Chemical Shift Scales on an Absolute Basis

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1 INTRODUCTION

Nuclear magnetic shielding is a second-order molecular electronic property which provides a severe test of the accuracy of molecular quantum mechanical calculations. While electric dipole polarizability and hyperpolarizabilities provide tests of the wavefunction at the outer regions, nuclear shielding is very sensitive, especially to contributions from high angular momentum functions, in the regions close to a particular nucleus. Precise measurements of differences in shielding are easy to carry out. In most NMR studies the resonance frequencies are measured and a chemical shift is defined as $\delta = (\nu_i - \nu_{\text{ref}})/\nu_{\text{ref}}$. From the relationship between the resonance frequency ν_i, the external magnetic field $\boldsymbol{B}_0$, the magnetogyric ratio γ, and the nuclear shielding σ_i, i.e. $\nu_i = (\gamma/2\pi)(1 - \sigma_i) B_0$, we can write the chemical shifts in terms of the nuclear shielding as $\delta = (\sigma_{\text{ref}} - \sigma_i)/(1 - \sigma_{\text{ref}})$.

Reasonably accurate calculations are now available for nuclei in the first row of the Periodic Table in molecules with a small number of first row atoms and for hydrides of the second row, as may be seen in the articles on IGLO, LORG and SOLO and GIAO shielding calculations described by Kutzelnigg, Hansen and Pulay in this Encyclopedia (***Shielding Calculations: LORG and SOLO Approaches***, ***Shielding Calculations: IGLO Method***, ***Shielding Theory: GIAO Method***). In making a comparison of theoretical ab initio values at the equilibrium molecular geometries with experimental chemical shifts, it is necessary to have absolute quantities (absolute shielding values) to compare with rather than shielding differences or chemical shift values. Accurate chemical shift measurements can be carried out by simultaneous measurement of two frequencies in the same physical sample in the field. If we know the absolute shielding value corresponding to the first frequency, then the accurate chemical shift between the two provides the absolute shielding of the second, or indeed of any number of systems whose chemical shifts can be related to the absolute shielding of any one system. But how do we establish the absolute shielding value of the very first one?

2 ABSOLUTE SHIELDING SCALES BASED ON THE PROTON IN LIQUID WATER

The absolute proton shielding in a spherical sample of pure liquid H_2O at 34.7 °C, $\sigma = 25.790 \pm 0.014$ ppm, has been established by two experiments. The first was a simultaneous measurement of the frequencies of an electronic transition and a nuclear magnetic transition in atomic hydrogen. The second was a simultaneous measurement of NMR frequencies of protons in a spherical sample of liquid water at 34.7 °C and in a spherical bulb filled with atomic hydrogen in the same magnetic field. The first experiment established the g-factor of the bare proton; the second experiment allows the determination of the absolute nuclear magnetic shielding of protons in liquid water.[1,2]

One standard technique for establishing an absolute shielding scale for a nucleus M is by combining the results of two experiments. The first is an atomic beam magnetic resonance experiment or an optical pumping experiment which measures the ratio of γ for the M nucleus to γ for the electron in the free M atom. Since the (electron) γ can be calculated from the known electron magnetic moment and electronic g-value of the atomic state, the value of γ(M, free atom) may be obtained precisely. The second is an NMR experiment which measures the ratio of the Larmor frequencies of M and ^{1}H in an infinitely dilute $\text{M}_{(\text{aq})}{}^{n+}$ ion in aqueous solution. This provides the ratio $\gamma(^1\text{H}, \text{H}_2\text{O}, \text{liq.})/\gamma(\text{M}, \text{M}_{(\text{aq})}{}^{n+})$. The key here is that $\gamma(^1\text{H}, \text{H}_2\text{O}, \text{liq.})$ is known precisely for pure liquid water from experiments and is assumed to be the same in the infinitely dilute aqueous solution of $\text{M}_{(\text{aq})}{}^{n+}$ ion, so $\gamma(\text{M}, \text{M}_{(\text{aq})}{}^{n+})$ can be obtained. Then, from the definition of the nuclear magnetic shielding σ relative to the bare nucleus, $\gamma = (1 - \sigma)\gamma_0$, where γ_0 is the magnetogyric ratio of the bare nucleus,

$$\frac{\sigma(\text{M, free atom}) - \sigma(\text{M}, \text{M}_{\text{aq}}{}^{n+})}{1 - \sigma(\text{M}, \text{M}_{\text{q}}{}^{n+})} = 1 - \frac{\gamma(\text{M, free atom})}{\gamma(\text{M}, \text{M}_{\text{aq}}{}^{n+})} \tag{1}$$

Since σ(M, free atom) is theoretically known[3] the absolute shielding of M in the aqueous solution of $\text{M}_{(\text{aq})}{}^{n+}$ is thereby established.

This method is applicable when the aqueous solution of the metal ion is a convenient reference and extrapolation to infinite dilution is possible. The ratio γ(M, free atom)/γ(M, liq. ref.) has to be known to 1 part in 10^5 if the σ(M, liq. ref.) $-$ σ(M, free atom) is to be determined to ± 10 ppm. The absolute shielding scales for Li, Na, K, Rb, Cs, Zn, Cd, Ga, Hg, and Pb were determined in this way and are summarized in Table 1 in 'Multinuclear NMR' edited by Mason.[4]

3 ABSOLUTE SHIELDING INFORMATION FROM SPIN-ROTATION CONSTANTS

With the gauge origin at the nucleus in question, σ^{p} in Ramsey's expression is related to another molecular property,

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Table 1 Absolute σ_0 ^{15}N Shieldings

Molecule	σ_0(^{15}N in the molecule, 300 K) (ppm)
N_2	−61.6
NNO	99.5
N**N**O	11.3
HCN	−20.4

the nuclear spin-rotation tensor. The nuclear spin-rotation tensor arises from the coupling of the magnetic moment of a nucleus with the magnetic field generated by the molecular rotation at that nucleus. Ramsey[5] and Flygare[6] have shown that

$$\sigma^{\mathrm{p}}_{\mathrm{gg}} = (m_{\mathrm{p}}/2mg_N)C_{\mathrm{gg}}/B^{(\mathrm{e})}_{\mathrm{gg}} - (\mu_0/4\pi)(e^2/2m) \times \sum_N Z_{N'}[R^2_{NN'} - (R^2_{NN'})_{\mathrm{gg}}]/R^3_{NN'} \tag{2}$$

in which m_{p} and m are the masses of the proton and the electron, g_N is the g-factor for the nucleus of interest, C_{gg} and $\sigma_{\mathrm{gg}}{}^{\mathrm{p}}$ are the diagonal components of the spin-rotation tensor and the paramagnetic shielding tensor in the principal axis system of the molecular moment of inertia, while $B_{\mathrm{gg}}{}^{(\mathrm{e})}$ is the rotational constant at the equilibrium configuration.

The $\sigma_{\mathrm{gg}}{}^{\mathrm{p}}$ values can be related to the components along the principal axes of the shielding tensor by a rotational transformation using the known molecular goemetry. The second term in the equation is the nuclear contribution which depends only on the coordinates and atomic number of all the other nuclei N' in the molecule. The total absolute shielding can then be determined by adding the diamagnetic contribution σ^{d}, which is obtained from theory, calculated at the nucleus of interest N as the gauge origin:

$$\sigma^{\mathrm{d}} = (\mu_0/4\pi)(e^2/3m)\left\langle \psi^0 \middle| \sum 1/r_i \middle| \psi^0 \right\rangle \tag{3}$$

It is very important to calculate the nuclear terms using the same structure as that used for calculating diamagnetic terms.

Experimental values of spin-rotation constants are available from molecular beam magnetic and electric resonance experiments and also from high-resolution microwave spectroscopy. In the first two types of experiments the radiofrequency spectrum corresponding to the reorientation of the ^{15}N nuclear moment in a magnetic field, or the interaction of the electric dipole moment of the molecule with a strong external electric field, is composed of transitions from many J and M_J states which may be individually resolved. In the third type of experiment, a specific purely rotational transition is observed. Vibrationally averaged constants are obtained, usually for the ground vibrational state, occasionally for a vibrationally excited state as well. The exact relation between σ^{p} and C holds for a vibrationless molecule at the equilibrium nuclear configuration. Experimentally one usually obtains $\langle C \rangle_{\mathrm{v}=0}$ components of the vibrationally averaged spin-rotation constant.

The first absolute shielding scale which was compiled in an internally consistent way is the one for ^{19}F in a small set of molecules whose chemical shifts have been measured in the limit of zero pressure at room temperature.[6] To establish the first absolute shielding for ^{19}F in a molecule,[7] Hindermann and Cornwell corrected the observed spin-rotation constant in HF to the equilibrium configuration, from which they obtained $\sigma_{\mathrm{e}}{}^{\mathrm{p}}$. The latter combined with the theoretical value of $\sigma_{\mathrm{e}}{}^{\mathrm{d}}$ gave σ_{e}, which was then converted to σ_0 at room temperature by making the rovibrational correction. Once the absolute σ_0 for HF was known, they could then find the absolute σ_0 for their secondary reference molecule (SiF_4) by measuring the chemical shift between HF and SiF_4 at the zero-pressure limit. The absolute σ_0 for the other molecules on their scale were then determined from measured chemical shifts from SiF_4. Since all the measured chemical shifts correspond to the zero-pressure limit, Hindermann and Cornwell's scale is a list of absolute σ_0 (i.e., for the isolated molecule) at room temperature. In addition, they found the absolute shielding σ(liq., T) of $CFCl_3$. With this connection, other measurements of shifts relative to liquid $CFCl_3$ can be converted to absolute σ(liq. or soln., T) by other workers.

In general, once the absolute shielding of a primary reference molecule (in this case the HF molecule) has been established, the absolute ^{19}F shielding of a series of other molecules can be systematically determined. What is required are simultaneous accurate chemical shift measurements between the primary reference molecule and all the other molecules in the isolated molecule limit. Frequently, the primary reference molecule is not a convenient internal reference and a secondary reference molecule is used instead. In this case, the SiF_4 molecule is ideal, it is relatively inert, and has a long ^{19}F relaxation time in the gas phase so that the signal is sharp. To extend the ^{19}F absolute shielding scale, observed resonance frequencies in gas samples were reduced to the zero-density limit at 300 K using previously measured density and temperature-dependent chemical shifts for each gas. The results corresponding to a rovibrationally-averaged isolated molecule at 300 K are expressed relative to SiF_4 as a standard. The values of $[\sigma_0(300\,\mathrm{K}) - \sigma_0{}^{\mathrm{SiF_4}}(300\,\mathrm{K})]/[1 - \sigma_0{}^{\mathrm{SiF_4}}(300\,\mathrm{K})]$ were obtained by dividing the frequency differences by the resonance frequency of SiF_4. The shielding differences $[\sigma_0{}^{\mathrm{A}}(300\,\mathrm{K}) - \sigma_0{}^{\mathrm{SiF_4}}(300\,\mathrm{K})]$ were obtained for a large number of molecules[8,9] and were found to be identical to Hinderman and Cornwell's values for all of their molecules (six) which were included in the new set. Based on σ_0(HF, 300 K) = 410.0 ppm, absolute σ_0(SiF_4, 300 K) = 363.2 ppm. The absolute σ_0 for a large number of F-containing molecules have been determined from the ^{19}F chemical shift limit at 300 K, $[\sigma_0(\mathrm{A}, 300\,\mathrm{K}) - \sigma_0(\mathrm{SiF_4}, 300\,\mathrm{K})]$.[8,9] Neat liquid $CFCl_3$ and C_6F_6 provide the connection for converting chemical shifts measured in other laboratories using these references into absolute shielding values; σ(^{19}F neat liq. $CFCl_3$, spherical, 300 K) = 188.7 ppm; σ(^{19}F neat liq. C_6F_6, spherical, 300 K) = 355.5 ppm.

How large can the errors be if the corrections shown in Figure 1 are not carried out, i.e. if $\langle C_{\mathrm{gg}}\rangle_{\mathrm{v}=0}/\langle B_{\mathrm{gg}}\rangle_{\mathrm{v}=0}$ are used to calculate $\langle \sigma_{\mathrm{gg}}{}^{\mathrm{p}}\rangle/_{\mathrm{v}=0}$ directly? The difference between the vibrational average of the ratios $\langle C_{\mathrm{gg}}/B_{\mathrm{gg}}\rangle_{\mathrm{v}=0}$ and the ratio of the vibrational averages $\langle C_{\mathrm{gg}}\rangle_{\mathrm{v}=0}/\ \langle B_{\mathrm{gg}}\rangle_{\mathrm{v}=0}$ can be as much as 10% in molecules containing hydrogen. Incomplete knowledge of the first and second derivatives of C with nuclear configuration presently makes it impossible to correct for this error, as Hindermann and Cornwell had done for HF. The thermal average of σ^{p} can be approximated by using the spin-rotation tensor for the ground vibrational state. However, when a low-frequency vibration exists and the spin-rotation constants

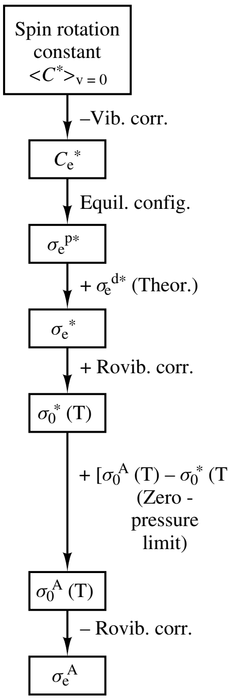

Figure 1 Building up an absolute shielding scale from the absolute shielding of one primary reference whose spin-rotation constant is accurately known. The following notations are used: * denotes the primary reference molecule, A any other compound, subscript 0 the isolated molecule, and subscript e the equilibrium configuration

for the first excited vibrational state are substantially different from those of the ground vibrational state (such as in NNO), a proper thermal average has to be carried out. There are also rotational (centrifugal distortion) corrections which have to be made.

Given the possible sources of error which we have mentioned above, some discrepancies may be observed in comparing shielding values derived from spin-rotation constants with differences in thermal averages of shielding observed in nuclear magnetic resonance spectroscopy in the zero-pressure limit. However, the precision of most available spin-rotation constants is still such that the sources of errors discussed above are not limiting.

Ab initio calculations of the diamagnetic part of the shielding are generally reliable since these depend only on the ground-state wavefunctions. The changes resulting from configuration interaction are very minor, no more than a few tenths of a ppm in σ^d, over the Hartree–Fock value. Where ab initio calculations are not available, it is possible to estimate σ^d to within 1–2 ppm even without wavefunctions. Flygare has proposed an easy method for evaluating σ^d which has been shown to be sufficiently reliable for evaluating the average and the components of σ from the spin-rotation tensor.**10,11** The success of this method is due to the fact that most of σ^d is given by the diamagnetic shielding of the free atom and the rest can then be approximately calculated by the method of atomic dipoles. It has been found that the method of Flygare and co-workers is accurate to within 1–2 ppm. Let us consider this method briefly.

By formally partitioning the sum of $1/r_j$ over all j electrons into two sums, one over electrons 'on' nucleus N and the other over all electrons 'on' all the other nuclei, N', Flygare has been able to write the average diamagnetic shielding in terms of a free atom term, a contribution of the electronic point charges centered at the other nuclei, and a third term which arises if the point charges are not centered on the N' nucleus but are displaced by a distance $\langle\rho\rangle_{N'}$:

$$\sigma_{\mathrm{av}}^{\mathrm{d}} = \sigma^{\mathrm{d}}(\text{free atom}) + (\mu_0/4\pi)(e^2/3m)\sum_{N'} Z_{N'}/R_{N'} - (\mu_0/4\pi)(e^2/3m)\sum_{N'} R_{N'}\cdot\langle\rho\rangle_{N'}/R_{N'}^3 \qquad (4)$$

The second term in the above equation is identical in form and opposite in sign to the nuclear terms in equation (1) and the last term is a small correction. Thus, the absolute shielding σ can be written in the Flygare method, as

$$\sigma_{\mathrm{av}} = \sigma^{\mathrm{d}}(\text{free atom}) - (\mu_0/4\pi)(e^2/3m) \times \sum_{N'} R_{N'}\cdot\langle\rho\rangle_{N'}/R_{N'}^3 + \frac{m_{\mathrm{p}}}{2mg_N}\cdot\frac{1}{3}\sum\frac{C_{\mathrm{gg}}}{B_{\mathrm{gg}}^{(\mathrm{e})}} \qquad (5)$$

This applies to the equilibrium configuration, with extension to thermal averages requiring some corrections which may be a few ppm.

Using the Flygare approximation for the diamagnetic shielding then leads to

$$\sigma_{\mathrm{av}} \simeq \frac{m_{\mathrm{p}}}{2m_{\mathrm{e}}g_N}\cdot\frac{1}{3}\sum\frac{C_{\mathrm{gg}}}{B_{\mathrm{gg}}^{(\mathrm{e})}} + \sigma^{\mathrm{d}}(\text{free atom}) \qquad (6)$$

The diamagnetic shieldings of the free atoms are well known from the tabulations of Malli and Froese.**3** For a spherical top molecule,

$$\left.\begin{aligned} \sigma_{\mathrm{av}} &\simeq \frac{m_{\mathrm{p}}}{2m_{\mathrm{e}}g_N}\cdot\frac{C_{\mathrm{av}}}{B} + \sigma^{\mathrm{d}}(\text{free atom}) \\ \sigma_{\parallel} - \sigma_{\perp} &\simeq \frac{m_{\mathrm{p}}}{2m_{\mathrm{e}}g_N}\cdot\frac{C_{\parallel} - C_{\perp}}{B} \end{aligned}\right\} \qquad (7)$$

and for a linear molecule

$$\left.\begin{aligned} \sigma_{\perp} &\simeq \frac{m_{\mathrm{p}}}{2m_{\mathrm{e}}g_N}\cdot\frac{C_{\perp}}{B} + \sigma^{\mathrm{d}}(\text{free atom}) \\ \sigma_{\parallel} &= \sigma_{\parallel}^{\mathrm{d}} \end{aligned}\right\} \qquad (8)$$

since $\sigma_{\parallel}{}^{\mathrm{p}}$ is identically zero for a linear molecule.

The spin-rotation tensor has been used to determine the ^{15}N absolute shielding in NH_3, ^{19}F in HF, ^{13}C and ^{17}O in CO, and ^{31}P in PH_3, and these absolute shieldings have been used to establish all other absolute shieldings in various molecules containing these nuclei. Gas-phase studies provide the relative differences at the zero-density limit and these can be converted to $\sigma_0(300\,\mathrm{K})$ values absolutely. If the commonly used liquid reference is also measured relative to this one molecule, then all past and future measurements of chemical shifts relative to this liquid reference can be converted to absolute shieldings. As we have seen above, rovibrational corrections should be calculated and added to theoretical σ_{e}

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before comparing with the experimental values $\sigma_0(300\,\mathrm{K})$. For some molecules this latter value is not very different from the zero-point vibrational average shielding $\sigma_0(0\,\mathrm{K})$. Similarly, the observed spin-rotation constants should be corrected for rovibrational effects before using the identity to obtain σ_e. Nevertheless, the agreement between absolute shielding values derived from spin-rotation constants and those from gas-phase measurements in the zero-pressure limit is remarkably good as shown in Figure 2, which indicates the reliability of the spin-rotation constants.

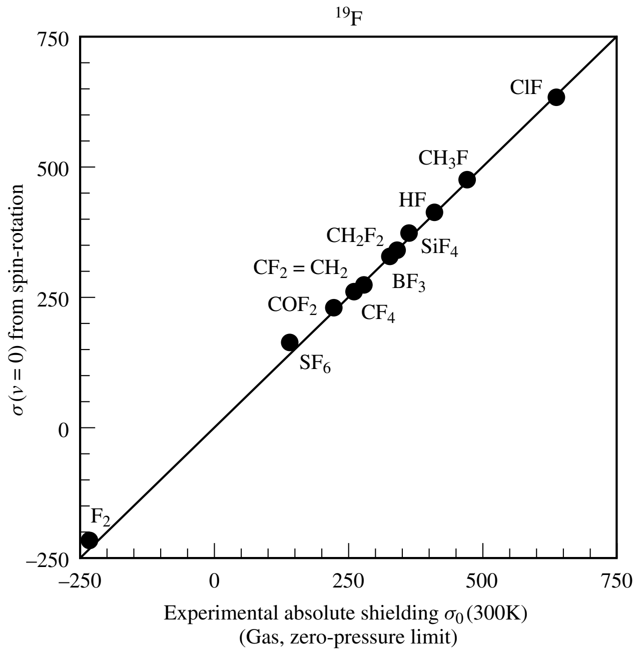

Figure 2 Experimental absolute shielding values of ^{19}F from gas-phase measurements in the zero-density limit. The gas-phase measurements are converted to absolute shielding by using HF as the primary reference molecule. These are compared with the individual absolute shielding values derived from independent measurements of the ^{19}F spin-rotation constants in various molecules

The ^{15}N absolute shielding scale is based on the spin-rotation tensor in the primary reference molecule, NH_3. The spin-rotation-derived shielding for NH_3 is 264.54 ppm.[12] Nitrogen-15 chemical shifts in the gas phase taken to the zero-pressure limit lead to absolute $\sigma_0(^{15}\mathrm{N})$ shieldings in the N_2, NNO, and HCN molecules,[13] see Table 1. At the same time, the absolute shielding of the liquid references were obtained: $\sigma(^{15}\mathrm{N}, \mathrm{NH_3}, \text{liq.}, 300\,\mathrm{K}) = 380.4\,\mathrm{ppm}$; $\sigma(^{15}\mathrm{N}, \mathrm{CH_3NO_2}, \text{liq.}, 300\,\mathrm{K}) = -135.8\,\mathrm{ppm}$.

The ^{17}O absolute shielding scale is based on the spin-rotation tensor in $C^{17}O$, $C_\perp = 30.4 \pm 1.2\,\mathrm{kHz}$ which leads to $\sigma(^{17}\mathrm{O}, \mathrm{CO}) = -42.3 \pm 17.2\,\mathrm{ppm}$.[14] The gas-phase measurements of ^{17}O chemical shifts in H_2O, CO_2, NNO, OCS, OF_2, and CO lead to the absolute $\sigma_0(^{17}\mathrm{O})$ shielding values[14] shown in Table 2.

Table 2 Absolute σ_0 ^{17}O Shieldings

Molecule	σ_0(^{17}O in the molecule, 300 K) (ppm)
H_2O	344.0
CO_2	243.4
NNO	200.5
OCS	107.9
OF_2	−473.1
CO	(−42.3 ± 17.2)

The ^{13}C shielding scale is based on the primary reference ^{13}C in the $^{13}C^{16}O$ molecule in which $C_\perp = 32.70 \pm 0.12\,\mathrm{kHz}$ in the v = 0, J = 1 state [15] is in good agreement with the previous value of $32.59 \pm 0.15\,\mathrm{kHz}$. Rovibrational corrections on the spin-rotation constant to obtain $\sigma_e(^{13}\mathrm{C}\text{ in }^{13}\mathrm{C}^{16}\mathrm{O}) = 3.0 \pm 0.9$ and then rovibrational corrections on the latter lead to $\sigma_0(^{13}\mathrm{C}\text{ in }^{13}\mathrm{C}^{16}\mathrm{O}, 300\,\mathrm{K}) = 1.0 \pm 1.2\,\mathrm{ppm}$.[16] With measurements of ^{13}C chemical shifts in the low-density gas phase under conditions such that intermolecular effects and bulk susceptibility effects are less than 0.05 ppm, the $[\sigma_0 - \sigma_0(\mathrm{CO})]$ have been obtained for a large number of molecules ranging from CH_4 where $\sigma_0(^{13}\mathrm{C}, \mathrm{CH_4}, 300\,\mathrm{K}) = 195.1\,\mathrm{ppm}$ to $CH_2{=}C{=}CH_2$ where $\sigma_0(^{13}\mathrm{CH_2}, 300\,\mathrm{K}) = 115.2\,\mathrm{ppm}$, $\sigma_0({=}^{13}\mathrm{C}{=}, 300\,\mathrm{K}) = -29.3\,\mathrm{ppm}$. The independent spin-rotation-derived absolute shieldings in $^{13}CH_4$, $D^{13}CN$, and $O^{13}CS$ are completely consistent with the values of σ_0 obtained for these molecules based on $\sigma_0(^{13}\mathrm{CO}) = 1.0 \pm 1.2\,\mathrm{ppm}$.

The σ_0(^{13}C in the molecule, 300 K) values for a large number of molecules have been published by Jameson[16] and Jameson (Table 16).[17] A missing value from the latter is isopentane ⋯ (CH)**C**H_3, for which σ_0(^{13}C in the molecule, 300 K) = 165.0 ppm. These measurements also provide $\sigma(^{13}\mathrm{C}, \text{TMS liquid, spherical}, 300\,\mathrm{K}) = 184.1\,\mathrm{ppm}$ and $\sigma(^{13}\mathrm{C}, \mathrm{C_6H_6}\text{ liquid, spherical}, 300\,\mathrm{K}) = 55.7\,\mathrm{ppm}$, which are convenient references for converting chemical shift measurements to absolute shieldings.

The ^{31}P absolute shielding scale is based on the primary reference molecule PH_3, in which the spin rotation tensor $C_\perp = -114.90 \pm 0.13\,\mathrm{kHz}$ and $C_\parallel = -116.38 \pm 0.32\,\mathrm{kHz}$ (where the quoted errors are for 99% confidence limits),[18] leading to $\sigma_0(^{31}\mathrm{P}, \mathrm{PH_3}, 300\,\mathrm{K}) = 594.45 \pm 0.63\,\mathrm{ppm}$. If the spin-rotation tensor is rovibrationally corrected, one gets[19] σ_e(^{31}P in the PH_3 molecule) = 599.93 ppm and $(\sigma_\parallel - \sigma_\perp)_e = -64.5\,\mathrm{ppm}$.

The PF_3 molecule serves as a suitable secondary reference since its chemical shift has a smaller dependence on density. Extrapolation of gas-phase mixtures in argon to the zero-density limit provides the absolute shieldings[20] listed in Table 3. At the same time the absolute shielding of ^{31}P in convenient reference liquids has been obtained: $\sigma(^{31}\mathrm{P}, 85\%\ \mathrm{H_3PO_4}\text{ aq., spherical}, 300\,\mathrm{K}) = 328.35\,\mathrm{ppm}$ and $\sigma(^{31}\mathrm{P}, \mathrm{P(OMe)_3}\text{ liquid, spherical}, 300\,\mathrm{K}) = 187.54\,\mathrm{ppm}$. A ^{33}S absolute shielding scale has been derived from the spin-rotation constant $C_\perp = 870 \pm 50\,\mathrm{Hz}$ in the OCS molecule, which leads to $\sigma_0(^{33}\mathrm{S}, \text{OCS molecule}) = 843 \pm 12\,\mathrm{ppm}$.[21] The ^{33}S chemical shift measurements in the gas phase lead (without full corrections for intermolecular effects) to the values shown in Table 4. A convenient liquid reference is CS_2 for which $\sigma(^{33}\mathrm{S}, \mathrm{CS_2}, \text{liquid, spherical}, 300\,\mathrm{K}) = 581\,\mathrm{ppm}$.

Although the proton absolute shielding for water was the first to be established, proton shifts have not been systematically measured in the gas-phase zero-pressure limit and connected to either liquid water or liquid TMS. This situation should be remedied soon as improving proton shielding calculations need some good experimental tests. There are, however, absolute shieldings that can be individually derived

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Table 3 Absolute σ_0 ^{31}P Shieldings

Molecule	σ_0(^{31}P in the molecule, 300 K) (ppm)
PMe_3	391.71
OPF_3	363.43
PF_3	222.69
PCl_2Me	138.65
PCl_3	111.29
P_4	−551.5
PH_3	(594.45 ± 0.63)

Table 4 Absolute σ_0 ^{33}S Shielding Values

Molecule	σ_0(^{33}S in the molecule, 300 K) (ppm)
H_2S	752
CH_3SH	707.3
SF_6	425.6
SO_2	−125.9
OCS	(843 ± 12)

from measured spin-rotation constants by the methods already described, and these are shown in Table 5.

Table 5 Absolute σ_0 Proton Shieldings

Molecule	σ_0 (^{1}H in the molecule, 300 K) (ppm)	Other values (ppm)
CH_3F	28.27 ± 0.5	
PH_3	27.89 ± 0.15	
NH_3	32.10 ± 0.02	
H_2	26.363 ± 0.004	
CH_4	30.80 ± 0.23	30.611 ± 0.024
HCl	31.16 ± 0.09	
HF	28.64 ± 0.01	28.51 ± 0.20
H_2S	31.26 ± 0.40	
SiH_4	27.52 ± 0.44	27.63 ± 0.03

The errors quoted include only those arising from the uncertainty in the spin-rotation tensor itself. Other values reported in the last column are based on a variety of chemical shift measurements which are indirectly connected to liquid water whose absolute shielding is $\sigma(^1\mathrm{H}, \mathrm{H_2O}, \text{liq., spherical}, 34.7\,^\circ\mathrm{C}) = 25.790 \pm 0.014$ ppm.

4 THE CONNECTION BETWEEN ABSOLUTE SHIELDING SCALES OF TWO NUCLEI

Spin-rotation constants of any two nuclei in the same molecule can be related to one another provided that both nuclei relax entirely by the spin-rotation mechanism. In the gas phase, in the exchange-narrowing limit, there is a single characteristic correlation time τ which is identical for both nuclei.

The nuclear spin relaxation time characteristic of this mechanism is given by

$$(1/T_1)_{\mathrm{SR}} = \frac{2}{3}\langle J(J+1)\rangle 4\pi^2 C_{\mathrm{eff}}^2 \tau \qquad (9)$$

with C in units of rad s^{-1}, so that for two nuclei k and k' in the same molecule, in the same gas sample,

$$T_1(k)/T_1(k') = C_{\mathrm{eff}}^2(k')/C_{\mathrm{eff}}^2(k) \qquad (10)$$

For linear molecules $C_{\mathrm{eff}}{}^2 = C_\perp{}^2$. For spherical tops

$$\begin{aligned} C_{\mathrm{eff}}^2 &= C_{\mathrm{av}}^2 + \frac{4}{45}(\Delta C)^2 \\ &= \left[\frac{1}{3}(2C_\perp + C_\parallel)\right]^2 + \frac{4}{45}(C_\parallel - C_\perp)^2 \end{aligned} \qquad (11)$$

A nucleus in the center of a spherical top is a favorable choice since all $C_{\mathrm{gg}}{}^{(k)}$ are equal by symmetry and only $C_{\mathrm{av}}{}^2$ enters into the relaxation expression. If both nuclei k and k' relax entirely by spin rotation, and if $C_{\mathrm{eff}}{}^2$ is known for one nucleus, e.g. ^{19}F in SeF_6 or TeF_6, then C_{av} for the central nucleus (and thus the shielding) can be obtained from the measured ratio of relaxation times in the gas phase. This is supported by empirical observations for CH_4 in various buffer gases, in which the ratio of measured ^{13}C and ^{1}H relaxation times in the gas phase was found to be independent of buffer gas, temperature, or density, and was within experimental error of the inverse ratio of the $C_{\mathrm{eff}}{}^2$ values from molecular beam data. These molecular beam data, in turn, were consistent with the ^{13}C shielding scale (based on $C_\perp$ in CO) and the ^{1}H shielding scale (based on γ of the H atom).

It is also possible to determine $C_{\mathrm{eff}}{}^2$ from the density dependence of T_1 in the region of the minimum. However, for most systems, the minimum T_1 occurs at such low densities that appropriate measurements are feasible only for ^{1}H and ^{19}F nuclei which have the highest NMR sensitivity, and which also have well-established shielding scales based on spin-rotation constants from molecular beam and high-resolution microwave measurements.

This method was used to establish the ^{77}Se and ^{125}Te shielding scales by concurrent measurement of the ^{19}F and ^{77}Se (or ^{125}Te) spin-relaxation times in SeF_6 (or TeF_6) molecules in the dilute gas phase,**22** and also the ^{29}Si shielding scale based on both SiH_4 and SiF_4 molecules.**23** The sample was gaseous (e.g. SeF_6 or TeF_6, or an equimolar mixture of SiH_4 and SiF_4) contained in a sealed glass tube at a well-regulated temperature. Inversion–recovery experiments were set up in both the observe channel and the decoupling channel, the decoupling channel having been modified so that it could be tuned to ^{19}F as well as ^{1}H.

In one cycle, one-eighth of the total number of transients were taken and stored for each delay time for one nucleus and then the other. The next cycle went through the delay list for one nucleus and the other, acquiring the next eighth and so on. Thus the T_1 experiments were undertaken in the same molecule in the same sample essentially simultaneously. Only the magnitude of C could be obtained from the experiments. The signs were assigned on the basis of the σ values obtained. Defined with the gauge origin at the nucleus in question, σ^{p} is usually negative for most heavy nuclei. For SeF_6 the two possible values of σ^{p} which can be calculated from C are 1559.7 or −2160.7 ppm, from which we choose the latter, i.e. $C(^{77}\mathrm{Se})$ is negative. For TeF_6 the two possible values of σ^{p} are 2570 or −3070 ppm and we choose the latter, which with a negative $g(^{125}\mathrm{Te})$ implies that $C(^{125}\mathrm{Te})$ is positive.

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Although the relationship between σ^{p} and C is exact only for the rigid isolated molecule at its equilibrium configuration, we have used rovibrationally averaged values at room temperature for all quantities. The errors in σ associated with this are smaller than the rovibrational corrections to shielding (-8 and -9 ppm, respectively, for ^{77}Se and ^{125}Te in SeF_6 and TeF_6) since the vibrational corrections to C and σ^{p} tend to increase slightly the magnitudes of both. Hence, σ_0 (^{77}Se in SeF_6 molecule, 300 K) = 1437.8 ± 64 ppm, σ_0 (^{77}Se in H_2Se molecule, 300 K) = 2401 ± 64 ppm, and σ_0 (^{125}Te in TeF_6 molecule, 300 K) = 3790 ± 130 ppm.

These values are based on 3298 ppm and 6580 ppm for σ^{d} of the free Se and Te atoms, respectively, including relativistic corrections. Using the absolute shielding values for ^{77}Se in SeF_6(g) and for ^{125}Te in TeF_6(g), and the known gas-to-liquid shifts for SeF_6 and TeF_6, the absolute shielding for the reference liquids σ(^{77}Se, Me_2Se, liq.) = 2069 ppm and σ(^{125}Te, Me_2Te, liq.) = 4333 ppm are obtained. Concurrent measurement of ^{29}Si and ^{1}H spin-relaxation times in a sample of SiF_4 gas provides the ratio $C^2_{\mathrm{av}}(^{29}\mathrm{Si})/C^2{}_{\mathrm{eff}}$ (^{1}H), and concurrent measurement of ^{29}Si and ^{19}F spin-relaxation times in SiF_4 gas provides the ratio $C^2_{\mathrm{av}}(^{29}\mathrm{Si})/C^2_{\mathrm{eff}}(^{19}\mathrm{F})$. The spin-rotation tensors are independently known for ^{1}H and ^{19}F in these molecules. Using $g_{\mathrm{Si}} = -1.1106$ and the theoretical value for the diamagnetic shielding σ^{d} free Si atom = 874.1 ppm, and choosing positive signs for $C(^{29}\mathrm{Si})$ in both molecules, leads to[23] σ_0(^{29}Si in SiH_4 molecule, 300 K) = 475.3 ± 10 ppm and σ_0(^{29}Si in SiF_4 molecule, 300 K) = 482.0 ± 10 ppm.

The T_1 experiments in SiH_4 and SiF_4 provide two completely independent determinations of very nearly the same point (separated by only 6.7 ppm) on the ^{29}Si shielding scale. The coincidence of these two truly independent results is remarkable. Since a large part of C^2_{eff} (^{1}H or ^{19}F) is the isotropic average C^2_{av} (^{1}H or ^{19}F) which is directly related to σ_{av} (^{1}H or ^{19}F), the values are constrained to be consistent with the absolute shielding scales of both ^{1}H and ^{19}F and also the 6.7 ppm ^{29}Si shielding difference between SiH_4 and SiF_4. All these conditions are well satisfied within realistic error estimates of ±10 ppm. The ^{19}F shielding scale is well established, with several independent determinations based on the spin-rotation constants in a number of small molecules agreeing with the chemical shifts in the zero-pressure limit. The ^{1}H shielding scale is also well established on the basis of hydrogen atomic beam data. It is satisfying to find that the Si shielding scale is consistent with these. Finally, the measured ^{29}Si chemical shifts in SiH_4 and SiF_4 gas relative to neat liquid Me_4Si lead to σ(^{29}Si, Me_4Si, liquid, spherical) = 368.5 ± 10 ppm.

In favorable systems, simultaneous measurements of T for two spin-$\frac{1}{2}$ nuclei in the same molecule in the gas phase provide a means of determining the absolute nuclear shielding scale of the second nucleus from that of the first. This method can be applied when the spin-rotation tensor of the first nucleus is independently known or can be calculated from its known shielding tensor. The latter can be obtained by measurement of the chemical shift anisotropy and the isotropic absolute shielding based on some primary reference (such as ^{1}H in the H atom, ^{13}C in CO, ^{15}N in NH_3, ^{17}O in CO, ^{19}F in HF, ^{31}P in PH_3, or ^{33}S in OCS). In a linear molecule only the isotropic shielding is necessary since $\sigma_{\|}$ is entirely diamagnetic. For spherical tops the $(\Delta C)^2$ term is 4/45-times as small as the $C^2{}_{\mathrm{av}}$ term, so that even when $(\Delta C)^2$ and $\Delta\sigma$ are unknown an estimate may be adequate. An appropriate molecule in which two nuclei relax nearly exclusively by spin-rotation in the gas phase effectively provides a bridge between the absolute shielding scales of these nuclei.

Finally, a method of obtaining the absolute shielding directly from the measured anisotropy $\Delta\sigma \equiv (\sigma_{\|} - \sigma_{\perp})$ in a linear molecule takes advantage of the symmetry requirement that the paramagnetic shielding contribution along the axis parallel to the molecular axis vanishes: $\sigma^{\mathrm{p}}_{\|} = 0$. A theoretically calculated diamagnetic term $\sigma^{\mathrm{d}}_{\|}$ provides the rest of the required information:

$$\sigma_{\perp} = \sigma^{\mathrm{d}}_{\|} - \Delta\sigma, \qquad \sigma_{\|} = \sigma^{\mathrm{d}}_{\|} \tag{12}$$

so that the absolute average shielding is

$$\sigma = \sigma^{\mathrm{d}}_{\|} - \left(\frac{2}{3}\right)\Delta\sigma \tag{13}$$

albeit containing some unwanted intermolecular effects in $\Delta\sigma$ which is usually obtained from a condensed-phase measurement. One can therefore establish a shielding scale for a nucleus by choosing an appropriate linear molecule. Some examples are shown in Table 6. The absolute shieldings obtained from the anisotropy differ slightly from those obtained in the gas in the zero-pressure limit, from which we see that intermolecular effects are 1 to -8 ppm in the solid. It should be noted that the above relationships hold only for a linear molecule, not for a quasilinear or pseudolinear molecule. Any off-axis atoms break the symmetry and lead to $\sigma^{\mathrm{p}}_{\|} \neq 0$. For example, $CH_2{=}^{13}C{=}CH_2$ has $\sigma^{\mathrm{p}}_{\|} = -250$ ppm for the central ^{13}C. Furthermore, $\sigma^{\mathrm{p}}_{\|} = 0$ holds for a linear molecule only at the level of the nonrelativistic theory of shielding.

5 MAGNITUDES OF THE CORRECTIONS LINKING THE SHIELDING IN THE CONDENSED PHASE TO THE ISOLATED MOLECULE AT ITS EQUILIBRIUM GEOMETRY

The exquisite sensitivity of the shielding to the electronic environment is what makes the NMR chemical shift a very

Table 6 Absolute Shielding (ppm) Derived from the Shielding Anisotropy

Molecule/ion	$\Delta\sigma$, solid	$\sigma_{\|} = \sigma_{\|}{}^{\mathrm{d}}$	$\sigma_{\perp}$	σ_{av}	σ_0(^{13}C in the molecule, 300 K)
OCO	335	274.1	−60.9	50.8	58.8
OCS	365	274.1	−90.9	30.8	30.0
SCS	424	276.1	−147.9	−6.6	−8.0
NCS^-	321	264.7	−56.3	50.7	
SeCSe	506	294	−212	−43.3	

powerful tool in studying structure, intermolecular effects, and dynamic averaging. For the purpose of comparing with theoretical ab initio calculations of the shielding, however, this exquisite sensitivity to the environment appears at first to be a distinct disadvantage. Nevertheless, if one knows the precise relationship between the quantities being calculated (the shielding at some specific set of nuclear coordinates) and the quantities being measured, then the appropriate comparisons against theory can still be made. In fact, a more complete comparison becomes possible when the true connection between the experimental milieu and the theoretical constructs is understood. Since it is never possible to observe a molecule as a fixed arrangement of nuclei (even in the molecular beam where no neighbor effects need to be considered, there is always at least the zero-point vibrational motion), let us consider the nature of the connection between what is measured and what can be calculated. In this respect, the NMR chemical shift is in by far a more advanced stage compared with other molecular electronic properties such as electric dipole polarizability, electric field gradient tensors, etc. It is partly a theoretical advantage, but more important an experimental advantage, that NMR spectroscopy provides. The very high resolution that is possible under the conditions of isotropic averaging in gases and solutions makes it possible to measure chemical shifts of the order of parts per billion. The more advanced temperature control of experiments in NMR spectroscopy, compared with other forms of spectroscopies, combined with the high resolution, has made it possible to measure the temperature dependence of the shielding in a nearly isolated molecule over a 200 K range almost routinely. The small chemical shifts that are the differences in shielding between two molecules differing only in the isotopic masses of some of the nuclei can be measured to a few ppb as well.

Both of these phenomena are related to the dynamic averaging of the vibrating molecule through its various nuclear configurations, each configuration having its appropriate shielding value for a particular nucleus. There are also intermolecular effects, again associated with shielding values that change with nuclear configurations, this time the configurations of supermolecules including not only the molecule bearing the NMR nucleus but all the neighboring interacting molecules. Solvent shifts are a manifestation of this, as are adsorption shifts, as well as a portion of the discrimination between different locations of the same amino acid residues in a protein. The dynamic averaging is discussed further in ***Isotope Effects on Chemical Shifts and Coupling Constants*** and some aspects of the intermolecular shifts are discussed further in the article on ***Gas Phase Studies of Intermolecular Interactions and Relaxation***. In this article, we merely take note of the mechanisms that give rise to the phase-dependent and temperature-dependent differences and how large the corrections are.

Let us first consider an isolated or nearly isolated molecule, i.e. one in which the frequency of collisions with other molecules is still enough to allow the molecule to sample its many rotational and vibrational states while being observed in the NMR spectrometer but not frequent enough to lead to a measureable intermolecular contribution. As the molecule undergoes vibrations, the distances between nuclei change in a periodic fashion, bonds being alternately compressed and expanded, bond angles being alternately enlarged and made smaller, with torsions or frustrated internal rotations possibly occuring as well. For each frozen configuration the shielding of an NMR nucleus in the molecule is different. In the context of the Born–Oppenheimer approximation, the nuclei are moving slowly enough relative to the electronic motion that it is possible to talk about a shielding surface, a highly multidimensional mathematical surface akin to the intramolecular potential energy surface, which describes the shielding at each configuration of the collection of nuclei that make up the framework of the molecule. Of course, the parts of this shielding surface that are sampled during the vibrations are those regions that correspond to the deep pockets in the intramolecular potential energy surface (PES), located at what we call the ‘equilibrium’ molecular geometry. Thus, it would seem that for the most part, the only interesting regions that we should concern ourselves with are those in the immediate vicinity of the single deep pocket in the PES. This may indeed be the case for the dynamic averaging in small molecules such as diatomics and methane. However, as soon as torsion angles come into the picture, the nature of the averaging changes. Wider excursions are possible, perhaps passing though *cis*-eclipsed, *gauche*, *gauche*′, *trans*-staggered, etc. Even in a simple molecule like NH_3, the umbrella inversion has to be considered in its entirety—no minor small amplitude excursions here! Thus, it becomes necessary to think in terms of not a single shielding tensor associated with a particular nucleus in a molecule, but a continuum, of such tensors changing smoothly with nuclear displacements away from the lowest energy point in the deep pocket. Some shielding surfaces are shown in the article on ***Isotope Effects on Chemical Shifts and Coupling Constants***, and the consequences of the dynamic averaging are discussed there as well.

How large are the shielding changes in going from the equilibrium geometry to the dynamically-averaged shielding? This depends on the molecule. For the ^{19}F shielding in the F_2 molecule, the difference is of the order of 40 ppm; for the ^{15}N in the N_2 molecule it is smaller, about 3 ppm, and for ^{1}H in the HF molecule it is around 0.3 ppm. Most of the dynamic averaging effects lead to a decreased shielding, but instances of increased shielding can also be found. At the time when the theoretical calculations were only good to within 50 ppm for ^{13}C in various molecules, for example, the direct comparison of the shielding calculated in a molecule rigidly fixed at its equilibrium geometry with the chemical shift measurements in solution could be excused. With the present theoretical capability discussed in the articles by Hansen and Kutzelnigg in this Encyclopedia, the real test of the quality of a calculation is really in the shape of the surface in the immediate vicinity of the equilibrium geometry, not just the value at a single one point on the surface. The rationale for determining absolute shielding scales is to be able to compare shieldings rather than differences of shieldings between two different molecules, thereby disallowing any fortuitous agreements in chemical shifts while the shieldings themselves could be far off. We go further at this point and make note not only of the absolute shielding of a nucleus in the particular molecule, but the dynamic average over a portion of the shielding surface for this nucleus; the shape of the surface itself is being tested. Typical magnitudes of the vibrational corrections that arise from this dynamic averaging are shown in Table 7.

Most of the time, we observe molecules in some medium rather than in the zero-pressure limit in the gas phase. Most of the full shielding tensor information is obtained in the solid

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Table 7 Vibrational Corrections from Dynamic Averaging

	$[\sigma_0(T) - \sigma_e]$, theor. (ppm)
^{1}H in HF	−0.4
^{13}C in CH_4	−3.6
^{15}N in NH_3	−8.8
^{17}O in H_2O	−13.6
^{19}F in HF	−9.7
^{31}P in PH_3	−12.8
^{77}Se in H_2Se	−58.9

state or in liquid crystal solutions. It is therefore important to understand the ways in which that which we are measuring is affected by the surrounding molecules. We know that medium effects can be large because the gas-to-liquid shifts have been measured in pure substances. The magnitudes of some of these are shown in Table 8, where the chemical shift between the liquid and the vapor in equilibrium with it have been measured at the same temperature. We also know that intermolecular effects in physisorption can be large. Now, this is strictly an intermolecular effect, not involving a change in chemical structure. For ^{129}Xe nuclei of xenon atoms physisorbed in zeolites, the adsorption shifts are of the order of several hundred ppm! In other words, a xenon atom adsorbed in a zeolite cavity or channel has a shielding that differs from that in the gas phase by several hundred ppm. (See ***Adsorbed Species: Spectroscopy and Dynamics***.) This is strictly an intermolecular effect, not much different from the solvent effect in solution, with the only difference being that the solvent is stationary while the solute is relatively free to move. This too is a result of dynamic averaging, just as in solutions. This is clearly a many-body type of situation and the interpretation involves making some approximations.

Table 8 Gas-to-Liquid Shifts

		T(K)	$[\sigma(\text{liquid}, T) - \sigma\ (\text{vapor}, T)]$ (ppm)
^{1}H in	H_2O	298	−4.4
	NH_3	300	−1.75
	HCN	346.6	−2.0
^{13}C in	CO_2	220	−1.28
	HCN	336.6	−7.68
	C_6H_6	300	−1.5
^{15}N in	NH_3	300	−19.47
	HCN	346.7	+10.4
	CH_3CN	227.5	+11.3
^{17}O in	H_2O	488	−36.0
^{19}F in	CF_3H	280	−2.26
	CH_2F_2	280	−3.17
	CF_3Cl	280	−3.65
	CF_2Cl_2	300	−5.15
	CF_3CH_3	300	−4.65
	$CFCl_3$	340	−6.00
	CH_3F	260	−7.7
	SeF_6	300	−4.8
	TeF_6	300	−5.4
	WF_6	300	−7.4
^{31}P in	P_4	526	−77
^{77}Se in	SeF_6	300	−1.38
	H_2Se	300	−120
^{125}Te in	TeF_6	300	−2.0
^{129}Xe in	Xe	244	−200

A simpler situation is found in the gas phase. Intermolecular effects can be treated in the gas phase by the method of Buckingham and Pople by considering a virial expansion of the molecular electronic property, in this case the NMR shielding, in powers of density, i.e. $\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \sigma_3(T)\rho^3 + \dots$, where $\sigma_0(T)$ is the temperature-dependent shielding in the nearly isolated molecule. By making measurements of the shielding in gas samples of various densities at various temperatures, it is possible to obtain directly the second virial coefficient of nuclear shielding, $\sigma_1(T)$. This is a dynamic average which has a precise interpretation, as shown below.

$$\sigma_1(T) = \int_0^\infty 4\pi R^2\, \mathrm{d}R[\sigma(R) - \sigma(\infty)] \exp^{-V(R)/kT} \qquad (14)$$

In other words, the dynamic averaging occurs over an intermolecular shielding surface, $[\sigma(R) - \sigma(\infty)]$, with various weighting factors, as determined by the intermolecular potential energy, $V(R)$, surface. In a sense, this is entirely analogous to the averaging which occurs in vibration, except that the pockets are very deep in the intramolecular potential surface, whereas they are relatively shallow for intermolecular surfaces. Thus a very wide range of distances are included, and the temperature dependence is explicitly seen in the integration. The intermolecular shielding surface looks rather similar to the shielding surface of a nucleus in a diatomic molecule, except that all parts of the intermolecular surface are important other than at very very close range where the repulsive interactions dominate so strongly that such configurations are not effectively sampled.

This shielding surface is also amenable to theoretical calculations. In effect, the system under consideration is a supermolecule made up of the interacting molecules at all possible orientations and separations. A direct comparison of an intermolecular surface to an intramolecular one is not possible. However, the known differences in shielding sensitivities of nuclei across the Periodic Table allow us to scale the chemical shifts of one type of nucleus relative to another. For example, proton shifts are about 20 ppm to the fluorine shifts of about six hundred ppm. If we do this, then we can put an intramolecular shielding surface on the same plot as an intermolecular shielding surface, keeping their magnitudes in the same proportion as the well-known relative magnitudes of the ranges of their chemical shifts. One such example is shown in Figure 3, where the intramolecular shielding surface for the ^{23}Na nucleus in the NaH molecule is superimposed on the intermolecular shielding surface for the isoelectronic system, the ^{21}Ne nucleus in a Ne atom interacting with a He atom. On an absolute scale the shielding surface for ^{21}Ne in Ne–He has a much steeper change than the ^{23}Na shielding surface, but only because the nuclei on the right-hand side of the Periodic Table have much larger expectation values for the $1/r^3$ value of the electrons. When this is taken into account, it is seen that intramolecular shielding surfaces involve a much greater response of the nucleus to the changing electronic environment (bond extension or compression) than the response of the nucleus to the approach of a neighboring solvent molecule described by the intermolecular shielding surface.

If the shielding of a nucleus in a molecule surrounded by six neighbors, say, can be considered as a sum of six pairwise contributions between itself and each neighbor molecule,

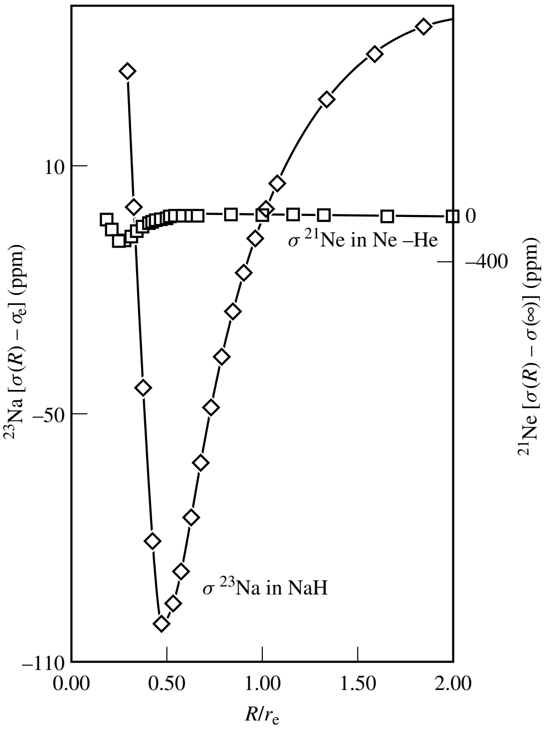

Figure 3 The intramolecular shielding surface for ^{23}Na in NaH and the intermolecular shielding surface for ^{21}Ne in NeHe

and if each pairwise intermolecular shielding function is known (similar to the ^{21}Ne shielding function for NeHe in Figure 3), then dynamic averaging amounts to sampling all such configurations of molecule and neighbors and calculating the intermolecular shielding for each configuration. This has been done for ^{129}Xe shielding in zeolite NaA. The same intermolecular shielding function that reproduces the $\sigma_1(T)$ for xenon in the gas phase reproduces the chemical shifts between the Xe, Xe$_2$, Xe$_3$, … , Xe$_8$ clusters trapped inside the cages of zeolite NaA.[**24,25**] In principle, chemical shifts in condensed phases can be obtained by a similar dynamic averaging.

6 RELATED ARTICLES

Shielding Calculations: LORG and SOLO Approaches; Gas Phase Studies of Intermolecular Interactions and Relaxation; Isotope Effects on Chemical Shifts and Coupling Constants; Shielding Calculations: IGLO Method; Shielding: Overview of Theoretical Methods; Shielding Theory: GIAO Method.

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Biographical Sketch

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