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Calculation of Hypershielding Contribution to Isotropic Nitrogen Shielding in Strong Magnetic Fields

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Abstract: Hypershielding contributions to magnetic shielding of the nitrogen **N** nucleus have been evaluated for some nitroso (R**N**O) and isodiazene (R$_1$R$_2$**NN**) compounds in the presence of an external spatially uniform, time-independent magnetic field, accounting for cubic response via Rayleigh–Schrödinger perturbation theory. Numerical estimates have been obtained at the coupled Hartree–Fock level of accuracy within the conventional common-origin approach. Medium-size basis sets of gaugeless (that is, without gauge-including phase factors) Gaussian functions have been employed in a numerical test to show that the isotropic hypershielding contribution $\tau^N B^2$, $\tau^N = 1/2\langle\Sigma_{\alpha\beta\gamma\delta}^N\rangle$, eqs 2–4 in the text, to average nitrogen shielding in Ph**N**O ($\tau^N \approx 1.1 \times 10^{-5}$ ppm T^{-2}), (CH$_3$)$_3$C**N**O ($\tau^N \approx 2.3 \times 10^{-5}$ ppm T^{-2}), and (CH$_3$)$_2$**NN** ($\tau^N \approx 4.4 \times 10^{-5}$ ppm T^{-2}) are similar and quite large. For ^{15}N at the highest currently available high-resolution NMR field strength of 22.3 T ($\omega^H/2\pi = 950$ MHz, $\omega^{15N}/2\pi = 96.3$ MHz) the change due to the additional shielding contribution for these compounds is between $\sim$0.5 and $\sim$2 Hz to lower frequency (upfield). Employing modern NMR instrumentation, shielding perturbations of this magnitude are, in principle, within detection limits, although instrumental instabilities and other field-dependent shielding phenomena make unambiguous detection at different field strengths difficult.

I. Introduction

Matter in the presence of intense external magnetic fields changes its basic properties and structure and leads to a multitude of interesting phenomena. As a result, strong fields are of interest in several branches of physics like atomic, molecular, or solid-state physics. A growing interest in the problem of molecules and clusters in strong magnetic fields is motivated by various technological applications in different branches of nanoscience,[1–5] and the relationship between the strength of the applied magnetic field and superconductivity has long been known.[6]

A few studies discussing effects observable in systems exposed to fields with intermediate strength (conventionally in the range from 30 to 10^4 T) are available. A review on atoms, molecules, and bulk matter has recently been published.[7] Earlier references are the conference proceedings on *Atoms and Molecules in Strong External Fields*[8] and the issue of the *International Journal of Quantum Chemistry* concerning The Properties of Molecules in Strong Magnetic Fields.[9]

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Experimental evidence in the lower limit of the intermediate regime, where conventional methods of perturbation theory are applicable, has been sought by some authors.[10−19] Vaara and co-workers reported theoretical investigations of nuclear magnetic shielding in closed-shell atomic systems as a function of even powers of a strong perturbing magnetic field[11] and analyzed the magnetic-field dependence of ^{59}Co nuclear magnetic shielding in Co(III) complexes.[12] A computational scheme based on Rayleigh−Schrödinger perturbation theory has been developed to evaluate 10 propagators appearing in the quantum mechanical definition of the fourth-rank hypershielding $\langle \Sigma_{\alpha\beta\gamma\delta}^I \rangle$ of the Ith nucleus in a molecule.[18]

Attempts have recently been made to evaluate fourth-rank hypermagnetisabilities in small-[13] and medium-size molecules,[15] conjugated systems, and fullerene.[16] Sum rules for invariance of the fourth-rank hypermagnetizability in a gauge translation have been examined in small molecules.[17] The effects of an intense magnetic field on the electron distribution and on the magnetizability have been studied for rare gas atoms.[14] Induced electron current densities depending on the third power of the applied field have been considered for aromatic and antiaromatic compounds, showing that the nonlinear response can cause a switch from diatropic to paratropic behavior and vice versa.[20]

Tellgren et al. implemented a nonperturbative scheme using London orbitals and applied it to boron monohydride and cyclobutadiene, showing the highly nonlinear behavior of the former, which is typical of a system turning from paramagnetic to diamagnetic and going through an energy minimum in the presence of a strong magnetic field.[21]

The investigations reported so far for small molecules indicate that hypermagnetizabilities and magnetic hypershieldings of H, C, N, and O nuclei are very small.[13,15] Therefore, nonlinear response to strong magnetic fields seems to be quite difficult to detect experimentally. On the other hand, the present study shows that the fourth-rank magnetic hypershielding for the nitrogen nucleus, $\Sigma_{\alpha\beta\gamma\delta}^N$, of some nitroso (RNO) and isodiazene (R_1R_2NN) compounds could, in principle, be experimentally detectable. The theoretical approach employed in this study is described in ref 18; only a brief summary is outlined in section II. Numerical results for the hypershielding contribution to the isotropic nitrogen shielding are reported and discussed in section III.

II. Fourth-Rank Nuclear Magnetic Hypershielding

The interaction energy of a diamagnetic molecule, i.e., a closed-shell system even under time reversal, in the electronic reference state a, in the presence of a static and spatially uniform external magnetic field **B**, and of an intramolecular magnetic dipole $\mathbf{m}_I$ at the Ith nucleus with position $\mathbf{R}_I$, can be expressed as a Taylor series[18]

$$\Delta W_a = W_a^{(2)} + W_a^{(4)} + ...$$

$$= \sigma_{\alpha\beta}^I m_{I\alpha} B_\beta + \frac{1}{6}\Sigma_{\alpha\beta\gamma\delta}^I m_{I\alpha} B_\beta B_\gamma B_\delta + ... \quad (1)$$

Only terms relevant for the following discussion are retained in expression 1, e.g., $\sigma_{\alpha\beta}^I$ is the second-rank magnetic shield-

ing at nucleus I,[22] and the fourth-rank tensor $\Sigma_{\alpha\beta\gamma\delta}^I$ accounts for nonlinear response in **B**. NMR relaxation phenomena in liquids are typically treated using semiclassical relaxation theory, where the imaginary part of the time-dependent quantum mechanical master equation gives rise to a small change to the energy (1) of the system and a small shielding perturbation.[23] An estimate of the magnitude of this phenomenon is presented later for a small molecule in a nonviscous liquid.

The field-dependent magnetic shielding of nucleus I in a molecule in the presence of the magnetic field **B** is defined by the expression[18]

$$\sigma_{\alpha\beta}^I(\mathbf{B}) = \sigma_{\alpha\beta}^I + \frac{1}{2}\Sigma_{\alpha\beta\gamma\delta}^I B_\gamma B_\delta + ... \quad (2)$$

The hypershielding tensor is defined as the fourth derivative of the molecular energy in the limit of vanishing perturbations, that is

$$\Sigma_{\alpha\beta\gamma\delta}^I = \frac{\partial^4 W_a^{(4)}}{\partial m_{I\alpha} \, \partial B_\beta \, \partial B_\gamma \, \partial B_\delta} \quad (3)$$

The hypershielding $\Sigma_{\alpha\beta\gamma\delta}^I$ can be expressed as a sum of 10 propagators[18]

$$\Sigma_{\alpha\beta\gamma\delta}^I = -\{\hat{B}_{I\alpha}^n, \hat{m}_\beta, \hat{m}_\gamma, \hat{m}_\delta\}_{-3} - \\ \{\hat{B}_{I\alpha}^n, \hat{m}_\beta, \hat{\chi}_{\gamma\delta}^d\}_{-2} - \{\hat{B}_{I\alpha}^n, \hat{m}_\gamma, \hat{\chi}_{\beta\delta}^d\}_{-2} - \{\hat{B}_{I\alpha}^n, \hat{m}_\delta, \hat{\chi}_{\gamma\beta}^d\}_{-2} + \\ \{\hat{\sigma}_{\alpha\beta}^{dI}, \hat{m}_\gamma, \hat{m}_\delta\}_{-2} + \{\hat{\sigma}_{\alpha\gamma}^{dI}, \hat{m}_\beta, \hat{m}_\delta\}_{-2} + \{\hat{\sigma}_{\alpha\delta}^{dI}, \hat{m}_\gamma, \hat{m}_\beta\}_{-2} + \\ \{\hat{\sigma}_{\alpha\beta}^{dI}, \hat{\chi}_{\gamma\delta}^d\}_{-1} + \{\hat{\sigma}_{\alpha\gamma}^{dI}, \hat{\chi}_{\beta\delta}^d\}_{-1} + \{\hat{\sigma}_{\alpha\delta}^{dI}, \hat{\chi}_{\gamma\beta}^d\}_{-1}, \quad (4)$$

where $\hat{m}_\alpha$ and $\hat{\chi}_{\gamma\beta}^d$ are the electronic operators for the orbital magnetic dipole and for the diamagnetic contribution to the susceptibility tensor, $\hat{B}_{I\alpha}^n$ is the operator for the magnetic field of n electrons on nucleus I, and $\hat{\sigma}_{\alpha\beta}^{dI}$ denotes the operator for the diamagnetic contribution to the nuclear shielding.[18]

The sum of the terms in eq 4 is invariant in a gauge transformation of the vector potential in ideal cases, for instance, for exact eigenfunctions to a model Hamiltonian, or optimal variational eigenfunctions.[24] In actual calculations allowing for the algebraic approximation, the total hypershielding $\Sigma_{\alpha\beta\gamma\delta}^I$ varies in a gauge translation, that is, a change of coordinate system. Computed results would be origin independent only in the limit of complete basis sets: the closeness of values obtained in different coordinate systems is a measure of quality of the basis set. Nonetheless, the addenda in eq 4 are not uniquely defined in any case. They transform among themselves in a change of gauge, which makes an assessment of the physical meaning of individual terms quite problematic in general. However, the use of an ad hoc gauge origin, e.g., the nucleus in question, turns out to be practical in some cases.

$\Sigma_{\alpha\beta\gamma\delta}^I$ quantitatively accounts for small changes to magnetic flux density at the nucleus caused by the Lorentz magnetic force of the external magnetic field acting to deform (compress) the electron density to a new equilibrium configuration. The magnitude of the response functions in relationship 4 depends on inverse powers (specified by the subindices −1, −2, and −3) of the excitation energies.

For the systems considered here, $\{\hat{B}_{I\alpha}^n, \hat{m}_\beta, \hat{m}_\gamma, \hat{m}_\delta\}_{-3}$ is strongly influenced by (i) the excitation energies $\hbar\omega_{ja}$ for

an electronic transition, $|a\rangle \rightarrow |j\rangle$, from the reference state to an excited state, e.g., electronic transitions involving low-lying states, such as $n_N \rightarrow \pi^*$, which often have the lowest excitation energies, and (ii) the energy differences $\hbar\omega_{jk}$ between two excited states, which becomes very small for near degeneracies. In the present case of RNO compounds the first term in relationship 4 makes the largest contributions to $\Sigma_{\alpha\beta\gamma\delta}^N$ (typically $\geq 85\%$) for the gauge origin on the reference nucleus.

In an isotropic medium, the molecule rotates freely with respect to a set of axes fixed to the laboratory's frame, where the stationary magnetic field, **B**, is usually aligned with the z direction. Therefore, since we want to relate shielding and hypershielding to intrinsic molecular properties, we must transform the tensors specified in space fixed axes, $\sigma_{\alpha\beta}^I(\text{lab})$ and $\Sigma_{\alpha\beta\gamma\delta}^I(\text{lab})$, to an axis system fixed to the molecule, by averaging over the surface of the unit sphere to yield the isotropic invariants. The isotropic shielding, $\langle\sigma^I\rangle$, of an NMR experiment is

$$\langle\sigma\rangle^I = \langle\sigma_{\alpha\beta}^I(\text{lab})\rangle + \frac{1}{2}\langle\Sigma_{\alpha\beta\gamma\delta}^I(\text{lab})\rangle\mathbf{B}^2$$

$$= \frac{1}{3}\sigma_{\alpha\alpha}^I(\text{mol}) + \frac{1}{30}[\Sigma_{\alpha\alpha\beta\beta}^I(\text{mol}) + \Sigma_{\alpha\beta\alpha\beta}^I(\text{mol}) + \Sigma_{\alpha\beta\beta\alpha}^I(\text{mol})]\mathbf{B}^2 \quad (5)$$

We note that in solution other processes lead to field-dependent shielding. Molecules with an anisotropic susceptibility tensor, $\chi_{\alpha\beta}$, are partially aligned when placed in a magnetic field, resulting in incomplete averaging of the anisotropy $\Delta\sigma^I = \sigma_{zz}^I - 1/2(\sigma_{xx}^I + \sigma_{yy}^I)$ of the second-rank shielding tensor $\sigma_{\alpha\beta}^I$ of nucleus I and leading to an isotropic shielding contribution with $\mathbf{B}^2$ field dependence.[25] Assuming $\sigma_{\alpha\beta}^I$ axial symmetry ($\sigma_{xx}^I = \sigma_{yy}^I$ and $\Delta\sigma^I \equiv \sigma_{\parallel}^I - \sigma_{\perp}^I$) and limited amplitude fast internal motion, the contribution due to partial orientation is

$$\sigma_\chi^I(\text{ppm T}^{-2}) = (S/15k_\text{B}T)\Delta\sigma^I\left(\frac{2}{3}\Delta\chi P_2(\cos\theta) + \frac{1}{2}\chi_R\sin^2\theta\cos 2\varphi\right) \quad (6)$$

where T is the absolute temperature and θ and ϕ are the angles between the chemical shielding anisotropy (CSA) unique axis and susceptibility tensor principal axes with $\Delta\chi = \chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$, $\chi_R = \chi_{xx} - \chi_{yy}$. $P_2(\cos\theta)$ is the Legendre polynomial of second degree, and S is the generalized order parameter, which acts to scale the degree of magnetic alignment depending upon the extent of any internal motions.[26] S varies between 0 and 1, with 1 corresponding to a static rigid model. The concept of a generalized order parameter has been introduced to NMR by Lipari and Szabo.[27,28]

In addition, small relaxation-induced field-dependent shielding occurs due to the dynamic frequency shift. The imaginary part of the spectral density, derived from the Fourier transform of the autocorrelation function, can be viewed as an oscillation; therefore, NMR relaxation processes can lead to frequency shifts; however, for a spin 1/2 nucleus, assuming the fast motion limit, these are often smaller than the line width.[29]

III. Results and Discussion

The shielding range for ^{15}N is large, and notably some systems show anti (that is, negative) shielding.[30] According to Saika and Slichter,[31] the wide range is primarily due to a change in local paramagnetic shielding, σ^{pI}, and for nitrogen this proposal has found qualitative support in correlation between isotropic shielding and $1/\Delta E$ (ΔE is the excitation energy from the ground state to low-lying excited states important in σ^{pN}, mainly $n_N \rightarrow \pi^*$ transitions).[32,33] Here, $\Sigma_{\alpha\beta\gamma\delta}^N$ is also assumed to be larger in systems with low-lying excited states. Solutions of isodiazenes (R_2NN) and monomers of nitroso species (RNO) are often colored, indicative of long-wavelength electronic absorption, and σ^{pN} in $-$NN and $-$NO groups is large.[33-35]

We calculated $\Sigma_{\alpha\beta\gamma\delta}^N$ for a series of nitroso compounds RNO, where the electronegativity of the R$-$ group is varied, so its inductive effect, $\mathscr{I}$, ranges from electron-withdrawing ($-\mathscr{I}$) to electron donating ($+\mathscr{I}$). The groups considered are R$-$ = F$-$, Cl$-$, Br$-$, FO$-$, HO$-$, H$_2$N$-$, C$_6$H$_5-$, H$-$, CF$_3-$, CH$_3-$, and (CH$_3$)$_3$C$-$. Molecules containing these substituents range from colorless FNO to red ClNO, brown BrNO, blue-green C$_6$H$_5$NO, blue CH$_3$NO, and deep blue C(CH$_3$)$_3$NO. $\Sigma_{\alpha\beta\gamma\delta}^N$ was also calculated for two isodiazenes, H$_2$NN and (CH$_3$)$_2$NN: solutions of persistent isodiazenes are deep purple,[34] and the terminal nitrogen exhibits large (negative) antishielding.

The computational procedure is based on the coupled Hartree$-$Fock (CHF) approach implemented in the DALTON package.[36] The calculations employed medium-size basis sets, referred to as I $\rightarrow$ VI, that is, I, aug-cc-pCVTZ, from refs 37 and 38 for ClNO and BrNO; II, aug-cc-pCVTZ-CTOCD-uc, (C, N, O, F: 11s11p6d2f/H: 6s5p2d) contracted to [C, N, O, F: 5s11p6d2f/H: 4s5p2d] from ref 39 and 40 for FONO, HONO, H$_2$NNO, H$_2$NN, and HNO; III, sp$_{tt}$d$_{td}$f$_2$/sp$_t$d, (C, N, O: 12s9p5d2f/H:7s4p1d) contracted to [C, N, O: 9s9p5d2f/H: 4s4p1d] from refs 41 and 42 for HONO; IV, Huz-III for CF$_3$NO, C$_6$H$_5$NO, (CH$_3$)$_3$CNO, (CH$_3$)$_2$NN; V, Huz-IV for FNO, C$_6$H$_5$NO, CH$_3$NO, (CH$_3$)$_2$NN from ref 43; VI, aug-cc-pCVQZ from ref 37 and 38 for BrNO. These basis sets were found to be large enough to obtain reasonable estimates of nitrogen hypershielding at the Hartree$-$Fock (HF) level of accuracy.

Simple chemical-bonding consideration would suggest that the wave function of the systems of this investigation, nitroso compounds and, even more so, isodiazenes, has a significant multireference character. As Hartree$-$Fock perturbation theory is likely to suffer from triplet and, possibly, singlet instabilities, random-phase approximation (RPA) singlet and triplet excitation frequencies were evaluated in a check on FNO and H$_2$NN via the SYSMO code.[44] We found 1908 positive singlet excitation frequencies for the former and 1936 for the latter, excluding any problem of singlet instability in the calculation of $\langle\sigma^N\rangle$ and $\langle\Sigma^N\rangle$. On the other hand, triplet instabilities were found for both systems, which however do not affect shielding and hypershielding estimates.

The molecular geometries were optimized at the density functional theory (DFT) B3LYP level[45] employing the 6-31G** basis set.[46,47]

Table 1. Nitrogen Isotropic Hypershielding for Some Nitroso RNO and Isodiazene RNN Compounds[a]

molecule	basis set	$\langle \Sigma_{iiii}^N \rangle \times 10^{-4\,b}$	$\langle \sigma^N \rangle^c$	$(1/2)\langle \Sigma^N \rangle B^{2\,d}$
FNO	V	3.51 (3.35)	−335.3 (−264.6) [−236[e]]	3×10^{-3} (3×10^{-3})
FONO	II	7.20	−441.0	7×10^{-3}
ClNO	I	9.99	−431.9	9×10^{-3}
HONO	II	10.09	−484.2	9×10^{-3}
	III	10.16	−485.6	9×10^{-3}
H_2NNO	II	10.29	−531.5	9×10^{-3}
BrNO	I	17.80	−384.1	0.02
	VI	21.19	−441.9	0.02
C_6H_5NO	IV	125.5 (65.8)	−1067.2 (−631.7)	0.11 (0.06)
	V	120.3 (64.0)	−1063.0 (−629.9) [−667[f]]	0.11 (0.06)
CF_3NO	IV	145.9	−431.9	0.13
CH_3NO	V	203.6	−1269.3	0.18
HNO	II	229.8	−1240.5	0.21
$C(CH_3)_3NO$	IV	248.4 (87.4)	−1373.2 (−791.1) [−735[g]]	0.23 (0.07)
H_2NN	II	423.1	−2025.8	0.38
$(CH_3)_2NN$	IV	482.3	−2110.0	0.44
	V	437.0	−2064.7	0.40

[a] Hartree−Fock results. The gauge origin is taken at the nucleus in question. Corresponding values via DFT- Keal-Tozer KT3 functional[48,49] are given in parentheses, and experimental values are reported in brackets. [b] In SI atomic units. The conversion factor to SI units is $1.80997698 \times 10^{-11}$ T^{-2}, using the CODATA values of the fundamental constants 2002.[56] [c] In ppm. [d] Isotropic contribution to $\langle \sigma^N \rangle$, eqs 2 and 5, in ppm, for $B = 100$ T. [e] Estimated from the average ^{15}N chemical shift, 128 ppm, of FNO with respect to aqueous nitrite, ref 57, the ^{15}N chemical shift of the aqueous nitrite ion, 608 ppm, with respect to anhydrous NH$_3$, ref 33, and the absolute shielding, 244.6 ppm, of nitrogen in NH$_3$, ref 58. [f] Estimated from the ^{15}N shielding, −531.52 ppm, from ref 59 (sample in acetone and referenced to CH$_3$NO$_2$); converted to the shielding scale assuming σ_{av}^N (CH$_3$NO$_2$) = −135.8 ppm from ref 58. The experimental ^{15}N shielding measured in this work (sample in acetone) σ_{av}^N = −666.4 ppm. [g] Estimated from the ^{15}N shielding, −599.40 ppm, from ref 35 (sample in acetone and referenced to CH$_3$NO$_2$); converted to the shielding scale assuming σ_{av}^N (CH$_3$NO$_2$) = −135.8 ppm from ref 58.

The calculated isotropic contribution from hypershielding $\langle \Sigma^N \rangle$ to isotropic shielding $\langle \sigma^N \rangle$ will be origin independent only for complete basis sets; see the previous discussion. However, for $(CH_3)_2NN$ and HONO, it was found for two different origins of the vector potential, namely, the nucleus in question and the center of mass (CM), hypershielding differs by less than 2×10^{-9} ppm T^{-2} with basis sets in Table 1. Therefore, relying on that criterion for these types of molecular systems, we conclude that basis sets I−VI are suitable for quantitative estimates of nitrogen hypershielding.

Although we do not claim that the calculated second- and fourth-rank shielding tensors of the N nucleus have converged to the HF limit, the values reported in Table 1 for HONO, C_6H_5NO, and $(CH_3)_2NN$ for two basis sets document the quality of the present predictions. However, we also note that for these types of molecular systems the HF approach, due to lack of electron correlation, often provides quite poor values for $\langle \sigma^N \rangle$. Very much better agreement with experimental isotropic shielding data is achieved via the DFT approach, allowing for the Keal and Tozer KT3 functional,[48,49] as implemented in the DALTON package.[36] The KT3 functional was found to be the most efficient for calculating shielding constants in a series of small molecules[50] and for studies of hydrogen bonding.[51] Also, in the present research the computed isotropic shielding values for FNO, C_6H_5NO and $(CH_3)_3CNO$ are each quite close to experiment.

An indication obtained here is that electron-correlation effects act to lower the magnitude of $\langle \sigma^N \rangle$ and $\langle \Sigma^N \rangle$. On the other hand, DFT methods employed in this work are not designed to properly deal with nondynamical correlation. Therefore, further work will be required to assess the importance of electron correlation in nuclear hypershielding of nitrogen in RNO and R_1R_2NN compounds; however, this is beyond the scope of the present paper, whose primary concern is to identify molecular systems as potential candidates for experimental detection.

Clearly for this series of nitroso derivatives the magnitude of nitrogen hypershielding is sensitive to the inductive character of R−; as the electronegativity of R increases, hypershielding is reduced, whereas electron-donating groups such as $(CH_3)_3C-$ markedly increase hypershielding. The model isodiazenes show similar large hypershielding effects with $\tau^N \equiv 1/2\langle \Sigma^N \rangle \approx 4.4 \times 10^{-5}$ ppm T^{-2}.

The dominant contribution to hypershielding arises from the response function $\{\hat{B}_{l\alpha}^n, \hat{m}_\beta, \hat{m}_\gamma, \hat{m}_\delta\}_{-3}^{mol}$; see the previous discussion. This term is positive for the systems studied assuming the origin of the gauge on the N nucleus and, therefore, acts to *increase* isotropic shielding.

For PhNO, $\tau^N \approx 1.1 \times 10^{-5}$ ppm T^{-2} and assuming spectrometer magnetic field strengths for ^{15}N of 8.45 T ($\omega^N/2\pi = 36.5$ MHz) and 22.3T ($\omega^N/2\pi = 96.3$ MHz), the shielding change due to hypershielding as the field increases from 8.45 T to 22.3 T is $\approx 4.7 \times 10^{-3}$ ppm (≈ 0.5 Hz) upfield, i.e., to lower resonance frequency. In principle, although small, a shielding change of this magnitude is detectable as modern high-resolution NMR spectrometers are capable of resolving differences of ~0.15 Hz, as occurs for the H resonance in CHCl$_3$ due to[35,37] Cl isotope shifts.[52]

However, several experimental factors, including sample stability (over periods of many days) and the requirement for identical sample temperature on spectrometers operating with different field strengths, have made it difficult to achieve the required experimental accuracy and reproducibility to adequately test the predictions. The measured ^{15}N temperature coefficient, $\Delta\langle\sigma^N\rangle/\Delta T$, of Ph^{15}NO in acetone-d_6 over the small range 20−21 °C is ca. -2.6×10^{-3} ppm per 0.1 °C. Furthermore, in solution NMR due to the effect of susceptibility anisotropy, PhNO is expected to be weakly oriented

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by the static magnetic field. A calculation of $\Delta\chi$, χ_R, and $\Delta\sigma^N$ for PhNO gave -1.94×10^{-27} J T^{-2}, 1.05×10^{-27} J T^{-2}, and -1685 ppm, respectively, with $\theta = \pi/2$ and $\phi = 4.3°$. Assuming $T = 293$ K and limited fast internal motion, $S = 0.8$, sample orientation could lead to an isotropic field-dependent shielding contribution to σ_χ^N as big as -2.6×10^{-5} ppm T^{-2}.

The magnitude is similar but opposite in sign to the hypershielding effect. The calculated CSA, $\Delta\sigma^N$, for PhNO is large; however, the shielding tensor characteristics are similar to experimental data from *p*-nitroso-*N,N*-dimethyl-alanine.[53] Furthermore, the average shielding estimated for the nitrogen nucleus via some preliminary DFT calculations,[54] using the KT3 scheme functional[48,49] available in the DALTON code,[36] -629.9 ppm, is in good agreement with experiment, -666 ppm (sample in acetone).

Assuming the rotational diffusion characteristics of PhNO are similar to toluene[55] with symmetric top rotational diffusion and $D_{\parallel} = 3.8 \times 10^{10}$ s^{-1}, $D_\perp = 9.1 \times 10^{10}$ s^{-1}, $1/\tau_{2n} = 6D_\perp + n^2(D_{\parallel} - D_\perp)$, and $\omega^N\tau_{2n} \ll 1$, the calculated dynamic frequency shift from autocorrelated ^{15}N$-$H dipolar and ^{15}N CSA relaxation is small ($<10^{-8}$ ppm T^{-2}) and field-dependent shielding contribution from the dynamic frequency shift can be neglected for PhNO.

IV. Concluding Remarks

Measurement of response properties of a molecule in a strong magnetic field, such as susceptibility and nuclear shielding, as a function of the field strengths currently attainable in laboratory, have so far been considered quite difficult.

Theoretical results obtained in this work at the Hartree$-$Fock and DFT levels of accuracy, within the common origin approach for the vector potential, indicate that the hyper-shielding of nitrogen nuclei in molecules containing nitroso and diazene moieties might be experimentally observed. Therefore, the recent introduction of NMR instruments using superconducting magnets with strong flux density increases the possibility that useful information may soon become available from the field dependence of spectral parameters such as chemical shielding of nitrogen in R**N**O and R$_1$R$_2$N**N** compounds.

The increased chemical shieldings (upfield) arising from quadratic dependence of the nuclear shielding constant in $(CH_3)_3CNO$ and $(CH_3)_2NN$ estimated via Hartree$-$Fock calculations are, respectively, $\sim$0.2 and $\sim$0.4 ppm for a field of 100 T, which supports the expectation that hypershielding effects in NMR spectra are, in principle, within detection limits, although other field-dependent processes, such as susceptibility-induced partial orientation effects, may act to reduce the magnitude of the hypershielding phenomenon as predicted here for C_6H_5NO. Electron correlation effects partially investigated here are quite sizable and should be considered for accurate quantitative predictions. However, further theoretical and experimental investigation of quadratic dependence of NMR parameters does now, at least, continue to merit consideration.

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