

## TODAY'S HEADLINES

---

**April 7, 2003**

Volume 81, Number 14

CENEAR 81 14 p. 9

ISSN 0009-2347

## NMR SPECTROSCOPY

# SHARPER SPECTRA

NMR method yields high-resolution spectra of disordered solids

### STU BORMAN

Nuclear magnetic resonance (NMR) spectra of disordered, noncrystalline solids such as glasses, polymers, and biological materials typically have peaks that are broad, relatively featureless, and of limited use for materials characterization. Now, using a two-dimensional NMR correlation approach, a team has obtained high-resolution NMR spectra of disordered solids [[J. Am. Chem. Soc., 125, 4376 \(2003\)](#)].

The new technique "could lead to the detailed structural characterization of these types of materials, which are central to many areas of chemical sciences," says chemistry professor [Lyndon Emsley](#) of the Ecole Normale Supérieure, in Lyon, France. His group carried out the study in collaboration with that of chemistry professor Alexander Pines at the University of California, Berkeley.

High-resolution NMR spectra can already be obtained routinely from ordered, homogeneous solids, using techniques like magic-angle spinning (MAS). But conventional solid-state NMR techniques don't help to narrow the broad distribution of NMR chemical shifts that arises in structurally disordered solids.

"By disordered systems, I mean things like polymers, glasses, surface species, or catalysts, where the local environment changes from one subunit to another due to a change in geometry," Emsley explains. "In silicate glasses, for example, the Si–O–Si bond angle changes slightly from one Si–O–Si unit to another. In a crystalline silicate, the Si–O–Si bond angle is always identical."

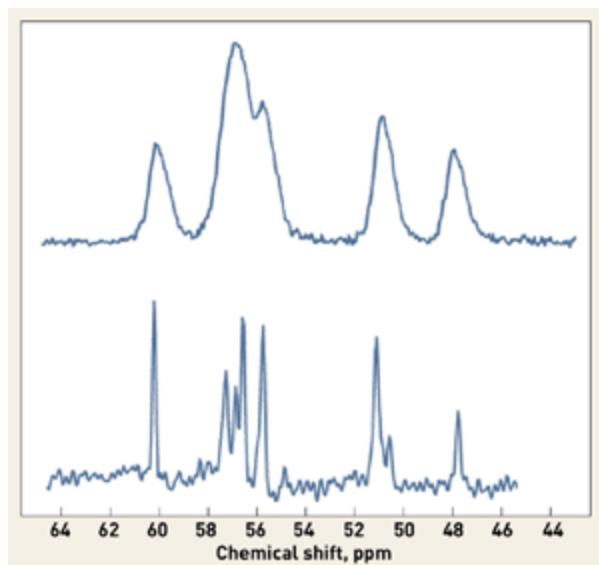
In disordered solids, resonance frequencies of otherwise equivalent nuclei vary because of such microenvironment differences. These variations aren't averaged out by rapid molecular tumbling, as occurs in solution NMR, nor can they be removed by conventional solid-state techniques like MAS. When NMR spectra of disordered materials are obtained, "people try to interpret them as best they can because this is all they can get, but the broadening severely limits the range of materials where the spectra are useful," Emsley notes.

"This has for a long time looked like an impossible problem," he says. But his group and Pines's have now shown that by going from one- to two-dimensional NMR and by making pairwise correlations between neighboring atoms, high-resolution spectra of disordered solids can finally be obtained.

The work "entails one of the earliest, and arguably cleverest, concepts put forward for narrowing wide lines in NMR--to combat one broadening with another broadening," comments professor of chemical physics [Lucio Frydman](#) of Weizmann Institute of Science, Rehovot, Israel. The technique "begins with the realization that in several kinds of heterogeneous, disordered solids--where NMR peaks tend to be particularly ill-defined because of dispersions arising in chemical shifts--the broadening exhibited by any particular chemical site parallels in a nearly one-to-one fashion the broadening exhibited by its nearest neighbor. Rather than attempting to average out these incapacitating broadenings, Emsley, Pines, and coworkers demonstrate that they can actually be exploited for achieving an increase in spectral resolution."

Despite the dispersion in chemical shift values that occurs in disordered solids, chemical shift differences between neighboring nuclei are often relatively constant. By focusing on those unvarying differences, line narrowing of the NMR spectrum can be obtained. "This gain in resolution is achieved at the price of increasing the dimensionality of the experiment by one--from 1-D to 2-D NMR--yet it offers a new window of opportunity toward the experimental characterization of numerous kinds of materials where disorder has hitherto proved problematic," Frydman says.

The new method may not represent a universal route to highly resolved spectra of disordered solids because chemical shift distances between neighboring atoms are constant in some disordered materials, but not all. Nevertheless, the technique demonstrates that obtaining such spectra is feasible. Emsley, Pines, and coworkers are now investigating the range of disordered solids and NMR-active nuclei to which the strategy is applicable and the range of correlation techniques that can carry it out.



**SPECTRAL WEIGHT LOSS** Conventional 1-D  $^{31}\text{P}$  spectrum (top) of a disordered solid amine has broadened peaks. These peaks are narrowed considerably in the correlation plot (bottom) derived from a 2-D  $^{31}\text{P}$  spectrum of the same material.

---

**Chemical & Engineering News**

**Copyright © 2003 American Chemical  
Society**