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A Double-Quantum Filter for Rotating Solids

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Abstract: A pulse sequence is demonstrated which effectively excites double-quantum coherences in solid samples rotating at the magic angle. A double-quantum filter using this sequence is presented and applied to ¹³C-labeled zinc acetate to demonstrate its effectiveness. The ¹³C-¹³C scalar coupling between the methyl and carboxyl resonances was observed as well as a shift of 31 Hz in the center of both resonances arising from the homonuclear dipole Hamiltonian. It was also noted that when the spinning sideband patterns of the two coupled resonances overlap, carbon flip-flop transitions are facilitated, resulting in significant broadening of the spectral lines.

During the last few years, *n*-quantum filters have proven their usefulness in simplifying spectra and establishing carbon-carbon connectivities in liquid-state nuclear magnetic resonance.¹⁻⁷ More sophisticated filtering techniques like topological filters which select only certain spin systems out of a complicated mixture have also been developed.^{8,9} These experiments have proven very useful to chemists interested in obtaining the structure of complicated molecules in solution. Multiple-quantum experiments, using homonuclear dipole coupling to generate the multiple-quantum coherence, have been used in static, solid samples.¹⁰⁻¹² These experiments have limited chemical application because of the line broadening due to chemical shift anisotropy. Multiple-quantum experiments are more difficult if one desires "high resolution" through magic angle sample spinning. However, Griffin and co-workers have demonstrated the possibility of obtaining double-quantum filtered spectra,¹³ and we have demonstrated a method to effectively excite multiple-quantum transitions¹⁴ in samples of abundant spins rotating at the magic angle.

The problem of simplifying complex spectra and of obtaining carbon-carbon connectivities in solids is of considerable interest. The two-dimensional spin-diffusion experiment^{15,16} originally used to determine the extent of mixing of two solids in a solid solution has been proposed as a solution to these problems.¹⁷ In this work we demonstrate an alternative solution, a double-quantum filter, used in conjunction with magic angle spinning. This experiment is a solid-sample analogue of the INADEQUATE experiment¹ which has proven quite useful in solution NMR. Two problems occur in the multiple-quantum NMR of rotating solids which do not apply in liquids.

The first problem is the experimental one of generating a double-quantum filtered spectrum with good signal to noise and peak amplitudes which are not dependent on offset of the carrier frequency. In a solid sample the multiple-quantum coherence is generated by the inhomogeneous part of the dipolar interaction; i.e., the sign and magnitude of the interaction depend on the

orientation of the internuclear vector relative to the applied magnetic field and therefore on time. Therefore, if one is to perform a conventional 90°-τ/2-180°-τ/2-90° sequence^{18,19} to generate the multiple-quantum coherence, the maximum excitation time must be kept much shorter than a rotor period¹³ or the dipole interaction will change sign in the course of rotation and partially or fully destroy the multiple-quantum coherence. In most cases, this means that the excitation will be much shorter than the optimum excitation time of 1/*D* where *D* is a "typical" dipolar coupling constant. Furthermore, the 180° refocusing pulse which makes the excitation independent of offset^{18,19} cannot be used

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because it scrambles the magnetization and prevents the occurrence of the rotational echoes.¹⁴ Without this refocusing pulse, the intensities of the excited multiple-quantum transitions become offset dependent. These experimental problems can be overcome by applying time reversal pulses in synchrony with the sample rotation.¹⁴ Compared to the conventional sequence,¹⁰⁻¹³ our pulse sequence offers improved signal to noise and offset-independent multiple-quantum excitation, and the resulting spectrum has pure positive absorption line shapes.

The second problem encountered in the application of double-quantum filtering to rotating solids is more fundamental. In spin systems containing only chemical shift anisotropy, MAS yields a pattern of sidebands. The line widths of the sidebands are identical and independent of spinning speed. However, Maricq and Waugh²⁰ have shown (both theoretically and experimentally) that in systems containing both chemical shift anisotropy and dipolar couplings, magic angle spinning fails to totally narrow the lines. In first-order average Hamiltonian theory, the line width is scaled by a factor of $1/\omega_r$ by the sample rotation. We will demonstrate that even in an acetate, where the chemical shift separation of the peaks is very large and therefore no strong coupling is encountered in any crystallite orientation, considerable broadening of the lines is observed if the spinning speed is such that any two rotational sidebands of the dipolar coupled carbons overlap. In addition to this broadening, a spinning speed independent shift in the "isotropic" ¹³C resonance frequency is observed because the static dipole-dipole coupling is not much smaller than the separation in resonance frequency.

Theory

As already mentioned, there are significant differences in the relevant spin interactions of liquid or solid samples. Even "isotropic looking" solid spectra obtained through the application of magic angle spinning cannot be completely described by the isotropic part of the spin interactions. Therefore, we will briefly outline the relevant parts of the theory.

A schematic representation of the pulse sequence for the double-quantum filtering experiment using time reversal is given in Figure 1. The basic physics of the time-reversal, multiple-quantum pulse sequence and the modifications necessary for its application to rotating solids are given elsewhere and will not be discussed in detail here.¹⁰⁻¹⁴

To the best of our knowledge, time-reversal sequences have only been applied to homonuclear spin systems. Therefore, we will briefly address the problem of heteronuclear dipolar couplings during the multiple-pulse sequence; i.e., we would like to excite ¹³C double-quantum coherence in the presence of strongly coupled protons. If the protons are polarized along the magnetic field direction, the heteronuclear dipolar interactions behave in the same way as the carbon chemical shift and do not appear in the zero-order average Hamiltonian of the double-quantum filter. Therefore, if the proton magnetization is flipped back along the magnetic field direction after the initial cross-polarization period, no proton decoupling need be applied during the carbon multiple-pulse sequence. However, if the proton decoupler were turned on during the carbon multiple-pulse sequence, averaging of the heteronuclear dipole interaction would not occur and the carbon-proton couplings would be reintroduced in the average Hamiltonian. If the ¹³C multiple-pulse cycle time is not much faster than the heteronuclear couplings, higher order average Hamiltonian terms may play a significant role and lead to a loss in the efficiency of the multiple-quantum excitation. This situation could be improved by inserting 180° pulses on the proton system applied in synchrony with the carbon multiple-pulse, similar to the way that such 180° pulses have been used in multiple-pulse line-narrowing experiments.²¹

Since carbon-carbon dipolar couplings between directly bonded carbons are comparable to carbon chemical shift differences, strong

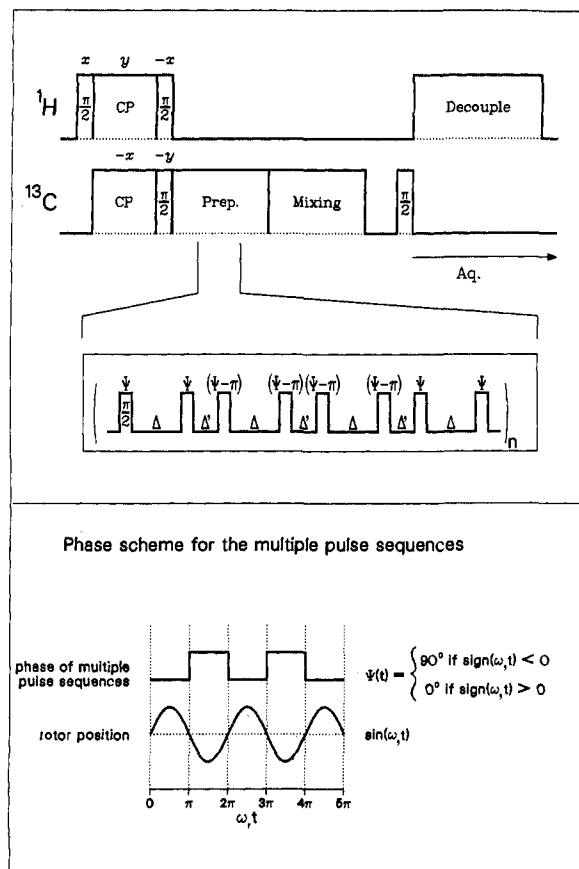


Figure 1. A schematic representation of the pulse sequence used to obtain the double-quantum filtered ¹³C spectra. The upper part of the figure illustrates the time-reversal double-quantum filter with the ¹³C multiple pulse sequence. During the preparation multiple-quantum pulse sequence, even quantum transitions, are excited. The phase of the pulses in the multiple-quantum sequence must be altered synchronously with the rotation of the magic angle spinner, as indicated in the bottom part of the figure. This phase alternation avoids the "self-time-reversal" effect.¹⁴ During the mixing period, the multiple-quantum intensity is transferred back into z-magnetization which allows it to be detected with a 90° read-out pulse. Because an additional 90° phase shift is applied to every pulse in the mixing period (relative to the preparation period), the Hamiltonian during the mixing period is the negative of the Hamiltonian during the preparation period. This leads to a time reversal which results in all transitions observed during acquisition having a pure positive absorption line shape.

coupling effects must be considered. The four transition frequencies for a two-spin system with dipolar coupling and chemical shift are given by:

$$\omega_{1,2,3,4} = \frac{1}{2} \left[\Sigma \pm D + \left(\frac{D^2}{4} \pm \Delta^2 \right)^{1/2} \right] \quad (1)$$

where Σ and Δ are the sum and difference of the rotating frame frequencies Ω_1 and Ω_2 of the two spins and D is the dipolar coupling between them.

The resonance frequencies and the dipolar coupling are functions of the orientation of the crystallite in the static field. Therefore, magic angle spinning makes them time dependent.

$$\Omega_i(t) = \omega_0^i \text{Tr} \sigma^i + C_1^i \cos(\gamma_i + \omega_r t) + C_2^i \sin(\gamma_i + \omega_r t) + C_3^i \cos(2\gamma_i + 2\omega_r t) + C_4^i \sin(2\gamma_i + 2\omega_r t) \quad (2)$$

$$D(t) = C_5 \cos(\gamma_{12} + \omega_r t) + C_6 \cos(2\gamma_{12} + 2\omega_r t) \quad (3)$$

where σ^i is the chemical shift tensor of spin i , ω_r is the angular frequency of the sample rotation, ω_0 is the Larmor frequency, and the constants C_1 to C_6 are given by:^{14,22}

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$$C_1 = \omega_0 \sin \theta \cos \theta (-3 \sin \beta_i \cos \beta_i (\sigma_{33} - \sigma_i) + \sin \beta_i \cos \beta_i \cos 2\alpha_i (\sigma_{11}^i - \sigma_{22}^i)) \quad (4)$$

$$C_2 = -\omega_0 \sin \theta \cos \theta (\sin \beta_i \sin 2\alpha_i (\sigma_{11}^i - \sigma_{22}^i)) \quad (5)$$

$$C_3 = \omega_0 \sin^2 \theta (\frac{3}{4} \sin^2 \beta_i (\sigma_{33}^i - \sigma_i) + \frac{1}{4} (1 + \cos^2 \beta_i) \cos 2\alpha_i (\sigma_{11}^i - \sigma_{22}^i)) \quad (6)$$

$$C_4 = -\omega_0 \sin^2 \theta (\frac{1}{2} \cos \beta_i \sin 2\alpha_i (\sigma_{11}^i - \sigma_{22}^i)) \quad (7)$$

$$C_5 = -6d \sin \theta \cos \theta \sin \beta_{12} \cos \beta_{12} \quad (8)$$

$$C_6 = \frac{3}{2}d \sin^2 \theta \sin^2 \beta_{12} \quad (9)$$

where θ is the angle between the applied field, B_0 , and the rotor spinning axis; σ_{11} , σ_{22} , and σ_{33} are the eigenvalues of the chemical shift tensor; and d is the dipole coupling constant. The angles α_i , β_i , γ_i and α_{12} , β_{12} , γ_{12} are the Euler angles which describe the orientations of the eigensystems of the two chemical shift tensors and the carbon-carbon dipolar tensor in the rotor frame.

Let us now consider a case where the chemical shift difference is larger than the dipolar splitting for all Euler angles $\alpha\beta\gamma$. The square root in eq 1 can then be approximated by:

$$\left(\frac{D^2}{4} + \Delta^2\right)^{1/2} = \Delta - \frac{D^2}{8\Delta} + \frac{3D^4}{128\Delta^3} - \dots \quad (10)$$

and the expressions for the resonance frequencies are:

$$\omega_{1,2} = \Omega_1 \pm \frac{D}{2} + \frac{D^2}{16\Delta} \pm \dots \quad (11)$$

$$\omega_{3,4} = \Omega_2 \pm \frac{D}{2} - \frac{D^2}{16\Delta} \pm \dots \quad (12)$$

As long as the spinning frequency is less than the chemical shift separation, the frequency of the center band of the magic angle spinning spectrum can now be calculated by averaging eq 11 and 12 over a full rotor period:

$$\omega_{1,2} = \frac{\omega_0 \text{Tr } \sigma^1}{3} + \left\langle \frac{D^2}{16\Delta} \right\rangle + \dots \quad (13)$$

$$\omega_{3,4} = \frac{\omega_0 \text{Tr } \sigma^2}{3} - \left\langle \frac{D^2}{16\Delta} \right\rangle + \dots \quad (14)$$

If, for simplicity, Δ is assumed to be isotropic, eq 13 and 14 can be rewritten as:

$$\omega_{1,2} = \frac{\omega_0 \text{Tr } \sigma^1}{3} + \frac{\langle D^2 \rangle}{16\Delta} + \dots \quad (15)$$

$$\omega_{3,4} = \frac{\omega_0 \text{Tr } \sigma^2}{3} - \frac{\langle D^2 \rangle}{16\Delta} + \dots \quad (16)$$

with:

$$\langle D^2 \rangle = d^2 (4 \sin^2 \beta_{12} \cos^2 \beta_{12} + \frac{1}{2} \sin^4 \beta_{12}) \quad (17)$$

Because $\langle D^2 \rangle$ is dependent on the crystallite orientation with respect to the rotor axis, the MAS line shape will not be a single narrow line, but a distribution of frequencies. The width of this pattern is proportional to d^2/Δ . The average value of the distribution is obtained by performing a powder average of eq 17. The following result is obtained:

$$\langle \langle D^2 \rangle \rangle_B = \frac{4}{5}d^2 \quad (18)$$

Note that the second and all higher terms in eq 15 and 16 have their origin in a perturbation theory treatment of the B term of the dipolar Hamiltonian:

$$B \propto (I_1^+ I_2^- + I_1^- I_2^+) \quad (19)$$

The bigger the chemical shift difference Δ between the two spins, the less important these terms are since the flip-flop processes are no longer energy conserving. A second-order perturbation treatment can therefore be applied. If the energy difference in the flip-flop can be supplied by sample rotation, or, in other words, if any two lines of the sideband pattern of the two carbons overlap, the flip-flop term will gain importance, and, since it does not commute with the chemical shift Hamiltonian, it will introduce considerable additional broadening into the MAS spectrum.

Experimental Section

The experiments reported were performed on two different ^{13}C -labeled samples of zinc acetate dihydrate. One sample (referred to as doubly labeled) was prepared from 95% ^{13}C acetate. This was diluted with natural abundance acetate in the ratio of 1:19 (i.e., 5%). Since the 95% sample contains about 90% of the doubly labeled acetate, the final ratio of double- to single-labeled material is ≈ 3 . The zinc acetate was crystallized from aqueous solution as the dihydrate. The second labeled sample was prepared from 5% methyl labeled acetate, 5% carboxyl labeled acetate, and 90% natural abundance acetate, mixed and crystallized from aqueous solution. This sample has about the same overall loading of ^{13}C as the doubly labeled sample, and the intermolecular ^{13}C - ^{13}C dipole couplings should be roughly equivalent. The doubly labeled acetate was used purely for sensitivity reasons; at natural abundance the concentration of double-labeled acetate would be about 0.01%. However, the method is by no means restricted to doubly labeled compounds.

Measurements were performed at 4.7 T on a Bruker CXP-200 spectrometer equipped with a Merimac PSDW-84 digital phase shifter. The quadrature phases in the multiple pulse sequences were generated by the spectrometer modulator unit which was carefully tuned by means of tune-up sequences.²³ The additional phase shift ψ (see Figure 1) was generated by means of the digital phase-shifter. The phase, ψ , is altered synchronously with the spinner rotation according to the scheme given in Figure 1. This overcomes the "self-time-reversal" as previously noted.¹³ The mixing period consists of exactly the same pulse sequence as preparation with the exception that all pulses are shifted by 90° with respect to preparation. To eliminate zero-quantum transitions as well as four-quantum transitions (even though the latter are extremely weak for a dilute spin system), an additional phase cycle of 0° , 90° , 180° , 270° is applied. This phase shift is added to all preparation pulses. An add-subtract cycle is performed for the detection. This phase cycling also eliminates remaining z -magnetization as well as all odd-order transitions caused by imperfections in the preparation and mixing pulse sequences.²⁴ For a double-quantum filter the additional phase shifts are all multiples of 90° and the digital-phase shifter is convenient but not necessary. In all experiments, the 90° pulse length was $3.22 \mu\text{s}$, the cross-polarization contact time was $850 \mu\text{s}$ with rf fields matched at about 77 kHz, and the recycling time was 30 s. The times Δ and Δ' in the multiple-pulse sequences of preparation and mixing were chosen to be 9.28 and 3.03 μs , respectively. The delay between mixing and the read-out pulse was 100 ms. More ideal behavior of the spin system during preparation and mixing would be expected for a shorter multiple pulse cycle time. Because of hardware limitations in our pulse programmer, we were not able to realize this.

Results and Discussion

Figure 2 contains the ^{13}C CP MAS spectra of zinc acetate taken under several different conditions. The uppermost trace (A) is the spectrum of the sample of 5% singly labeled acetate in natural abundance material. Spectrum B is the "normal" CP MAS spectrum of the 5% doubly labeled material. Trace C is the two-quantum filtered spectrum of the 5% doubly labeled material obtained using the pulse sequence in Figure 1. The bottom spectrum (D) is the two-quantum filtered spectrum obtained with the same pulse sequence but without phase switching every half-rotor period. Spectra C and D were obtained under the same experimental conditions and contain the same number of scans per spectrum. It is immediately obvious that only the pulse sequence with synchronous phase shifting results in effective excitation of double-quantum coherence under MAS conditions. When applied to a sample spinning at the magic angle, the

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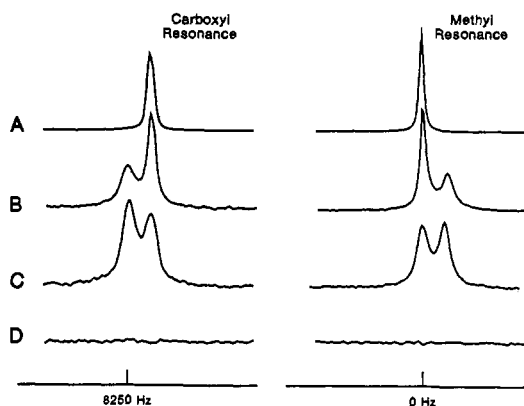


Figure 2. Four spectra of polycrystalline zinc acetate. The left set of spectra are due to the carboxyl carbon and the right set are due to the methyl carbon. The vacant, central portion of each spectrum has been eliminated. Spectrum A is the CP MAS spectrum of a sample composed of 5% acetate labeled at C1, 5% labeled at C2, and the remainder natural abundance acetate. Both carbons give rise to a single narrow line. Spectrum B is the CP MAS spectrum of 5% doubly labeled acetate diluted in natural abundance. Compared to spectrum A, which has the same overall concentration of ^{13}C , there are additional lines with a broader line width. These are caused by ^{13}C spins which have another ^{13}C as a nearest neighbor. Spectrum C is the double-quantum filtered spectrum of the same sample as spectrum B using the pulse sequence depicted in Figure 1. In this spectrum *only* ^{13}C spins with ^{13}C as a nearest neighbor are detected. Each carbon gives rise to a broadened doublet. The preparation and mixing sequences each had a length of 300 μs , corresponding to a full spinner rotation period. Spectrum D is the double-quantum filtered spectrum of the same sample as spectrum C. The phase of the multiple-pulse sequence has not been changed synchronously with the sample rotation; otherwise, all parameters were the same as for spectrum C. A nearly perfect "self-time-reversal" is seen, causing the intensity of the double-quantum filtered lines to vanish. For spectra A and B, 16 scans were accumulated; for C and D, 1000 scans were added. The sample rotation speed for all spectra was 3.33 kHz. The timing parameters for the pulse sequences are given in the text.

standard time reversal sequence used in static solids results in perfect "self-time-reversal" over the full rotor period.¹³ This is a clear demonstration of the necessity of synchronous phase shifting in MAS multiple-quantum NMR spectroscopy.

The double-quantum filtered spectrum (C) selects the resonances of ^{13}C nuclei which are dipolar coupled to another ^{13}C nucleus, while the CP MAS spectrum results from all of the ^{13}C in the sample. We note that the resonances of the doubly labeled material are broader than those of the singly labeled acetate and that they are split into a doublet. These two effects explain the relative peak heights seen in spectrum B which is a superposition of spectra A (singly labeled in zinc acetate) and C (doubly labeled in zinc acetate). The asymmetry of the doublets in spectrum C is possibly due to strong coupling effects. The lack of perfect alignment of the peak maxima in spectra A through C results from small shifts associated with peak overlap.

The center of the doublet resonance observed in trace C of Figure 1 is shifted with respect to the resonance position of the singly labeled material. The splitting is due to the scalar (J) coupling between the ^{13}C nuclei which is 52 Hz as determined by solution NMR of the doubly labeled zinc acetate. The shift of the center of the doublet resonance as well as part of the broadening can be attributed to strong coupling effects described in the Theory section above. If, for simplicity, the chemical shifts are assumed to be isotropic, the shift in the mean frequency can be calculated using eq 15, 16, and 18. A shift of 33 Hz between the singly and doubly labeled resonances was computed using a dipolar coupling constant of 2.34 kHz corresponding to the carbon-carbon internuclear distance of 1.48 Å in zinc acetate²⁵ and using the measured chemical shift difference of 8.25 kHz between the methyl and carboxyl carbons. The measured shift is 31 Hz

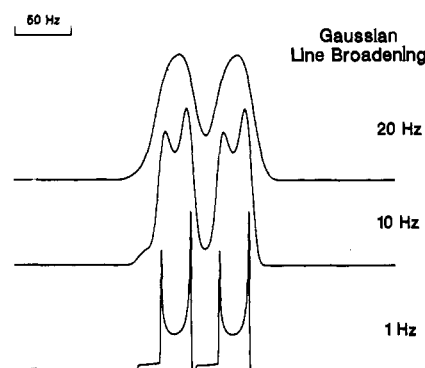


Figure 3. Computer-simulated spectra for the methyl resonance of doubly labeled acetate with 1, 10, and 20 Hz of Gaussian line broadening. The equations and parameters for this simulation are described in the text. The spectra for the carboxyl carbon are the mirror image of those shown.

which is in excellent agreement with the simplified calculations. This additional shift is caused by homonuclear dipolar interactions and is therefore of different origin from the shifts discussed by VanderHart²⁶ which have their origin in heteronuclear interactions.

There are relatively few reported observations of scalar couplings in solid samples. In principle, scalar couplings are an excellent structural tool and should be as useful in solids as they are in liquids. There are several conditions which must be met in order to observe carbon-carbon J couplings in solids. First, the line width of the MAS spectral lines must be less than the J coupling. Since the coupling is constant and the line widths are generally linear with field, this condition may not be easily met at higher fields. The frequency distribution resultant from the dipolar coupling must be smaller than J ; i.e. the structure of the lines in the bottom trace of Figure 3 must not obscure the J coupling. The broadening due to the B term (flip-flops) in the dipolar alphabet must be smaller than J .

Under the simplifying assumption of an isotropic chemical shift, the line shape, including the additional shift, can be calculated using eq 15 and averaging the dipolar coupling over all crystallite orientations and over the spinner rotation according to eq 17. The results of such a calculation using the chemical shift and dipolar coupling values mentioned above are shown in Figure 3. This figure is a simulation of the upfield (methyl) resonance in Figure 2. The lower trace with only 1 Hz of Gaussian line broadening shows a structured resonance line similar to that noted by Maricq and Waugh²⁰ but different in origin. The width of this resonance is independent of the rotor spinning frequency as long as the spinning is slower than the chemical shift separation. After application of 20-Hz line broadening the computed spectrum is very similar to the observed data. The implications of this comparison are that the line width of the experimental spectrum is about 20 Hz broader than the optimal width of the acetate resonance. We estimate the magnetic field inhomogeneity to contribute no more than 3 Hz to the line width; insufficient decoupling with proton decoupling fields of greater than 70 kHz should contribute less than 3 Hz to the width. The remainder of the observed line width must be due to intrinsic factors which include residual broadening due to ^{13}C - ^{13}C dipolar coupling, possible motional destruction of the coherent averaging of the decoupling or MAS, and, most likely, a dispersion in chemical shifts due to imperfections in crystallite structures or bulk susceptibilities.²⁷ The observed line widths of about 30 Hz are consistent with the line widths observed in most organic materials in MAS experiments at 4.7 T. If eigenvalues and eigenvectors of the chemical shift tensors are known, eq 13 can be evaluated in a similar way to simulate the exact spectrum.

The very earliest applications of magic angle spinning NMR by Andrew and co-workers²⁸ and Lowe²⁹ were intended to reduce

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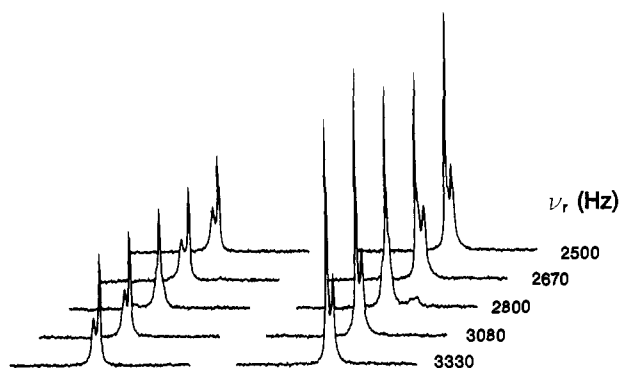


Figure 4. Normal CP MAS spectra of 5% doubly labeled zinc acetate taken as a function of the sample rotation frequency. The methyl and carboxyl resonances each consist of a sharp line, arising from carbon spins with no neighboring ^{13}C and a broadened and shifted doublet arising from carbon spins with a ^{13}C neighbor (cf. Figure 2). While the single line is independent of spinner speed, the doublet is severely broadened around $\nu_r = 2.8$ kHz. At this spinning speed, the sidebands of the two resonances, separated by 8.25 kHz, overlap considerably. Similar broadening effects were observed at rotation speeds of 2.10 and 4.15 kHz (spectra not shown).

the homonuclear dipole coupling in dense spin systems and thus reduce the rate of flip-flop processes and spin exchange. The reduction of spin-spin effects has been discussed in the context of the now common CP MAS experiment.^{30,31} Qualitatively, this can be rationalized in terms of the energy needed to accomplish a flip-flop transition. When two resonance lines are narrowed sufficiently that there is no overlap between them, an amount of energy equal to the chemical shift difference between the resonances must be provided to make the exchange allowed. This drastically slows spin exchange between clearly separated lines³⁰⁻³². Figure 4 contains a series of simple CP MAS spectra of doubly labeled zinc acetate taken as a function of the spinning frequency. Note that at a spinning frequency of 2.8 kHz, the lines which result from the doubly labeled material are broadened to the extent that the doublet nearly disappears. Recall that these spectra contain a narrow resonance due to the natural abundance (singly labeled) ^{13}C as well as the doublet due to the labeling. The reason for the observed broadening is that the first spinning sideband of one resonance overlaps with the second sideband of the other resonance at this spinning speed. Effectively, the sample rotation is providing the energy necessary to make spin exchange relatively rapid, thus broadening the lines. This indicates that the B term in the dipolar Hamiltonian has an important influence on the spectrum when the flip-flop energy can be provided by spinning. Similar line broadening effects have been observed at spinning speeds of 2.10 and 4.15 kHz (not shown), where again an overlap in the sideband pattern occurs. This is not the first observation of such line broadening effects; equivalent observations have been made by Andrew and co-workers³³ in the ^{31}P spectrum of solid PCl_5 . This solid is actually a mixture of PCl_4 and PCl_6 with different ^{31}P chemical shifts. At a spinning speed equal to one-half the shift between the two species, the resonances become significantly broadened.

Finally, we would like to make a few comments about the effectiveness of the double-quantum filter. The maximum double-quantum filtered signal (Figure 2C) was obtained with a multiple-quantum preparation time of 300 μs , corresponding to one full rotor period. The signal-to-noise ratio of this spectrum is compared to that of spectrum 2B, obtained through a

normal cross-polarization. Taking into account the number of scans, about 15% of the signal intensity from the ^{13}C pairs passes through the double-quantum filter, we believe that the majority of this loss is due to experimental difficulties and could be recovered if it were possible to truly optimize the spectrometer for this particular NMR experiment.

Conclusions

In this work, we have demonstrated a double-quantum filter applicable to solid samples with magic angle spinning. For purposes of demonstration, we have used isotopically labeled samples of zinc acetate dihydrate to improve the signal to noise. At the 5% enrichment level used, the doubly labeled signal should be a factor of 500 more intense than in a natural abundance sample. The sensitivity of the double-quantum filtered experiment is about 15% of the standard spin-locked cross-polarization experiment. With minor experimental modifications, the sensitivity with respect to the cross-polarization experiment could be improved significantly. Under optimum conditions, at natural abundance the signal to noise of the double-quantum spectrum would be 0.1% of a spin-locked cross-polarization spectrum. At first glance this appears rather poor, but it is about the same as found in an INADEQUATE¹ experiment in solution. The alternative approach of using a two-dimensional spin diffusion experiment as demonstrated by Frey¹⁷ has equal considerations of poor signal to noise coupled with the fact that the huge diagonal peaks are bound to obscure the desired connectivity information when the chemical shifts are small. Furthermore it is much less effective when combined with magic angle spinning because the spinning greatly slows spin diffusion. Obviously, such double-quantum or spin diffusion experiments become easier with slight isotopic enrichment in the sample. There are many cases where the information obtained from a multiple-quantum filtered spectrum is sufficient to warrant long spectrometer accumulation times or isotopic labeling. A clearly useful application of multiple-quantum filtering occurs when a compound can be "doubly labeled" and the resulting spin pair followed through a set of chemical or biochemical reactions, in analogy to Schaefer, Stejskal, and McKay's ^{13}C - ^{15}N double-cross-polarization spectra.³⁴ In many solution structural studies, the J coupling is a powerful indicator of structure.³⁵ To our knowledge, this fact has not been exploited in solids because of the difficulty in obtaining coupling constants. Double-quantum filtering may well make it possible to use these "liquid techniques" in structural studies in solids.

We would like to reiterate the "lesson" clearly discussed by Maricq and Waugh²⁰ that homonuclear dipole couplings are a serious perturbation in MAS spectra. "High-resolution solid-state NMR spectra" show important differences from spectra of samples in an isotropic phase. Additional shifts, spectral line-shape changes, and line broadening can be expected. Following Waugh's earlier example, we have demonstrated that these effects are understandable and can be calculated, but exploitation of statistical ^{13}C pairs or isotopic labeling must be used with caution. In cases like zinc acetate, where the coupling is not too strong, easily interpretable double-quantum filtered spectra can be obtained as long as the sideband pattern of the two coupled resonance does not include severe overlap. This can always be achieved by adjusting the spinner frequency. More severely broadened spectra could be expected with samples with stronger coupling.²⁰ In cases where the overlap of peaks is severe, it will be difficult to deconvolute them and extract connectivities unless one knows quite a bit about the shift and dipole coupling tensors. Performing the experiment at a higher resonance frequency would help to reduce these second-order effects.

Despite the discussed complications, we expect the application of n -quantum filtering to MAS spectroscopy to become a powerful tool in reducing the complexity of MAS spectra and in the as-

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signment of geometrical proximity of spins in polycrystalline or glassy solids.

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Laser Photolysis and CIDEP Studies of the Formation of Phenyl-Substituted Group 4B Element (Silicon, Germanium, and Tin)-Centered Radicals in Direct Photoejection of the Group 4B Element-Centered Anions

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Abstract: Phenyl-substituted group 4B element-centered radicals generated by the direct photoejection from the group 4B element-centered anions were observed by laser photolysis at room temperature. In order to clarify the mechanism of this process, CIDEP study of the photolysis of the group 4B element-centered anions was carried out at 77 and 4.2 K. From the emissive patterns observed for the germyl and stannyl anions after the excitation by a pulse laser, the photoejection reactions were most probably considered to occur from triplet anions.

Organic anions, especially of the group 4B elements (silicon, germanium, and tin) have received considerable interest in synthetic chemistry and reaction mechanisms.¹⁻⁷ Although extensive thermal reactions of the group 4B element-centered anions have been made, there are few reports on photochemical studies of these anions.⁸⁻¹⁰ By near-UV photolysis at 93 K of rigid glasses of triphenylstannyl anions, the triphenylstannyl radical was confirmed to be generated from a stationary ESR measurement.⁸ Upon steady-light illumination of aromatic compounds at room temperature in the presence of the triphenylsilyl and triphenylstannyl anions in tetrahydrofuran (THF), anion radicals of the aromatic compounds were found to be produced.^{9,10} Although it was suggested that one-electron transfer would occur from the silyl and stannyl anions to the aromatic compounds, the resulting silyl and stannyl radicals have not yet been observed directly.

On the other hand, the photoejection process from the organic anions, including the group 4B element-centered anions, has received much attention recently in relation to the intermediates of photostimulated $\text{S}_{\text{RN}}1$ reactions¹¹⁻¹⁵ and ion-pair phenomena.^{16,17} Among them, the key problem in this process is the identification of labile intermediates formed during reaction. The laser-photolysis technique is a good method for direct observation of transient species generated immediately after excitation of the anions. Furthermore, chemically induced dynamic electron polarization (CIDEP) has recently become a powerful tool for investigating fast radical reactions. CIDEP is expected to give us unique information about short-lived radicals and their precursors.

In this paper, we describe the direct observation of phenyl-substituted group 4B element (silicon, germanium, and tin)-centered radicals generated by photoejection of the corresponding anions with the aid of a laser-photolysis measurement at room temperature.¹⁸ Furthermore, CIDEP spectra obtained by the photolysis of these anions at 77 and 4.2 K are discussed.

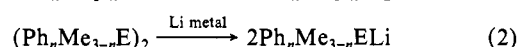
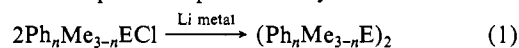
Results and Discussion

Absorption Spectra of Phenyl-Substituted Group 4B Element-Centered Anions. The phenyl-substituted group 4B element-centered anions ($\text{Ph}_n\text{Me}_{3-n}\text{ELi}$: 1-3 for E = Si and $n = 1-3$, 4-6

Table I. Absorption Data of UV Spectra for Phenyl-Substituted Group 4B Element-Centered Anions in THF

compound	λ_{max} (nm) for E =		
	Si	Ge	Sn
PhMe_2ELi	335	290	
Ph_2MeELi	335	310	
Ph_3ELi	335	310	310

for E = Ge and $n = 1-3$, and 7 for E = Sn and $n = 3$, respectively) were prepared from the corresponding chlorides and lithium metal in THF at room temperature quantitatively.



E = Si, Ge, and Sn; $n = 1-3$

The formation of the anions (1-7) from the chlorides and lithium

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