

THE DETERMINATION OF LOCAL STRUCTURE IN ORGANOFLUORIDES
USING FLUORINE-19 CARBON-13 DIPOLAR COUPLING

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INTRODUCTION

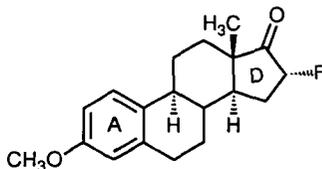
A facet of our research has been directed toward the elucidation of "reactive sites" in the organic milieu of coals. The conceptual framework for these experiments is the chemical introduction of a unique, NMR active nucleus at or adjacent to a reactive site in the coal network and the subsequent utilization of this nucleus to extract site specific structural information by solid state ^{13}C NMR spectroscopy. Fluorine-19 and phosphorus-31 nuclei are good NMR choices, having large magnetic moments, 100 % natural abundance, and spin 1/2. The absence of a quadrupole moment translates into narrow, well-resolved spectral resonances. Both are suitable in applications to coal derivatization, having small natural concentrations in the organic matrix of most coals.¹ Fluorine is attractive from the standpoint of chemical manipulation of coals in that a large and increasing number of fluorinating reagents are available to specifically incorporate fluorine into organic substances. It should be possible to label diverse sites in the coal by a judicious choice of fluorinating reagent and reaction conditions.

The use of an introduced magnetic nucleus in an organic environment as a probe of local structure utilizes in some fashion the dipolar interaction between the probe nucleus and proximate ^{13}C nuclei to selectively observe the interactive carbons. Since ^{13}C is dilute by virtue of low natural abundance, these dipolar couplings are often isolated spin pair interactions. Two experiments that selectively detect carbons dipolar coupled to a probe nucleus are cross polarization between the nuclear pair, and dephasing of ^{13}C magnetization by interference with rotational echo formation. The first class of experiments are known as double cross polarization (DCP) NMR^{2,3}; the second as rotational-echo double resonance (REDOR) NMR⁴. This paper reports experiments that demonstrate the REDOR experiment is ineffective when applied to the ^{19}F - ^{13}C nuclear pair in models of molecular weight < 300. A new experiment that uses the cause for the REDOR failure, ^{19}F spin diffusion, is used to regain site specific structural information encoded by the ^{19}F - ^{13}C dipolar coupling.

RESULTS AND DISCUSSION

We have examined the perturbation of the conventional CP/MAS ^{13}C NMR spectrum of organic substances due to the incorporation of a of a single ^{19}F atom in the structure. In molecules in which the

fluorine atom undergoes little motion in the solid, e.g., as in 16 α -fluoroestrone-3-methyl ether, (1), the carbon directly bonded to fluorine has a resonance so broad (> 2500 Hz) that it is not observed in the spectrum. In molecules that exhibit motion in the crystal that modulates the ^{19}F - ^{13}C dipolar interaction, as in *ortho*-fluorophenylglycine, the ^{19}F - ^{13}C dipolar coupling is partially averaged by the motion and the directly fluorinated carbon is observed. In this case the resonance is narrowed enough that the J-coupling (250 Hz) between the directly bonded pair is apparent in the conventional spectrum. Longer range ^{19}F - ^{13}C dipolar interactions result in a graded, r^{-3} internuclear distance dependent broadening of near neighbor carbon resonances in the spectrum. Simultaneous ^1H and ^{19}F high power decoupling applied during the free induction decay acquisition time efficiently eliminates heteronuclear dipolar coupling from the spectrum. This triple resonance capability is required to obtain high quality CP/MAS ^{13}C NMR spectra on organofluorides obtained at routine (< 5 kHz) MAS speeds.



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The spectral response described above may not be anticipated on first glance since the dipolar interaction between two spin $1/2$ nuclei has the form $(r^{-3})(3\cos^2\theta-1)$ and should be averaged to zero by MAS. However, MAS is successful only when the rotation rate is large in comparison to the dipolar interaction linewidth. The maximum dipolar linewidth, $2D_{\text{CF}}$, for a directly bonded pair is about 26 kHz, the consequence of the large magnetic moment of F19 and short C-F bond distance ($r \approx 0.13$ nm). In this instance the actual 4.2 kHz spinning used in these experiments is ineffective. This MAS speed is just comparable to typical ^{19}F - ^{13}C dipolar linewidths for atoms separated by two bonds ($r \approx 0.23$ nm, $D_{\text{CF}} \approx 4.5$ kHz). In the absence of ^{19}F dipolar decoupling, these resonances have a ca. 50 Hz residual linewidth contribution due to incomplete averaging of the dipolar interaction by MAS.

The REDOR experiment requires that the dipolar coupled spin pair (^{19}F - ^{13}C in the present case) in a system be isolated. If so, the time average of the resonance frequencies over one MAS rotor period is zero, i.e., full recovery of signal intensity occurs after each rotor cycle, producing a train of rotational echoes. REDOR uses π pulses applied to the probe nucleus (^{19}F) to intentionally cause echo destruction of those ^{13}C resonances dipolar coupled to ^{19}F . These are detected in a difference experiment. In 1, for example,

the anticipated REDOR difference spectrum would contain only ring D carbon resonances with intensities that reflect an r^{-3} distance dependence. The placement of π pulses and signal acquisition are timed to rotor position; REDOR signals can be accrued over even, integral multiples of the rotor cycle.⁵

Attempts to perform REDOR on 1 and smaller molecules has met with marginal success in our laboratory. Initial REDOR difference signal intensities in 3-fluoro-4-methoxybenzoic acid (evolution for two rotor cycles) do not exhibit the expected intensity ratios based on ^{19}F - ^{13}C internuclear distance. The resonances of C(2) and C(4) have greater integrated areas than the fluorinated carbon resonance, C(3). Continued evolution (4-20 rotor cycles) yields a strong selective attenuation of the REDOR signal set. We have shown in separate ^{13}C T_2 experiments, with and without ^{19}F decoupling, that the signal decay is governed by the ^{19}F T_2 . In effect, ^{19}F intermolecular spin diffusion provides a dephasing mechanism for coupled ^{13}C nuclei that competes with the experimentally imposed π pulses of REDOR, violating the isolated pair precondition in this experiment. This failure mode has been observed in ^{15}N - ^{13}C REDOR experiments in which spin diffusion among ^{13}C nuclei defeat the REDOR difference signal.⁶

For isolated spin pairs, REDOR accesses the dipolar interaction between the pairs, and, hence, is a direct method to obtain structural information. This experiment will work for the ^{19}F - ^{13}C pair in high molecular weight molecules where ^{19}F spin diffusion is suppressed by large internuclear distances. The applicability of this experiment in coal structure analysis is great for chemical derivatizations that introduce low concentrations of fluorine into the material. For more highly fluorinated coals, an new experiment has been created that uses the dipolar interaction to provide site selective structural information. The experiment accrues the difference signal between spectra that measure C13 T_2 over even integral multiples of the rotor period (to allow refocussing of ^{13}C chemical shift anisotropy), with alternate scans employing ^{19}F heteronuclear decoupling during the rotor evolution period. Signals arise from those carbons that show differences in T_2 arising from ^{19}F - ^{13}C dipolar dephasing mediated by the ^{19}F spin diffusion. Carbon signal intensities in this T_2 difference map do not provide a direct measure of ^{19}F - ^{13}C dipolar coupling. The structural information that can be gleaned from this and related experiments is under current investigation. Further studies are planned to delineate ^{19}F internuclear distance boundaries that are appropriate for these experiments.

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