Elimination of Heteronuclear Dipolar Interaction Effects from ^{13}C-Detected Proton Spectra in Wideline-Separation Nuclear Magnetic Resonance Spectroscopy

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It is well-known that abundant spin systems (mostly proton) can be used to polarize a dilute spin system more rapidly and to a higher level than is thermally attainable.[1,2] In fact, cross-polarization is routinely used to increase the magnitude of the NMR signal from a rare spin species, and it simultaneously allows the experiment to be repeated more frequently for better signal averaging. A further advantage of this technique is the possibility of investigating one nucleus indirectly by means of the other nucleus involved in the polarization transfer. The complementary advantages of high sensitivity and high chemical shift dispersion offered by ^{1}H and ^{13}C spins have been exploited previously in heterogeneous organic solids for indirect measurement of T_2 relaxation times of protons attached to various types of carbons and for indirect selective observation of proton spin diffusion.[3–9] It was shown that a proper image of the structural heterogeneity can be deduced from indirect measurements on static and magic-angle spinning samples of polymers and coals. Good agreement between the domain sizes estimated in direct and indirect measurements has been noted for poly(oxymethylene). The restrictions on the qualitative analysis of the extent of the different morphological regions were discussed in terms of their different cross-polarization characteristics.[6]

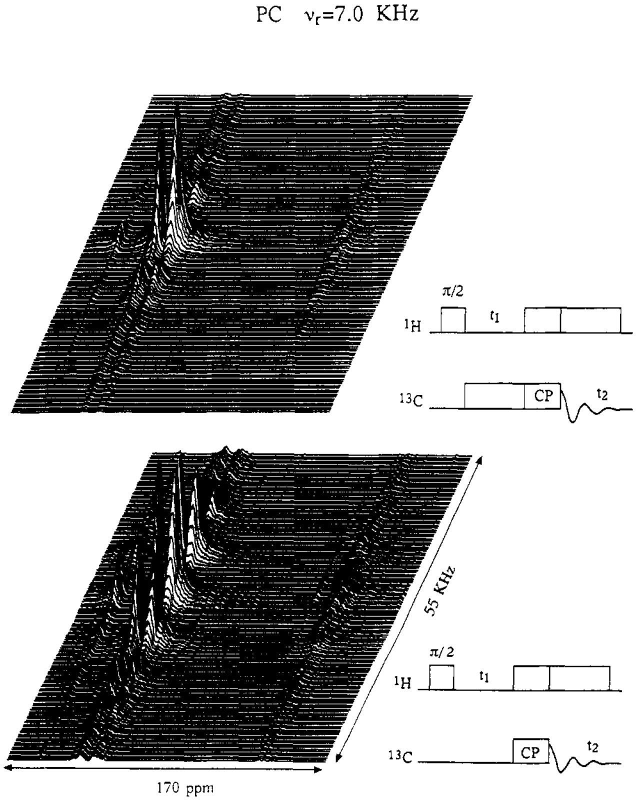

Figure 1. WISE-NMR spectra of PC obtained with (top) and without (bottom) carbon decoupling irradiation during the t_1 period. In both cases, a cross polarization time of 100 μs and 64 t_1 increments with a dwell time t_1 of 5 μs were used.

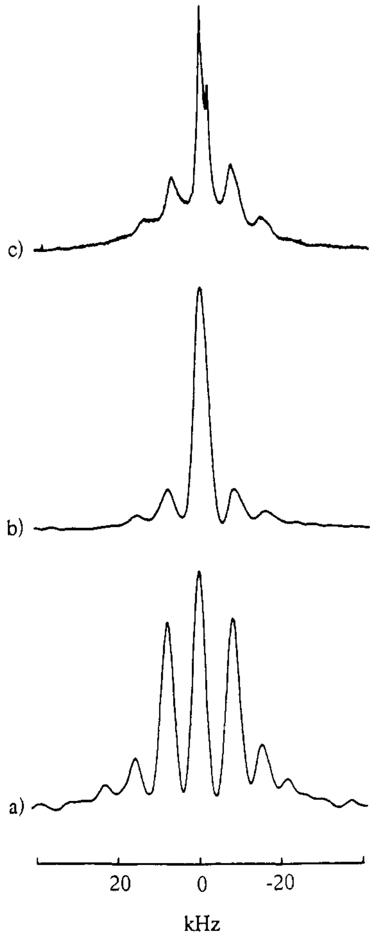

Figure 2. Cross sections of PC dipolar spectra along the frequency of the low-field aromatic protonated carbon obtained from experiments without (a) and with (b) carbon decoupling irradiation during the t_1 period. All experimental conditions are the same as in Figure 1. For comparison, a ^{1}H MAS NMR spectrum of PC obtained at ν_r = 7.0 kHz is shown (c). Note a small difference in chemical shift of methyl and phenyl proton signals.

The idea of using a second Fourier transform related to T_2 evolution was presented very recently by Schmidt-Rohr et al.[10] This leads to a two-dimensional experiment with the f_1 wideline shapes separated according to the chemical shift of the ^{13}C to which the protons are bonded. This shows the advantage of direct visualization of the variation in the dipolar local field of different functional groups with different molecular mobility; however, for morphologically heterogeneous samples, one gets several lines with overlap in the dipolar dimension f_1, making the analysis more difficult. By contrast, in the time domain, the different stages of the T_2 relaxation process in a heterogeneous sample are usually well separated and thus more easily analyzed.[6]

In this note, we provide experimental evidence that, by using a short contact time between ^{1}H and ^{13}C in a wideline separation (WISE) experiment, the heteronuclear dipolar effects manifest themselves in the separated wideline shapes. These effects may be suppressed by decoupling irradiation applied to the carbon channel during the t_1 period. This is shown in Figure 1, where WISE-NMR spectra of polycarbonate (PC) obtained with and without carbon decoupling irradiation during the t_1 period are compared. The corresponding cross sections at the frequency of the low-field aromatic protonated carbon are

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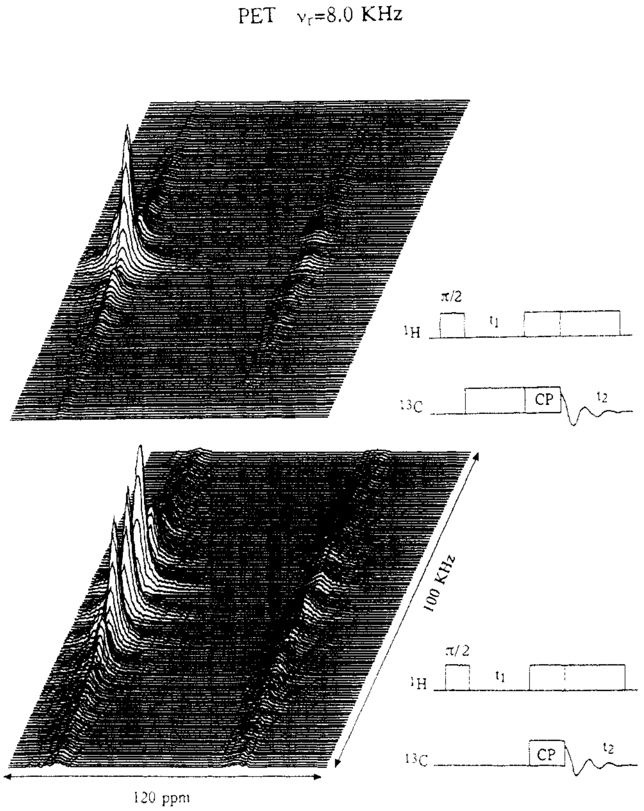

Figure 3. WISE-NMR spectra of PET obtained with (top) and without (bottom) carbon decoupling irradiation during the t_1 period. The macroscopic rotation was 8.0 kHz, and the contact time was 100 μs.

presented in Figure 2. Without decoupling irradiation, an important enhancement of spinning sidebands is observed during t_1. This is due to the heteronuclear dipolar interaction effects during the evolution period which lead to more pronounced dipolar echoes after each rotation period. Such dipolar echoes, resulting from the refocusing effect of macroscopic rotation, lead after a second Fourier transform to a family of sidebands whose intensity increases as the inhomogeneous character of the dipolar interactions becomes more pronounced. This will depend on the rate of flip-flop spin exchange in the proton system which is slowed down by rapid macroscopic rotation.[11] Local anisotropic motions such as phenyl flips may slow spin exchange, too, due to an averaging effect on the intermolecular dipolar interactions and may enhance additionally the intensity of spinning sidebands. We observed the presence of spinning sidebands in the f_1 dimension even in rigid organic solids without any internal high-amplitude motion. For polymers, the dipolar spinning sidebands not only are present for the flipping phenyl rings but also are visible for other functional groups experiencing sufficiently slow spin exchange during rapid macroscopic rotation. For example, a hint of it can be observed for the methyl groups in polycarbonate (Figure 1) and for the phenyl and methylene groups in poly(ethylene terephthalate) (PET) (Figures 3 and 4).

By analogy to PC, the heteronuclear dipolar interactions in PET induce an important enhancement of spinning sideband families. Here, the pronounced spinning sidebands are observed for aromatic and methylene groups in spite of the fact that only small-amplitude libration motions are expected at room temperature for both groups in a semicrystalline (40% crystallinity) powdered sample.[12] By taking only the initial part of the intensity evolution without dipolar echoes, no spinning sidebands are obtained in either experiment (Figure 4). For such short evolution times, the influence of a perturbing effect from flip-flop spin exchange is small, and this permits visualization of the difference in local dipolar field on different functional groups through the fine structure of the homo- and heteronuclear dipolar splittings. The dipolar powder pattern of the CH system in the phenyl ring (Figure 4a, top) shows a characteristic splitting of about 20 kHz, which is close to the value 23.2 kHz expected for a rigid isolated CH pair. For methylene groups, a doublet with splitting of about 26 kHz is visible in the experiment with carbon decoupling (Figure 4d, top), as compared to 31.6 kHz for rigid isolated CH_2 groups. It can be expected that the detailed analysis of the line shapes obtained in this manner could be useful in providing structural and motional information.

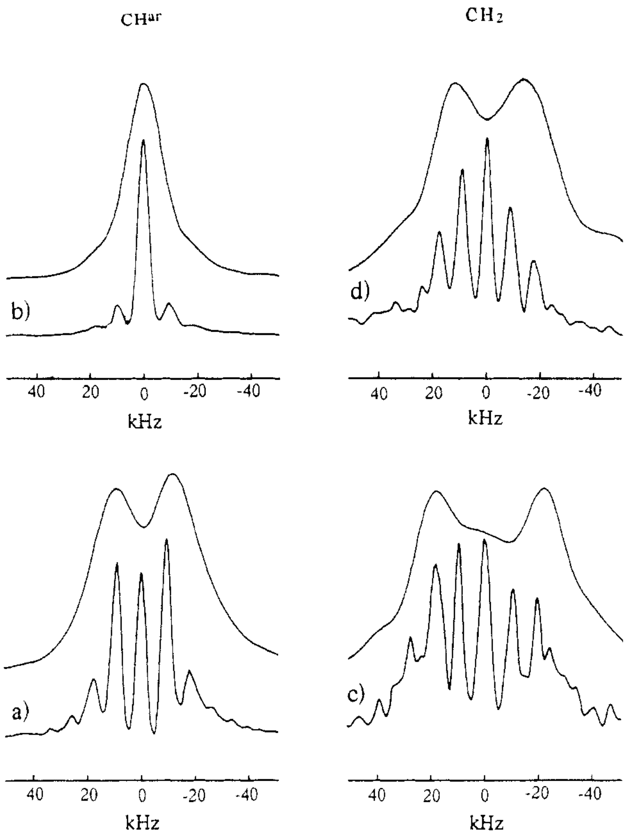

Figure 4. Cross sections of PET dipolar spectra along the frequency of aromatic protonated carbons (a, b) and of methylene groups (c, d) obtained from experiments without (a, c) and with (b, d) carbon decoupling irradiation during the t_1 period and taking 64 (bottom) or 16 (top) t_1 increments of 5 μs. Other experimental conditions are the same as in Figure 3.

In typical organic solids, the heteronuclear dipolar effects manifest themselves by using a short cross-polarization time of some hundreds of microseconds. For longer contact times approaching 1 ms, the ^{13}C-detected dipolar spectra obtained without carbon irradiation during t_1 are essentially determined by proton dipolar interactions mediated by flip-flop spin exchange. A detailed discussion of these effects will be presented elsewhere.

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