Application of Multiple-Pulse Experiments to Characterize Broad NMR Chemical-Shift Powder Patterns from Spin-$^1/_2$ Nuclei in the Solid State

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The utility of the Carr-Purcell Meiboom-Gill (CPMG) experiment and a modified-CPMG experiment in characterizing NMR chemical-shift powder patterns for spin-$^1/_2$ nuclei is demonstrated. Heavier NMR-active nuclei such as ^{195}Pt, ^{199}Hg, and ^{207}Pb are known to be extremely sensitive to their local environment and as such have very large chemical-shift ranges. In the solid state, such nuclei commonly exhibit chemical shifts that range well over 1000 ppm, depending upon the orientation of the molecule within the applied magnetic field. Thus, acquiring NMR spectra of polycrystalline samples is often an experimental challenge because of these very broad powder patterns. In acquiring chemical-shift powder patterns of these nuclei, we provide several examples that demonstrate that a considerable saving in time is realized by using the CPMG experiment as opposed to the standard one-pulse or spin-echo experiment. In general, this time saving is even greater if a modified-CPMG experiment is used. Homonuclear dipolar interactions are considerably reduced in the CPMG experiment and are almost completely removed in the modified-CPMG experiment. For samples containing ^{1}H, larger enhancements are realized by combining the CPMG experiment with cross polarization. By use of the CPMG and the modified-CPMG experiments, the principal components of the chemical-shift tensors are determined for each of the samples studied.

1. Introduction

In 1950, Hahn[1] reported the first multiple-pulse NMR experiment, now known as the spin-echo or Hahn-echo experiment. The original purpose of this technique was to measure the transverse relaxation time, T_2, of nuclei in a liquid sample. Four years later, Carr and Purcell[2] proposed a variation of the Hahn-echo experiment by employing a combination of pulses $[90°_x − \tau − (180°_x − 2\tau−)_n]$ in order to reduce the effects of translational diffusion and to obtain better refocusing of the chemical-shift interaction. Meiboom and Gill[3] then improved the Carr-Purcell pulse sequence to compensate for small cumulative errors due to mis-settings of the pulse widths by using a different phase cycling (see Figure 1a), which is now known as the Carr-Purcell Meiboom-Gill (CPMG) experiment. A multiple-pulse technique, inspired by the well-known solid-echo experiment and employing a train of $\pi/2$ pulses (Figure 1b), was independently reported by Mansfield and Ware[4] and Ostroff and Waugh.[5] In the case of solid samples, the multiple-pulse technique proved to be more efficient than the CPMG pulse sequence in removing homonuclear dipolar interactions. Years later, Garroway[6] demonstrated that one could Fourier transform spin-echo trains and obtain a spikelet spectrum that mimicked the spectrum of a stationary sample. He compared the widths of the spikelets from ^{13}C NMR spectra of stationary samples of adamantane obtained with these three different methods in order to determine the origin of the static line broadening. Garroway concluded that for a stationary sample, the ^{13}C−^{13}C intermolecular dipolar coupling was responsible for the 40 Hz line width of the ^{13}C peaks. This homonuclear dipolar interaction was not removed using the
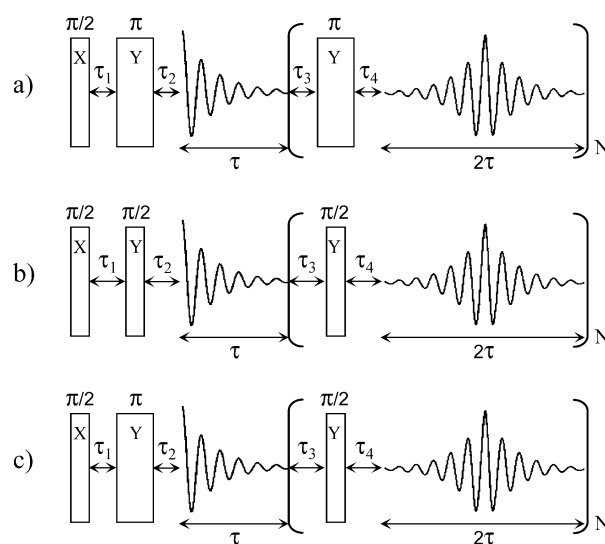

Figure 1. Timing diagram for (a) CPMG, (b) MW-4, and (c) modified-CPMG pulse sequences.

Carr-Purcell pulse sequence. On the other hand, the CPMG and Mansfield-Ware (MW-4) methods were found to reduce the homonuclear dipolar coupling considerably, with the MW-4 method being most effective. These methods were later applied to quadrupolar nuclei in the solid state by Bloom and Sternin[7] to investigate the slow motions of phospholipid bilayer membranes via ^{2}H NMR (MW-4) and by Cheng and Ellis[8] to examine the motion of rubidium cations on the surface of γ-alumina using ^{87}Rb NMR (CPMG). More recently, Cowans and Grutzner[9] rotor synchronized the CPMG experiment in order to obtain ^{13}C line widths of 0.8 and 1.3 Hz, respectively, for the aromatic and methyl peaks of polycrystalline hexamethyl-

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benzene. Until recently, these experiments were used to obtain information about homonuclear dipolar coupling[6,10,11] or molecular dynamics.[7,8,12-16] Larsen et al.[17] appear to be the first to suggest using the CPMG pulse sequence to acquire NMR spectra of half-integer quadrupolar nuclei (QCPMG) for the purpose of sensitivity enhancement. One advantage of the QCPMG experiment is that it allows one to separate homogeneous and inhomogeneous interactions as originally defined by Maricq and Waugh.[18] In fact, information about the homogeneous interactions can be obtained from the line width of the individual spikelets, while inhomogeneous interactions only affect the envelope of the spikelet manifold. From the [87]Rb and [59]Co QCPMG spikelet spectra obtained for the central $^1/_2 \leftrightarrow -^1/_2$ transitions in RbClO$_4$, RbVO$_3$, and [Co(NH$_3$)$_5$Cl]Cl$_2$, respectively, Larsen et al. characterized the quadrupolar and chemical-shift interactions as well as their relative orientations. The results obtained from these experiments were in good agreement with those obtained previously by other NMR techniques (e.g., single crystal, quadrupolar echo, magic angle spinning (MAS) NMR). Shortly after introducing the QCPMG experiment for studying stationary samples, Larsen et al. demonstrated that one could investigate spinning samples by synchronizing the echo with the spinning frequency.[19] More recently, QCPMG has also been combined with cross polarization[20] and MQ-MAS.[21,22] Because of the significant sensitivity gain realized using the QCPMG experiment, researchers have been able to examine some nuclei that were never or rarely studied in the solid state before, specifically low-γ nuclei, such as [35]Cl,[23] [39]K,[24] [25]Mg,[24] or [67]Zn.[20,24-27]

To our knowledge, no one has used the CPMG experiment (or one of its variants) to improve the signal-to-noise ratio of spectra arising from spin-$^1/_2$ nuclei in a stationary sample. (After the submission of this manuscript, we became aware of a paper by J. Z. Hu and R. A. Wind titled "Sensitivity-enhanced phase-corrected ultra-slow magic angle turning using multiple-echo data acquisition".[28] The sensitivity gain realized in a conventional CPMG experiment is discussed in this interesting paper.) In the present report, we will demonstrate that this technique is very useful for spin-$^1/_2$ nuclei with large chemical-shift anisotropies (CSAs).[29] To date, these nuclei have been studied using spin-echo,[30-32] point-by-point,[33] MAS,[33-35] or CP-MAS[32,36-38] methods, but not without difficulty; in particular, the time to acquire such spectra is often prohibitively long. We will present, using [207]Pb NMR, a comparison of the results obtained for the CPMG experiment and two variants (the MW-4 and a new variant that we will refer to as the modified-CPMG, shown in Figure 1c). We will then use some of these pulse sequences on several spin-$^1/_2$ nuclei known to have large CSAs such as [207]Pb, [199]Hg, and [195]Pt. For samples containing ^{1}H, the CPMG experiment will be combined with cross polarization in order to increase sensitivity. We will also examine the sensitivity enhancement of these different experiments compared to the conventional spin-echo experiment[39] and determine the principal components of the chemical-shift tensors from the envelope of the spikelet spectra.

2. Experimental Section

All compounds were obtained commercially and used without further purification, except for (Ph$_3$P)$_2$Pt(C$_2$H$_4$), which was prepared following published procedures.[40]

The [207]Pb NMR experiments were performed using a Bruker Avance 300 (B_0 = 7.05 T, SF = 62.84 MHz) with a 90° pulse of 2.4 μs and recycle times varying from 20 to 40 s. The radio frequency (rf) field strength and chemical-shift reference were

calibrated using a powder sample of Pb(NO$_3$)$_2$. The [199]Hg and [195]Pt NMR spectra were acquired using a Bruker Avance 500 (B_0 = 11.75 T, SF = 89.60 and 107.06 MHz, respectively). The rf field strengths (100 kHz), chemical-shift reference, and CP Hartmann-Hahn matching condition (rf = 75 kHz and 50 kHz) were set using NEt$_4$Na[Hg(CN)$_4$][41] and (NH$_4$)$_2$PtCl$_6$[42] for [199]Hg and [195]Pt, respectively. Proton recycle delays were 125 s for Hg(CH$_3$COO)$_2$ and 10-30 s for the platinum samples; contact times between 5 and 15 ms were used. Proton decoupling using a two-pulse phase modulation (TPPM)[43] and an rf field strength of 50 kHz was used when the sample contained protons (^{1}H). The transmitter was generally set near the center of the spectrum and all spectra were acquired at room temperature. All spectra were obtained using Bruker MAS probes with cylindrical 4-mm o.d. rotors.

Except for the pulse sequence shown in Figure 1c, the other pulse sequences (CPMG, MW-4) have been previously detailed elsewhere.[2-5,44,45] The delays τ_1, τ_2, τ_3, and τ_4 were set to 40 μs, and the phase cycling used here is the one defined by Larsen et al.[17]

The response of a spin-$^1/_2$ system to the various pulse sequences used in this study was calculated using the program SIMPSON.[46,47] This program was also used to obtain the principal components of the chemical-shift tensors by visually comparing calculated and experimental spectra.

3. Results and Discussion

[207]Pb NMR Spectra. As previously mentioned, lead compounds tend to give rise to [207]Pb NMR spectra with quite large spans (i.e., large CSAs);[29,31] consequently, the [207]Pb NMR line shapes of solid compounds often cover 100 kHz or more. Uniform pulse excitation of such large sweep widths is an experimental challenge. Furthermore, relatively long [207]Pb spin-lattice relaxation times[33] result in long spectral accumulation times because of the need for long relaxation delays. Finally, lead chemical shifts are very sensitive to temperature[48] (e.g., the [207]Pb NMR of solid Pb(NO$_3$)$_2$ is commonly used to set and calibrate the temperature in NMR MAS experiments);[49-55] hence, due to sample heating and temperature gradients across the sample caused by spinning,[49] slow MAS techniques are not an ideal means of characterizing [207]Pb NMR chemical-shift tensors. An alternative method involves using the static spin-echo technique; however, as explained by Van Bramer et al.,[30] the acquisition and analysis of broad chemical-shift powder patterns is not straightforward and significant errors can result. Despite these problems, many solid-state [207]Pb NMR analyses have been published so far[30,31,33,34,56] due to the importance of lead in various fields of chemistry (environment, glasses, conducting materials, etc). A good overview of solid-state [207]Pb NMR is given in a recent review by Dybowski and Neue;[55] Wrackmeyer has also reviewed applications of [207]Pb NMR parameters.[57]

The CPMG experiment splits the spectrum into a manifold of spikelets separated by $(2\tau)^{-1}$ (with 2τ equal to the time of the full echo; see Figure 1) and exhibits an envelope similar to the spin-echo spectrum. In the solid state, the CPMG experiment was originally designed to reduce/remove the homonuclear dipolar coupling, but as already demonstrated,[6,44] this is not the most efficient homonuclear decoupling technique one can use. Since the development of CPMG, there have been many other homonuclear dipolar decoupling techniques using the same pulse-sequence skeleton (i.e., a series of pulses separated by small delays and/or acquisition times, τ). However, the more recent and efficient experiments do not sample the signal
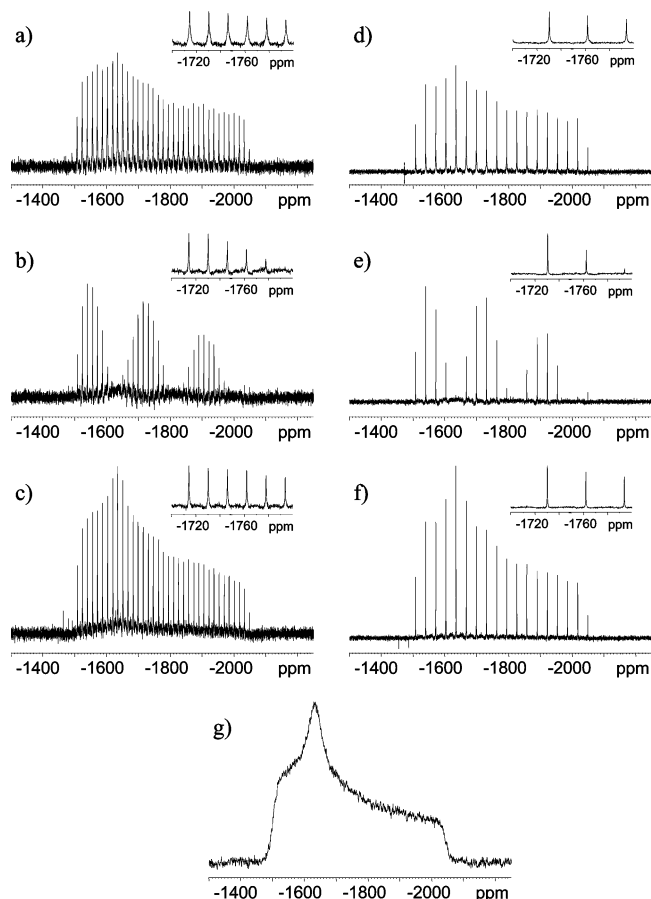
Figure 2. ^{207}Pb NMR spectra of PbCl$_2$ with $\tau = 500\ \mu$s and 512 scans (left column) and $\tau = 250\ \mu$s and 256 scans (right column). The pulse sequences are CPMG (a, d), MW-4 (b, e), and modified-CPMG (c, f) and spin−echo with 2048 scans with a line broadening of 50 Hz added prior to Fourier transformation (g). All spectra were acquired at 7.05 T.

Figure 3. Comparison of experimental (512 scans and $\tau = 500\ \mu$s) free induction decay (a) and spectrum (c) with calculated (using parameters given in Table 1) free induction decay (b) and spectrum (d) for ^{207}Pb NMR of PbCl$_2$ at 7.05 T for the MW-4 pulse sequence. The desired echoes occur at 1.0, 2.0, 3.0, ...ms.

Figure 4. Comparison of experimental (1024 scans and $\tau = 500\ \mu$s) free induction decay (a) and spectrum (c) with calculated (using parameters given in Table 1) free induction decay (b) and spectrum (d) for ^{207}Pb NMR of PbCl$_2$ at 7.05 T for the modified-CPMG pulse sequence.

between each pulse; the sampling of a time 2τ only occurs every 6τ (WHH-4[58] and MREV-8[59−62]) or even at longer times (BR-24 and BR-52[63−66]), thus involving a loss of signal compared to CPMG and other methods. Often these multipulse experiments also scale the chemical-shift Hamiltonian, making them more complicated to exploit. We therefore employed only the CPMG experiment and two of its variants using ^{207}Pb NMR to investigate the lead CS tensor of PbCl$_2$. This sample is used to check the efficiency of the various spin-echo experiments on a model spin-$^1/_2$ system which exhibits a large CSA. Figure 2 shows the ^{207}Pb NMR spectra of solid PbCl$_2$ acquired applying these three different techniques, CPMG (parts a and d of Figure 2), MW-4 (parts b and e of Figure 2), and a modified-CPMG (parts c and f of Figure 2), all giving spikelet spectra. A close examination of the line widths of the individual spikelets (see insets of Figure 2) shows that both the MW-4 and the modified-CPMG experiments result in narrower spikelets and consequently are more effective in removing homonuclear dipolar coupling than the CPMG experiment. However, the MW-4 experiment is clearly unsuitable for broad chemical-shift patterns. In fact, it creates equally spaced repetitive Gaussian filters of which one is centered on the offset resonance, even if the transmitter is placed exactly on the isotropic shift value (which is very important for quadrupolar nuclei with integer spin, from unpublished results). Thus, the CPMG and modified-CPMG experiments seem to be the best methods to obtain reliable NMR spectra of stationary powder samples.
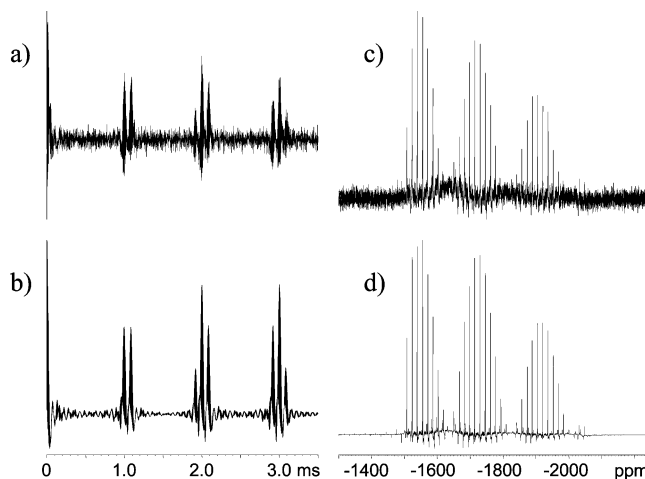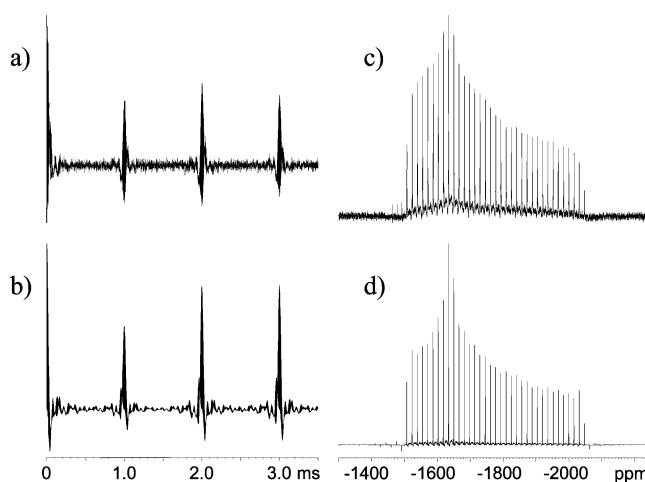
To understand why the MW-4 pulse sequence fails (i.e., Figure 2b) and why the CPMG and modified-CPMG experiments work (see Figs. 2a and 2c), we have calculated the response of a typical spin-$^1/_2$ system that experiences anisotropic magnetic shielding (e.g., PbCl$_2$) to the pulse sequences shown in Figure 1 using the program SIMPSON.[46,47] Calculated free-induction decays and their corresponding Fourier transforms are shown in Figures 3 and 4, for the MW-4 and modified CPMG experiments, respectively. In the MW-4 sequence, it is clear that three spin-echoes are created (see Figure 3a); this leads to the demise of the MW-4 sequence. The echoes occur at $(2\tau - 2\tau_1)$, 2τ, and $(2\tau + 2\tau_1)$. On the other hand, as shown in Figure 4, echo refocusing is achieved in the modified-CPMG experiment. Product operator formalism[67] indicates that the unwanted echo modulation in the MW-4 experiment results from mixing of the -1 and $+1$ coherence levels. This formalism also reproduces the echo refocusing of the modified-CPMG experiment.

As already indicated, the modified-CPMG experiment is more efficient in removing homonuclear dipolar interactions even for nuclei with moderate natural abundances, such as ^{207}Pb (22.6%). Reduction of the homonuclear dipolar broadening results in

TABLE 1: Optimized Chemical-Shift Parameters for Studied Samples Using the Program SIMPSON

compound		technique	$\delta_{iso}{}^a$ (ppm)	$\delta_{cs}{}^b$ (ppm)	$\eta_{cs}{}^c$	ref
PbCl₂		modified-CPMG	−1730 ± 5	−319 ± 3	0.42 ± 0.02	this work
		spin-echo	−1716	−303	0.41	30
		MAS	−1717 ± 2	323	0.30	34
PbCrO₄		modified-CPMG	−2287 ± 3	455 ± 3	0.89 ± 0.01	this work
		static	−2292 ± 11	457 ± 15	0.87 ± 0.02	56
		spin-echo	−2236.2 ± 2.9	441.2 ± 5.4	0.890 ± 0.013	31
		spin-echo	−2286	460	0.85	30
PbTiO₃		modified-CPMG	−1407 ± 3	−772 ± 4	0	this work
		MAS	−1419	−772	0.0	33
		spin-echo	−1395.1 ± 8.4	−753.1 ± 14.5	0	31
		spin-echo	−1409	−759	0	30
PbZrO₃	site 1	modified-CPMG	−1345 ± 4	−536 ± 4	0.26 ± 0.02	this work
	site 2	modified-CPMG	−992 ± 4	−897 ± 4	0.20 ± 0.02	
	site 1	MAS	−1363	−546	0.2	33
	site 2	MAS	−1017	−838	0.2	
	site 1	spin-echo	−1349.5 ± 1.5	514.8 ± 2.2	0.211 ± 0.007	31
	site 2	spin-echo	−994.7 ± 2.4	−892.9 ± 4.5	0.211 ± 0.004	31
Hg(CH₃COO)₂		CP-CPMG	−2497 ± 4	−1165 ± 4	0.093 ± 0.01	this work
		CP-MAS	−2490	−1176	0.0	36
		CP-MAS (4.869 kHz)	−2497	−1131	0.0	32
		CP-MAS (5.508 kHz)	−2497	−1204	0.23	
		CP-spin-echo	−2497	−1154	0.08	
		CP-MAS	−2497	−1188	0.074	41
(Ph₃P)₂Pt(C₂H₄)			−488 ± 4	−205 ± 4	0.85 ± 0.02	this work
((C₂H₅)₃P)₂Pt-						
(OCO)₂·xH2O site 1		CP-CPMG	157 ± 4	2720 ± 4	0.21 ± 0.01	this work
	site 2	CP-CPMG	52 ± 4	2308 ± 4	0.15 ± 0.01	this work

^{a} $\delta_{iso} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$. ^{b} $\delta_{cs} = \delta_{33} - \delta_{iso}$; ($|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$). ^{c} $\eta_{cs} = (\delta_{22} - \delta_{11})/\delta_{cs}$.

longer "T_2" values and, thus, longer echo trains. Consequently, in a given time period, we obtained better signal−noise ratios using the modified-CPMG than the CPMG experiment. Preliminary results obtained in this lab involving half-integer quadrupolar nuclei show the same improvement using the modified-QCPMG instead of the QCPMG experiment. However, in the absence of homonuclear dipolar interactions, experiments and simulations carried out using SIMPSON indicate the conventional CPMG experiment will result in superior sensitivity for both spin-$^1/_2$ and quadrupolar nuclei.

Figure 2a shows a small distortion of the envelope of the CPMG spectra as compared to that obtained from the spin-echo experiment (Figure 2g); however, this distortion is not present using the modified-CPMG method. The relative merits of the CPMG and modified-CPMG techniques become more comparable when the acquisition time for one echo (2τ) is decreased (parts d and f of Figure 2). In fact, the homonuclear dipolar decoupling is more efficient when the sampling time of the echo, 2τ, is short (see insets in parts d and f of Figure 2). The shorter this time, the better the homonuclear dipolar decoupling and the smaller the difference in the spikelet line width between the CPMG and modified-CPMG methods is, especially when this dipolar coupling is weak.

The modified-CPMG ^{207}Pb NMR spectra of PbCl₂ acquired with different τ delays, along with the spin-echo spectrum, are shown in parts c and f of Figure 2. The signal gain depends on the separation of the spikelets and on the number of echoes acquired. Therefore, we required only 2.1 h (Figure 2f) and 4.2 h (Figure 2c) to acquire the modified-CPMG spectra versus 17 h for the spin-echo spectrum (Figure 2g). As expected, the spikelet spectra have an envelope which mimics the stationary sample powder pattern (Figure 2g); however, there are some small distortions in the baseline. Cowans and Grutzner[9] attribute these artifacts to magnetization that was originally generated off axis, magnetization that has recovered through spin-lattice relaxation during the τ period and/or imperfect echo pulses. This first explanation does not seem to be correct in our case since

tests on the CPMG and modified-CPMG experiments revealed that these two methods were not very sensitive to pulse imperfections. According to Mansfield and Ware[68] these artifacts come from Zeeman-dipole energy exchange of the spins viewed as being partially spin locked in the mean-pulse field, thus affecting the first few odd echoes. This latter explanation appears to be the most likely as in our case the distortions disappeared after left shifting the train of echoes to the top of the third echo. The nonflat baseline, having the shape of the spectrum's envelope, comes from the first echo corresponding to the classic spin-echo experiment. However, the acquisition of these spectra would be of little value if we were unable to correctly extract the principal components of the chemical-shift tensor δ_{ii} ($i = 1, 2, 3$). To a first approximation, one can simply obtain the δ_{ii} values by inspection of the spectra. To obtain more precise values, one may also fit the spectra using the program SIMPSON.[46,47] The closer the spikelets, the more precise the resulting simulated values will be. Figure 4c shows the ^{207}Pb NMR spikelet spectrum of PbCl₂ obtained with the same experimental parameters as those used to obtain the spectrum in Figure 2c, along with the theoretical spectrum calculated using SIMPSON (Figure 4d). The simulated spectrum is in very good agreement with experiment, and the values obtained for the chemical-shift tensor (Table 1) are also in good agreement with previous results.[30,34]

^{207}Pb NMR spectra of PbCrO₄ were also obtained with the modified-CPMG experiment (not shown). The ^{207}Pb chemical-shift powder pattern for lead chromate has a small span but is an interesting sample to examine because, to our knowledge, the ^{207}Pb chemical-shift tensor has the highest asymmetry parameter, η_{cs}, of any lead compound. This asymmetry is explained by the absence of a 3-fold (or higher) symmetry axis at the Pb site. We optimized the chemical-shift tensor and simulated the spectrum using SIMPSON to obtain the values presented in Table 1; our values are in very good agreement with some earlier results.[30,56] Nevertheless, we note
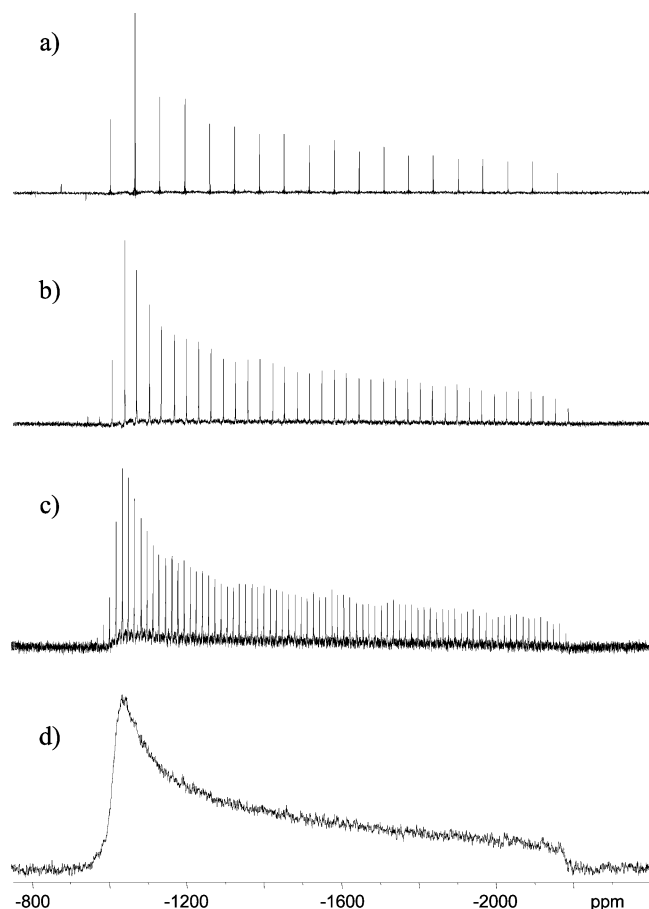
a)

b)

c)

d)

Figure 5. [207]Pb NMR modified-CPMG (a-c) and spin-echo (d) spectra of PbTiO$_3$ at 7.05 T. The modified-CPMG spectra were acquired with (a) 128 scans and $\tau = 125$ μs, (b) 512 scans and $\tau = 250$ μs, and (c) 1024 scans and $\tau = 500$ μs; a line broadening of 5 Hz was added prior to Fourier transformation. The spin-echo spectrum was acquired with 2880 scans, and a line broadening of 50 Hz was added prior to Fourier transformation.

some discrepancies between different papers for the isotropic shift value.[30,31,56]

PbTiO$_3$, which has been the subject of several NMR studies,[30,31,33,69] is another very interesting lead compound. The lead CS tensor for PbTiO$_3$ has a large span and the site symmetry[70] at the lead nucleus (C$_4$ axis at Pb) imposes an asymmetry parameter of zero on the [207]Pb chemical-shift tensor. Van Bramer et al. used this sample to test NMR data acquisition and analysis techniques for broad chemical-shift powder patterns.[30] PbTiO$_3$ is also interesting because, like Pb(NO$_3$)$_2$, its [207]Pb chemical-shift tensor is temperature dependent. Bussian et al.[69] clearly showed that its chemical-shift tensor, especially the anisotropy, varies with temperature, and from that determined an empirical relationship between lead coordination, unit cell distortion, and the lead NMR chemical shift. Nevertheless, when we examine our spectra (Figure 5), the asymmetry parameter seems to be slightly nonzero, contrary to that expected for a nucleus with a C$_4$ symmetry axis and all previous [207]Pb NMR results. An optimization of the spectrum (Figure 5c) with $\eta_{CS} = 0$ (as imposed by the structure) gives, however, a simulated spectrum (Figure 6b) in good agreement with the experimental one. The apparent asymmetry comes from the relative position of the isotropic peak compared to the positions of the spikelets. The value obtained for the CSA (Table 1) is in good agreement with previous studies.[30,31,33] This example clearly shows that, as usual, one has to be very careful when dealing with an axially symmetric chemical-shift tensor. We
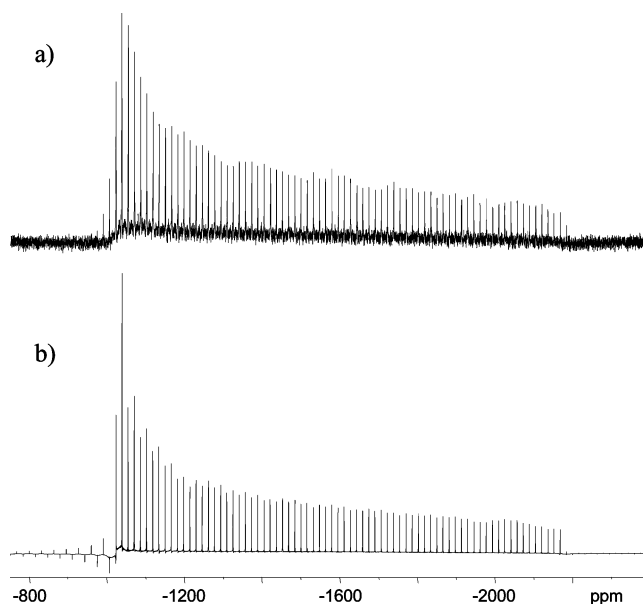
a)

b)

Figure 6. Comparison of experimental and calculated [207]Pb NMR spectra of PbTiO$_3$ at 7.05 T. (a) Experimental spectrum corresponding to Figure 5c; (b) optimum simulated spectrum using the chemical-shift parameters given in Table 1.

recommend that one acquires spectra with small spikelet separation in such cases. It would be interesting to see if the very small orthorhombic distortions of PbTiO$_3$, recently detected in powder X-ray work[71,72] and unlikely detectable via classic NMR experiments, could be detected with the modified-CPMG experiment at low temperatures.[69]

Lead zirconate, PbZrO$_3$, is one of the rare lead compounds having two nonequivalent Pb sites and seems to be an excellent candidate for examining the utility of the modified-CPMG method for a sample with multiple sites. Both lead sites of PbZrO$_3$ have asymmetric chemical-shift tensors as shown in Figure 7. Note that the envelope of the modified-CPMG spectra (parts a-c of Figure 7) mimics the spin-echo line shape; however, in general, the correspondence is not so obvious when there are 2 nonequivalent sites. The echo train decay is only due to homogeneous fluctuations, such as molecular motion, so the signal-to-noise ratio is proportional to "the spin-spin relaxation time", T_2. Lefort et al.[73] calculated the improvement of the signal-to-noise ratio, $G_{S/N}$, one can expect, and found that $G_{S/N} \approx 2(T_2 T_{off})^{1/2} \nu_{CPMG}$, where T_{off} is defined as the time needed for the free induction decay (FID) signal to become comparable to the noise level and ν_{CPMG} is the frequency of the periodic train of spin-echoes. Thus, the fact that there is little difference between the modified-CPMG spectrum and the spin-echo envelope is because these two sites have nearly equal T_2 values. This is not surprising since the two sites also have similar T_1 values.[33] The chemical-shift tensor principal components were optimized, and the results are in good agreement with previous studies (Table 1).[31]

[199]Hg NMR Spectra. Mercury compounds in the solid state generally have relatively long [199]Hg spin-lattice relaxation times and large CSAs; hence, [199]Hg NMR studies were, for a long time, restricted to the solution state. The only measured mercury CSA values were obtained from liquid crystal[74,75] or from variable-field solution T_1 measurements.[76] The first solid-state [199]Hg NMR study was reported in 1987 by Harris and Sebald on mercury acetate using CP-MAS.[77] A few years later, several researchers studied [199]Hg NMR in various metalloproteins[78-81] because [199]Hg chemical shifts are very sensitive to the primary coordination sphere of mercury and because it is relatively easy

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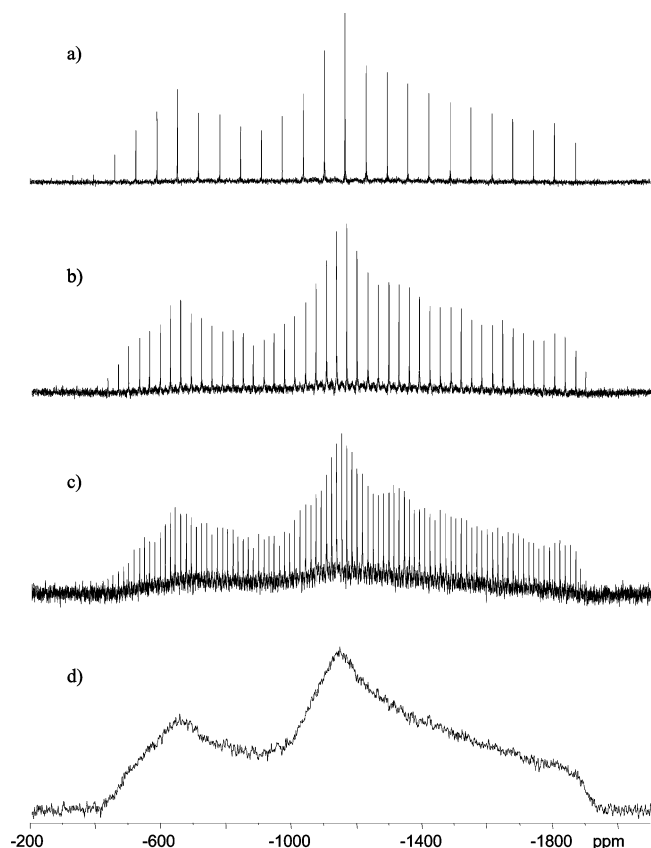*J. Phys. Chem. B, Vol. 108, No. 7, 2004* **2223**

Figure 7. ^{207}Pb NMR modified-CPMG (a-c) and spin-echo (d) spectra of PbZrO$_3$ at 7.05 T. The modified-CPMG spectra were acquired with (a) 512 scans and $\tau = 125$ μs, (b) 2048 scans and $\tau = 250$ μs, and (c) 4096 scans and $\tau = 500$ μs; a line broadening of 5 Hz was added prior to Fourier transformation. The spin-echo spectrum was acquired with 9680 scans, and a line broadening of 100 Hz was added prior to Fourier transformation.

to incorporate Hg(II) into metalloprotein sites. By analogy with ^{113}Cd, ^{199}Hg NMR has proven to be a powerful tool for characterizing metal-binding sites in proteins. In addition to these bio-NMR studies, several "inorganic" mercury compounds were studied and their ^{199}Hg chemical-shift tensors were usually characterized using slow MAS experiments.[82−90] The number of ^{199}Hg solid-state NMR investigations is however limited, partly due to its large CSA, which Ambrosius et al.[36] proposed to avoid by using a very low field spectrometer (e.g., $B_0 = 2.35$ T). However, considering the decreasing number of such spectrometers, this does not seem to be an ideal solution.

Thanks to its generally long T_2, ^{199}Hg is an excellent candidate for the CPMG experiment. As can be seen from Figure 8a, the echo intensities decrease very slowly, and acquisition times were only limited to shorter than optimum by the necessity to decouple protons. Since high-power ^{1}H decoupling is not advisable for acquisition times exceeding 100 ms, we had to truncate the echo train considerably. Without this problem, we would have been able to acquire more echoes, thus increasing the signal-to-noise ratio even more. ^{199}Hg usually also has long T_1 values in the solid state; therefore, we also used cross polarization prior to CPMG. At $B_0 = 11.75$ T, the spectral width of the signal is expected to be ~170 kHz,[29] and our CP rf field of 75 kHz is thus insufficient to uniformly excite the entire spectrum (see Figure 8b). Figure 8c shows the variable offset cumulative spectrum (VOCS)[91] of mercury acetate using the CP-CPMG pulse sequence that was obtained with nine steps separated by ~25.7 kHz. Because of the large spectral width of the ^{199}Hg spectrum of Hg(CH$_3$COO)$_2$, the spin-echo

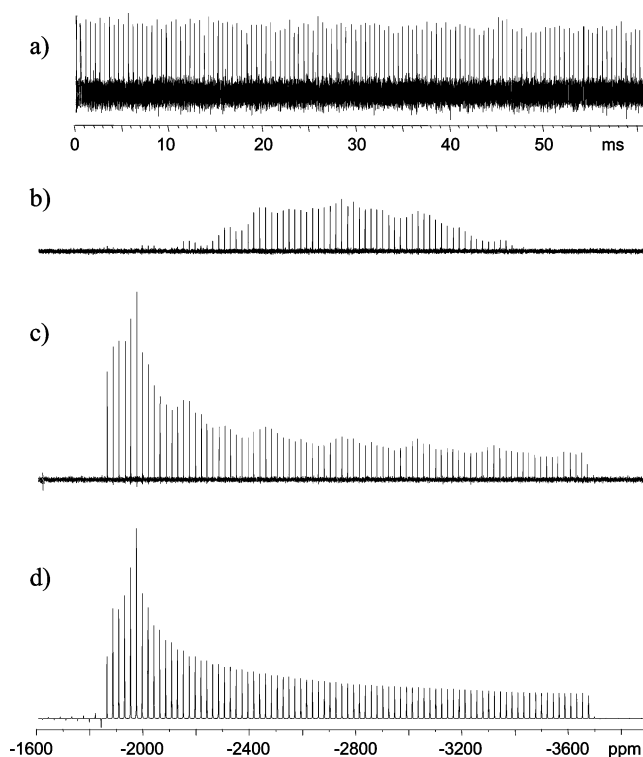**Figure 8.** ^{199}Hg NMR spectra of Hg(CH$_3$COO)$_2$ at 11.75 T. (a) CP-CPMG free induction decay; (b) central CP-CPMG subspectrum; (c) VOCS-CP-CPMG spectrum acquired with 9 subspectra of 16 scans each separated by ~25.7 kHz and with $\tau = 253$ μs; and (d) optimum simulated spectrum using an ideal pulse (infinitely short and hard) and the chemical-shift parameters given in Table 1.

experiment would have taken considerably longer and therefore was not acquired. Although the applied field and conditions are different, our results can be compared with previous CP-MAS and spin-echo experiments performed on this sample. The first one, which happens to be the first ^{199}Hg solid-state NMR spectrum reported,[77] was unfortunately recorded with the spinning axis slightly off the magic angle. The very poor sensitivity realized (4680 scans vs our 16 scans) resulted from an insufficiently long ^{1}H recycle delay. The extreme sensitivity of ^{199}Hg MAS spectra to the magic-angle setting was studied in depth by Groombridge.[32] He showed that for ^{199}Hg solid-state NMR spectra with large CSAs, a small deviation from the magic angle could broaden the spinning sidebands or even give the false appearance of multiple sites. After carefully setting the magic angle, the experiment was repeated and sharp spinning sidebands were obtained. Unfortunately, because the recycle delay was too short, several thousands of scans were required to acquire the signal. While trying to optimize the MAS spectra, Groombridge noted large estimated errors for the principal components of the chemical-shift tensor values. These errors were logically attributed to the fact that since the shift tensor is close to being axially symmetric, the sideband interpretation process could be ill-conditioned.[92] To avoid this problem, Groombridge acquired what, to our knowledge, is the only static spin-echo NMR spectrum of mercury acetate; however, the spectrum was noisy and seems to suffer from finite rf pulses. Later, Eichele et al.[41] measured the ^{1}H T_1 and performed the CP-MAS experiment with the proper recycle delay, obtaining a noisy but accurate spectrum in a single scan! The CPMG experiment appears however to have a better signal/noise ratio than MAS even if the spinning sidebands are very sharp. Note that none of these experiments was carried out with variable amplitude cross-polarization (VACP).[93,94] The VACP technique
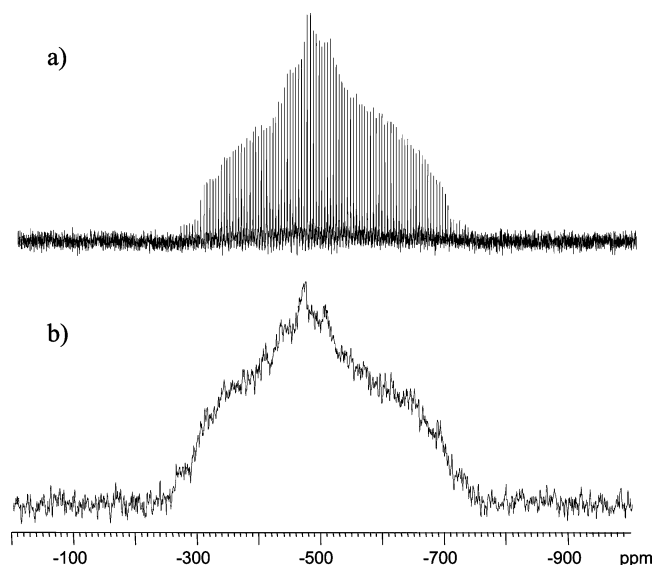
Figure 9. ^{195}Pt NMR spectra of $(PPh_3)_2Pt(C_2H_4)$ at 11.75 T. (a) CP-CPMG spectrum acquired with 3072 scans and $\tau = 1$ ms; a line broadening of 10 Hz was added prior to Fourier transformation. (b) Spin-echo spectrum acquired with 16384 scans; a line broadening of 100 Hz was added prior to Fourier transformation.

has the advantage of generating multiple Hartmann–Hahn matching conditions, which is very important, especially for fast MAS, and can also increase the signal intensity by compensating for the B_1 field inhomogeneity across the sample coil. As shown by Han et al.,[95] this can make a significant difference, especially for ^{199}Hg.

Figure 8d shows the simulated ^{199}Hg NMR spectrum of mercury acetate calculated using an isotropic chemical shift of -2497 ppm, a CSA of -1165 ppm, and an asymmetry parameter of 0.093 (Table 1), in good agreement with previous studies.[32,36,41] The slight oscillations observed in the experimental spectrum are due to the finite rf field; thus, the use of smaller offset variations would likely produce a smoother experimental spectrum.

^{195}Pt NMR Spectra. Despite the important role of platinum in transition-metal chemistry, solid-state NMR studies of ^{195}Pt are as rare as ^{199}Hg, if not more so.[96] In contrast, liquid-state ^{195}Pt NMR has become a standard technique.[97,98] Measuring the field-dependence of ^{195}Pt T_1 values in solution can provide an estimate of the CSA. If the CSA mechanism is the dominant relaxation mechanism, the rate of spin–lattice relaxation, $(T_1)^{-1}$, depends on the square of the CSA and the square of the applied magnetic field, B_0, thus providing a good estimate of the CSA.[99] With this method, many CSA values of square-planar Pt(II) compounds have been estimated to be in a range between 3000 and 10000 ppm.[99–102] The first solid-state ^{195}Pt NMR experiments (apart from single-crystal experiments)[103,104] were undertaken on compounds having relatively high symmetry with therefore relatively small CSAs (<1000 ppm).[37,38,42,77,105–107] Such species were also studied because of the scalar coupling between ^{195}Pt and other nuclei such as ^{13}C,[107] ^{31}P,[38,107] or ^{35}Cl.[42] To our knowledge, there are only three papers dealing with large ^{195}Pt CSAs,[35,36,108] from which K_2PtCl_4 with a CSA of 6943 ppm is the largest yet determined for ^{195}Pt.[35]

The effect of the CPMG experiment on systems where J-coupling is important was also examined. The square-planar platinum compound, $(PPh_3)_2Pt(C_2H_4)$, has a surprisingly small CSA but has a large J-coupling between ^{195}Pt and the two nonequivalent ^{31}P nuclei.[38] As expected, the CPMG experiment (Figure 9a) does not remove the J-coupling, which is inhomo-
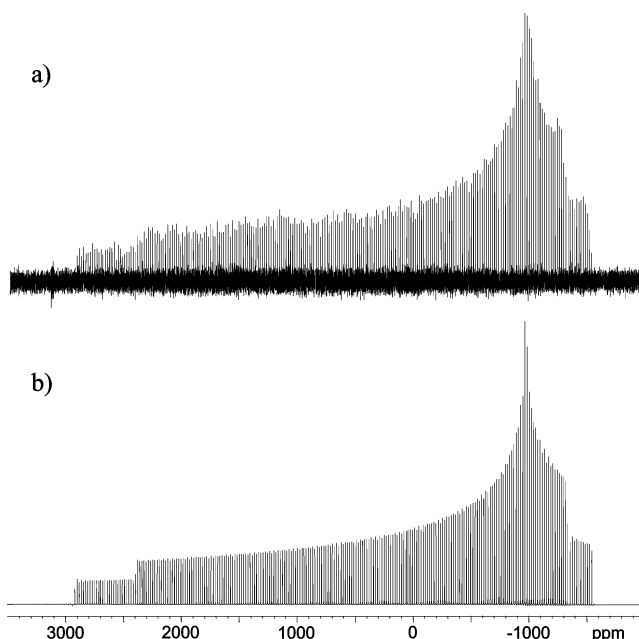

Figure 10. ^{195}Pt NMR spectra of $((C_2H_5)_3P)_2Pt(OCO)_2 \cdot xH_2O$ at 11.75 T. (a) VOCS-CP-CPMG spectrum acquired with 27 subspectra of 64 scans each separated by $\sim$19.9 kHz and with $\tau = 251\ \mu s$; (b) optimum simulated spectrum using an ideal pulse (infinitely short and hard) and the chemical-shift parameters given in Table 1.

geneous. In the ^{195}Pt CP-MAS spectrum of Challoner et al.,[38] the broadening of the central ^{195}Pt sideband enabled them to distinguish the two nonequivalent phosphorus nuclei that were evident in the ^{31}P NMR spectrum and by X-ray diffraction. The very small difference in the $^1J(^{195}Pt,^{31}P)$ values is not apparent in our ^{195}Pt NMR spectra. We could however determine the principal components of the chemical-shift tensor that, surprisingly, Challoner et al.[38] did not determine. By use of their values for the two different $J(^{195}Pt,^{31}P)$ values (3656 and 3772 Hz), the principal components of the chemical-shift tensor were optimized (Table 1).

The final compound discussed here, bis(triethylphosphine) platinum(II) oxalate hydrate, plays an important role in catalytic chemistry.[109–111] In the presence of UV irradiation, it releases two CO_2 molecules and creates a highly reactive platinum species, $Pt(PEt_3)_2$, used to produce a series of Pt(0) or Pt(II) compounds containing $Pt(PEt_3)_2$.[109] Because of its square-planar structure, a rather large CSA is expected and therefore the VOCS method was used to collect the data. Figure 10a shows the experimental ^{195}Pt variable offset cumulative CP-CPMG spectrum obtained with 27 steps separated by $\sim$19.9 kHz. This spectrum extends over a range of $\sim$4500 ppm and shows the presence of two sites with similar chemical-shift tensor principal components. Unfortunately, to our knowledge, no X-ray data exists for this compound. The presence of these two sites is however confirmed by the ^{13}C spectrum (not shown), which clearly indicates two different oxalate ^{13}C sites. The ^{31}P spectrum (not shown) surprisingly shows four sites, all J-coupled to the platinum. A closer examination reveals a scalar coupling $^2J(^{31}P,^{31}P)$ of 21 Hz between two phosphorus nuclei and 29 Hz for the two others. Thus, there are two nonequivalent phosphorus atoms per molecule and two different molecules per unit cell. From the ^{31}P MAS spectrum, $J(^{195}Pt,^{31}P)$ values of 3447, 3524, 3480, and 3440 Hz can be deduced, which are similar to that for $(PPh_3)_2Pt(C_2H_4)$. However, considering the relatively large frequency separation (2 kHz) between the spikelets compared to the coupling constant, these couplings are not expected to be apparent in the ^{195}Pt CPMG spectrum and, therefore, were

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not taken into account in the simulation. The chemical-shift parameters obtained for the two ^{195}Pt sites (Table 1) are similar and give a spectrum in good agreement with the experiment (Figure 10b).

4. Conclusions

In conclusion, the CPMG and modified-CPMG pulse sequences both give rise to spikelet spectra whose envelope is similar to that obtained from the classic spin-echo experiment. The CPMG method was used on spin-$1/2$ nuclei with large CSAs to significantly enhance the signal sensitivity compared to the spin-echo technique. The CPMG sequence was also modified in order to remove the homonuclear dipolar coupling more efficiently, resulting in sensitivity enhancements compared to the standard CPMG experiment. As previously discussed, these techniques are a good alternative to the MAS experiment for several reasons: one does not require an MAS probe, sample heating due to rapid MAS is avoided, the NMR coil (transmitter and receiver) can be perpendicular to the applied magnetic field resulting in a significant gain in signal/noise, and finally the sharper spikelet resonances due to reduced homonuclear dipolar couplings further enhances the sensitivity. The only limit of the CPMG and modified-CPMG experiments occurs when T_2 is very short, in which case only the first echo can be collected, resulting in a spectrum corresponding to the classic spin-echo experiment. Another small disadvantage occurs when one has multiple sites; proper separation of these sites may be difficult, especially if they have similar intensities. The CPMG and modified-CPMG methods can be combined with other experiments, such as CP, to obtain even greater signal enhancements. The chemical-shift tensor principal components and *J*-couplings were determined from these spikelet spectra. Some preliminary results show the same efficiency to reduce the homonuclear dipolar coupling using the modified CPMG on half-integer quadrupolar nuclei instead of the standard QCPMG. Like the CPMG and QCPMG experiments, the modified-CPMG experiment can be rotor synchronized to obtain narrower line widths and thus a better signal/noise ratio. This experiment could also be an alternative to the recently introduced ROCSA[112] technique that uses fast MAS (to remove the homonuclear dipolar coupling) combined with a recoupling of the CSA.

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