

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.³ The magnitude and the sign of J_{AB} is, then, proportional to those of the induced electron spin density on H_A .²

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 $H_A-C---C-H_B$ fragment.³ From an analogous correlation between induced spin density and the H_A-H_B coupling constant in $H_A-C---C-H_B$, it is inferred that upfield contact shift of proton H_A in $H_A-C---N-Ni(II)$ system corresponds to the positive H_A-H_B coupling constant in the corresponding fragment $H_A-C---C-H_B$. This relation was established in the experiment, as was noted above. However, it should be noted that nuclear spin-spin coupling is caused by the electron spin polarization mechanism only, while for the paramagnetic complex, an electron spin is transferred by both spin polarization and spin delocalization mechanisms. Accordingly, the above correlation holds only for the limited case where electron spin polarization mechanism predominates or the case where the relative importance of spin polarization to spin delocalization for the ligand protons is comparative.

¹ (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Am. Chem. Soc.* **92**, 1267 (1970); (b) I. Morishima, K. Takeuchi, K. Fukuta, and T. Yonezawa (to be published); (c) I. Morishima, K. Takeuchi, K. Fukuta, and T. Yonezawa (to be published); (d) I. Morishima, K. Takeuchi, and T. Yonezawa (unpublished).

² J. A. Happe and R. L. Ward, *J. Chem. Phys.* **39**, 1211 (1963).

³ J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.* **49**, 2960, 2965 (1968).

⁴ Along with the similar discussions, a correlation between nuclear spin coupling constant J_{AB} and the nuclear (A)-electron spin hyperfine coupling constant for the radical fragment $H_A-C---C$ obtained by breaking the $C-H_B$ bond homolytically has been presented [W. T. Dixon, *Mol. Phys.* **11**, 601 (1966)].

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

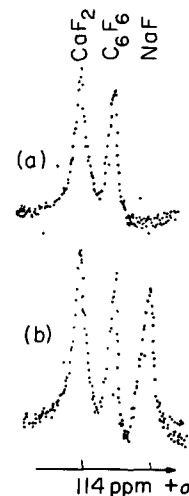
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Recent communications from this laboratory have described a number of pulsed NMR experiments aimed

Fig. 1. Fourier transform of the ^{19}F transient nuclear signal sampled once every cycle in a four-pulse experiment on the ^{19}F spins of a sample containing CaF_2 , NaF , and hexafluorobenzene: (a) with no rf applied at the ^{23}Na resonance frequency; (b) with a train of 180° pulses applied simultaneously to the ^{23}Na spins. One 180° pulse is applied every four-pulse cycle. The ^{19}F chemical shifts of CaF_2 and NaF are ± 57 ppm relative to hexafluorobenzene.



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

$$\mathcal{H}_R = \sum_i \delta_i I_{zi} + \sum_{i < j} \sum J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j + \sum_{i < j} \sum b_{ij} \times (\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{zi}I_{zj}) + \sum_i \sum_j a_{ij} I_{zi} S_{zj} + \mathcal{H}_{RF}. \quad (1)$$

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 \mathcal{H}_{RF} 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

$$\bar{\mathcal{H}}_{TR} = 3^{-1/2} \sum_i \delta_i I_{zi} + \sum_{i < j} \sum J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j + 3^{-1/2} \sum_{i < j} \sum a_{ij} I_{zi} S_{zj}. \quad (2)$$

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

remaining dipolar interactions usually obliterate any fine structure we may wish to observe.

We suggested previously¹ 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,⁷ the double irradiation removes the last term in (2) leaving us with the required high-resolution 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 (¹⁹F and ²³Na) and the total dipolar coupling is strong enough to provide a good test for the efficiency of the method, and to demonstrate an advantage of the rf pulse technique over that of sample rotation,⁸ even in compounds with more than one active nuclear species. Line narrowing by the latter method is an unenviable task in compounds with such strong dipolar couplings⁹ and does not benefit from the preservation of any chemical or Knight shift anisotropies.^{3,9}

In Fig. 1(a) we see the spectrum of a mixture of CaF₂ (powdered), NaF (single crystal with the 100 axis oriented approximately along *H*₀) and hexafluorobenzene (liquid), obtained by fourier transformation of the ¹⁹F transient nuclear signal sampled one per cycle during application of a four-pulse sequence^{2,3} at the ¹⁹F resonance frequency. This reduces the inter-¹⁹F dipolar coupling, and we obtain peaks from hexafluorobenzene and the narrowed ¹⁹F absorption of CaF₂, as is well known.² The absorption peak of the ¹⁹F spins in NaF is too broad to be observed on this scale due to coupling with ²³Na spins as in (2). Figure 1(b) shows the result of an identical experiment except with the ²³Na spins irradiated with a 180° resonant rf pulse once per ¹⁹F four-pulse cycle, exhibiting an additional narrowed line due to NaF. It can be seen that there is a ¹⁹F chemical shift of 114±6 ppm between NaF and CaF₂, 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.¹⁰ The cycle time for the four-pulse sequence was 24 μsec and the ¹⁹F and ²³Na 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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⁴ J. D. Ellett, Jr., U. Haeberlen, and J. S. Waugh, *Polymer Letters* **7**, 71 (1969).

⁵ J. D. Ellett, Jr., U. Haeberlen, and J. S. Waugh, *J. Am. Chem. Soc.* **92**, 411 (1970).

⁶ M. Mehring, R. G. Griffith, and J. S. Waugh, *J. Am. Chem. Soc.* (to be published).

⁷ An indiscriminate continuous irradiation of the *S* spins does not do the job unless $\gamma_s H_{1s} \gg 2\pi t_c^{-1}$, where *t_c* is the four-pulse cycle time. A convenient method of irradiation that does, is a train of 180° pulses synchronized with the four-pulse train on the *I* spins.³ This also allows continuous observation of the signal.

⁸ E. R. Andrew, A. Bradbury, and R. G. Eades, *Arch. Sci. (Geneva)* **11**, 223 (1958); *Nature* **182**, 1659 (1958).

⁹ In compounds where molecular motion is sufficient to aid the line-narrowing by sample rotation, one does observe the scalar coupling between *I* and *S* spins. The double resonance, on the other hand, provides a complete decoupling of these spins.

¹⁰ J. D. Ellett, Jr. *et al.*, *Advan. Magnetic Resonance* (to be published).

Comments

Comment on "Further Calculations of Equilibrium Dimer Properties"

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The thermodynamics of dimer formation in magnesium, beryllium, and manganese vapors has been discussed recently by Ewing and Mellor.¹ They calculated equilibrium dimer properties (e.g., dimer mole fractions and equilibrium constants) using equations derived by Stogryn and Hirschfelder.^{2,3} Values of the dissociation energy of Mg₂ determined spectroscopically by Hamada⁴ (6.92 kcal mole⁻¹) and Soulen *et al.*⁵ (7.2±0.2 kcal mole⁻¹) were advanced by Ewing and Mellor as experimental confirmation of their calculations.

In connection with these results we wish to point

TABLE I. Molar thermodynamic properties of ²⁴Mg₂ vapor.

Temp (°K)	<i>G</i> ^o - <i>E</i> ₀ (kcal)	<i>S</i> ^o (cal/degree)	<i>H</i> ^o - <i>E</i> ₀ (kcal)	<i>C</i> _p ^o (cal/degree)
500.	-28.41	63.66	3.415	5.668
600.	-34.83	64.67	3.971	5.474
700.	-41.34	65.50	4.512	5.348
800.	-47.93	66.21	5.042	5.264
900.	-54.58	66.83	5.566	5.204
1000.	-61.29	67.37	6.084	5.161