^{19}F NMR chemical shifts due to intermolecular interactions in $F_2C=CFX$. A quantitative measure of the nuclear site effect

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In $CF_2=CFX$ (X = H, Cl, Br, I) there are three probe nuclei for studying the magnitudes of intermolecular effects on nuclear shielding. The values of $\sigma_1 = \lim_{\rho\to 0}(\partial\sigma/\partial\rho)_T$, the change in the nuclear shielding due to interactions between pairs of molecules, have been obtained from the resonance frequencies in medium to low density gas samples. The nuclear site effect gives the most exposed one of the three probe nuclei the largest magnitude of σ_1, i.e., the F *trans* to X = Cl, Br, I or the F *cis* to X = H. The gas-to-liquid shifts show exactly the same ordering as the σ_1 in the dilute gas. A model is described which relates a calculated site factor to the observed σ_1 values. With this model, the observed density dependence of the NMR isotope shift in D_2/HD is calculated. This model provides a mechanism for nonspecific solvent effects on the NMR isotope shift.

INTRODUCTION

The nuclear magnetic shielding σ of a nucleus in a molecule in a dilute gas of density ρ can be written in the form of a virial expansion

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

$\sigma_0(T)$ is the rovibrationally averaged shielding at any temperature in the limit of zero density. The leading term in the shielding due to intermolecular interactions $\sigma_1(T)\rho$ can be interpreted in terms of a binary collision statistical mechanical model proposed by Raynes, Buckingham, and Bernstein:[1]

$$\sigma_1 = \sigma_{1b} + \sigma_{1W} + \sigma_{1a} + \sigma_{1E}. \quad (2)$$

Here σ_{1b} is due to nonvanishing volume susceptibility effects in a nonspherical sample, which is easily calculated from the molecular magnetic susceptibility, σ_{1W} is the dispersion contribution to shielding from van der Waals interactions, σ_{1a} is due to magnetic anisotropy effects, and σ_{1E} the shielding effects arising from that part of the intermolecular interaction which is due to permanent electrical moments of the molecules.

A corollary to this model was added by Rummens and Bernstein[2] to explain the empirical observation that nuclei on the periphery of a molecule have larger values of σ_1 than nuclei which are less exposed. An analogous site factor was also introduced into the reaction field model for gas-to-liquid shifts[3] and this was used to explain the differences in ^1H gas-to-liquid shifts in $M(CH_3)_4$, M = C, Si, Ge, Sn, Pb. In this series, the gas-to-liquid shifts at 30 °C were 0.217, 0.228, 0.260, 0.296, and 0.358 ppm, respectively, in the usual direction, the liquid being less shielded. The conclusion that the differences in gas-to-liquid shifts in these systems can be attributed to differences in site factors is not unequivocal because the quantities which go into the model (polarizability α, ionization energy I, intermolecular potential parameters r_0 and ϵ, and the model parameter B) all vary in the systems which are being compared, and are estimated with some margin of error.

In our gas phase studies of intermolecular effects on nuclear magnetic shielding, we have found some differences in σ_1 which could partly be attributed to the nuclear site effect, such as the trends in σ_1 for ^{19}F in the series CF_3X (X = H, F, Cl, Br, I)[4] or in CF_4 compared to CF_3CF_3,[5] or in σ_1 for ^{31}P in PF_3 compared to PF_5.[6] We have also noted that the σ_1 of central nuclei have very small magnitudes, as ^{13}C in CH_4, the middle ^{15}N in NNO, ^{13}C in CO_2, etc.[7] While there may be site effects in these cases just as in the $M(CH_3)_4$ gas-to-liquid shifts, a quantitative determination of the site effect is difficult in these systems since the factors which enter into σ_1 are different for the systems being compared. In the case of NNO, the comparison is more meaningful, the shielding of the two ^{15}N nuclei due to interaction between a given pair of molecules can be compared for the same intermolecular potential. The two nitrogens in NNO do indeed show consistently large differences in σ_1 values between the end and central N in NNO interacting with NNO, CF_4, SiF_4, and Xe.[7] However, even in this case, the site effect cannot be established because the very different electronic sites of the two nitrogen nuclei makes dubious the assumption of a common B. One N has a lone pair, whereas the other is bonded to two different atoms. There are sometimes unusually large intermolecular effects on nuclei associated with the lone pair ($n\rightarrow\pi^*$) excitations. This can not be ruled out as the possible reason for the larger σ_1 of the end N. Quantitative comparison in this system is also difficult in practice because a large fraction of the measured σ_1 for the central N is from bulk susceptibility effects.

In this work, we compare three nuclei in the same molecule so that all the parameters of the model remain the same, except for the site factor (and possibly B). In this study of ^{19}F

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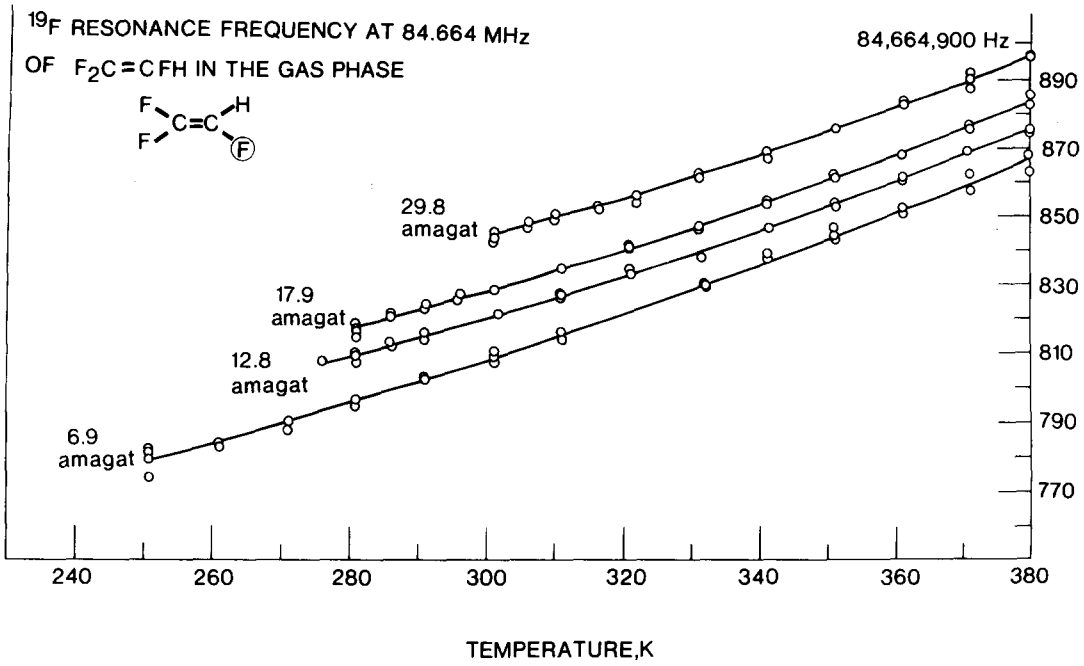

FIG. 1. Typical raw data showing the temperature dependence of the resonance frequency of one of the F nuclei in $CF_2=CFH$ in samples of various densities.

in $CF_2=CFX$ (X = H, Cl, Br, I) we have chosen nuclei with fairly sizable $(\sigma_1-\sigma_{1b})$ values, all attached to the same type of carbon so that the assumption of a constant B parameter in the RBB model is a logical one. We study three different sites on the same interacting pair of molecules so that σ_1 is an average over the same intermolecular potential. We study four sets of such systems in which the effect can be systematically compared. Furthermore, each of the three F nuclei in the substituted fluoroethylenes can be compared to $CF_2=CF_2$, a limiting case in which all fluorines are equivalent.

EXPERIMENTAL RESULTS

^{19}F FTNMR spectra were taken with a Bruker spectrometer operating at 21.15 kG with a Nicolet data acquisition system. Regulation of the temperature (with a precision of $\pm$ 0.2 deg) of the spinning 5 mm sample assembly (sealed gas sample with lock substance in the annular region) was provided by a previously calibrated Bruker BST 100/700 variable temperature unit. The CD_3 signal of toluene-d_8 provided field stabilization. ^{19}F spectra were acquired in 2 K data points, zero filling to 8 K. Gases were obtained from PCR Chemicals. The resonance frequencies were measured in pure gas samples of known density in the range 1–20 amagat, except for $CF_2=CFBr$ which had some $CF_2=CFCl$ as an impurity. Typical data are shown in Fig. 1 for one of the F nuclei in $CF_2=CFH$. For ^{19}F in gas samples, resonance frequencies typically increase with increasing temperature and increasing density, as shown in Fig. 1, since σ_1 is negative and σ_0 decreases with increasing temperature. In Fig. 1, the temperature dependence of σ_1 is apparent in the raw data. The frequency separations between samples increase with decreasing temperature. Only for $CF_2=CFH$ of this series was this observed. For the others (X = Cl, Br, I), the experimental curves are strictly parallel.

We have determined the values $\sigma_1=\lim_{\rho\to 0}-(\partial\nu/\partial\rho)_T/\nu_0=(\partial\sigma/\partial\rho)_T$, a measure of the change in nuclear magnetic shielding due to interactions between pairs of molecules. The signs of σ_1 and the temperature dependence of $CF_2=CFH$ are all usual; deshielding with increasing density, more pronounced at lower temperature. The results are shown in Table I. Because of the presence of some $CF_2=CFCl$ in the $CF_2=CFBr$ samples, the σ_1 values given in Table I for $CF_2=CFBr$ are for an average buffer molecule. They are somewhat lower than they would be for $CF_2=CFBr$ interacting with $CF_2=CFBr$ alone. These σ_1 values are corrected for the bulk susceptibility contribution $\sigma_{1b}=-2\pi\chi/3$ which is the same for all nuclei in the same molecule. The labels A, B, C are shown in the figures.

Although the differences between $\sigma_1(F_A)$, $\sigma_1(F_B)$, and $\sigma_1(F_C)$ in the same molecule are of the same order of magnitude as the errors in the absolute σ_1 values in some cases, these differences are nevertheless real. The variation of the internal chemical shifts with density gives the differences $\Delta\sigma_1$ directly, and these were found to agree with Table I. This is consistent with our previous experience that the errors in density measurement are largely responsible for the standard deviations in the absolute σ_1 values.

We have also measured gas-to-liquid shifts $(\sigma_{LIQ}-\sigma_{VAP})(T)$ by observing liquid and vapor signals simultaneously in the same spectrum. In this difference, the intrinsic temperature dependence of the shielding due to rovibrational averaging substracts out, leaving only the intermolecular effects. We note that the gas-to-liquid shifts, shown in Fig. 2 and described by quadratic functions in Table II, show the same trends as the σ_1. The F_A, F_B, and F_C nuclei in the same molecule show differences in the gas-to-liquid shifts which are magnified versions of the differences in the values of σ_1.

A MODEL

The order of the magnitudes of σ_1 are $F_A>F_B>F_C$ for X heavier than F and a different order for X = H (lighter than F): $F_B\gtrsim F_C>F_A$, indicates a nuclear site effect. The intermolecular force between a pair of freely rotating mole-

TABLE I. The change in ^{19}F nuclear shielding due to intermolecular interactions, $\sigma_1 = \lim_{\rho\to 0}(\partial\sigma/\partial\rho)_T$, for $F_2C=CFX$, in ppb amagat^{-1}. The measured quantities corrected for bulk susceptibility ($\sigma_1 - \sigma_{1b}$) are shown in parentheses.[a]

X	T,K	F_A[b]	F_B	F_C
F	270–380	$-17.8 \pm 2.0 + 5.25\times10^{-2}(T-300)$ (-14.8)		
Cl	320–380	-26.7 ± 1.8 (-22.7)	-25.1 ± 1.6 (-21.1)	-24.8 ± 1.6 (-20.8)
Br[c]	340–380	-31.4 ± 2.3 (-26.9)	-26.8 ± 1.7 (-22.3)	-26.7 ± 4.0 (-22.2)
I	370–380	-61.8 ± 5.0 (-55.6)	-51.2 ± 5.3 (-45.0)	-49.7 ± 6.1 (-43.5)
H	300–380	$-11.8 \pm 0.9 + 3.5\times10^{-2}(T-300)$ (-9.2)	$-19.0 \pm 1.2 + 3.8\times10^{-2}(T-300)$ (-16.4)	$-18.9 \pm 0.9 + 5.5\times10^{-2}(T-300)$ (-16.3)

[a] $\sigma_{1b} = -2\pi\chi/3$, where χ are molecular magnetic susceptibilities estimated with Pascal's constants: -28.3, -42.4, -51.9, -65.9×10^{-6} emu mol^{-1}, respectively, for $CF_2=CFH$, Cl, Br, I. For $CF_2=CFBr$ in the mixture, the average buffer χ was used.
[b] See Figs. 2 and 3 for labeling of F nuclei.
[c] Since our $CF_2=CFBr$ samples had some $CF_2=CFCl$ impurity, these values of σ_1 and ($\sigma_1 - \sigma_{1b}$) are for an average perturber.

cules depends on the separation R between their center of masses (neglecting anisotropy), but the local effects on nucleus F depends on the separation r between the nucleus and the center of the collision partner. When the ensemble average is carried out over all orientations and distances, a nucleus which is further from the center of mass samples somewhat shorter interaction distances than one which is closer to the center of mass in the same molecule. Our results on the substituted fluoroethylenes are completely consistent with this model.

In the model of Raynes, Buckingham, and Bernstein, the van der Waals contribution to σ_1 is given by[1]

$$\sigma_{1W} = -3B\alpha_2 I_2\langle R^{-6}\rangle, \tag{3}$$

where B is a constant which in this case is characteristic of the F nuleus in a C–F bond, and is of the order of 24×10^{-18} esu.[2] The average is taken over all configurations of the buffer molecule, with an interaction potential $V(R,\theta,\phi)$. Nuclei located on the periphery of the molecule rather than at its center experience perturbing fields which depend on the instantaneous distance r of the observed nucleus from the center of the perturbing solvent molecule. Thus, the R^{-6} in the RBB model should be replaced by r^{-6}. If $q = d/R$, where d is the distance of the observed nucleus from the center of mass of the molecule, then it can be shown that averaging over all rotational orientations leads to[2]

$$\langle r^{-6}\rangle = \langle R^{-6}(1+q^2)/(1-q^2)^4\rangle. \tag{4}$$

When incorporated into the RBB binary collision model for σ_1, the site effect can be taken into account by a multiplicative factor (the site factor s)[3]:

$$s = 1 + 3.45q_0^2 + 7.42q_0^4 + 12.9q_0^6 + 19q_0^8 + \cdots, \tag{5}$$

where $q_0 = d/r_0$, r_0 being the characteristic distance parameter of the potential, as in $V_{LJ} = -4\epsilon[(r_0/R)^6 - (r_0/R)^{12}]$. According to this model, then, the three nuclear probes in the molecule will exhibit σ_1 values which are related to each other in the same manner as the site factors, e.g.,

$$\frac{\sigma_1(F_A)-\sigma_{1b}}{\sigma_1(F_C)-\sigma_{1b}} \cong \frac{\sigma_{1W}(F_A)}{\sigma_{1W}(F_C)} = \frac{s_A}{s_C}. \tag{6}$$

This relationship between σ_1 values and s values is based on having a constant parameter B for C–F bond in the RBB model. It may be expected that the different electronic environments of the F_A, F_B, and F_C nuclei described by shielding values which range over 100 ppm might require different B parameters in Eq. (3). Therefore, we expect Eq. (6) to hold only semiquantitatively.

Values of d (shown in Table III) were obtained from structural data derived from microwave spectroscopy or electron diffraction.[8] Values of r_0 were estimated from the critical volumes[9] using the empirical relationship of Stiel and Thodos[10] $r_0/\text{Å} = 0.785\,(V_c/\text{cm}^3)^{1/3}$. The site factors calculated using Eq. (5) for the three F nuclei are shown in Table III. Upon comparison of Table III with Table I, we note a

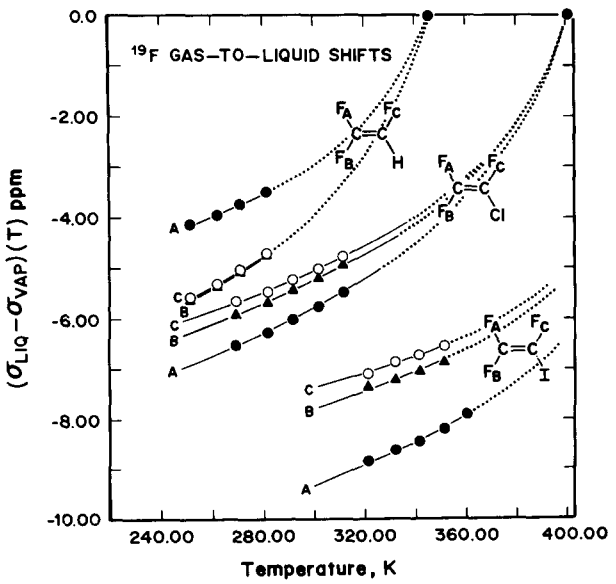

FIG. 2. The measured gas-to-liquid shifts, $(\sigma_{LIQ} - \sigma_{VAP})(T)$, shown above are represented by quadratic functions of T in Table II. They are expected to approach zero at the critical temperature.

TABLE II. The ^{19}F gas-to-liquid shifts, $(\sigma_{LIQ} - \sigma_{VAP})(T)$, for $F_2C = CFX$, in ppm. These values have not been corrected for the bulk susceptibility contribution, $-(2\pi/3)\chi(\rho_{LIQ} - \rho_{VAP})(T)$, which is the same for all three nuclei in the molecule.

X	T,K	F_A	F_B	F_C
Cl	245–310	-5.798 $+2.66\times10^{-2}(T-300)$ $+7.0\times10^{-5}(T-300)^2$	-5.242 $+2.41\times10^{-2}(T-300)$ $+6.0\times10^{-5}(T-300)^2$	-5.052 $+2.28\times10^{-2}(T-300)$ $+7.0\times10^{-5}(T-300)^2$
I	300–350	-8.693 $+2.31\times10^{-2}(T-300)$ $+5.0\times10^{-5}(T-330)^2$	-7.258 $+1.92\times10^{-2}(T-330)$ $+4.2\times10^{-5}(T-330)^2$	-6.929 $+1.66\times10^{-2}(T-330)$ $+6.6\times10^{-5}(T-330)^2$
H	250–280	-3.546 $+2.37\times10^{-2}(T-280)$ $+8.0\times10^{-5}(T-280)^2$	-4.791 $+3.45\times10^{-2}(T-280)$ $+1.8\times10^{-4}(T-280)^2$	-4.770 $+3.4\times10^{-2}(T-280)$ $+1.8\times10^{-4}(T-280)^2$

clear correlation between σ_1 and the site factors for the three F nuclei in a given molecule. The plots of these respective quantities in Fig. 3 are consistent with the model. However, the value of B is evidently not a constant, otherwise all the curves should be straight lines with slopes $B\alpha I\langle R^{-6}\rangle$. The three F nuclei in $CF_2 = CFI$, Cl do show straight line plots of σ_1 with s in Fig. 3, but $CF_2 = CFH$, Br do not. Another reason for inadequacy of Eq. (6) is the neglect of the other contributions to σ_1. In all the molecules except for $CF_2 = CF_2$, there are electrical contributions, σ_{1E}. All have magnetic anisotropy contributions due to the planar structure of the ethylene-derived molecules and the anisotropy of their molecular magnetic susceptibility. These contributions will also have site factors associated with them. For σ_{1E} the form of the site factor for a nonpolar molecule interacting with a dipolar one is the same as Eq. (5) since both depend on r^{-6} in the RBB model. For interacting dipolar molecules σ_{1E} has an r^{-9} dependence. σ_{1a} depends on the anisotropy of the magnetic susceptibility of the collision partner and also has an r^{-9} dependence. By its nature, the averaging over all orientations of the pair of molecules that gives rise to σ_{1a} has to be done in an anisotropic intermolecular potential. It is very likely that σ_{1a} contributes significantly in these $CF_2 = CFX$ collision pairs. The anisotropy of the magnetic susceptibility in each of these molecules is expected to be greater than in ethylene, for which the components are χ_{xx} ($\perp$ to the plane of the molecule) $= -30.16$, $\chi_{yy} = -23.47$, and χ_{zz} (along the C = C bond) $= -21.36\times10^{-6}$ emu-mol^{-1}.[11] With the high orbital angular momentum contributions to the anisotropy in χ coming from Cl, Br, and I atoms, the intramolecular magnetic anisotropy term should be considerably greater.

DENSITY DEPENDENCE OF THE ISOTOPE SHIFT

In order to eliminate any ambiguity due to (a) possibly different values of B for different electronic environments of compared nuclei, and (b) contributions of electrical and mag-

TABLE III. Average distance d/Å of the ^{19}F nuclei from the center of mass of the molecule $CF_2 = CFX$. Site factors s are shown in parentheses.[a]

X	F_A	F_B	F_C
F[b]	1.77 (1.83)		
Cl[b]	2.13 (2.18)	1.85 (1.78)	1.78 (1.69)
Br[c]	2.72 (3.46)	2.13 (2.08)	1.89 (1.77)
I[c]	3.15 (4.69)	2.38 (2.33)	2.11 (1.91)
H[b]	1.37 (1.44)	1.73 (1.82)	1.89 (2.07)

[a] Site factors were calculated according to Eq. (5) using the following r_0 values: 4.29, 4.39, 4.69, 4.82, and 5.04 Å for X = H, F, Cl, Br, and I, respectively. These were estimated from critical volumes 163.1, 174.4, 213.0, 232.1 and 264.7 cm^3 respectively, as described in the text.

[b] Coordinates of the F nuclei were calculated using bond angles and bond lengths derived from the microwave spectra. [J. L. Carlos, R. R. Karl, and S. H. Bauer, J. Chem. Soc. Faraday Trans 2, **70**, 177 (1974); R. G. Stone and W. H. Flygare, J. Mol. Spectrosc. **32**, 233 (1969); A. Bhaumik, W. V. F. Brooks, and S. C. Dass, J. Mol. Struct. **16**, 29 (1973).]

[c] The following average bond lengths and angles were used: r(C–F) = 1.33, $r(C=C) = 1.312$, r(C–Br) = 1.891, r(C–I) = 2.092 Å, $\langle C=C-F = 123.8°$. [*Tables of Interatomic Distances and Configurations in Molecules and Ions* (The Chemical Society, London, 1958), Suppl. 1965.]

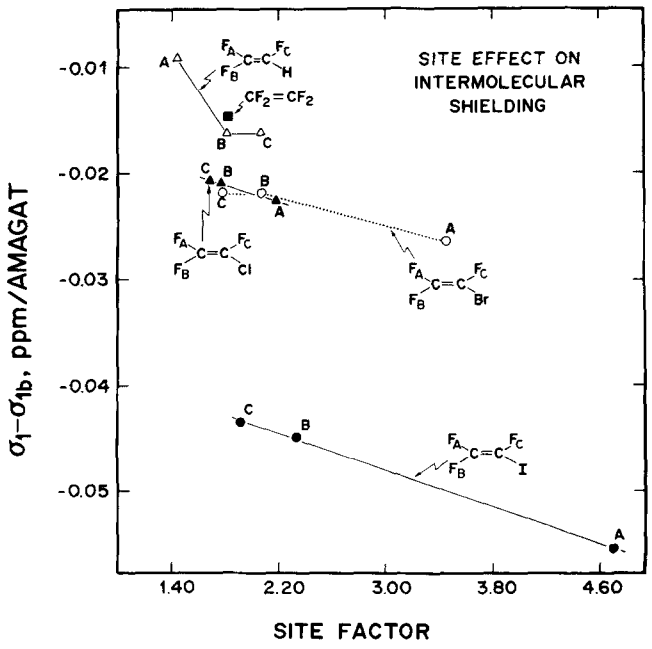

FIG. 3. Correlation between observed $(\sigma_1 - \sigma_{1b})$ and the site factors calculated with Eq. (5) for the three F nuclei in various $CF_2 = CFX$ molecules. For $CF_2 = CFBr$ interacting with an average buffer the site factors are only slightly different than for pure $CF_2 = CFBr$.

netic anisotropy terms, the true test of a nuclear site effect would be in isotopically related molecules of high symmetry. The ideal case is that of the ^{1}H σ_1 in the isotopomers CH_nD_{4-n}. We have calculated the site factors for these molecules. Let us assume that σ_1 has been corrected for the bulk susceptibility effects. The differences in σ_1 due to the site factors for the proton is

$$\delta\sigma_1 = \sigma_1(CH_4)(s' - s)/s, \tag{7}$$

where s is the site factor for CH_4 and s' for any one of the CH_nD_{4-n} (other than CD_4). Using the measured ^{1}H σ_1 for CH_4 interacting with CH_4, -3.4×10^{-4} ppm/amagat,[12] we get

$$\begin{aligned}&\sigma_1(CH_3D) - \sigma_1(CH_4)\\ &\quad = -1.5\times10^{-5}\ \text{ppm amagat}^{-1},\\ &\sigma_1(CH_2D_2) - \sigma_1(CH_4) = -2.9\times10^{-5},\\ &\sigma_1(CHD_3) - \sigma_1(CH_4) = -4.0\times10^{-5}.\end{aligned} \tag{8}$$

These differences are just large enough to be measured from the ^{1}H chemical shifts between isotopomers in the vapor phase (very low density) and the chemical shifts between isotopomers in the liquid phase (density of several hundred amagat) at the same temperature in a mixture of the isotopic species. Note that $\delta\sigma_1$ gives the density dependence of the isotope shift.

An interesting application of the nuclear site effect is to the previously unexplained density dependence of the NMR isotope shift in hydrogen gas. Beckett and Carr measured the isotope shift $\sigma(D_2) - \sigma(HD)$ in gas and liquid samples (10, 18, 808, and 840 amagat) of HD with a small amount of D_2 at nearly the same temperature (23 K).[13] They find that

$$\sigma(D_2) - \sigma(HD) = a + b\rho. \tag{9}$$

This observation can be explained as follows:

$$\begin{aligned}&\sigma^{HD}(T,\rho) = \sigma_0^{HD} + \sigma_1^{HD}(T)\rho + \cdots,\\ &\sigma^{D_2}(T,\rho) = \sigma_0^{D_2} + \sigma_1^{D_2}(T)\rho + \cdots.\end{aligned} \tag{10}$$

$(\sigma_0^{D_2} - \sigma_0^{HD}) = a$, is the isotope shift at 23 K in the zero-density limit, and $(\sigma_1^{D_2} - \sigma_1^{HD}) = b = -(0.059 \pm 0.026)\times10^{-4}$ ppm amagat^{-1}. The result $\sigma_1^{D_2} < \sigma_1^{HD}$ means $|\sigma_1^{D_2}| > |\sigma_1^{HD}|$, since all σ_1 are known to be negative. The greater magnitude of the σ_1 in D_2 is due to the more exposed deuterium nuclei in D_2 ($r_e/2$ from the center of mass) compared to HD (the D is $r_e/3$ from the center of mass). Thus, the nuclear site effect gives rise to the observed density dependence in the isotope shift. One should also find that the σ_1 for the proton is in the order $|\sigma_1^{HD}| > |\sigma_1^{H_2}|$, for the same reason. There is a reported value for σ_1 for H_2 gas, 11.0 ppm mol^{-1} cm^3,[14] from which we calculate $(\sigma_1 - \sigma_{1b}) = 1.34\times10^{-4}$ ppm amagat^{-1}. The site factors for D_2 and HD can be calculated using the Lennard-Jones $r_0 = r_m(1/2)^{1/6}$ and $r_m = 3.0$ Å from spectroscopic measurements in $(H_2)_2$.[15] We obtain $s_{D_2} = 1.0692$ and $s_{HD} = 1.0301$ from which we calculate $\sigma_1^{D_2} - \sigma_1^{HD} = (s_{D_2} - s_{HD})/s_{D_2}\cdot(\sigma_1 - \sigma_{1b}) = -0.049\times10^{-4}$ ppm-amagat^{-1} which compares favorably with Beckett and Carr's $-(0.059 \pm 0.026)\times10^{-4}$. Thus the site factor provides a mechanism for a nonspecific solvent effects on the isotope shift. The ratio $(\sigma_1^* - \sigma_1)/\sigma_1$ where σ_1 and σ_1^* refer to two isotopomers should be entirely in terms of site factors which can be estimated for any solute–solvent pair. Since differences in site factors are small for most isotopic substitution, the solvent effects on isotope shifts in NMR are expected to be generally small (and in any case can be easily estimated) except when specific interactions such as hydrogen bonding are involved.

CONCLUSIONS

The nuclear site effect appears to be real. Although the site factors may not be the same for all contributions to σ_1, they are in the same relative order for the nuclei being compared. This model predicts a density dependence of the isotope shift which will normally be too small to observe. In the D_2/HD system, the calculated density dependence agrees with the observation of Beckett and Carr.

That the differences in the gas-to-liquid shifts parallel the differences in σ_1 values of the F_A, F_B, F_C nuclei in $CF_2=CFX$ for all X clearly shows that equivalent effects are operating in the dilute gas and in the liquid. If the site effect explanation of the differences in the gas is valid, then similar site factors should apply to shielding in the liquid. It is not necessary to propose mechanisms in the liquid phase which are fundamentally different from those which are believed to operate in the dilute gas phase.[16]

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