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High-Resolution NMR Correlation Spectra of Disordered Solids

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Abstract: We show how high-resolution NMR spectra can be obtained for solids for which the spectra are normally broadened due to structural disorder. The method relies on correlations in the chemical shifts between pairs of coupled spins. It is found experimentally that there are strong correlations in the chemical shifts between neighboring spins in both phosphorus-31 and carbon-13 spectra. These correlations can be exploited not only to provide resolution in two-dimensional spectra, but also to yield "chains" of correlated chemical shifts, constituting a valuable new source of structural information for disordered materials.

1. Introduction

High-resolution NMR spectroscopy has revolutionized many areas of chemistry over the last 50 years, and today it has become the cornerstone analytical technique. The key to this success has been that "high-resolution" spectra can be obtained from a range of molecular systems, allowing the identification of a single narrow resonance line for each chemically different nucleus.[1,2] The most obvious example is in the NMR of isotropic solutions, where today one can identify all the resonances belonging to the thousands of different atoms in a protein.[3] The high resolution of solution-state NMR spectra is a direct result of the rapid molecular tumbling in solution and the homogeneity of the sample, which lead to each chemically different nucleus having a different resonance frequency but which is perfectly identical for that nucleus in all the molecules in the sample.

The same is not true in the NMR of solids, where the spectrum is often dominated by broadening of the resonances due to an inhomogeneous local field in the sample. Under these conditions it is difficult to extract structural parameters from spectra, though many groups have worked on disordered systems,[2] and it is clear that NMR is a potentially very powerful probe. The local field variations can be caused by the anisotropy of the NMR interactions, by chemical disorder, or by differences in magnetic susceptibility over the sample.[1,4,5] Over the years some very ingenious techniques, such as MAS,[6] CRAMPS,[7,8] DAS,[9,10] DOR,[11] MQMAS,[12] and STMAS,[13,14] have been introduced to selectively remove the anisotropic broadening to yield high-resolution spectra of ordered, homogeneous solids.[1,2]

The two remaining types of broadening, that due to chemical disorder and that due to differences in magnetic susceptibility in different parts of the sample, pose more of a problem. The first is particularly important in glasses, catalysts, or polymers, and the latter will be important in any heterogeneous sample. Both mechanisms are similar in that variations in susceptibility lead to a change in the Larmor frequency from one part of the sample to another, and structural disorder leads to a change in the isotropic chemical shift from one molecule to another. The effect of this type of broadening (often referred to as "inhomogeneous" broadening[5,15]) is shown schematically in Figure 1. In the following we show how high-resolution spectra can be obtained free of this broadening, and we illustrate the idea with experimental examples.

Figure 1a shows a ^{31}P MAS NMR spectrum of *N*,*N*-bis-(diphenylphosphino)-*N*-((*S*)-α-methylbenzyl)amine (**1**), where there are in fact eight chemically distinct phosphorus atoms in the crystal structure arising from four inequivalent molecules per unit cell.[16] However, each resonance is inhomogeneously broadened as illustrated in Figure 1b, probably due to a slight

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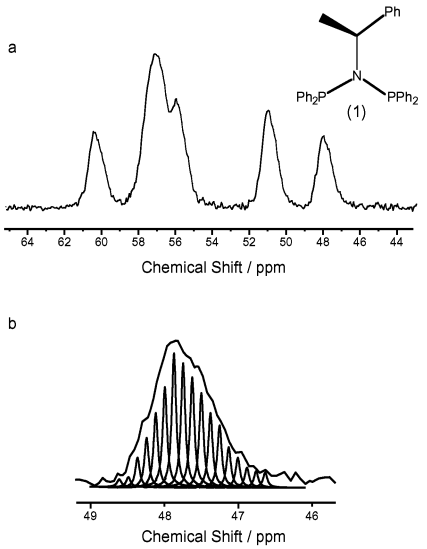

Figure 1. A typical CPMAS NMR spectrum is shown in (a), in this case a ^{31}P spectrum of **1**. Each peak is broadened by a distribution of chemical shifts, as illustrated schematically in (b).

structural disorder. The result is that the eight different chemical sites are not resolved, so this spectrum cannot be used to characterize the sample. In principle one would like to be able to obtain a "spectrum of sites" free of the inhomogeneous broadening, and where there would be only one narrow peak per site, with a line width determined only by the so-called "homogeneous" broadening.

The reason the obtention of such a spectrum looks so daunting is that broadening due to disorder or to susceptibility differences is simply due to a change in the isotropic resonance frequency. For example, a slight change in the orientation of the aromatic groups in **1** from one molecule in the crystal to another will slightly change the isotropic chemical shift of the phosphorus nuclei. *The Hamiltonians for two such phosphorus nuclei are functionally identical*. The two phosphorus nuclei are now just slightly inequivalent, and it is not obvious how to remove the chemical shift differences due to disorder without removing the chemical shift differences that distinguish different sites from each other.

Susceptibility broadening, or broadening due to an inhomogeneous applied magnetic field (but not broadening due to disorder), is also present in certain liquid samples, and clever techniques adapted to liquids or liquid crystals have been developed to remove this broadening.[17−30] All these techniques in fact exploit the fact that the shifts produced by susceptibility broadening at one nucleus are perfectly correlated in a one to one fashion with the shifts produced at another nearby nucleus. Thus, *while the individual chemical shifts change, the chemical shift differences remain the same.* This is most clearly observed in zero-quantum (ZQ) correlation spectra which are free from inhomogeneous broadening,[18] and most of the existing methods involve recording inter[26−29] or intra[21−25] molecular ZQ spectra. More generally, certain homonuclear[30] or heteronuclear[17] single-quantum correlations have also been shown to correlate inhomogeneous broadening, as well as multiple-quantum correlations appropriate for liquid crystalline samples with the "total spin coherence".[18,19] Along the same lines, the degree of correlation between the distribution of rf's in an inhomogeneous rf field and the distribution of Larmor frequencies due to a distribution of B_0 fields can be exploited to yield a spectrum of narrow lines.[31] For solids we are aware of only one study, by Spaniol et al.,[32] where ZQ spectra were used to remove susceptibility broadening from sideband spectra of paramagnetic compounds.

Here we demonstrate how ZQ-like spectra can be recorded under MAS for inhomogeneously broadened solids. More importantly, in the examples we give here, where the broadening is shown to be due to chemical disorder, the chemical shifts are found to be highly correlated between sites, and the result is high-resolution spectra free of the effect of structural disorder.

2. Experimental Section

All experimental results in this paper were obtained on a Bruker Avance spectrometer, operating at ^{1}H, ^{13}C, and ^{31}P resonance frequencies of 500.1, 125.8, and 202.5 MHz, respectively, using a 4 mm CPMAS probe with an MAS frequency of 12.0 kHz. For all experiments, ^{1}H decoupling was achieved using the TPPM method,[33] with a ^{1}H decoupling field amplitude of approximately 100 kHz. For two-dimensional experiments quadrature detection in F_1 was obtained by the States method.[34] The pulse programs and phase cycles used to record the spectra are available from our website or upon request from the authors.[35]

3. High-Resolution DQ Correlation Spectra

First we remark that the ZQ spectrum is by no means the only way to obtain a spectrum free from inhomogeneous broadening. Narrow spectra can in principle be observed in any spectrum where the broadening is correlated between sites through the generation of a coherence transfer echo.[17] Indeed, any nQ → mQ correlation will yield a coherence transfer echo which refocuses the broadening for each site at a certain well-defined time. Thus, *if the broadening is correlated in the right way*, as discussed below, there will always be a projection of such a spectrum that will yield a high-resolution spectrum. Different choices of m and n will simply yield projections with peaks at different frequencies. We note that in particular a 2Q → 1Q correlation spectrum yields a spectrum that under certain

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conditions has a high-resolution projection along the 2:1 axis, and this projection is identical to the ZQ spectrum. This has previously been recognized in a completely different context for medical imaging applications.[29] Recording the projection of this spectrum, which we dub the pseudo-ZQ (p-ZQ) spectrum, has several technical advantages over that of the equivalent ZQ sequence, most notably that it eliminates the presence of a large axial peak in the center of the spectrum inherent to ordinary ZQ spectra.[38]

We have recently shown that 2Q → 1Q spectra can be easily recorded in solids under MAS using refocused INADEQUATE.[39−41] The solid-state refocused INADEQUATE sequence[39] generates correlations between scalar coupled nuclei (as does its liquid-state and solid-state precursor cousins[42−45]). As a result the spectrum contains only directly bonded correlations. In this case this provides a significant advantage over dipolar-based methods of obtaining 2Q or ZQ spectra since the dipolar methods often yield additional long-range correlations[41] which would result in more peaks in the projection spectrum. The refocused INADEQUATE spectrum of **1** is shown in Figure 2a. In this spectrum we see for each correlation between a pair of phosphorus atoms that, while the spectrum is broad in both dimensions, *the distribution of chemical shifts, caused by structural disorder, is highly correlated*. In this spectrum, the F_1 dimension contains the double-quantum frequency, and the F_2 dimension the single-quantum frequency for a pair of *J*-coupled spins. We also see that *each pair of spins can be distinguished by the chemical shift difference* $\Delta\sigma$*, which is (virtually) a constant.* The p-ZQ projection (obtained by shearing the spectrum by arctan(1/2) = 26.6° and projection onto the F_2 axis) is shown in Figure 2b, and compared to the normal one-dimensional spectrum in Figure 2d. (We note that we have also recorded the 2D ZQ → 1Q correlation spectrum (not shown) and that (apart from an axial peak at $F_1 = 0$) the F_1 projection of that spectrum is essentially identical to the projection of Figure 2b.)

We see that the p-ZQ spectrum of Figure 2b has eight clearly resolved peaks at ± the difference in chemical shifts for the four pairwise correlations between the eight distinguishable sites in the structure (arising from four inequivalent molecules per unit cell). In the p-ZQ spectrum each line is around 0.25 ppm (50 Hz) full width at half-height, whereas in the normal 1D spectrum of Figure 2d, each line is around 0.95 ppm (190 Hz) broad, corresponding to an improvement of a factor of ∼4 in line width for the p-ZQ spectrum. In the p-ZQ spectrum the spectral broadening due to chemical shift distributions or to susceptibility effects has been largely removed, but the remaining parameter $\Delta\sigma$ still allows a spectrum of different frequencies to be recorded, in this case immediately showing that there are eight sites and thereby allowing the proper characterization of the sample.

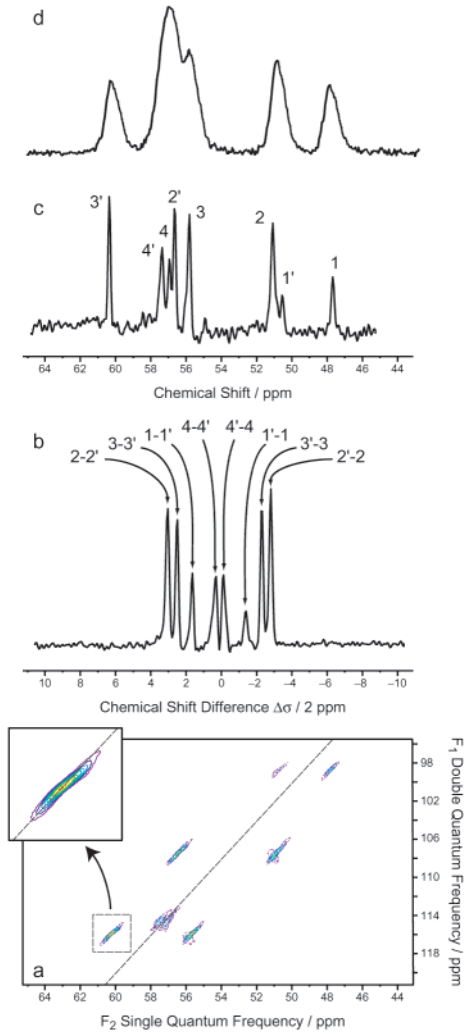

Figure 2. (a) Contour plot of a two-dimensional refocused INADEQUATE spectrum of **1**. The spectrum was recorded with 856 increments in t_1 for a spectral width of 12.0 kHz (rotor-synchronized acquisition) in both F_1 and F_2 with 32 transients per increment. The recycle time was 6 s between scans, and the τ period in the INADEQUATE sequence was 4.0 ms. (b) Projection of (a) onto the single-quantum axis after the spectrum was sheared along F_1. The shearing transformation was achieved using methods widely established in the literature[36] using the versatile data processing program RMN.[37] The resulting high-resolution spectrum yields narrow peaks at the chemical shift differences between *J*-coupled spin pairs. In (c) we show a spectrum constructed by adding traces taken through the 2D spectrum parallel to F_2 at double-quantum frequencies of 98.5, 107.8, 114.6, and 116.0 ppm. (d) reproduces the normal 1D spectrum on the same scale for comparison.

4. Criteria for Obtaining High Resolution

It is particularly important to note that the p-ZQ spectrum will be completely free of broadening only to the extent that the distribution of resonance frequencies is not only (i) perfectly correlated but also (ii) correlated with a 1:2 ratio for the single- and double-quantum frequencies. Both conditions are guaranteed for a distribution of Larmor frequencies due to susceptibility broadening or B_0 field inhomogeneity, but *neither condition is guaranteed for broadening due to disorder*. Indeed the extremely

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high degree of correlation we observe in the figure is surprising and had not been predicted. Specifically, the two-dimensional line shapes we observe imply that the structural disorder is such that when one of the phosphorus atoms in a P−N−P group changes its chemical shift due to a local change in structure, the other phosphorus atom in the group reacts to the structural change and changes its chemical shift in a perfectly well determined way. If, on the other hand, the changes experienced at both nuclei were independent of each other, then we would not observe narrow correlation peaks. The structural mechanisms leading to this correlation effect (and even more so to those observed for cellulose below) are not immediately obvious.

A closer inspection of the correlation peak shown in the inset in Figure 2 in fact shows that while the shifts are extremely well correlated, there is a clear deviation from the 1:2 behavior, most clearly seen from the "bend" in the middle of the resonance. (Indeed, it is this feature, in conjunction with a comparison with line widths recorded in carbon-13 spectra, which allows us to conclude that a significant part of the broadening is due to disorder rather than due entirely to susceptibility effects). As a result, we notice that an individual slice through the spectrum parallel to F_2 will yield narrower lines than the p-ZQ projection of this spectrum after shearing. In fact, the "ideal" spectrum discussed in the Introduction can be obtained by taking slices through the spectrum parallel to F_2 and adding them to reconstruct a spectrum which has narrow lines centered at the center of gravity of each of the broad overlapping resonances in the 1D spectrum. The spectrum of Figure 2c clearly resolves all eight resonances, and the line widths are now around 0.17 ppm (35 Hz) (over a factor of 5 increase in resolution). This method of reconstructing a spectrum from traces through the correlation spectrum, although limited in its applicability in the current implementation, will always yield line narrowing to the extent that condition i above is met. *There is no need for the second condition or indeed for any particular functional distribution for the correlation.*

5. Correlated Chemical Shift Chains

A more general example of the application of this method is given in Figure 3, where we show the refocused INADEQUATE spectrum of a sample of randomly 10% labeled cellulose extracted from wood.[46] In the ordinary 1D spectrum shown in Figure 3c, the resonances are substantially broadened by disorder, with the C6 resonance being about 500 Hz broad, and the C4 resonance spanning more than twice that range. In the refocused INADEQUATE spectrum of Figure 3a we remark that the chemical shifts of coupled pairs of carbon nuclei are strongly correlated, but we note that they are by no means all correlated in the same way. For example, the C3 and C2 resonances seem to be strongly correlated with an almost constant positive slope; i.e., when C3 is shifted by ΔHz, C2 is also shifted by ΔHz. In contrast the C6 and C5 resonances have a different type of correlation where it appears that when C5 is shifted by ΔHz, C6 is shifted by −0.2ΔHz. An even richer correlation structure is observed for the C1,C2 correlation.

Clearly this spectrum can be used to determine *chains of connected high-resolution carbon-13 chemical shifts* by following the INADEQUATE connectivity patterns through the entire carbon skeleton, and an example of two such chains is shown in blue and red in Figure 3a,b. Notably Figure 3b shows the schematic spectra for the two chains through the cellulose unit, and we remark that there are substantial nontrivial changes in the chemical shift patterns. These two patterns in fact correspond to the chemical shifts for two different cellulose units in the structure that are clearly seen to be in two significantly different structural environments. We will not treat the particular implications of these data for the structure of cellulose here, but we do remark that the structure of cellulose microfibrils in plant cell walls is not well understood at the molecular level and is still the subject of controversy. This controversy is largely due to the difficulty in obtaining the type of detailed experimental data relevant to structure that we obtain easily from the spectrum of Figure 3 presented here. As demonstrated by this example, the potential of the method lies in the fact that even though both dimensions yield broad spectra, the 2D spectrum yields high-resolution chemical shift correlations for each site, even though in this case the 1:2 correlation is not at all relevant (in this case the p-ZQ projection would yield a broad spectrum). The resolution available in Figure 3 is around 70 Hz, corre-

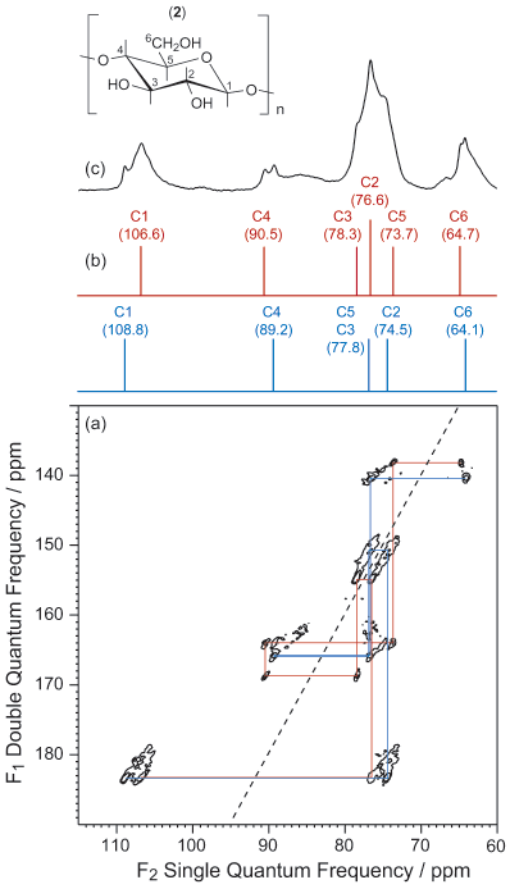

Figure 3. (a) Contour plot of a carbon-13 two-dimensional refocused INADEQUATE spectrum of 10% carbon-13 labeled cellulose extracted from a wood sample. The sample preparation has been described elsewhere.[46] A total of 456 increments in t_1 were used for a spectral width of 15 kHz, and 160 transients per increment, with a recycle delay of 1 s. Two chains of connected chemical shifts are illustrated in (a), and the stick spectra corresponding to these chemical shifts are shown in (b), with the chemical shifts given in parentheses. These spectra represent the chemical shifts for two different structural conformations of the cellulose unit. (c) shows the normal 1D spectrum on the same scale for comparison.

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sponding to a factor of >7 enhancement in resolution of the 2D correlation spectrum compared to the 1D spectrum.

It is essential to note that relatively fast MAS spinning rates (>10 kHz) are necessary to obtain spectra of this quality. Previously published spectra of the cellulose sample[39] recorded with a 6 kHz sample spinning frequency do not display the correlation structure which is obscured by residual broadening. A similar effect is observed for compound **1**. This raises the important and interesting question of what the limits of resolution are in this type of correlation spectrum. In the phosphorus spectrum we observe line widths of around 90 Hz, whereas spin−echo measurements suggest the homogeneous line width should be around 10 Hz or less, and both these values vary with the spinning speed. Notably, if the broadening were perfectly correlated, one would expect to recover the homogeneous line width from these experiments.[47] This issue is under-investigation.

6. Conclusion

In conclusion, the method we present here may not be a universal solution to obtain high-resolution spectra in disordered materials, but it does clearly demonstrate that it is possible, and that under appropriate conditions strong correlations can be observed between the changes in chemical shifts induced by disorder for adjacent nuclei in solids. It is worth noting that if the broadening is due to susceptibility effects, then the chemical shifts will always be perfectly correlated (applications to HRMAS spectra would certainly be interesting in this sense). It is less clear to what extent broadening due to disorder in the structure will always be correlated between coupling partners, but there are indications in the literature that lead us to believe that the effect may be widespread.[41,48] Perhaps more important than the application to resolution enhancement, the entire structure of these two-dimensional correlated chemical shift distributions could be a rich new source of chemical information in disordered systems, as indicated by the cellulose example. It can easily be appreciated that the reproduction of the shift chains in Figure 3b using quantum chemical calculations and structural models is a considerable challenge, and that these data (and more generally the whole 2D spectrum) provide very strong experimental constraints for such models. We are currently further investigating these phenomena in other systems, for other nuclei (for example, silicon, oxygen, and aluminum, all of which are particularly relevant in materials such as catalysts or polymers), and for other types of correlation apart from the homonuclear double-quantum single-quantum correlation exploited here.

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