VIII. MAGNETIC RESONANCE*

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A. NUCLEAR SPIN INTERACTIONS IN SOLIDS

We have shown in a recent paper[1, 2] that the response of a spin system to a suitable train of RF carrier pulses can be made asymptotically independent of the dipole-dipole interaction by reducing the pulse spacing to small values. In the experiments reported, the effects of the other terms in the spin Hamiltonian, in particular the inhomogeneous interactions such as chemical shifts, also vanish. By a suitable modification of the experiment (180° carrier phase shifts of alternate pulses), the effects of chemical shifts can be retained while the dipole-dipole effects are still annihilated. This experiment, just performed,[3] may be useful in studying chemical shifts in solids. Unlike other methods, it preserves information about the anisotropy of chemical shifts.

To understand the effect consider a simple model: the RF carrier, instead of being pulsed, is sinisoidally modulated about an average value. The Hamiltonian (in units of $\hbar$), including dipole-dipole couplings A_{ij} and chemical shifts δ_i, can be written in a suitable representation[2] as

$$
\begin{aligned}
\mathcal{H}_{\text{eff}} &= \sum_{i<j} \sum A_{ij}(\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{zi}I_{zj}) \\
&+ \frac{3}{2} \sum_{i<j} \sum A_{ij} \left[I_{+i}I_{+j}\, e^{-i\phi(t)} + I_{-i}J_{-j}\, e^{+i\phi(t)} \right] \\
&+ \frac{1}{2} \sum_{i} \delta_i \left[I_{+i}\, e^{-i\phi(t)/2} + I_{-i}\, e^{+i\phi(t)/2} \right],
\end{aligned}
$$

with

$$\phi(t) = 2 \int_0^t \gamma H_1(t')\, dt'.$$

Here the z-axis is along the RF field, H_1, in the rotating frame, and it will be

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understood that the spins have been initially polarized in the same direction: $\rho(0) = I_z$.

The change of magnetization with time is initially given by

$$\frac{\partial\rho}{\partial t} = -i[\mathcal{H}_{\text{eff}}, \rho(0)].$$

It will not decay if $[\mathcal{H}, \rho(0)]$ is either zero (cf. the first term of $\mathcal{H}_{\text{eff}}$) or rapidly oscillatory. Choose

$$H_1(t) = H_1 \cos \Omega t.$$

Then

$$e^{\pm i\phi} = \sum_{\ell=-\infty}^{\infty} J_\ell\left(\frac{2\gamma H_1}{\Omega}\right) e^{\mp i\ell\Omega t}.$$

For large Ω this makes the second term of $\mathcal{H}_{\text{eff}}$ oscillatory, except the part for $\ell = 0$. This part can be made to vanish by adjusting $z = (2\gamma H_1/\Omega)$ to match one of the zeros of $J_o(z)$; for example, $z = 2.405$. There will then be no decay of magnetization from dipole-dipole interactions. The third term of $\mathcal{H}_{\text{eff}}$ contains, however, $\exp(i\phi/2)$, and under the above-mentioned conditions will be secular, with a coefficient $J_o(z/2) = 0.671$. The magnetization will show beats corresponding to the various $\delta_i - \delta_j$, each reduced in frequency by the factor .671.

This example for sinusoidal modulation of H_1 has its counterpart for other modulations of arbitrary waveform, in particular a train of pulses.

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References

1. E. D. Ostroff and J. S. Waugh, Phys. Rev. Letters 16, 1097 (1966).
2. J. S. Waugh and C. H. Wang (Phys. Rev., in press).
3. J. S. Waugh and L. M. Huber (J. Chem. Phys., in press).