{31}P	0.0023-0.266
^{129}Xe	0.166-0.75

PH_3 the temperature dependences of σ_1 in PF_5 and POF_3 are so small as to be within experimental error. This is another example of a centrally located nucleus (similar to ^{13}C in CH_4) which has been found to always have a small σ_1 as well as a very small temperature dependence of σ_1.[10] The values of σ_1 for various nuclei are compared in Table V. It is obvious that the order of magnitudes of σ_1 are fairly predictable from the range of chemical shifts of the various nuclei. As a rule nuclei with wide chemical shift ranges also have large σ_1 values.

From Table V we can see that the solvent effects on ^{31}P nuclei can be expected to be sizeable, quite unlike solvent effects on ^{13}C or ^{1}H. Special caution should be used in interpreting very small ^{31}P shifts in biological systems, for example. In large part they could be nonspecific medium effects of the same type that occur in gas-phase spectra. The temperature dependence of solvent effects are in large part due to the temperature dependence of the density of solvents. In biological systems even more caution than usual should be used due to the complexity of the molecules being studied. Sometimes shifts observed are so small as to be entirely accountable by temperature dependences of the lock substance used as reference but have been mistakenly attributed to conformation changes or specific biologically important interactions.[24]

Intramolecular Dynamics

The temperature dependence of σ in the isolated molecule can be explained in terms of the averaging over rovibrational states which occurs in a gas sample even at a very low pressure. There are sufficient collisions to allow a particular molecule to sample many different rovibrational states during the acquisition of one free induction decay. As with any other molecular electronic property the nuclear magnetic shielding in a molecule which obeys the Born–Oppenheimer approximation can be expanded in terms of the normal coordinates[25]

$$\sigma = \sigma_e + \sum_i \frac{\partial\sigma}{\partial q_i}\langle q_i\rangle + \tfrac{1}{2}\sum_{i,j}\frac{\partial^2\sigma}{\partial q_i \partial q_j}\langle q_i q_j\rangle + \ldots \qquad (3)$$

The averages $\langle q_i\rangle$ and $\langle q_i q_j\rangle$ etc. are either averages over a given vibrational state in which case the σ obtained is characteristic of that vibrational state, or else the averages $\langle q_i\rangle$ and $\langle q_i q_j\rangle$ are thermal averages so that the σ obtained is a thermally averaged magnetic shielding constant. In a bulk gas the thermal average is observed. Unless some means is used to vibrationally select the system as can be done with a molecular beam, only the thermal average is observed.

The expansion in terms of the dimensionless normal coordinates is a convenient one to use because the leading linear terms in $\langle q\rangle$ are zero unless the coordinate is a totally symmetric one. No such restriction occurs for the quadratic terms except that $\langle q_i q_j\rangle$ = zero unless $i = j$, and when i and j refer to degenerate modes[25]

$$\langle q_{i\sigma} q_{j\sigma'}\rangle = \langle q_{i\sigma}\rangle^2 \delta_{ij}\delta_{\sigma\sigma'} \qquad (4)$$

The linear term is entirely due to anharmonic vibration and centrifugal distortion since a rigid rotor harmonic oscillator system will have zero $\langle q\rangle_v$ or $\langle q\rangle^T$. The thermal average of the dimensionless normal coordinates in a pyramidal AX_3 molecule is given by the anharmonic vibrational contribution and the centrifugal distortion contribution as follows:[4]

$$\langle q_i\rangle^T{}_{\text{anh}} = -\frac{1}{2\omega_i}\{3k_{iii}\coth(hc\omega_i/2kT) + \sum_{s\neq i}^{4} k_{iss}\coth(hc\omega_s/2kT)\} \qquad (5)$$

$$\langle q_i\rangle^T{}_{\text{cent}} = \frac{kT}{4\pi c\omega_i}\left(\frac{1}{hc\omega_i}\right)^{1/2}\sum_\alpha \frac{a_i^{\alpha\alpha}}{I_{\alpha\alpha}{}^{(e)}} \qquad (6)$$

for $i = 1, 2$ (the totally symmetric modes). The harmonic frequencies (ω_i), the cubic force constants (k_{iss}), the equilibrium moments of inertia ($I_{\alpha\alpha}{}^{(e)}$), the constants which appear in the expansion of the moments of inertia in terms of the dimensionless normal coordinates ($a_i^{\alpha\alpha}$), and the transformation matrix between the dimensionless normal coordinates (q_i) and the internal coordinates (Δr and $\Delta\alpha$) are obtained from spectroscopic constants which are available for some simple molecules. The difficulty which arises in defining the cubic force constants is that there sometimes are not enough spectroscopic constants to allow the many force constants to be determined unequivocally.

Once molecular symmetry has been used to advantage in limiting the number of nonvanishing $\langle q_i\rangle$ and $\langle q_i q_j\rangle$, it is usually necessary to transform to internal coordinates because the dimensionless normal coordinates are *not* mass independent; thus, neither are $\partial\sigma/\partial q$ mass independent. To be able to compare various isotopically substituted species, it is necessary to express the derivatives of σ with respect to nuclear configuration in terms of mass independent internal coordinates.[26] Thus, we may write the temperature dependence of σ for a bent AX_2 molecule in terms of

$$\frac{d\langle\sigma\rangle^T}{dT} = \left(\frac{\partial\sigma}{\partial\Delta r}\right)_e \frac{d\langle\Delta r\rangle^T}{dT} + \left(\frac{\partial\sigma}{\partial\Delta\alpha}\right)_e \frac{d\langle\Delta\alpha\rangle^T}{dT} + \left(\frac{\partial^2\sigma}{\partial\Delta\alpha^2}\right)_e \frac{d\langle(\Delta\alpha)^2\rangle^T}{dT} + \left(\frac{\partial^2\sigma}{\partial\Delta r^2}\right)_e \frac{d\langle(\Delta r)^2\rangle^T}{dT} + \left(\frac{\partial^2\sigma}{\partial\Delta r\partial\Delta\alpha}\right)_e \frac{d\langle(\Delta r)(\Delta\alpha)\rangle^T}{dT} + \ldots \qquad (7)$$

For a diatomic molecule, including terms up to the second derivative, the expression becomes

$$\frac{d\langle\sigma\rangle^T}{dT} = \left[-3a_1\left(\frac{\partial\sigma}{\partial\xi}\right)_e + \left(\frac{\partial^2\sigma}{\partial\xi^2}\right)_e\right]\frac{B_e}{2\omega}\frac{d(\coth(hc\omega/2kT))}{dT} \qquad (8)$$

where $\xi = (R - R_e)/R_e$. It has been found that in practically all diatomic molecules a_1 is of the order of -2 to -4.[27] Thus, for the linear terms to be comparable to the quadratic terms, the second derivative $(\partial^2\sigma/\partial\xi^2)_e$ must be 6 to 12 times the magnitude of $(\partial\sigma/\partial\xi)_e$. This is probably not the case, thus we may be able to have reasonable quantitative results with only the linear term.[28] For diatomic molecules, including the quadratic terms does not cause undue complication. It merely adds one parameter ($(\partial^2\sigma/\partial\xi^2)_e$) to be determined by empirically fitting the $\sigma_0(T)$. However, in polyatomic molecules, including the quadratic terms poses a large increase in complexity because the number of distinct second derivatives increases very rapidly with the

TABLE VI: Mean Displacements in Some Small Molecules, Å

	$\langle \Delta r \rangle^{300}$	10^4-($\langle \Delta r \rangle^{400} - \langle \Delta r \rangle^{200}$)	10^4-($\langle \Delta r \rangle_D - \langle \Delta r \rangle_H$)
H_2O	0.0151	5.4	−36.9
D_2O	0.0114	4.9	
H_2S	0.0167	7.0	−40.1
D_2S	0.0127	6.6	
H_2Se	0.0166	7.6	−41.8
D_2Se	0.0125	7.8	
SO_2	0.0045	3.4	
$^{35}ClO_2$	0.0050	5.1	
$^{15}NO_2$	0.0047	3.3	
CH, CH_3F	0.0057	2.1	
CF, CH_3F	0.0060	8.4	
CH_4	0.0170	3.5	
BF_3	0.0097	4.2	

number of atoms, even for fairly small symmetric systems. For example, in CF_4, there are 7 distinct second derivatives to be considered, and in CF_3Cl there are 16. Since there is not sufficient curvature in most observed $\sigma_0(T)$ functions, there is little likelihood of being able to determine the second derivatives even from extremely accurate measurements of $\sigma_0(T)$. Thus, we will limit our discussion to the linear terms. For a bent AX_2 and a pyramidal AX_3 molecule they are

$$\frac{\mathrm{d}\langle \sigma \rangle^T}{\mathrm{d}T} \simeq \left(\frac{\partial \sigma}{\partial \Delta r}\right)_e \frac{\mathrm{d}\langle \Delta r \rangle^T}{\mathrm{d}T} + \left(\frac{\partial \sigma}{\partial \Delta \alpha}\right)_e \frac{\mathrm{d}\langle \Delta \alpha \rangle^T}{\mathrm{d}T} \quad (9)$$

This theory of the temperature dependence of σ_0 is also related to the theory of isotope shifts.[26,29] The same derivatives of σ are involved:

$$\langle \sigma \rangle_{\text{heavy}} - \langle \sigma \rangle_{\text{light}} \simeq \left(\frac{\partial \sigma}{\partial \Delta r}\right)_e [\langle \Delta r \rangle_{\text{heavy}} - \langle \Delta r \rangle_{\text{light}}] + \left(\frac{\partial \sigma}{\partial \Delta \alpha}\right)_e [\langle \Delta \alpha \rangle_{\text{heavy}} - \langle \Delta \alpha \rangle_{\text{light}}] \quad (10)$$

Again, for simplicity, only the linear terms have been considered.

Derivatives of Magnetic Shielding, $\partial\sigma/\partial\Delta r$ and $\partial\sigma/\partial\Delta\alpha$

Empirical determination of the derivative $\partial \sigma/\partial \Delta r$ from eq 9 is possible if there is only one totally symmetric mode (stretching), if the approximate anharmonic force field of the molecule is known,[30] and if the relative precision of the experimental $\sigma_0(T)$ is good. In cases where a totally symmetric angle deformation also exists (as in bent AX_2 and pyramidal AX_3 molecules), there will be two unknown derivatives to determine: $\partial \sigma/\partial \Delta r$ and $\partial \sigma/\partial \Delta \alpha$, so the anharmonic force field has to be more accurately known and the $\sigma_0(T)$ data have to be very precise.

The general behavior of $\langle \Delta r \rangle^T$ appears to be uniform among the various molecules we have previously studied.[12,31,32] It increases with increasing temperature in the temperature range of 200–400 K. This is not surprising. If a Morse of similar potential is used to describe a diatomic molecule, $\langle \Delta r \rangle^T$ will indeed be increasing with increasing temperature.[33] Using triatomic molecules for which reliable anharmonic force fields are available,[34] we have calculated $\langle \Delta r \rangle^T$. The results are shown in Table VI, together with our previous results for BF_3, CH_4, and CH_3F.[12,31] We see that, in general, $\langle \Delta r \rangle^T$ increases with increasing temperature. In some cases, the heavy isotopic species has also been calculated and the difference $\langle \Delta r \rangle^T_{\text{heavy}} - \langle \Delta r \rangle^T_{\text{light}}$ shown in Table VI. We note that $\mathrm{d}\langle \Delta r \rangle^T/\mathrm{d}T > 0$ and also that $(\langle \Delta r \rangle^T_{\text{heavy}} - \langle \Delta r \rangle^T_{\text{light}}) < 0$ uniformly.

TABLE VII: Empirical Derivatives of Magnetic Shielding, ppm/Å

	$(\partial \sigma/\partial \Delta r)_e$
^{19}F in F_2	−4530
^{19}F in ^{35}ClF	−2073
^{19}F in CF_4	−1115[a]
^{19}F in SiF_4	−1170[a]
^{19}F in BF_3	−1115[a]
^{13}C in $^{13}C^{16}O$	−240
^1H in HBr	−400[b]
^1H in $H^{35}Cl$	−78.2

[a] This empirical value is for the sum $(\partial \sigma^{F1}/\partial \Delta r_1)_e + (\partial \sigma^{F1}/\partial \Delta r_2)_e + (\partial \sigma^{F1}/\partial \Delta r_3)_e + \ldots$. However, $(\partial \sigma^{F1}/\partial \Delta r_1)$ will be the dominant contribution. [b] W. T. Raynes and B. P. Chadburn, *J. Magn. Reson.*, 10, 218 (1973); *Mol. Phys.*, 24, 853 (1972).

From eq 9 and the anharmonic force fields available for some molecules[35-38] we have been able to determine $(\partial\sigma/\partial\Delta r)_e$ as an empirical parameter in the fitting of the observed $\sigma_0(T)$ by the calculated temperature dependence of $\langle \Delta r \rangle^T$. These results are summarized in Table VII. It is seen that all these empirical derivatives of shielding are negative. Indeed, if all $\mathrm{d}\langle \Delta r \rangle^T/\mathrm{d}T$ values are the same sign (if the results in Table VII are general in nature for most molecules) and if $\langle \Delta r \rangle^T_{\text{heavy}} - \langle \Delta r \rangle^T_{\text{light}}$ is always less than zero[39] (as may be the case if the results in Table VI are generally applicable), then if most derivatives $\partial \sigma/\partial \Delta r$ are negative, the observed sign of $\mathrm{d}\sigma_0(T)/\mathrm{d}T$ and of the isotope shift would be nearly universally uniform.[40] Although these are found to be true in general, there appear to be some exceptions. $\mathrm{d}\sigma_0/\mathrm{d}T$ for ^{31}P in PH_3 was found to be opposite in sign[11] to all others although the PD_3–PH_3 isotope shift was normal.[41] Unusual isotope shifts have also been reported recently; downfield shifts upon heavy isotopic substitution were found in ^{119}Cd shielding[42] and in ^{199}Hg shielding[43] by ^{13}C substitution in the dimethylcadmium and -mercury compounds.

We have not addressed the question of $\langle \Delta \alpha \rangle^T$ or $(\langle \Delta \alpha \rangle^T_{\text{heavy}} - \langle \Delta \alpha \rangle^T_{\text{light}})$ in bent AX_2 or pyramidal AX_3 molecules. There is not much known about the temperature dependence of $\langle \Delta \alpha \rangle^T$. For a bent AX_2 molecule we would normally expect $\langle \Delta \alpha \rangle$ to increase with temperature. Although we can calculate $\langle \Delta \alpha \rangle^T$ for the AX_2 molecules in Table VI, using the same anharmonic force fields that gave us $\langle \Delta r \rangle^T$, this will not necessarily lead to unequivocal results. The problem is that, even in triatomic molecules, the bending anharmonicities are less well known than the stretching anharmonicities.[44] Since the $\langle \Delta \alpha \rangle^T$ are very strongly dependent on the bending anharmonic force constants,[44] our results would not have the same sound basis as those of $\langle \Delta r \rangle^T$. The same comments can be made about $(\langle \Delta \alpha \rangle_{\text{heavy}} - \langle \Delta \alpha \rangle_{\text{light}})$. It may appear obvious that bending anharmonicity would lead to $\mathrm{d}\langle \Delta \alpha \rangle^T/\mathrm{d}T > 0$ and $(\langle \Delta \alpha \rangle_{\text{heavy}} - \langle \Delta \alpha \rangle_{\text{light}}) < 0$, but this is by no means supported by calculations which use the available anharmonic force fields for bent AX_2 molecules.[34] Although we have calculated $\langle \Delta \alpha \rangle^T$ for the molecules in Table VI, we have chosen not to report them since the results may not be valid for the reasons just stated.[45]

If we assume that $\langle \Delta \alpha \rangle^T$ behaves as normally expected, increasing with temperature, then the unusual $\mathrm{d}\sigma_0/\mathrm{d}T$ observed in PH_3,[10] coupled with the "normal" isotope shift,[41] would indicate that the derivatives $\partial \sigma/\partial \Delta r$ and $\partial \sigma/\partial \Delta \alpha$ are not both negative but are opposite in sign. Using a modified Kuchitsu approximation to the anharmonic force field of PH_3,[46] we found that our PH_3, PD_3

data could be consistent with $\partial \sigma / \partial \Delta\alpha$ less than zero and $\partial \sigma / \partial \Delta r$ greater than zero, with the term in $\partial \sigma / \partial \Delta r$ dominating in $d\sigma_0/dT$ and the term in $\partial \sigma / \partial \Delta\alpha$ dominating the isotope shift.[14] We hoped to clarify the situation with this program of study.

It is with both relief and chagrin that we report $\sigma_0(T)$ of ^{31}P in PF_3, POF_3, and PF_5 to be normal. Our previous results in obtaining empirical $\partial \sigma / \partial \Delta r$ and $\partial \sigma / \partial \Delta\alpha$ for ^{31}P in PH_3 were not unequivocal due to the defects of the model used by Kuchitsu in the anharmonic force fields for PH_3 and PD_3. Now that our new results for PF_3, POF_3, and PF_5 show a normal $d\sigma_0/dT$ for all three ^{31}P environments, we are left with the task of explaining why PH_3 behaves exceptionally whereas the others are "normal". The precision of our ^{31}P $\sigma_0(T)$ data shown in Figure 4 do not warrant a two-parameter fit, so we will be unable to extract both $\partial \sigma / \partial \Delta r$ and $\partial \sigma / \partial \Delta\alpha$ even with very good anharmonic force fields for these molecules, which incidentally are not yet available.[47] In the light of these new results, it is even more important to carry out the ^{15}N studies in the NH_3, ND_3, and NF_3 molecules. Apparently, ^{31}P $\sigma_0(T)$ values are not typically different from those of the other nuclei shown in Figure 2. So far, only PH_3 appears to be exceptional. Since the experimental results on ^{31}P $\sigma_0(T)$ offer no answer to this dilemma, let us look at the theoretical determination of the derivatives of σ.

The derivative $\partial \sigma / \partial \Delta\alpha$ for ^{31}P in PZ_3 molecules has been investigated by Letcher and Van Wazer.[48] Here, the average energy approximation was used and the σ and π contributions to the paramagnetic term were calculated as ζ_i:

$$\sigma^{p} \simeq -\frac{2e^2h^2}{3\Delta E m^2 c^2}(\langle r^{-3}\rangle_{p}\zeta_1 + \langle r^{-3}\rangle_{d}\zeta_2) \qquad (11)$$

Ignoring the π contributions, the angular dependence of σ^{p} would be entirely that due to the angular dependence of ζ_1. Their results for the latter are reproduced in Figure 5. In this approximation, $\partial \sigma / \partial \Delta\alpha$ is approximately directly proportional to $-\partial \zeta_1 / \partial \alpha$. Figure 5 shows that for Z = H and F, $\partial \zeta_1 / \partial \alpha > 0$, being much larger for PF_3 than PH_3. This leads to $\partial \sigma / \partial \Delta\alpha < 0$ for both PH_3 and PF_3, with $|\partial \sigma / \partial \Delta\alpha|_{PF_3} > |\partial \sigma / \partial \Delta\alpha|_{PH_3}$. If this is the case, then the bond angle deformation term in eq 9 could be more dominant in PF_3 than in PH_3, consistent with a normal $d\sigma_0/dT$ in PF_3. However, it is not possible to make quantitative arguments until theoretical studies of $\partial \sigma / \partial \Delta r$ for ^{31}P in PZ_3 molecules become available.[49] Unfortunately, this requires a more sophisticated calculation than does the determination of $\partial \sigma / \partial \Delta\alpha$. Unlike the latter, there is no simple approximation which can be used for the dependence of ^{31}P σ on bond distance. Calculations at the level of the coupled Hartree–Fock method are not yet available for ^{31}P, although a recent application of the pseudopotential method to PH_3 shows some promise.[50] A detailed theoretical study of $\partial \sigma / \partial \Delta r$ even for lighter molecules at the level of the coupled Hartree–Fock method would be very useful. There are a few examples already in the literature,[49] and a series of theoretical studies is currently under way, with the $\partial \sigma / \partial \Delta r$ for ^{1}H and ^{19}F in HF as a test case.[51]

Conclusions

We have determined the effects of intermolecular interaction and intramolecular dynamics on the ^{19}F and ^{31}P shielding in the molecules NF_3, PF_3, POF_3, and PF_5. The ^{19}F results show that the effects of intermolecular interactions are of the same magnitude as those previously measured, and the effect of intramolecular dynamics (anharmonic vibration and centrifugal distortion) is not unusual and fits very well with our previous data on ^{19}F. The ^{31}P results given here are the only ^{31}P gas phase NMR results currently available, other than the PH_3/PD_3 system which we reported earlier. The ^{31}P shielding in PF_3, POF_3, and PF_5 do not show any unusual shifts which may be attributed to inversion in PF_3 or pseudorotation in PF_5. The intermolecular effects are not as large in P_4 or PH_3, especially for the centrally located ^{31}P in POF_3 and PF_5. The ^{31}P $\sigma_0(T)$ behavior in PF_3, POF_3, and PF_5 is normal, that is, a decrease in shielding with increasing temperature. Thus, only the PH_3/PD_3 system appears anomalous in this respect. We expect to complete this program of study by observing the temperature and density dependence of ^{15}N in gaseous NF_3, NH_3, and ND_3. Already, tentative results for ^{15}N in NH_3 indicate a behavior similar to ^{31}P in PH_3. However, very careful experimental ^{15}N results in these molecules are necessary in order that the shielding of the apical nuclei in molecules of the pyramidal AX_3 type can be understood.

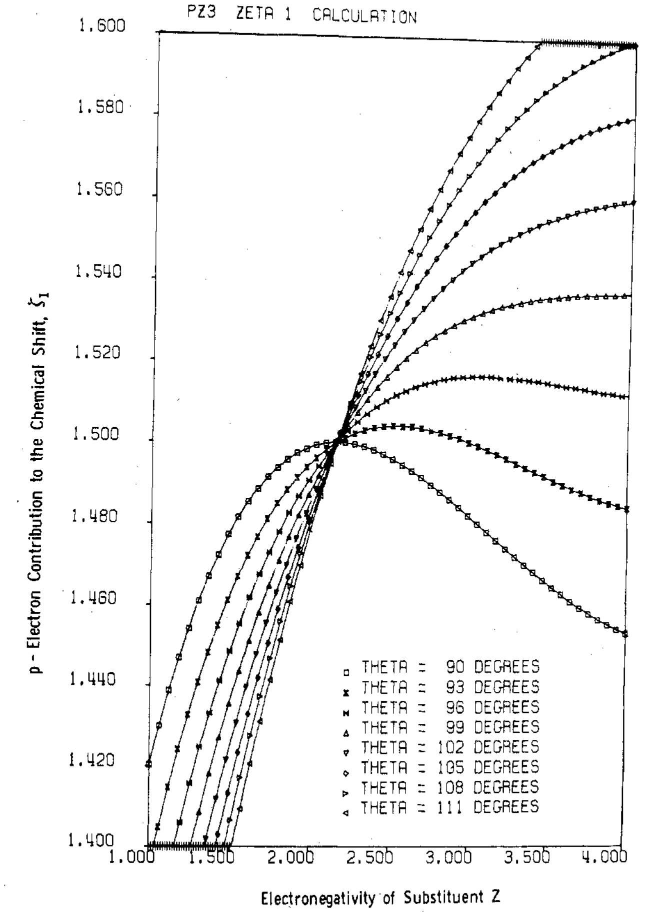

Figure 5. Angular dependence of the σ contribution (ζ_1 defined in the text) to the ^{31}P chemical shielding in PZ_3 molecules. This figure is reproduced with kind permission from J. R. Van Wazer, from J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966). Copyright 1966 American Institute of Physics.

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Electron Spin–Echo Modulation Studies of Silver Atom Solvation in Methanol. Geometrical Model for the Methanol Solvation Shell

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Electron spin echo modulation studies have been carried out for Ag^0 in CD_3OH and CH_3OD at 4.2 K. The data have been analyzed by using ratio analysis and complete simulation. The results indicate that Ag^0 is surrounded by four methanol molecules with their oxygen ends pointing toward Ag^0. The average distance between the silver atom and both the hydroxyl and methyl protons is about 3.3 Å. There is no observable geometrical change in the solvation shell around Ag^0 on warming the sample to 77 K in contrast with the ice matrix. This is consistent with weaker hydrogen bonding interactions in methanol than in water.

Introduction

Recent magnetic resonance studies[1-4] of the molecular environment of Ag^0 in ice have yielded a fascinating picture of solvation. It was found that when Ag^0 is initially formed at 4.2 K by reaction of Ag^+ with electrons it is surrounded by four water molecules with their oxygens pointing toward Ag^0. However, brief warming of the sample to 77 K induces an environmental change toward equilibrium, or solvation, involving the rotation of a single water molecule about its OH bond. The driving force for this solvation probably involves a hydrogen bonding interaction.

To contrast Ag^0 interactions in ice, we here investigate the molecular environment of Ag^0 in methanol matrices in which the hydrogen bonding interactions may be