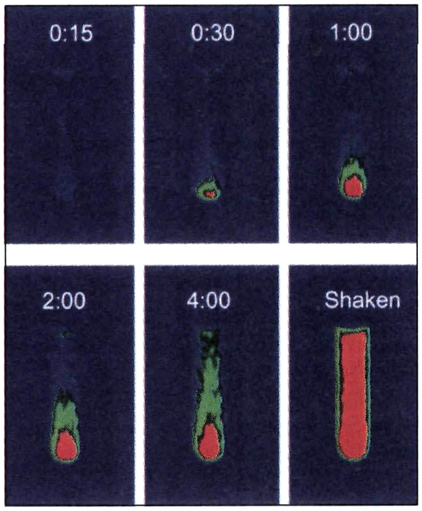
NMR and MRI

Sensitivity is a persistent challenge in NMR spectroscopy and magnetic resonance imaging (MRI), in part because of the small population difference between "up" and "down" spins (low spin polarization). Strategies to enhance polarization include optical pumping (OP) methods, which transfer angular momentum from circularly polarized light to electronic and nuclear spins, and dynamic nuclear polarization arising from the cross-relaxation between coupled spins—the basis for the nuclear Overhauser effect (NOE) for determining interatomic distances by solution NMR.

Alex Pines and colleagues at the University of California–Berkeley described preliminary experiments that combine OP and NOE to transfer enhanced polarization from hyperpolarized ^{129}Xe gas to the solution, an effect they labeled "spin polarization-induced NOE" (SPINOE). The new technique did not require radiofrequency irradiation of spins; OP with laser light polarized the nuclear spins of the Xe gas.

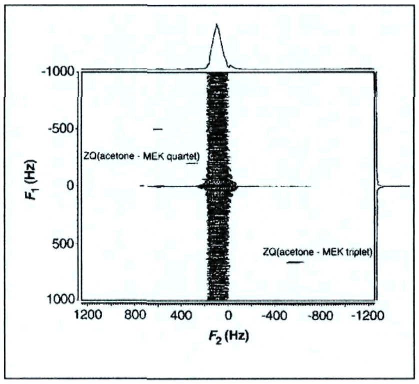
When hyperpolarized ^{129}Xe was dissolved in liquids, they observed a time-dependent change in the proton spin polarization from its thermal equilibrium. The variation in magnetization was a consequence of cross-relaxation between the solution proton spins and dissolved ^{129}Xe. It thus became possible to indirectly image the distribution and evolution of dissolved Xe by ^{1}H MRI, and the ^{1}H chemical shifts may provide an indication of Xe distribution, said the authors. As a result, it may be possible to image the hyperpolarized Xe and the environment in which it is accommodated. The effect could find application in NMR spectroscopy of surfaces and proteins as well as in MRI. (*Science* **1996**, *271*, 1848–51)



Time-resolved, two-dimensional magnetic resonance images of ^{129}Xe dissolved in benzene, taken after the benzene was exposed to hyperpolarized ^{129}Xe. (Adapted with permission from the American Association for the Advancement of Science.)

New NMR detection method

High magnetic fields are known to simplify and enhance the resolution of NMR spectra. Although magnets with fields higher than those in commercial instruments are available, their inhomogeneity makes them unacceptable for high-resolution NMR. Intermolecular zero-quantum coherences—flipping up one solute spin while simultaneously flipping down a neighboring solvent spin—give a simple spectrum that is the single quantum spectrum of the solute offset by the chemical shift of the solvent. Warren S. Warren and co-workers at Princeton University have described a detection method, called HOMOGENIZED (HOMOGeneity ENhancement by Intermolecular ZEro-quantum Detection) that gives a high-resolution spectrum in an inhomogeneous magnetic field without removing chemical shifts or J couplings. The HOMOGENIZED pulse sequence consists of $\pi/2$, $\pi/4$, and π pulses. The $\pi/4$ pulse acts as a gradient filter; the π pulse compensates for radiation damping and magnet inhomogeneities. They demonstrated the effectiveness of this approach on the NMR spectrum of 5% methyl ethyl ketone in acetone. (*Science* **1996**, *272*, 92–96)



The 2-D zero-quantum NMR spectrum of 5% MEK in acetone obtained using the HOMOGENIZED pulse sequence. (Adapted with permission from the American Association for the Advancement of Science.)

XPS of etched InP surfaces

Although InP is widely used in optoelectronic applications, little is known about the semiconductor's surface chemistry. Modification of the surface could introduce functional groups that would affect the behavior of the material. Marcel Sturzenegger and Nathan S. Lewis of the California Institute of Technology introduced a new general strategy for functionalizing the semiconductor's surface and used X-ray photoelectron spectroscopy (XPS) to characterize reactions performed on (111)B-oriented, n-type, single-crystal InP specimens of various doping densities.

The spectral results indicated the oxidation state of the surface P atoms. The authors found that it is unlikely that P lone pairs dominate the surface chemical reactivity, but rather are dominated by classical –OH group reactivity. (*J. Amer. Chem. Soc.* **1996**, *118*, 3045–46)