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Pines A, Gibby M G & Waugh J S. Proton-enhanced NMR of dilute spins in solids.
J. Chem. Phys. 59:569-90, 1973.
[Department of Chemistry and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA]

The NMR signals of isotopically or chemically dilute nuclear spins "S" can be enhanced by repeated cross-polarization under the Hartmann-Hahn condition from a more abundant species "I" (usually hydrogen). High-frequency resolution is obtained by decoupling of the I spins during observation of the S spin free induction decay. The theory and experimental requirements are discussed, and illustrative applications to carbon-13 NMR in organic solids are demonstrated. [The *SCI*® indicates that this paper has been cited in more than 1,000 publications.]

Carbon-13 NMR in Solids

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As a small boy, I often wondered about the chemical shift anisotropy of benzene. After my application for graduate school was rejected at Berkeley, I settled for the Massachusetts Institute of Technology (MIT), Cambridge.

At that time, MIT chemists were primarily interested in polywater, but J.S. Waugh had also developed the famous coherent averaging of spin interactions by means of multiple-pulse sequences that revealed the chemical shifts of hydrogen in solids. It occurred to us that, because of its low natural abundance (and correspondingly weak magnetic dipole-dipole couplings), carbon-13 should yield high-resolution Fourier-transform spectra with reasonable sensitivity by spin decoupling following polarization transfer from hydrogen to carbon. After building a spectrometer with Michael G. Gibby and arguing for two weeks about whether the double-resonance sequence should be called pulse program or pulse programme, we needed

a model sample to try the experiment. Henry A. Resing (known affectionately as Mr. Adamantane because of his work on plastic crystals) was visiting, and I asked him what would be a cheap compound with at least two inequivalent carbon sites, solid at room temperature but with the molecules reorienting roughly isotropically, and with T_1 and $T_1 \rho$ relaxation times of about one second. He suggested adamantane. Indeed, after we vaporized a number of samples in the probe with high radiofrequency power, the first successful experiments showed two resolved carbon-13 peaks with good signal/noise in solid adamantane. We subsequently obtained reasonable spectra for solid benzene and many other organic compounds, leading some innocent bystanders to believe that this cross-polarization and solid-state NMR stuff might actually be useful in chemistry.

It was during this period that Gibby became known as a hermitian operator because he would lock himself in the lab and run the spectrometer for weeks on end.

In our 1973 paper, we called the technique proton-enhanced nuclear induction spectroscopy, a term erected from the foundations of nuclear induction laid by physicists.¹ The early applications were to carbon-13, but we did extend the experiments to nitrogen-15 and silicon-29. Later, J. Schaefer and E.O. Stejskal added magic-angle spinning and, today, CP/MAS is widely available on royalty-yielding commercial spectrometers.

I left the east coast to come to Berkeley when Simkins was just completing the quantum theory of phlogiston at MIT. I'm not sure why our paper is cited so often. Perhaps one reason is that it talks openly and frankly about the Hartmann-Hahn condition, an affliction suffered by many chemists in the rotating frame of reference.

1. Pines A. NMR in physics, chemistry, and biology: illustrations of Bloch's legacy. *Int. J. Mod. Phys. B* 4:1241-67, 1990.