Isotropic Mixing, Sign Discrimination, and Sensitivity in Solid-State Wideline Heteronuclear Correlation Experiments

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A variant of the solid-state wideline heteronuclear NMR correlation experiment is described which overcomes some of the drawbacks associated with the routine experiment. The modified experiment results in spectra which are sign-discriminated in the ω_1 dimension, but without the loss in sensitivity expected for a standard hypercomplex implementation. In favorable cases sensitivity enhancements over comparable routine experiments are obtained. As well as these advantages, the method retains the selectivity of modified WISE experiments proposed previously which give spectra containing correlations between directly bonded nuclei only. © 1999 Academic Press

Key Words: heteronuclear correlation experiments; sensitivity; spin diffusion; isotropic mixing; semicrystalline polymers.

INTRODUCTION

Several solid-state two-dimensional proton carbon-13 NMR correlation experiments have been developed in recent years. An important early example was the high-resolution variant originally due to Caravatti *et al.* (*1*). In addition to magic angle spinning (MAS), this experiment makes use of multiple-pulse sequences in order to eliminate both homonuclear and heteronuclear dipolar couplings, so that protons evolve in the first dimension under a scaled chemical shift interaction. The required heteronuclear magnetization transfer is mediated by an isotropic mixing sequence which simultaneously nulls the proton dipolar couplings. This ensures that proton spin diffusion is quenched, so that only direct heteronuclear correlations are observed in the resulting two-dimensional plot which correlates the high-resolution proton spectrum with the isotropic carbon-13 chemical shifts. This type of heteronuclear correlation experiment has been applied to studies of polymers (*2*), lipid bilayers (*3*), and solid peptides (*4*). Modified versions suitable for use with fast MAS rates have also been described recently (*5*).

Another variant which has proved particularly useful for studying motionally heterogeneous materials, such as semicrystalline polymers, block copolymers, and polymer blends, is the "Wideline Separation" (WISE) experiment (*6*). It is this wideline variant of the heteronuclear correlation experiment which is of interest here. In WISE experiments with relatively slow MAS proton magnetization is initially generated by a $\pi/2$ pulse and subsequently evolves under the residual, but significant, dipolar coupling and chemical shift interactions. At the end of the evolution period t_1 a component of the proton magnetization present is transferred to carbon-13 by a standard Hartmann–Hahn cross-polarization step. Carbon-13 magnetization is detected during t_2 with heteronuclear dipolar decoupling, so that the resulting two-dimensional spectrum correlates isotropic carbon-13 chemical shifts which probe the molecular environment with proton MAS dipolar lineshapes which give an indication of mobility. A spin diffusion mixing period, in which the proton magnetization is stored along the z-axis of the rotating frame, is often introduced before the cross-polarization step in order to investigate heterogeneities on a longer length scale.

The routine WISE experiment described above suffers from two problems. First, the proton lineshapes mapped out along ω_1 are normally symmetrized around the center of the spectrum in that dimension. This is a consequence of an experimental protocol which results in the transfer of a single (cosine) component of the proton magnetization present at the end of t_1 to carbon-13 during the cross-polarization step. Obtaining sign-discriminated ω_1 spectra requires a separate experiment to be recorded in which the orthogonal (sine) component of the proton magnetization present at the end of t_1 is transferred to carbon-13. For broad proton lines this procedure results in a significant loss in sensitivity, since the second experiment contributes almost nothing to the signal, while doubling the total measuring time. However, symmetrization around $\omega_1 = 0$ is a significant drawback if the proton spectrum also contains relatively narrow lines with resonance offsets or spinning sidebands. Such a situation is commonly encountered in motionally heterogeneous polymers, but neither the routine WISE experiment nor a modification incorporating ω_1 sign discrimination appears to provide a satisfactory solution for these types of materials.

A second problem with the WISE experiment is the occurrence of proton spin diffusion during the cross-polarization step, since the spin-locking pulse merely reduces the dipolar

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interaction by a factor of two. This causes indirect magnetization transfer between protons and carbon-13 nuclei without a significant heteronuclear dipolar coupling and the observed correlations contain contributions from the lineshapes of distant protons. This problem is often minimized in routine WISE experiments by use of a severely truncated cross-polarization time which reduces the proton spin diffusion at the expense of sensitivity (7). For experiments with a mixing period, additional spin diffusion during the cross-polarization time prevents accurate measurement of the spin diffusion rate unless appropriate corrections are made. Kubo and McDowell (8) have proposed another solution which involves replacing the Hartmann–Hahn cross-polarization step with an isotropic mixing sequence as in the high-resolution experiment described above.

In this paper we show that in fact both the problems associated with the routine WISE experiment (spin diffusion and lack of sign discrimination) can be largely overcome by incorporating an isotropic mixing sequence in this way. In addition to quenching spin diffusion the isotropic mixing sequence plays an important auxiliary role in our new WISE experiment. This is because it simultaneously transfers all components of magnetization from proton to carbon-13 and preserves the phase of the transferred magnetization. The latter property coupled with data-processing methods borrowed from solution-state NMR spectroscopy (9) allows WISE spectra which are sign discriminated in ω_1 to be recorded without prohibitively large sensitivity losses. Indeed, in favorable cases sensitivity enhancements over comparable symmetrized spectra can be obtained. The new variant of the WISE experiment is demonstrated on a sample of semicrystalline low-density poly-(ethylene), an appropriate test case which consists of rigid crystalline domains and relatively mobile amorphous domains. The proton lines associated with the former are greater than 50 kHz in width, while those arising from the latter are motionally narrowed and show spinning sidebands even at moderate MAS rates. In the carbon-13 dimension resonances from the two domains are resolved due to the γ-gauche effect (10).

The pulse sequence used in this work is shown in Fig. 1. Proton magnetization generated by the initial $\pi/2$ pulse evolves during time t_1. A second proton $\pi/2$ pulse of phase 0 rotates the y-component of the proton magnetization present at the end of t_1 time onto the z-axis leaving the x-component unaffected. The windowless WIM-24 isotropic mixing sequence (1) is applied simultaneously to both channels in order to transfer proton magnetization to carbon-13, while quenching spin diffusion. The final carbon-13 $\pi/2$ pulse of phase 0 rotates carbon-13 z-magnetization into the transverse plane and leaves x-magnetization unaffected. Since the isotropic mixing sequence conserves the phase of the transferred magnetization, this sequence ensures that the y-component of the t_1 proton magnetization is transferred to, and detected as, carbon-13 y-magnetization and similarly the x-component is transferred to, and detected as, carbon-13 x-magnetization. A CYCLOPS
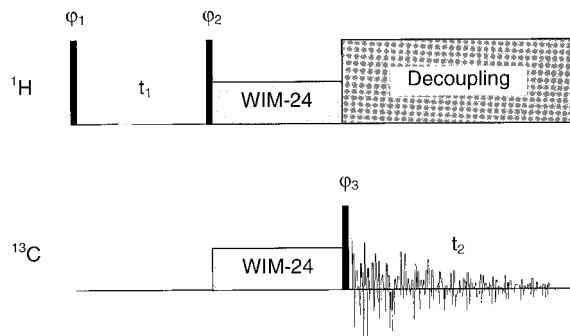
FIG. 1. The pulse sequence used to record the novel variant of the WISE experiment described in this work. Proton magnetization generated by the initial $\pi/2$ pulse evolves during time t_1. A second proton $\pi/2$ pulse of phase 0 rotates the y-component of the proton magnetization present at the end of t_1 time onto the z-axis leaving the x-component unaffected. The windowless WIM-24 isotropic mixing sequence is applied simultaneously to both channels in order to transfer proton magnetization to carbon-13. The final carbon-13 $\pi/2$ pulse of phase 0 rotates carbon-13 z-magnetization into the transverse plane and leaves x-magnetization unaffected. A CYCLOPS phase cycle of all pulses including those comprising the isotropic mixing sequence and a two-step phase cycle on the first proton pulse to remove axial peaks appearing at $\omega_1 = 0$ are applied. Further phase cycling is not commensurate with the processing protocol described.

phase cycle of all pulses including those comprising the isotropic mixing sequence and a two-step phase cycle on the first proton pulse to remove axial peaks appearing at $\omega_1 = 0$ are applied. Further phase cycling is not commensurate with the processing procedure described below. It should be noted that the pulse sequence of Fig. 1 is similar to that proposed by Kubo and McDowell (8) with the addition of two $\pi/2$ pulses which bracket the isotropic mixing sequence. Without the extra pulses pure absorption phase two-dimensional spectra cannot be obtained, since both components of the t_1 proton magnetization are simultaneously transferred to carbon-13 by the WIM-24. In fact, Kubo and McDowell used an absolute-value two-dimensional Fourier transform for this reason. The extra pulses allow the t_1 proton components to be separated during the processing, as described below.

Figure 2 shows a comparison between heteronuclear correlation spectra of poly(ethylene) recorded using the routine WISE experiment (left) and the novel "enhanced" experiment (right). These were recorded at Larmor frequencies of 300.07 and 75.46 MHz for proton and carbon-13, respectively, with a MAS rate of 3.33 kHz. The routine WISE spectrum was recorded using a Hartmann–Hahn cross-polarization time of duration 25 μs which was sufficiently brief to remove the effects of spin diffusion, while the new experiment incorporated a single cycle of the WIM-24 sequence of duration 100 μs for isotropic mixing. Incorporation of a Hartmann–Hahn cross-polarization time of 100 μs into the routine WISE experiment resulted in ω_1 proton lineshapes (not shown) with contributions from both the amorphous and crystalline parts due to spin diffusion. Both experiments were recorded with the
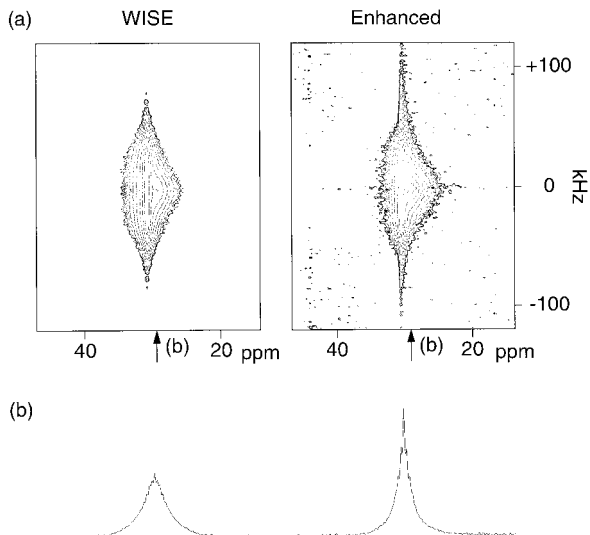
FIG. 2. (a) A comparison between heteronuclear correlation spectra of poly(ethylene) recorded using the routine WISE experiment (left) and the novel "enhanced" experiment (right). These were recorded at Larmor frequencies of 300.07 and 75.46 MHz for proton and carbon-13, respectively, with a MAS rate of 3.33 kHz. The routine WISE spectrum was recorded using a Hartmann–Hahn cross-polarization time of duration 25 μs which was sufficiently brief to remove the effects of spin diffusion, while the new experiment incorporated a single cycle of the WIM-24 sequence of duration 100 μs for isotropic mixing. Further experimental parameters were as follows: relaxation delay, 2 s; dwell time, 2.5 and 66.6 μs in t_1 and t_2, respectively; acquisition time, 136.5 ms; maximum t_1 time, 480 μs; B$_1$ field strengths, 59 kHz on proton and carbon-13 for $\pi/2$ pulses, cross-polarization, and isotropic mixing and 49 kHz on proton for decoupling. The proton resonance frequency was set to the center of the proton spectrum. (b) ω_1 cross-sections through the amorphous carbon-13 resonance as indicated by the arrow.

same total number of scans and the proton carrier frequency was set in the middle of the nonspinning proton spectrum. Data from the WISE experiment were subjected to a real (cosine) Fourier transform in the ω_1 dimension, while that from the new experiment were processed according to a procedure to be described in the Theory section below. Other processing details, such as weighting functions applied in the two dimensions prior to the Fourier transform, were identical for the two spectra. For the two-dimensional plots (Fig. 2a) 10 contour lines were drawn at heights scaled relative to the maximum intensity in the individual spectra. Figure 2b shows cross-sections parallel to the ω_1 dimension at the ω_2 frequency corresponding to the carbon-13 chemical shift for the amorphous domain (as indicated by the arrow in the figure). Two differences between the spectra should be noted. First, the overall signal to noise ratio in the WISE spectrum is greater than in the new experiment, but the former is dominated by the contribution from the crystalline region. On the other hand, the signal associated with the amorphous region (Fig. 2b) is larger in the new experiment. The relative sensitivities are mainly due to the different magnetization transfer sequences. A second difference is that the spinning sidebands apparent in the cross-

section taken from the new experiment are obscured in the WISE experiment due to the symmetrization around the center of the ω_1 dimension. In this case the amorphous contribution has a small resonance offset with respect to the center of the total proton spectrum. Figure 2 demonstrates that the new experiment does indeed produce a sign-discriminated proton spectrum in the ω_1 dimension and illustrates the advantage of doing so in systems with motionally narrowed proton lines. This could have been achieved using a standard procedure, such as the hypercomplex method due to States *et al.* (*11*), but only at the expense of sensitivity. To demonstrate how the new experiment largely overcomes this loss, a more detailed analysis is given below.

THEORY

For a proton (I) carbon-13 (S) system the isotropic mixing Hamiltonian is (*12*)

$$H = \sum_k D_{IS}^k I_k \cdot S,$$

where D_{IS} is an effective heteronuclear dipolar coupling which contains a scaling factor characteristic of the pulse sequence and is modulated by magic angle spinning. For a two-spin system the resulting magnetization transfer can be written (*12*)

$$I_\alpha \xrightarrow{D_{IS}I \cdot S\tau} \frac{1}{2} I_\alpha(1 + \cos D_{IS}\tau)$$

$$+ \frac{1}{2} S_\alpha(1 - \cos D_{IS}\tau) + (I_\beta S_\gamma - I_\gamma S_\beta)\sin D_{IS}\tau, \quad [1]$$

where α, β, $\gamma = x, y, z$. This process is isotropic in the sense that all components of the I-spin magnetization are transferred simultaneously to their S-spin counterparts and the phase of the transferred magnetization is preserved. This behavior is crucial to the correct operation of the experiment described here and contrasts with that observed with standard Hartmann–Hahn cross-polarization for which components of the I-spin magnetization perpendicular to the spin-locking field are dephased. If there are many heteronuclear interactions, as is usually the case in solids, the oscillations in Eq. [*1*] are rapidly damped, leading to a quasi-equilibrium state of $\frac{1}{2}(I_\alpha + S_\alpha)$.

If the cycle time of the WIM-24 sequence is short compared to the MAS period, the zero-order average Hamiltonian has the required isotropic form (*8, 13*)

$$H = \sum_k \frac{2}{3} \omega_{IS}^k(t)I_k \cdot S,$$

where the modulation of the spatial part by the spinning at a rate ω_R can be expressed as a Fourier series

$$\omega_{IS}^k(t) = \sum_{m=-2}^{+2} \omega_{IS}^{k(m)} exp(im\omega_R t)$$

with coefficients

$$\omega_{IS}^{k(m)} = -\chi^k d_{-m,0}^2(\beta_0) D_{0,-m}^2(\alpha_k \beta_k \gamma_k),$$

where β_0 is the magic angle. These depend on the Euler angles α_k, β_k, and γ_k which relate the principal axis system of the heteronuclear dipolar coupling tensor to a frame fixed on the MAS rotor as well as the coupling constant

$$\chi^k = \frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar}{r_k^3}$$

with r_k the distance between the carbon-13 nucleus in question and the kth proton. The Wigner rotation matrices $D_{p,q}^2 (\alpha\beta\gamma)$ are defined in (14). Kubo and McDowell (8) have analyzed the situation where magic angle spinning interferes with operation of the WIM-24 sequence. They demonstrated that anisotropic terms are introduced into the effective Hamiltonian, particularly when the MAS period lasts for an integral number of WIM-24 cycles. However, the effect was shown to be negligible for short mixing times and significantly less important than similar problems caused by experimental imperfections, such as mismatched proton and carbon-13 field strengths or pulse phase errors.

The evolution of the density operator during the experiment from the end of evolution time t_1 to the start of acquisition time $t_2 = 0$ can be represented as a series of product operator transformations. For proton pulse phases $\phi_1 = \pi/2$ and $\phi_2 = 0$ these are

$$(I_x\cos \Omega_I t_1 + I_z\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \xrightarrow{D_{IS}I \cdot S\tau}$$

$$(S_x\cos \Omega_I t_1 + S_z\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \xrightarrow{(\pi/2)S_x}$$

$$(S_x\cos \Omega_I t_1 - S_y\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2), \qquad [2]$$

where Ω_I is the proton offset and the effect of the proton homonuclear dipolar couplings has been accounted for by a Gaussian broadening term with σ related to the linewidth. Proton terms in the density operator remaining after the mixing have been disregarded and all numerical prefactors have been omitted for simplicity. The damping of the oscillations in Eq. [1] is assumed to be rapid compared to the time τ for which the

isotropic mixing sequence is applied. Repeating the experiment with a π phase shift of the second proton $\pi/2$ pulse so that $\phi_2 = \pi$ results in a similar series of transformations:

$$(I_x\cos \Omega_I t_1) - I_z\sin\Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \xrightarrow{D_{IS}I \cdot S\tau}$$

$$(S_x\cos \Omega_I t_1 - S_z\sin\Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \xrightarrow{(\pi/2)S_x}$$

$$(S_x\cos \Omega_I t_1 + S_y\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2). \qquad [3]$$

If the datasets corresponding to the signals of Eqs. [2] and [3] are stored separately rather than combined in the receiver, then both the orthogonal components of t_1 proton magnetization can be obtained simultaneously by taking additive or subtractive combinations,

$$S(t_1)_{add}^y = 2S_x\cos \Omega_I t_1\exp(-\sigma^2 t_1^2/2)$$

$$S(t_1)_{sub}^y = -2S_y\sin \Omega_I t_1\exp(-\sigma^2 t_1^2/2),$$

where the superscript refers to the phase ϕ_1. Allowing for a $\pi/2$ relative phase correction in the ω_2 dimension, the two datasets can be Fourier transformed according to the hypercomplex method of States et $al.$ This procedure follows that proposed previously for solution-state experiments (9) and results in a spectrum which is sign discriminated in the ω_1 dimension. Such a procedure resulted in the spectrum shown in Fig. 2 (right). It is important to note that sign discrimination has been achieved without the need to perform a separate experiment to obtain the sine component, and the loss of sensitivity incurred by a straightforward hypercomplex processing procedure is avoided. In the routine WISE experiment the sine component cannot be obtained in this way because the phase of the transferred magnetization is not preserved by the standard Hartmann–Hahn cross-polarization sequence. Hence, the incorporation of an isotropic mixing sequence into the experiment can be used to achieve sign discrimination without undue loss of sensitivity.

As demonstrated in Fig. 2, the sequence used for magnetization transfer has a significant effect on the relative sensitivities of the different variants of the heteronuclear correlation experiment. For example, the short Hartmann–Hahn cross-polarization time required by the routine WISE experiment favors rigid solids at the expense of more mobile ones. To compare the new data-processing procedure to that used with the routine WISE experiment, as well as to the hypercomplex method of States et $al.$, two further datasets were acquired using the pulse sequence of Fig. 1. These are obtained from experiments with proton pulse phases $\phi_1 = \pi$ and $\phi_2 = 0, \pi$ represented by the transformations

$$(I_z\cos \Omega_I t_1 - I_x\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \xrightarrow{\;\;D_{IS}I \cdot S\tau\;\;}$$

$$(S_z\cos \Omega_I t_1 - S_x\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \xrightarrow{\;\;(\pi/2)S_x\;\;}$$

$$(-S_y\cos \Omega_I t_1 - S_x\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \qquad [4]$$

$$(-I_z\cos \Omega_I t_1 - I_x\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \xrightarrow{\;\;D_{IS}I \cdot S\tau\;\;}$$

$$(-S_z\cos \Omega_I t_1 + S_x\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2) \xrightarrow{\;\;(\pi/2)S_x\;\;}$$

$$(S_y\cos \Omega_I t_1 - S_x\sin \Omega_I t_1)\exp(-\sigma^2 t_1^2/2). \qquad [5]$$

Additive and subtractive combinations of datasets [4] and [5] are therefore

$$S(t_1)_{add}^{-x} = -2S_x\sin \Omega_I t_1\exp(-\sigma^2 t_1^2/2)$$
$$S(t_1)_{sub}^{-x} = -2S_y\cos \Omega_I t_1\exp(-\sigma^2 t_1^2/2),$$

where once again the superscript refers to the phase ϕ_1. Hence,

the signal $S(t_1)_{add}^{y} + iS(t_1)_{sub}^{-x}$ contains only the cosine component of the t_1 modulation. Multiplication by the factor i indicates that the real and imaginary parts of a dataset must be exchanged. For this combination of the four datasets [2] to [5] a real Fourier transform must be applied in the ω_1 dimension, and this results in a symmetrized proton spectrum. This processing procedure is equivalent to that carried out for the routine WISE experiment, although the data have been acquired with the pulse sequence of Fig. 1, including the isotropic mixing sequence. In this way the sensitivity obtained with the WISE processing procedure can be compared to that obtained with both the hypercomplex method of States et al. and the novel procedure, avoiding interference from effects arising from the choice of magnetization transfer sequence. The corresponding sign-discriminated spectrum can be obtained from the same four datasets [2] to [5] using the hypercomplex method of States et al. with the $S(t_1)_{add}^{y}$ and $S(t_1)_{add}^{-x}$ combinations as the real and imaginary parts of the t_1 Fourier transform. Compared to the WISE processing procedure this method is expected to result in a loss of up to a factor two in signal to noise ratio. The largest decreases are expected for a broad proton line on resonance, while for narrow lines with an offset there is no loss in signal to noise. The origin of the loss is that while both combinations $S(t_1)_{add}^{y}$ and $S(t_1)_{add}^{-x}$ contribute to the noise, for a broad line on resonance the second contains
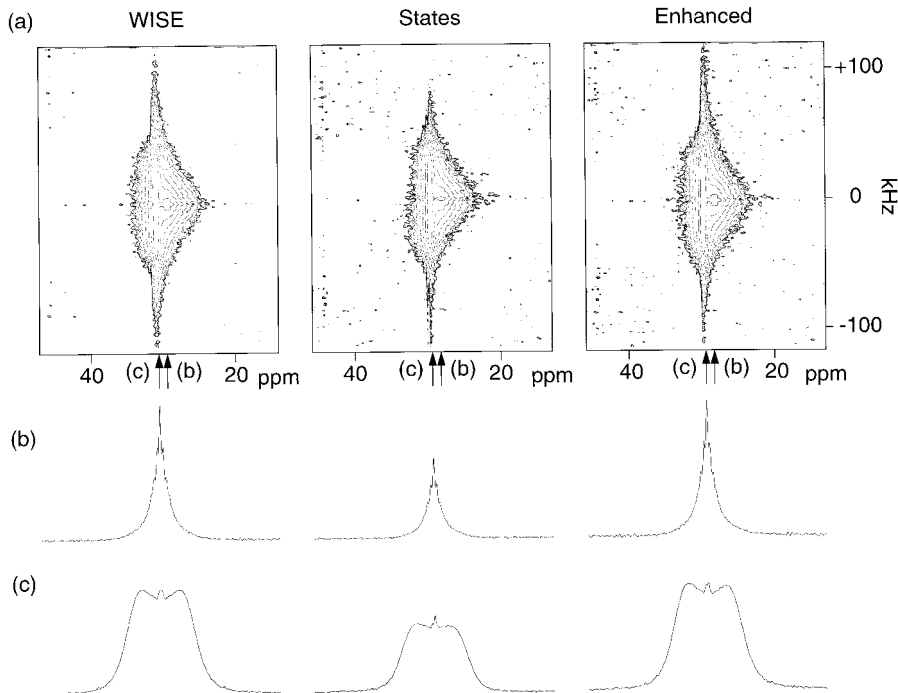
FIG. 3. (a) Results of the three processing procedures described in the text for the same experimental data: (left) WISE processing with a real ω_1 Fourier transform, (center) following the hypercomplex method of States et al., and (right) the new enhanced procedure. Four experimental datasets were recorded as described in the text, incorporating a single cycle of the WIM-24 sequence of duration 100 μs for isotropic mixing. The proton resonance frequency was set exactly on resonance with the narrow amorphous line. Other parameters were as for Fig. 2. (b and c) ω_1 cross-sections through the amorphous and crystalline carbon-13 resonance as indicated by the arrows.

negligible signal. However, an identical sign-discriminated spectrum can be obtained from the same four datasets [2] to [5] at no extra cost in terms of experiment time using the combinations $S(t_1)_{sub}^{y}$ and $S(t_1)_{sub}^{-x}$. The sum of these two sign-discriminated spectra in which the noise is uncorrelated (9) results in a gain in signal of a factor 2 and a gain in the noise of a factor $\sqrt{2}$. This corresponds to a $\sqrt{2}$ increase in signal to noise ratio relative to the standard States method. This third "sensitivity enhanced" (9) processing procedure is equivalent to that used to obtain the right-hand spectrum of Fig. 2.

RESULTS

Figure 3 shows the results of the three processing procedures described above on the same four experimental datasets, recorded with the proton carrier frequency set on resonance with the amorphous line. Experimental parameters were similar to those of Fig. 2; further details are given in the figure legend. For the two-dimensional plots, (a) 10 contour lines were drawn at heights scaled relative to the maximum intensity in the individual spectra. For the ω_1 cross-sections through the (b) amorphous and (c) crystalline carbon-13 resonances (as indicated by the arrows in the figure), an absolute scale of intensity was used. As expected, both the narrow on-resonance amorphous and broad crystalline proton lines show similar behavior. The WISE processing procedure (left) results in twice the signal and identical noise relative to the States method (center), while the new enhanced method (right) allows the full WISE signal to be regained at a cost of an extra factor of $\sqrt{2}$ in noise.

TABLE 1

Signal and Noise in Arbitrary Units Recorded for Poly(ethylene) with the Pulse Sequence in Fig. 1 as a Function of Processing Method

| Processing method[a]	Noise[b]	Signal (amorphous)[c]	Signal (crystalline)[c]
WISE (1)	0.295	3.73	20.05
States (1)	0.292	2.05	12.28
Enhanced (1)	0.421	3.75	20.26
WISE (2)	0.294	2.07	10.39
States (2)	0.299	2.00	6.30
Enhanced (2)	0.428	4.16	10.52

[a] As described in the text (1) and (2) denote amorphous protons on- and 2 kHz off-resonance in ω_1, respectively.

[b] Measured as the standard deviation of the intensities in a 25×50 data point section extracted from an empty region of the spectrum.

[c] Measured as the integral of the proton line in a ω_1 slice through the maximum of the relevant carbon-13 resonance.

The latter fact is most easily verified by looking at the noise in the two-dimensional contour plot. Quantitative details are given in the first three rows of Table 1 which shows the noise calculated by evaluating the standard deviation of intensities in a two-dimensional section of the spectrum extracted from a region well away from the resonances, as well as the integrals for the signals in the cross-sections of Figs. 3b and 3c. The values in the table confirm the expected signal to noise variation.

Figure 4 shows data which are identical to that of Fig. 3
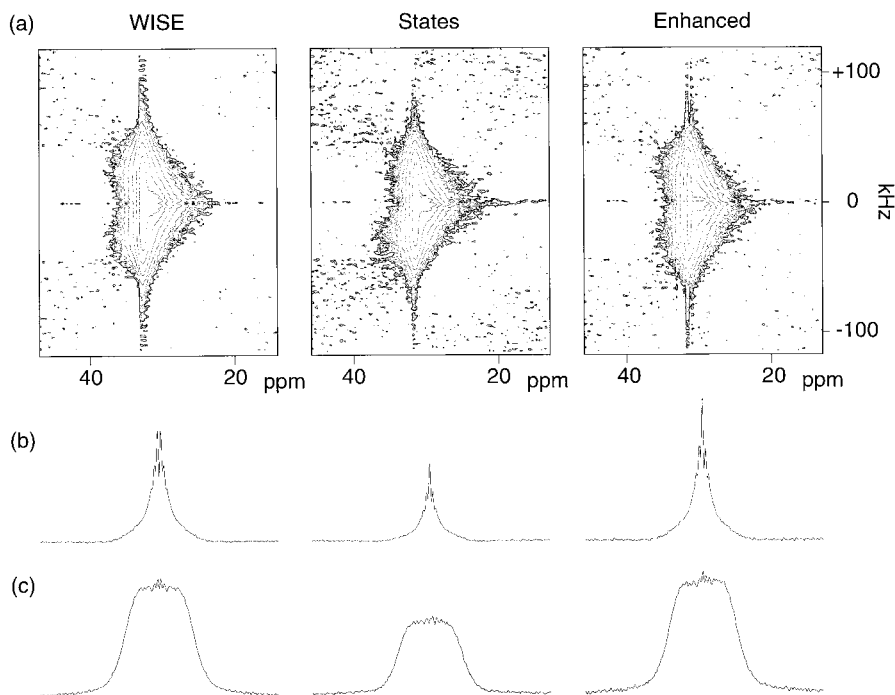
FIG. 4. Spectra produced as for Fig. 3 except that the proton resonance frequency was set 2 kHz off resonance with respect to the narrow amorphous line.

except that the proton carrier frequency was set 2 kHz off resonance with respect to the narrow proton line. In this case the symmetrization inherent in the WISE processing procedure is particularly apparent for the narrow amorphous proton line, as expected. There is no real gain in signal to noise for the WISE processing procedure relative to the States method for the narrow amorphous line. The apparent increase is solely due to the overlap of this line and its mirror image in ω_1. However, the WISE processing procedure still shows twice the signal relative to the States method for the broad crystalline line. Both lines show a twofold signal enhancement relative to the States method when the new processing procedure is used and there is the expected $\sqrt{2}$ enhancement in noise. Quantitative details are given in the last three rows of Table 1 and these confirm the expected signal to noise variations. In particular it should be noted that in the off-resonance case for the narrow line the signal to noise ratio is highest using the new procedure.

CONCLUSION

A novel variant of the WISE experiment which overcomes the problems of spin diffusion and lack of sign discrimination has been described. The combination of an isotropic mixing sequence for magnetization transfer with data-processing methods borrowed from solution-state NMR spectroscopy allows WISE spectra which are sign discriminated in ω_1 to be recorded without prohibitively large sensitivity losses. For relatively narrow proton lines this experiment has been shown to give sensitivity enhancements over comparable symmetrized spectra. The new variant of the WISE experiment has been demonstrated to be particularly useful in studies of semicrystalline polymers which consist of rigid crystalline domains and relatively mobile amorphous domains. In addition to the WIM-24 sequence mixing schemes have been proposed which are suitable for use with MAS at rates greater than the strength of the homonuclear and heteronuclear dipolar interactions (*15*). Finally, we note that sensitivity-enhanced variants of several other heteronuclear (*1*) and homonuclear (*16*) solid-state correlation experiments can be envisaged.

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