Communication

A simple one-dimensional method of chemical shift anisotropy determination under MAS conditions

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ABSTRACT

A method of determination of chemical shift anisotropy (CSA) tensor principal components under MAS condition is presented. It is a simple, one-dimensional, and robust alternative to the commonly exploited, but more complicated 2D-PASS. The required CSA components are delivered by simultaneous numerical analysis of a few regular MAS spectra acquired under different spinning rates.

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1. Introduction

Following the work of Maricq and Waugh [1], Herzfeld and Berger [2] demonstrated that the information about principal components of the chemical shift anisotropy (CSA) tensors is encoded in sideband pattern of NMR spectra of powder samples, acquired under MAS condition. Sufficient number of sidebands to extract the relevant information is obtained in experiments with suitably slow spinning. However, in the case of many nonequivalent nuclei with large shift anisotropies the spectrum measured under such conditions is usually overcrowded. In order to overcome this difficulty Antzutkin et al. [3] (following de Lacroix et al. [4] and Dixon [5,6]) introduced 2D-PASS pulse sequence which affords two-dimensional separation of spinning sidebands of different order. This leads to apparent simplification of the spectrum. The pulse sequence consists of cross-polarization block followed by five π pulses on X-nucleus (^{13}C, ^{15}N, etc.) RF channel, and acquisition. The timing of the π pulses is varied in consecutive traces of 2D spectrum according to the pattern resulting from Eqs. (28) and (29) of Ref. [3]. Since the equations are complicated, a numerical routine is required for correct setup of the experiment each time the number of 2D traces is changed. The whole procedure is, therefore, quite complicated. The spirit of the methods developed later [7–13] is similar to that of 2D-PASS: sophisticated pulse schemes are invented in order to visually simplify the NMR spectrum by separation of information in multiple dimensions. We test a different approach. Instead of using complicated pulse sequences, what

generates distortions the remedies to which are anything but simple (c.f. Liu et al. [7]), we focus on a numerical procedure aiming at a simultaneous analysis of several CP/MAS spectra obtained with various spinning rates.

2. Results and discussion

The determination of the principal CSA tensors' components in organic molecules is a very common problem. In most cases it can be solved by numerical lineshape analysis of a single one-dimensional MAS spectrum measured under slow spinning conditions. According to our experience acquired on molecules having up to 20 isotropic lines, this method works surprisingly well and fails only exceptionally. One of such rare failures is the case of porphycene (**1**). The structure of **1** is shown in Fig. 1. Although the ^{13}C MAS spectrum of **1** contains only five isotropic lines (see Fig. 2a), they overlap significantly due to a substantial broadening. Moreover, since the anisotropies of CSA tensors of all of the ^{13}C nuclei in **1** are large, a large number of spinning sidebands is present under slow MAS conditions (see Fig. 2b). Because of heavy overlap of so many resonances, such a spectrum appears intractable at a first glance. Indeed, if the initial approximations of the CSA tensors' components are insufficiently close to their real values, the fitting algorithm either diverges or converges to a false minimum (see Fig. 3a). The convergence is improved by the simple trick: instead to a single spectrum, the fit is performed simultaneously to several (at least two) MAS spectra measured at different spinning rates. In the case of two spectra, one, obtained under slow MAS, contains enhanced information about the anisotropies and asymmetries of
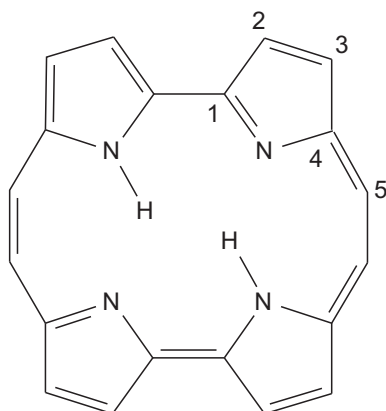
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Fig. 1. The structure of porphycene (**1**).

the shift tensors, encoded in the manifold of spinning satellites, while the other, acquired under fast MAS, is a kind of "guide" for the isotropic shifts. By the addition of second spectrum, the range of deviations of the initial shift anisotropies for which convergence to the true minimum is still warranted is extended at least twice. In
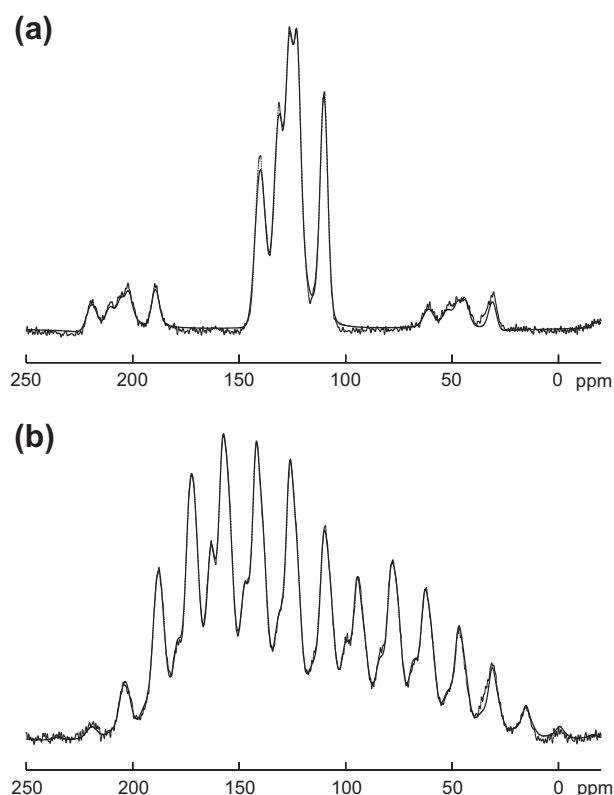

Fig. 2. The ^{13}C CP/MAS spectra of **1** obtained under 10 kHz (a) and 2 kHz (b) spinning rates, superimposed with "best fit" spectra obtained from the simultaneous analysis. Bruker AVANCE II 500 MHz spectrometer was used. The acquisition parameters were as follows: B_0 = 11.7 T, CP contact time 1.0 ms, recycle delay 10 s, acquisition time 41 ms, spectral width 400 ppm, RF field strength for TPPM-15 proton decoupling 66 kHz. The total acquisition time was about 8.5 h. The in-house written Fortran routine was used for numerical analysis. The least-squares minimization method based on the Newton–Raphson [14] algorithm was exploited. The theoretical spectra are calculated using Eq. (132) of Ref. [15]. The distortions introduced to the lineshapes by cross-polarisation, unsupressed X–H dipolar couplings, and off-resonance effects are taken into account by fitting both gaussian and lorenzian broadenings individually for each nucleus in each spectrum. The set of 538 Euler angles used for powder averaging was generated using ZCW scheme, described briefly in Appendix A of Ref. [16].
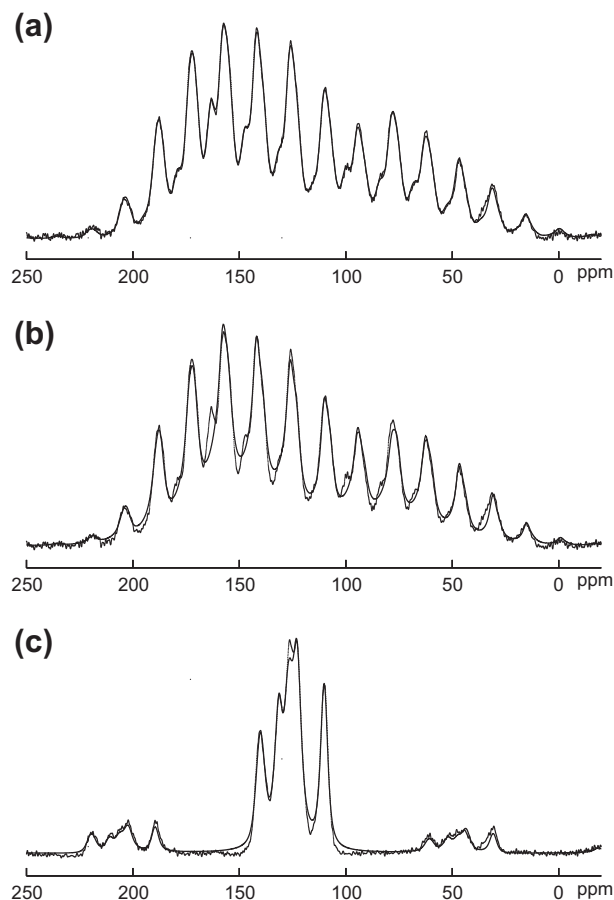

Fig. 3. Example of false minimum. (a) The experimental ^{13}C CP/MAS spectrum obtained under 2 kHz spinning, fitted alone, superimposed with the "best fit" spectrum obtained from convergence to a false minimum; in this minimum, Δ_2 has an opposite sign compared to its sign in the true minimum, while η_2 exceeds unity. (b) and (c): The result of simultaneous analysis of the spectra obtained under spinning of 2 and 10 kHz, respectively; in this fit, Δ_2 and η_2 are fixed at the values obtained from the fit in (a), while the other parameters are adjusted. The substantial misfits in (b) and (c) allow for an easy recognition that the essentially perfect fit in (a) involves a false minimum.

the fitting procedure, the overall intensity, baseline position, phase factor, spinning frequency and lorentzian/gaussian broadenings for each nucleus are unique to the individual spectra. The "global" parameters fitted for all spectra in the set include isotropic chemical shifts, δ_k, chemical shift anisotropies, Δ_k, and asymmetry parameters, η_k, for the individual nuclei. The "best fit" parameters delivered by the numerical algorithm at convergence are collected

Table 1
"Best fit" CSA tensor componets of ^{13}C nuclei in **1** compared to the values calculated at DFT level [17]. The geometry for calculations is taken from X-ray structure [20]; IGLO-III basis set [18] is used. Standard errors are given for the experimental results.

Nucleus	δ^a (ppm)	Δ^a (ppm)	η^a
1(exp)	131.65 ± 0.02	139.49 ± 0.30	0.1205 ± 0.0189
1(calc)		129.54	0.2876
2(exp)	122.86 ± 0.03	143.22 ± 0.47	0.6204 ± 0.0042
2(calc)		144.18	0.7715
3(exp)	126.62 ± 0.03	128.64 ± 0.54	0.7577 ± 0.0083
3(calc)		139.82	0.1930
4(exp)	140.32 ± 0.02	166.76 ± 0.29	0.1753 ± 0.0072
4(calc)		154.18	0.1980
5(exp)	110.29 ± 0.02	161.67 ± 0.29	0.4632 ± 0.0036
5(calc)		156.15	0.6348

^{a} $\delta = (\delta_{XX} + \delta_{YY} + \delta_{ZZ})/3$; $\Delta = \delta_{ZZ} - (\delta_{XX} + \delta_{YY})/2$; $\eta = (\delta_{YY} - \delta_{XX})/(\delta_{ZZ} - \delta)$.

in Table 1. The relevant CSA components calculated at DFT level [17,18] from X-ray geometry [20] are included for comparison. The agreement is good; the minor discrepancies could be explained in terms of intermolecular interactions in crystal, which are not taken into account. The latter argument concerns, in particular, carbon atoms 3 and 5 which have short contacts to neighbouring molecules and whose protons are engaged in van der Waals contacts too.

1,8-bis(dimethylamino)naphthalene (**2**) is another model compound used to test our method (see Fig. 4). We chose **2** since CSA tensors of its carbon atoms determined by the use of this method had already been successfully exploited [19] to determine its rotational diffusion tensor from liquid-state relaxation data. The latter task requires excellent consistency of all the CSA tensors in the molecule. The CSA components from Ref. [19] were determined from five CP/MAS spectra, while in Table 2 of the present contribution values obtained from one and three spectra are listed. In this case simultaneous fit allows for checking if the results obtained from a single slow-spinning spectrum are not distorted by line overlap. The results of simultaneous fit of the spectra obtained under spinning of 2.0, 2.5 and 10.0 kHz are shown in Fig. 5.

The idea of simultaneous numerical lineshape fits to several spectra acquired after different preparation of the spin system was earlier exploited by Szymanski et al. [21] in both the solid-
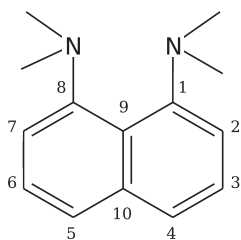

Fig. 4. The structure of 1,8-bis(dimethylamino)naphthalene (**2**).

Fig. 5. The ^{13}C CP/MAS spectra of **2** obtained under 10 kHz (a), 2.5 kHz (b) and 2 kHz (c) spinning rates, superimposed with "best fit" spectra obtained from the simultaneous analysis. Bruker AVANCE II 300 MHz spectrometer was used. The acquisition parameters were as follows: B_0 = 7.0 T, CP contact time 2.0 ms, recycle delay 30 s, acquisition time 39 ms, spectral width 350 ppm, RF field strength for TPPM-15 proton decoupling 48 kHz. The total acquisition time was about 42 h.

and liquid-phase NMR [22]. These authors fitted a family of "echo" spectra, obtained after quadrupolar (in solids) or Carr-Purcell (in liquids) echo sequences with different delay times. Such a procedure proved extremely sensitive to even subtle inadequacies of the theoretical model used to describe the lineshape effects. Fits to a single spectrum often happened to be fair, regardless of whether the correct or defective lineshape model was used. In the fits to whole sets of echo spectra, correct reproduction of the lineshapes could be obtained only for the correct model, while defects of the incorrect model were manifested as substantial, readily visible discrepancies between the experimental and theoretical spectra. The case reported presently involves remedies to convergence problems rather than discrimination between models. Nevertheless, the fact that no remarkable misfits are revealed in the simultaneous fit speaks strongly in favor of reliability of the parameter estimates obtained at convergence (see Fig. 3).

3. Conclusions

The presented method of simultaneous numerical lineshape analysis of several one-dimensional spectra acquired under different MAS rates seems to be an efficient, simple and robust alternative to the commonly exploited, but more complicated 2D-PASS scheme of CSA determination. Its usefulness was demonstrated for porphycene, where lineshape analysis of a single, slow MAS spectrum fails.

Table 2
"Best fit" CSA tensor componets of ^{13}C nuclei in **2** determined using the method of simultaneous analysis of three CP/MAS spectra of Fig. 5, compared with the results obtained from a single spectrum acquired under rotation of 2.5 kHz. Standard errors are given.

Nucleus	δ (ppm)	Δ (ppm)	η
1,8 (1 spc)	149.0	140.88 ± 0.32	0.5271 ± 0.0072
1,8 (3 spc)	149.0	143.19 ± 0.38	0.5786 ± 0.0063
2,7[a] (1 spc)	112.4	143.45 ± 0.51	0.6735 ± 0.0082
	111.3	147.26 ± 0.48	0.6600 ± 0.0076
2,7 (3 spc)	112.5	146.48 ± 0.56	0.6925 ± 0.0070
	111.3	150.14 ± 0.51	0.6728 ± 0.0063
3,6 (1 spc)	123.6	160.13 ± 0.75	0.8592 ± 0.0034
3,6 (3 spc)	123.6	160.35 ± 0.45	0.8779 ± 0.0038
4,5 (1 spc)	121.3	129.98 ± 0.53	1.0122 ± 0.0088
4,5 (3 spc)	121.3	130.53 ± 0.50	1.0018 ± 0.0068
9 (1 spc)	120.0	143.00 ± 0.35	0.7387 ± 0.0055
9 (3 spc)	120.0	144.41 ± 0.41	0.7546 ± 0.0052
10 (1 spc)	136.3	201.51 ± 0.72	0.0591 ± 0.0594
10 (3 spc)	136.3	196.83 ± 0.63	0.0617 ± 0.0641
CH$_3$[b] (1 spc)	43.7	61.95 ± 0.41	0.0349 ± 0.3413
	40.3	55.53 ± 0.38	0.0430 ± 0.6997
CH$_3$ (3 spc)	43.7	59.36 ± 0.30	0.1516 ± 0.0828
	40.3	56.18 ± 0.39	0.0932 ± 0.1317

[a] There are two resonances from nonequivalent carbons 2 and 7 of a single molecule in the solid state.
[b] There are two resonances from nonequivalent methyl carbons of a single molecule in the solid state.
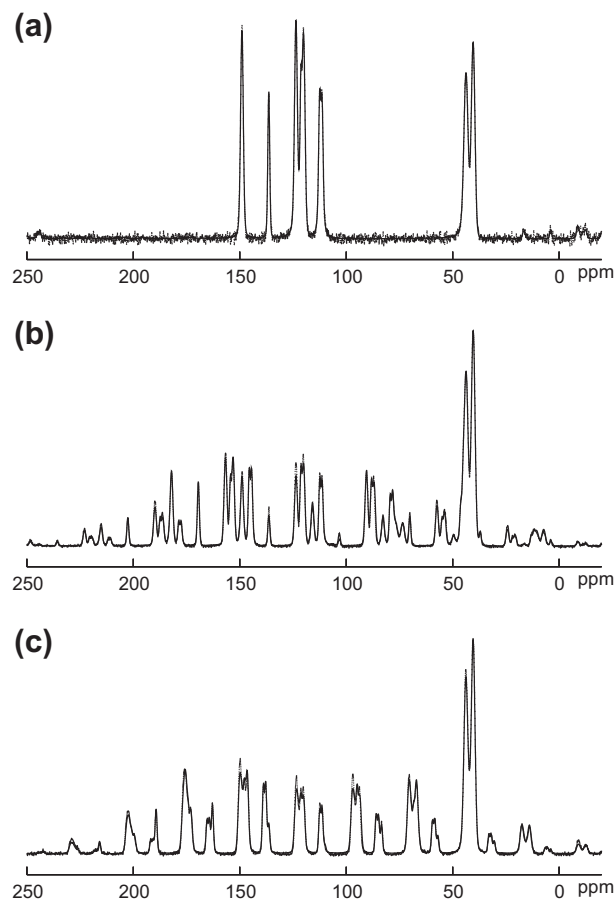
Acknowledgments

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