High-Resolution NMR Spectroscopy of Disordered Solids

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High-Resolution NMR



Solid-State NMR: Anisotropic Interactions

The resonance frequency of a given nucleus within a particular crystallite depends on the orientation of the crystallite



High-Resolution NMR of Ordered and Homogeneous Solids



+ MQMAS, STMAS, ...

NMR of Disordered Solids

Chemical Disorder (local effect)

a change in the isotropic chemical shift from one molecule to another *e.g., glasses, catalysts, polymers*



Magnetic Susceptibility (bulk effect) a change in the Larmor frequency from one part of the sample to another heterogeneous samples





How can the chemical shift differences due to disorder be removed without removing the chemical shift differences that distinguish sites from each other?

Intrinsic Linewidths in Disordered Solids



Zero-Quantum Spectroscopy

For susceptibility broadening or broadening due to an inhomogeneous applied field, the shifts at one nucleus are perfectly correlated in a one-to-one fashion with the shifts at another nearby nucleus

Thus, while the individual chemical shifts change, the chemical shift differences remain the same



Hall et al. 1981: Zero-quantum NMR spectra are free of B_0 broadening

Warren et al. 1996: Intermolecular solvent-solute ZQ coherences yield high-resolution spectra in unstable very high magnetic fields

Terao et al. 1999: ZQ sideband spectra are free of susceptibility broadening in paramagnetic solids



Double-Quantum Spectroscopy and Coherence Transfer Echoes





 $s(t_1, t_2) = \exp\{ \left[\Omega_A + \Omega_B \right] t_1 \}$ $x \exp\{ -\Omega_A t_2 \}$

A coherence transfer echo (Ernst 1978) forms at $t_2 = 2 t_1$:

$$s(t_2 = 2t_1) = \exp\{ [-\Omega_A + \Omega_B] t_1 \}$$

In the frequency domain, a projection perpendicular to the $F_2 = 2 F_1$ diagonal thus corresponds to a pseudo ZQ spectrum

Solid-State Spectra of Disordered Solids



To record this red spectrum we must refocus the chemical shift distribution due to disorder within a site, without refocusing the chemical shifts that distinguish sites from each other.

This cannot be done if the sites are isolated from each other.

It can be achieved if

(i) the sites can be connected in a multi-dimensional spectrum

(ii) the chemical shifts between coupled pairs of spins are highly correlated.

³¹P-³¹P Through-Bond Connectivities



High-Resolution Spectra of Disordered Solids

The pseudo-ZQ spectrum will be completely free of broadening only to the extent that the distribution of resonance frequencies is: (1) perfectly correlated

(2) correlated with a 1:2 ratio for the SQ and DQ frequencies





High-Resolution Spectra of Disordered Solids

The shifts are well correlated, but there are deviations from a 1:2 ratio for the SQ and DQ frequencies







reconstructed spectrum

FWHMH = *35 Hz*



Refocused INADEQUATE ¹³C Spectrum of Cellulose



cellulose from wood

Correlated Chemical Shifts in Disordered Solids



In more complex systems, correlations can be exploited to extract *chains of correlated shifts*. Each chain corresponds to the chemical shifts of an entire subunit with a given conformation. Conclusions

Strong correlations can be observed between the changes induced by disorder for adjacent nuclei in solids

These correlations can be exploited in refocused INADEQUATE spectra where peaks are only due to directly bonded pairs of nuclei

Significant resolution enhancement can be achieved

Two-dimensional correlated chemical shift distributions are a potential rich new source of chemical information about disordered systems

Sakellariou et al, J. Am. Chem. Soc. 125, 4376 (2003)

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