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Spectral Editing of Solid-State MAS NMR Spectra of Half-Integer Quadrupolar Nuclei

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The NMR characterization of materials containing half-integer quadrupolar nuclei received a propelling impetus due to the discovery of high-resolution techniques, such as dynamic angle spinning (DAS),[1,2] double rotation (DOR),[1,3] and multiple-quantum magic angle spinning (MQMAS).[4] This latter is a particularly straightforward application, because it requires only readily available technology. The method consists of a 2D experiment in which a dimension corresponding to a "normal" MAS spectrum (i.e., corresponding to single-quantum coherence) is correlated to a multiple-quantum (MQ) one. The enhanced resolution comes about because the different sources of spectral broadening under MAS possess different magnitude and sign in the two dimensions, so that their respective effects may compensate and cancel out reciprocally.

Many theoretical aspects of the MQMAS method have been explored in detail, due to its potential as a characterization technique for a wide selection of materials. Different excitation schemes have been proposed, using three-[4] or two-pulse[5,6] excitation, rotationally induced adiabatic coherence transfer (RIACT),[7] adapted RF schemes involving amplitude or frequency modulation,[8,9] transfer of intensities from satellite transitions,[10−12] or spectral simplification through adapted spin−echo pulse trains (QCPMG).[13] The reason for such a methodological effort is that the MQMAS experiment is intrinsically a low-efficiency and uneven process. Namely, the excitation−reconversion total yield for a given signal is a complex function of its quadrupolar parameters. The main point addressed by those methods is thus the achievement of an increased and as homogeneous as possible spectral intensity over a broad selection of quadrupolar parameters.

In any case narrow signals, associated with smaller quadrupolar couplings, are easier to excite. As a consequence, they tend to appear relatively more intense in the MQMAS spectrum with respect to the MAS one. A number of bothersome impediments descend from this fact. In the multiple-quantum dimension, those contributions die out at longer times, thus forcing longer overall acquisition times to avoid truncation of the signal and the associated spectral distortions. Moreover, still due to their dominant position in the spectrum, the tail of these signals may extend until it partially hinders neighboring broader sites. These drawbacks add onto the fact that pure-phase spectra are sometimes hard to obtain for MQMAS spectra, due to uneven excitation of the conjugate coherence transfer pathways required by common pure-phase methods.[14] This latter problem may be evaded by using *z*-filtering,[15] which allows one to record pure-phase spectra, albeit at the expense of sensitivity. Another possible solution would be to use a shifted-echo acquisition scheme,[14] but this method is prone to all of the problems concerning narrow signals we mentioned above. An ideal situation would be to produce an MQMAS spectrum in which the narrow signals are of much reduced intensity with respect to the broad ones, as the former ones do not carry much information that cannot be easily extracted from a simple MAS spectrum.

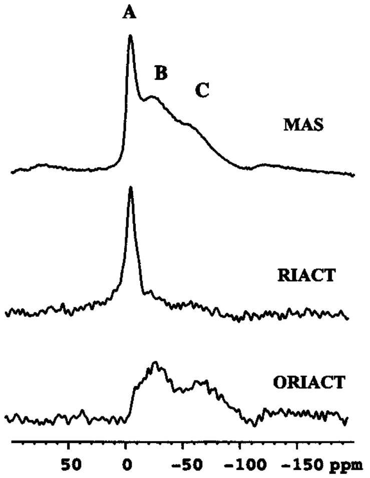

Figure 1. Demonstration of the editing capability of the ORIACT method on zeolite NaY. The top spectrum shows the three resonances in the ^{23}Na MAS line shape (128 scans). The standard MQMAS RIACT (middle) yields essentially the narrow signal (A), while the ORIACT spectrum (bottom) is mainly showing the broader resonances (B and C). All MQMAS spectra were obtained with a two-pulse sequence: $P1-t_1-P2-$Acq. $P1$ was set at 4 and 5 μs for spectrum ORIACT and ORIACT respectively, with a ω_{RF} of 150 kHz. $P2$ was set at 25 μs with a RF frequency of 75 kHz. The spinning rate was 10 kHz. The delay t_1 was fixed at 2.5 μs. 150 scans were acquired with a recycle delay of 500 ms. 3-quantum filtering was achieved through a six-step phase cycle on $P1$, with $\phi = \pi/6(0, 1, 2, 3, 4, 5)$. The phase of the second pulse was kept fixed, while the phase of the receiver was alternated of π. All frequencies are referenced to a 1 M aqueous solution of NaCl.

The aim of this report is to present a new version of the MQMAS technique which allows spectral editing along these lines. The method illustrated below consents to reduce dramatically and selectively the intensity of this type of signals in the MQMAS spectrum, while at the same time increasing the signal from broader peaks (Figure 1). The resulting MQMAS spectrum (Figure 2) shows much better resolved line shapes for the broader contributions. The narrow lines can be scaled down to an order of magnitude.

The Off-Resonance RIACT (ORIACT) Principle. Wu et al.[7] introduced the rotationally induced adiabatic coherence transfer (RIACT) method for converting MQ into 1Q coherences by exploiting the periodic variation of the energy level system for a half-integer quadrupolar nucleus under MAS. This is caused by

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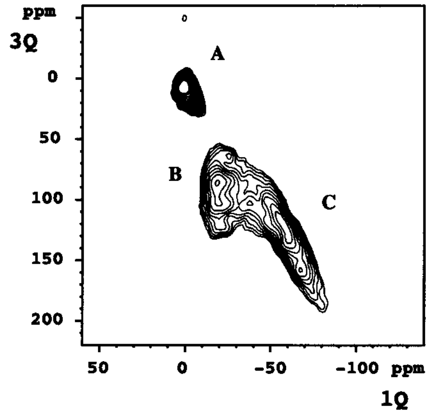

Figure 2. Pure-phase (TPPI) 2D ORIACT spectrum of zeolite NaY. The spectrum was acquired in the same conditions as the bottom 1D spectrum in Figure 1, by incrementing the delay t_1. A multiplication by a Gaussian weighting function of 10 Hz in the direct dimension and an exponential one of 500 Hz in the 3Q dimension were applied before double Fourier transform. 150 scans per spectrum and 32 t_1 increments were acquired, for an overall acquisition time of 81 min.

the modulation of the quadrupolar frequency ω_Q, due to spinning of the sample at a frequency ω_{ROT}. The presence of an irradiating field, ω_{RF}, may induce coherence transfers, provided the evolution of the level system is adiabatic. Vega[16] proposed an estimate of the energy level rate of change with the parameter $\alpha = \omega^2_{RF}/\omega_Q\omega_{ROT}$, adiabaticity being achieved when $\alpha \gg 1$. However, the modulation of the quadrupolar Hamiltonian under MAS is continuous, and the adiabatic condition should rather be defined at each point in time: $\alpha' \propto \omega^2_{RF}/|dQ/dt|$,[17-20] where Q is the effective quadrupolar interaction. Numerical simulations and experimental tests in the case of an analysis of spin-locking efficiency have shown that α' in a powder is very sensitive to an offset of the irradiating field. Optimum behavior for a spin $^3/_2$ was achieved when irradiating at an offset frequency equal and opposite in sign to the second-order quadrupolar shift.[20]

We demonstrate here that this property can be used in MQ-filtered NMR spectra to enhance the relative intensity of broad signals with respect to narrow ones. This new technique (that we dubbed ORIACT, for off-resonance RIACT) can be particularly useful in real life materials, in which several heterogeneous contributions to the spectrum are customary. We discuss as an example the case of zeolite NaY, a common catalyst. The ^{23}Na MAS spectrum of the dehydrated material presents a very narrow signal at −3.5 ppm (A), neighboring two broad ones, with maximum at −23 (B) and −55 (C) ppm (Figure 1 top). This is a typical case in which it may become difficult to extract quadrupolar parameters for the different sites from a simple MQMAS spectrum. We demonstrate this problem in Figure 1 (middle), where the RIACT MQ-filtered spectrum essentially contains the narrow contribution from site A. A dramatic inversion in the relative intensities is achieved when the carrier frequency of the RF pulses is shifted to 4 kHz off-resonance (Figure 1 bottom). This shift is too small compared to the RF frequencies used for the two-pulse experiment (respectively 150 and 75 kHz for the MQ excitation and the reconversion pulse) for this behavior to be explained in terms of just an offset effect. In fact, the editing effect is not observed when the carrier frequency is located symmetrically off-resonance to the other side with respect to the resonance position (not shown). The selected offset value lies between the (inverted in sign) second-order quadrupolar shifts of site B (3300 Hz) and site C (5200 Hz) and far off of the one of site A (950 Hz). This confirms that the variation in intensities is provided by a modulation of the adiabaticity parameter α', which is optimum for irradiation offsets balancing the second-order quadrupolar shift. Figure 2 shows the ^{23}Na 3Q-MAS spectra of dehydrated zeolite NaY, obtained with the same parameters used for the 3Q-filtered 1D spectrum shown in the bottom of Figure 1. The two contributions from the sites B and C are clearly dominating the spectrum, although site A still provides the most intense signal, due to the difference in line width. The signal of site A does not interfere with the measurement of the broader line shapes. Consequently, it can be clearly seen that signal B shows a line shape due to a disordered (partially rehydrated) local environment, whereas site C aligns along the characteristic direction of a distribution of quadrupolar couplings.

The enhanced resolution provided by this new technique should be particularly useful to follow the fine structural variations experienced by a given material in the course of its functional activity. For instance, we are currently applying the method to study the influence of organic molecules in the pores of several molecular sieves. Similar advantages should be encounterd in the case of metal-containing biomolecules.[21]

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