by causing unpairing of formally paired electrons on the valence s orbital of atom B only by a small amount. It is, therefore, likely that the nuclear spin coupling constant is related to the induced spin density on the valence s orbital of atom A when a small quantity of electron spin density is placed on the s orbital of atom B. Accordingly, a correlation roughly exists between the contact shift in $H_A - C - C - H_B$ and the corresponding $H_A - H_B$ coupling constant in the $H_A - C - C - H_B$ fragment. From an analogous correlation between induced spin density and the $H_A - H_B$ coupling constant in the $H_A - C - C - H_B$ fragment, it is inferred that upfield contact shift of proton HA in the $H_A - C - C - H_B$ fragment is comparative.

A σ-type nickel–ligand interaction also causes a small unpairing of the formally paired electrons of the oriented lone pair and induces positive or negative electron spin density on the various protons.1 Accordingly, a correlation roughly exists between the contact shift in $H_A - C - N - Ni(II)$ system and the corresponding $H_A - H_B$ coupling constant in the $H_A - C - N - Ni(II)$ system.2 It is inferred that upfield contact shift of proton HA in the $H_A - C - N - Ni(II)$ system corresponds to the electron spin density on HA.2

A notable feature of these experiments is the fact that they have been restricted primarily or compounds containing only one abundant nuclear species with nonzero magnetic moment (generally $^1H$ or $^{19}F$). The reason for this is simple: Imagine for example that our system contains two nuclear species labeled $I$, $S$ with the Hamiltonian for the observed $I$ spins (in their rotating reference frame) given by

$$\mathbf{P}_{RI} = \sum_i \delta_i I_i + \sum_{i<j} J_{ij} I_i I_j + \sum_{i<j} b_{ij}$$

$$\mathbf{X}(I_i, I_j - 3I_i I_j) + \sum_i a_q I_i S_{qi} + \mathbf{X}_{qB}.$$  (1)

The first two terms express the chemical shifts and isotropic scalar couplings we wish to observe; the second two are truncated dipolar interactions among the $I$ spins and truncated dipolar and scalar couplings between $I$ and $S$ spins; the last term is an interaction with externally applied rf fields. For the form taken by $\mathbf{X}_{qB}$ in the four-pulse experiment,2 it can be shown that the system evolves effectively to lowest order under the influence of a time-independent average Hamiltonian given in the tilted rotating frame (tilted along the 111 axis) by

$$\mathbf{X}_{TR} = 3^{-1/2} \sum_i \delta_i I_i + \sum_{i<j} J_{ij} I_i I_j$$

$$+ 3^{-1/2} \sum_{i<j} a_{ij} I_i S_{ij}.$$  (2)

Thus, while the pulse train succeeds in enormously reducing the effects of dipolar interactions between like spins, only a reduction by a factor of $\sqrt{3}$ is acquired by the secular interactions between unlike spins. The

Spin-Decoupling in the Resolution of Chemical Shifts in Solids by Pulsed NMR

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Recent communications from this laboratory have described a number of pulsed NMR experiments aimed at eliminating the effects of the normally predominant dipolar interactions between nuclear spins in solids, in order to expose weaker but perhaps more interesting effects such as chemical shifts (with any associated anisotropy) and electron-coupled spin–spin interactions.1–6 A notable feature of these experiments is the fact that they have been restricted primarily or compounds containing only one abundant nuclear species with nonzero magnetic moment (generally $^1H$ or $^{19}F$). The reason for this is simple: Imagine for example that our system contains two nuclear species labeled $I$, $S$ with the Hamiltonian for the observed $I$ spins (in their rotating reference frame) given by

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Thus, while the pulse train succeeds in enormously reducing the effects of dipolar interactions between like spins, only a reduction by a factor of $\sqrt{3}$ is acquired by the secular interactions between unlike spins. The
remaining dipolar interactions usually obliterate any fine structure we may wish to observe.

We suggested previously that this difficulty might be overcome in a double-resonance experiment by simultaneously subjecting the interfering \((S)\) spins to a suitable strong rf perturbation at their Larmor frequency. If selected carefully, the double irradiation removes the last term in (2) leaving us with the required high-solution Hamiltonian for the \(I\) spins. This would be extremely valuable in extending the applicability of the line-narrowing technique to a wider variety of chemically interesting compounds. Here we report preliminary results for an experiment of this type performed on a crystal of sodium fluoride. This compound serves as an ideal prototype for these experiments; there are two abundant species \((^{19}\text{F and }^{23}\text{Na})\) and the total dipolar coupling is strong enough to overcome high-solution Hamiltonian for the \(I\) spins. The double resonant \(rf\) pulse once per \(19\text{F}\) four-pulse cycle, exhibiting an additional narrowed line due to NaF.

In Fig. 1(a) we see the spectrum of a mixture of CaF\(_2\) (powdered), NaF (single crystal with the 100 axis oriented approximately along \(H_0\)) and hexafluorobenzene (liquid), obtained by fourier transformation of the \(^{19}\text{F transient nuclear signal sampled one per cycle during application of a four-pulse sequence}\)

at the \(^{19}\text{F resonance frequency}. This reduces the inter-

\(^{19}\text{F dipolar coupling, and we obtain peaks from hexafluorobenzene and the narrowed \(^{19}\text{F absorption of CaF}_2, as is well known. The absorption peak of the \(^{19}\text{F spins in NaF is too broad to be observed on this scale due to coupling with }^{23}\text{Na spins as in (2). Figure 1(b) shows the result of an identical experiment except with }^{23}\text{Na spins irradiated with a }180^\circ\text{ resonant rf pulse once per }^{19}\text{F four-pulse cycle, exhibiting an additional narrowed line due to NaF. It can be seen that there is a }^{19}\text{F chemical shift of }114\pm6\text{ ppm between NaF and CaF}_2, a surprisingly large value in view of the fact that both are considered ionic solids. An extension of this method to compounds of chemical interest as well as to other nuclei will be discussed in the future.}

The experiments were performed on a home-built pulsed double-resonance spectrometer, operating in the four-pulse mode. The cycle time for the four-pulse sequence was 24 \(\mu\)sec and the \(^{19}\text{F and }^{23}\text{Na rf fields had peak rotating components of 90 and 55 Oe and were produced in crossed coils tuned to 54 and 15.2 MHz, respectively.}

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