A. METHOD FOR HIGH RESOLUTION NMR IN SOLIDS

In Quarterly Progress Report No. 86 (pages 67-68), we described a pulsed NMR experiment by means of which the static magnetic dipole-dipole interactions in a solid could be reduced substantially in effect without at the same time annihilating the inhomogeneous interactions (e.g., chemical shifts, Knight shifts, etc.). Further analysis of that experiment shows that the extent to which the dipole-dipole interactions can be reduced is limited. One can say, in the language of steady-state absorption spectroscopy, that the dipole-dipole line broadening is reduced to the point where the chemical shifts are just resolved, but no farther. While this experiment has potential utility, for example, in the study of anisotropic shifts in crystals, it would be desirable to reduce the dipole-dipole interactions without limit (as occurs in a liquid through averaging of the angle factors in the dipole-dipole Hamiltonian).

We propose here a new method that accomplishes this aim. In its simplest form it involves the repeated application of a cycle of three equally spaced pulses. The first and third of these are 90° radiofrequency pulses differing in carrier phase by 90°. The second lasts twice as long and has its phase switched by 90° at the center. When the period of this cycle of pulses becomes small compared with the natural transverse relaxation time of the spin system, the system behaves as though it were subject to a time-independent Hamiltonian \( \overline{H} \), which is the average of the successive operators through which the actual Hamiltonian is transformed by the rotations corresponding to the pulses

\[
\overline{H} = \frac{1}{3} \left[ H + P_2 \left( H + P_1 H P_1^{-1} \right) P_2^{-1} \right].
\]

When

\[
H_d = \sum_i \sum_j a_{ij} \left( I_i^x \cdot I_j^x - 3 I_i^z I_j^z \right),
\]

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the static dipolar Hamiltonian, one finds that $\overline{H}_d = 0$. On the other hand, the scalar coupling

$$\overline{H}_j = \sum_{i < j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$$

is unaffected, and the chemical shifts

$$\overline{H}_6 = \sum_i \delta_i I_z i$$

give

$$\overline{H}_6 = \frac{1}{3} \sum_i \delta_i (I_{xi}^2 + I_{yi}^2 + I_{zi}^2).$$

The last form can be rewritten by a rotation of axes in the form

$$\overline{H}_6' = \frac{1}{\sqrt{3}} \sum_i \delta_i I_z i.$$

The total effective Hamiltonian thus becomes the ordinary Hamiltonian for scalar coupling and chemical shifts alone, except that all chemical shifts are scaled down by the factor $\sqrt{3}$.

The detected precessing magnetization that results from the application of such a pulse train is oscillatory. Its Fourier transform is identical to the steady-state unsaturated slow passage NMR spectrum that would be obtained if (a) dipolar interactions were absent, and (b) the Zeeman field intensity were reduced by a factor of $\sqrt{3}$.

A more detailed discussion of this and related effects has been submitted to the Journal of Chemical Physics.

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