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Fluorine chemical shift tensors in substituted fluorobenzenes using cross correlations in NMR relaxation

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Abstract

The effect of cross correlations between the chemical shift anisotropy of fluorine and its dipolar interaction with nearby protons has been investigated via multi-spin longitudinal relaxation studies in fluorinated benzenes. Experiments have been performed on four different fluorinated benzenes. Significant variations in the value/orientation of the chemical shift anisotropy tensors of fluorine have been observed as a function of substitution. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Cross correlations, or interference terms between two different relaxation pathways in a system of nuclear spins, have been the subject of theoretical and experimental studies for many years [1–7]. The potential of dipole–dipole (DD) cross correlated relaxation rates in providing information about structural parameters like dihedral angles in biomolecules and anisotropic motion, has been recognised and exploited recently [8–13]. At higher magnetic fields, studies of cross correlations between the chemical shift anisotropy (CSA) and dipolar interactions also provide useful structural information [14]. There have been several studies on the influence of cross correlations on the relaxation of nuclei with large CSA values (like ^{13}C, ^{15}N, ^{19}F) [15–17]. A systematic study of the longitudinal relaxation of fluorine to monitor the cross correlations between the CSA of fluorine and its dipolar interactions with nearby protons are described in this paper. Such a study provides insights into the variation of the value and the orientation of ^{19}F CSA tensors as a function of different substitutions in fluorinated benzenes. The cross correlations give rise to a differential longitudinal relaxation of various lines of a spin multiplet, which is then analysed by using appropriate magnetisation modes [18–25].

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2. The emergence of multi-spin order in a relaxation experiment

All experiments were carried out at 300 K on a Bruker AMX-400 NMR spectrometer operating at a ^{1}H resonance frequency of 400 MHz. Studies have been performed on four fluorinated samples: 1, 2-dichloro 4-fluoro 5-nitro benzene (DCFNB), 2, 4-dichloro 5-fluoro benzoic acid (DCFBA), 2, 6-dichloro 4-fluoro phenol (DCFP), and 1, 5-difluoro 2, 4-dinitro benzene (DFDNB) (see Fig. 1 for details). The samples have been de-gassed and the NMR tubes sealed, to eliminate the possibility of impurities like dissolved oxygen acting as external sources of relaxation.

Spin relaxation can be analysed using the Redfield method, wherein the evolution of populations and coherences is monitored after a perturbation [26]. Most relaxation studies, however, use the basis of 'modes', many of which can be directly related to physical observables. For longitudinal relaxation, these modes are essentially linear combinations of the level populations. Various single- and multi-spin modes can be constructed for weakly coupled spins, each with a well-defined parity under spin inversion. The evolution of these modes is given by [27]

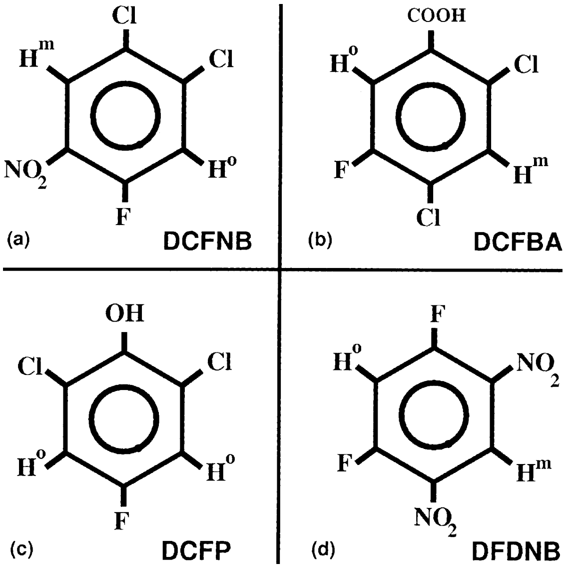

Fig. 1. Structure and parameters of the fluorinated ring molecules. The T_1 of a spin has been measured by observing its recovery towards equilibrium after inversion, with all other spins being decoupled during signal acquisition. (a) The structure of DCFNB. The fluorine spin (labeled F) and the two protons (labeled H^{o} and H^{m}, being ortho or meta to the fluorine, respectively) resonate at −123.39, 7.46 and 8.15 ppm, respectively. The values of the coupling constants measured are $J_{\mathrm{FH}^{o}} = 10.04$ Hz and $J_{\mathrm{FH}^{m}} = 7.16$ Hz. The proton–proton para-coupling constant $J_{\mathrm{H}^{o}\mathrm{H}^{m}}$ is too small to be resolved. Proton T_1's of $(T_1)_{\mathrm{H}^{o}} = 24.1$ s and $(T_1)_{\mathrm{H}^{m}} = 71.43$ s and a fluorine T_1 of $(T_1)_{\mathrm{F}} = 3.94$ s have been observed in the de-gassed sample. (b) The structure of DCFBA. The fluorine spin (labeled F) and the two protons (labeled H^{o} and H^{m}) resonate at −122.42, 7.84 and 7.58 ppm, respectively. The values of the coupling constants measured are $J_{\mathrm{FH}^{o}} = 9.02$ Hz and $J_{\mathrm{FH}^{m}} = 6.47$ Hz. The proton–proton para-coupling constant $J_{\mathrm{H}^{o}\mathrm{H}^{m}}$ is too small to be resolved. Proton T_1's of $(T_1)_{\mathrm{H}^{o}} = 8.06$ s and $(T_1)_{\mathrm{H}^{m}} = 62.5$ s and a fluorine T_1 of $(T_1)_{\mathrm{F}} = 3.32$ s have been observed in the de-gassed sample. (c) The structure of DCFP. The fluorine spin (labeled F) and the two equivalent ortho protons (labeled H^{o}) resonate at −127.02 and 7.04, ppm respectively. The values of the coupling constant measured is $J_{\mathrm{FH}^{o}} = 7.84$ Hz. A proton T_1 of 46.52 s and a fluorine T_1 of 12.9 s have been observed in the de-gassed sample. (d) The structure of DFNB. The equivalent fluorine nuclei (labeled F) resonate at −110.13 ppm while the protons (labeled H^{o} and H^{m}) resonate at 4.96 and 6.57 ppm respectively. The values of the coupling constants measured are $J_{\mathrm{FH}^{o}} = 9.71$ Hz and $J_{\mathrm{FH}^{m}} = 7.58$ Hz. The proton–proton para-coupling constant $J_{\mathrm{H}^{o}\mathrm{H}^{m}}$ is too small to be resolved. Proton T_1's of $(T_1)_{\mathrm{H}^{o}} = 20.41$ s and $(T_1)_{\mathrm{H}^{m}} = 90.91$ s and a fluorine T_1 of $(T_1)_{\mathrm{F}} = 3.22$ s have been observed in the de-gassed sample.

$$\frac{\mathrm{d}}{\mathrm{d}t}\vec{M} = \Gamma \Delta \vec{M}, \tag{2.1}$$

where $\Delta\vec{M}$ denotes the deviation of the mode $\vec{M}$ from its equilibrium value. The elements of the relaxation matrix Γ are linear combinations of different auto and cross correlation spectral densities. As an illustration, the rate equation for the DCFNB sample (a weakly coupled three spin system with one fluorine, denoted F and two protons, ortho and meta, to the fluorine denoted H^o and H^m, respectively) is

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} 1 \\ \mathrm{F}_z \\ \mathrm{H}^o_z \\ \mathrm{H}^m_z \\ 2\mathrm{F}_z\mathrm{H}^o_z \\ 2\mathrm{F}_z\mathrm{H}^m_z \\ 2\mathrm{H}^o_z\mathrm{H}^m_z \\ 4\mathrm{F}_z\mathrm{H}^o_z\mathrm{H}^m_z \end{bmatrix} = - \begin{bmatrix} 0 & & & & & & & \\ 0 & \rho_{\mathrm{F}} & & & & & & \\ 0 & \sigma_{\mathrm{FH}^o} & \rho_{\mathrm{H}^o} & & & \text{SYMMETRIC} & & \\ 0 & \sigma_{\mathrm{FH}^m} & \sigma_{\mathrm{H}^o\mathrm{H}^m} & \rho_{\mathrm{H}^m} & & & & \\ 0 & \Delta^{\mathrm{F}}_{\mathrm{FH}^o} & \Delta^{\mathrm{H}^o}_{\mathrm{FH}^o} & 0 & \rho_{\mathrm{FH}^o} & & & \\ 0 & \Delta^{\mathrm{F}}_{\mathrm{FH}^m} & 0 & \Delta^{\mathrm{H}^m}_{\mathrm{FH}^m} & \delta_{\mathrm{F}} + \sigma_{\mathrm{H}^o\mathrm{H}^m} & \rho_{\mathrm{FH}^m} & & \\ 0 & 0 & \Delta^{\mathrm{H}^o}_{\mathrm{H}^o\mathrm{H}^m} & \Delta^{\mathrm{H}^m}_{\mathrm{H}^o\mathrm{H}^m} & \delta_{\mathrm{H}^o} + \sigma_{\mathrm{FH}^m} & \delta_{\mathrm{H}^m} + \sigma_{\mathrm{FH}^o} & \rho_{\mathrm{H}^o\mathrm{H}^m} & \\ 0 & \delta_{\mathrm{F}} & \delta_{\mathrm{H}^o} & \delta_{\mathrm{H}^m} & \Delta^{\mathrm{F}}_{\mathrm{FH}^m} + \Delta^{\mathrm{H}^o}_{\mathrm{H}^o\mathrm{H}^m} & \Delta^{\mathrm{F}}_{\mathrm{FH}^o} + \Delta^{\mathrm{H}^m}_{\mathrm{H}^o\mathrm{H}^m} & \Delta^{\mathrm{H}^o}_{\mathrm{FH}^o} + \Delta^{\mathrm{H}^m}_{\mathrm{FH}^m} & \rho_{\mathrm{FH}^o\mathrm{H}^m} \end{bmatrix} \times \begin{bmatrix} 1 \\ \Delta\mathrm{F}_z \\ \Delta\mathrm{H}^o_z \\ \Delta\mathrm{H}^m_z \\ \Delta 2\mathrm{F}_z\mathrm{H}^o_z \\ \Delta 2\mathrm{F}_z\mathrm{H}^m_z \\ \Delta 2\mathrm{H}^o_z\mathrm{H}^m_z \\ \Delta 4\mathrm{F}_z\mathrm{H}^o_z\mathrm{H}^m_z \end{bmatrix}, \tag{2.2}$$

where the mode $\langle 1 \rangle$ is the total sum of the populations and is unobservable. The single spin order modes $\langle \mathrm{F}_z \rangle$, $\langle \mathrm{H}^o_z \rangle$ and $\langle \mathrm{H}^m_z \rangle$ are the total magnetisations of the corresponding spins. The modes $\langle 2\mathrm{F}_z\mathrm{H}^o_z \rangle$, $\langle 2\mathrm{F}_z\mathrm{H}^m_z \rangle$ and $\langle 2\mathrm{H}^o_z\mathrm{H}^m_z \rangle$ correspond to two-spin order. The mode $\langle 4\mathrm{F}_z\mathrm{H}^o_z\mathrm{H}^m_z \rangle$ is the three-spin order mode. The $\rho_i \equiv (1/T_{1i})$ are the self-relaxation rates while the σ_{ij} are cross relaxation rates that interconvert modes of the same order. These self- and cross relaxation rates have contributions from auto correlation spectral densities alone. In the initial rate approximation, the interconversion between the single-spin and two-spin modes is governed solely by the CSA(i)–DD(ij) cross correlation rate Δ^i_{ij}. The DD (ij,ik) cross correlation rate δ_i interconverts the single- and the three-spin order modes. Modes for the DCFBA sample (also a weakly coupled three-spin system) are defined identically. A different set of symmetrised modes have to be defined for the samples DCFP and DFDNB which have inherent symmetry (see later).

2.1. Nuclei selective inversion recovery experiments

The $^{19}\mathrm{F}/^{1}\mathrm{H}$ magnetisation is inverted with a π pulse and detected at different relaxation intervals. The fluorine spectra at different recovery times τ and the evolution of the single- and the two-spin order modes of the weakly coupled three-spin system (DCFNB) is shown in Fig. 2. Similar inversion recovery spectra have been obtained for all the four samples, with inversion of the fluorine and the proton nuclei separately [28] (spectra not shown here). The unequal relaxation of different lines of the fluorine multiplet is an evidence of the emergence of multi-spin order and is a direct measure of cross correlations in the system [27]. Hence, after an inversion of the F spin magnetisation, the buildup of the two-spin mode $\langle 2\mathrm{F}_z\mathrm{H}^o_z \rangle$ (using the

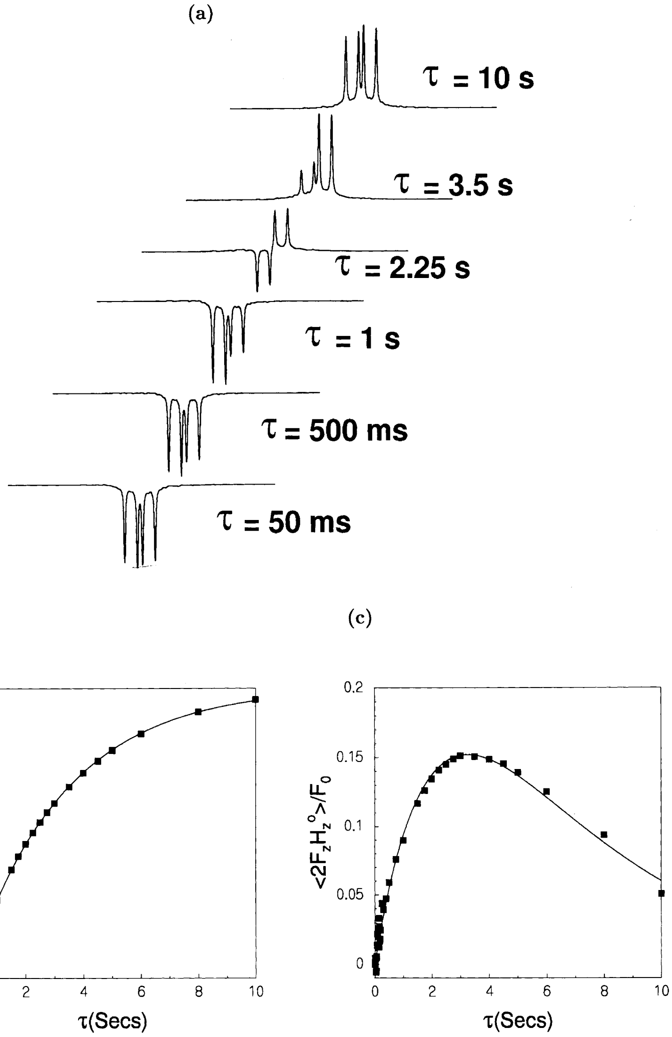

Fig. 2. (a) ^{19}F spectra of CFNB for different recovery times τ. The differential recovery of various lines indicates the presence of cross correlations in the molecule. The recovery of single-spin order and the buildup and decay of two-spin order as obtained from inversion recovery experiments are plotted in (b) and (c), respectively.

initial rate approximation), quantifies the CSA (F) – DD (F – H^o) cross correlation rate $\Delta^{F}_{FH^o}$. Longitudinal spin order is detectable by conversion to antiphase magnetisation by a selective pulse on the spin of interest, or for homonuclear spins, by a non-selective pulse of flip angle less than 90°. Since our studies are confined to heteronuclear spin systems, we use detection pulses of flip angle 90°. Cross correlation rates were determined from the initial slope of buildup curves of multi-spin modes, after a double-exponential fitting of the entire curve, the analytical first derivative at zero delay giving the buildup rate.

It can be clearly inferred from the experiments on DCFNB and DCFBA (both weakly coupled three-spin systems), that the cross correlated relaxation of the fluorine spin (F) is dominated by its CSA and its dipolar interaction with the nearest proton (H^o). A similar conclusion can be drawn for the H^o spin, with the main contribution to cross correlation in the ^{1}H inversion experiment coming from the CSA of spin H^o and its dipolar interaction with the fluorine spin. In consonance with smaller CSA values for protons, this

CSA–DD rate is much smaller than that of the fluorine spin. The proton H^m relaxes extremely slow, as is evident from its very gradual return to equilibrium after the perturbation (proton T_1 s of as large as 90 s have been observed in these de-gassed samples). The other cross correlation rates for e.g., the cross correlation between the CSA H^m and the $F - H^m$ dipolar interaction ($\Delta^{H^m}_{FH^m}$) and the DD cross correlation between $F - H^o$ and $F - H^m$ (δ_F) though observable, are rather small and have not been quantified.

It may be mentioned here that although all the samples were vacuum sealed after several freeze pump and thaw cycles, they show varying T_1 s and cross correlations (see Fig. 1). While the T_1 s can depend on the amount of residual oxygen in the sample, the cross correlation rates do not have such a dependence. Therefore the observed differences in the Δ^i_{ij} values are not due to residual oxygen, but are real variations. A fitting of the initial rate approximation to the evolution curves yields the values of $\Delta^{F}_{FH^o} = 0.128\ s^{-1}$ and $\Delta^{H^o}_{FH^o} = 0.018\ s^{-1}$ for DCFNB and $\Delta^{F}_{FH^o} = 0.33\ s^{-1}$, $\Delta^{H^o}_{FH^o} = 0.028\ s^{-1}$, and $\Delta^{F}_{FH^m} = 0.009\ s^{-1}$ for DCFBA for the CSA–DD cross correlation rates.

The modes of interest in the DCFP system (an FH_2 system with both protons being magnetically equivalent), are the two-spin order mode $\langle 2F_z(H^o_z + H^{o'}_z)\rangle$ and the three-spin order $\langle 4F_zH^o_zH^{o'}_z)\rangle$. Since the H spins are magnetically equivalent, the other modes are not observable. An analysis using the initial rate approximation yielded the CSA–DD cross correlation rates $1/2(\Delta^{F}_{FH^o} + \Delta^{F}_{FH^{o'}}) = 0.0255\ s^{-1}$, $1/2(\Delta^{H^o}_{FH^o} + \Delta^{H^{o'}}_{FH^{o'}}) = 0.0014\ s^{-1}$, and the DD cross correlation rate $\delta_F = 0.0078\ s^{-1}$ for this system. The cross correlation between $F - H^o$ and $F - H^{o'}$, quantified by the rate δ_F, has been observed and gives rise to a significant three spin order [28] (spectra not shown here).

The magnetisation modes for the DFDNB sample (an $F_2H^oH^m$ four-spin system, with both fluorine nuclei being magnetically equivalent) are defined in the usual manner [29]. CSA–DD cross correlation rates of $1/2(\Delta^{F}_{FH^o} + \Delta^{F'}_{F'H^o}) = 0.048\ s^{-1}$, $1/2(\Delta^{H^o}_{FH^o} + \Delta^{H^o}_{F'H^o}) = 0.00265\ s^{-1}$, $1/2(\Delta^{F}_{FH^m} + \Delta^{F'}_{F'H^m}) = 0.006\ s^{-1}$, and DD cross correlation rates of $\delta_{H^o} = 0.016\ s^{-1}$, and $1/2(\delta_F + \delta_{F'}) = 0.0015\ s^{-1}$ were obtained using the initial rate approximation.

The CSA–DD cross correlation rate $\Delta^i_{ij}(\omega)$ is proportional to the magnitude of the chemical shift anisotropy of a spin, times a geometric factor, which refers to the angle subtended by the internuclear vector and the CSA symmetry axis given by,

$$(\Delta\sigma_g)_i = \Delta\sigma_i \times \left[\frac{1}{2}(3\cos^2\phi_{i,ij} - 1)\right] = \left[\frac{10\pi}{\mu_0 B_0 \gamma_i^2 \gamma_j \hbar (r_{ij}^{-3})}\right] \times \Delta^i_{ij}(\omega_i) \times \left[\frac{1 + \omega_i^2\tau_c^2}{\tau_c}\right]. \tag{2.3}$$

Hence, this structural parameter $(\Delta\sigma_g)_i$, can be determined from the CSA–DD rate $\Delta^i_{ij}(\omega)$ and an independent measurement of the correlation time τ_c.

The correlation time τ_c is usually calculated from a measurement of the cross relaxation rate σ_{ij}, which can be determined from steady-state (SS)-NOE experiments. The NOE enhancement on the fluorine spin is measured, after irradiation of all the protons. The CSA tensor parameters estimated from CSA–DD cross correlation rates, for ^{19}F and ^{1}H in different fluorobenzenes, are given in Table 1. The $(\Delta\sigma_g)^{F}_{FH^o}$ as well as $(\Delta\sigma_g)^{H^o}_{FH^o}$ show significant variation in these samples with the variation in $(\Delta\sigma_g)^{F}_{FH^o}$ being larger. These variations can arise due to variations in the values of CSA tensors as well as the orientation of these tensors with respect to the FH dipolar vectors, arising from different substitutions, mainly at the ortho positions in these molecules (the 'ortho-effect' [30]).

Previous workers in the field [30,31] have determined the principal elements of the ^{19}F chemical shift tensor in different substituted fluorobenzenes in the solid-state. They have observed pronounced variations in the magnitude and orientation of the chemical shift anisotropy tensors, on chemical substitutions, with values ranging from $\Delta\sigma = 68$ ppm for para-fluorophenol to 175 ppm for Tetrafluoro-1,4-benzoquinone, and angles varying from 0° to 38°. In particular, they note the existence of an 'ortho-effect' on the principal values of the chemical shift anisotropy wherein a large shift in the CSA value (of up to 50 ppm) is observed when a phenol, toluene or another fluorine is substituted in an ortho position to the fluorine spin in the

Table 1
The CSA structural parameter $\Delta\sigma_g$ estimated for the ^{19}F and ^{1}H nuclei in different fluorobenzenes

System	NOE factor	ρ_{F} (s^{-1})	τ_c (ps)	$\Delta\sigma_g$ (ppm)
DCFNB	0.045	0.254	9.95	$(\Delta\sigma_g)^{\mathrm{F}}_{\mathrm{FH}^o} = 35.21$ $(\Delta\sigma_g)^{\mathrm{H}^o}_{\mathrm{FH}^o} = 4.66$
DCFBA	0.043	0.301	11.26	$(\Delta\sigma_g)^{\mathrm{F}}_{\mathrm{FH}^o} = 80.71$ $(\Delta\sigma_g)^{\mathrm{F}}_{\mathrm{FH}^m} = 11.52$ $(\Delta\sigma_g)^{\mathrm{H}^o}_{\mathrm{FH}^o} = 6.41$
DCFP	0.024	0.078	1.62	$(\Delta\sigma_g)^{\mathrm{F}}_{\mathrm{FH}^o} = 87.86$ $(\Delta\sigma_g)^{\mathrm{H}^o}_{\mathrm{FH}^o} = 4.45$
DFDNB	0.032	0.311	8.65	$(\Delta\sigma_g)^{\mathrm{F}}_{\mathrm{FH}^o} = 15.18$ $(\Delta\sigma_g)^{\mathrm{F}}_{\mathrm{FH}^m} = 8.2$ $(\Delta\sigma_g)^{\mathrm{H}^o}_{\mathrm{FH}^o} = 0.81$

solid-state. To the best of our knowledge, this is a first study of its kind in the liquid state where we find the sensitivity of cross correlation rates to chemical substitutions. Since these CSA–DD rates encode information about the chemical shift anisotropy tensors, we expect that these variations reflect the dependence of the magnitude and orientation of the CSA tensors on the chemical structure of the molecule. Ab initio quantum chemistry and molecular orbital calculations, in addition to the estimation of these cross correlation rates would lead to a meaningful model of the CSA tensors in these compounds.

3. Conclusions

It has been demonstrated that cross correlations between chemical shielding anisotropy (CSA) and DD interactions contribute significantly to the relaxation of nuclei with a large CSA, like fluorine. The contribution of such cross terms to the relaxation of various weakly coupled magnetically equivalent and non-equivalent spin systems has been studied. A pronounced variation in the cross correlation rate has been observed, indicating large variations in the value/orientation of the CSA tensors as a function of substitution in fluorobenzenes.

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