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Influencing the satellite transitions of half-integer quadrupolar nuclei for the enhancement of magic angle spinning spectra

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Abstract

Double frequency sweeps can induce spin transitions in a set of satellites of a half-integer quadrupolar nucleus by simultaneously passing through resonance for a satellite pair. It is shown that by transferring population from the outer spin levels to the inner $|1/2\rangle$ and $|-1/2\rangle$ levels an increased intensity for central transition spectra is obtained. Although Magic Angle Spinning in principle interferes with this process, and the adiabaticity of the passages is different for every crystallite in a powder, enhanced spectra with undistorted line shapes are obtained for $I = 3/2$ (^{23}Na) and $5/2$ (^{27}Al) spins experiencing quadrupolar interactions with ω_Q in the range 0.1–3 MHz. Even at spinning speeds up to 30 kHz significant enhancements are obtained. An analysis of the combined effects of double frequency sweeps (DFS) and MAS indeed shows strongly different effects for different crystallites in powder ranging from no gain at all to the theoretical maximum gain of $2I$. As the effects are randomly distributed over all orientations on a sphere this is averaged over the whole line shape. Therefore, undistorted powder patterns are obtained enhanced by the average gain over the individual crystallites. Saturation of the satellite transitions, which can only be achieved if spin–spin relaxation is sufficiently strong, leads to identical results. Optimization of the sweeps should be toward an optimal effect on the population transfer to the central levels and chosen short with respect to spin–lattice relaxation times.

Keywords: Double frequency sweeps; MAS; Quadrupolar nuclei; Sensitivity enhancement

1. Introduction

Half-integer quadrupolar nuclei such as ^{27}Al, ^{17}O, ^{23}Na, etc. are encountered in many interesting natural or synthetic compounds. Extracting information about the quadrupolar interaction to which these nuclei are subjected can give valuable insight in understanding structural and dynamical aspects of such compounds. The high external magnetic fields that are now available made it possible to record spectra of compounds with relatively large quadrupolar interactions were these interactions can still be treated as a perturbation. The central transition of the spins is then broadened by the quadrupolar interaction only in second order [1]. A second prerequisite to obtain well-resolved high-field spectra of compounds in which large quadrupolar interactions are encountered is the possibility of fast magic angle spinning [2–4] of several tens of kHz. Small diameter MAS rotors capable of reaching such speeds are now widely available. This has intensified NMR research of quadrupolar nuclei leading to much progress in understanding the NMR spectra of these nuclei [1].

However, increasing the sensitivity of the NMR experiments is still holding the attention of the NMR spectroscopist as for many nuclei, such as ^{17}O, sensitivity is a crucial issue which can determine the success or failure of an experiment. In a magnetic field, half-integer quadrupolar nuclei have $2I + 1$ energy levels. In equilibrium, the nuclei populate these energy levels according to the Boltzmann distribution. In the high-temperature approximation the spin levels are populated proportional to their magnetic quantum number m. Therefore, manipulation of the satellite transitions is a useful tool to increase the polarization of the central transition levels. A subsequent inversion from the outer

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to the inner satellite transitions brings the population from the outer levels into the central transition levels, so that the intensity of NMR spectra of the central transition can be enhanced by a factor of $2I$ [5–10]. Indeed such enhancements have been realized experimentally in single crystals [5–10].

In powders, the quadrupolar frequency of the crystallites is spread over a wide frequency range and therefore inversion of the satellite transition for every orientation in a powder is not trivial. Frequency sweeps are very suitable in this case as their sweep range can be chosen to traverse the satellite transitions of every crystallite in the powder distribution. Experimentally enhancements around 2 for $I = 3/2$ and around 3 for $I = 5/2$ were reported [8–10] in case of static samples. Frequency sweeps can invert specific transitions via an adiabatic passage [5–11]; the frequency of the rf-field is swept from far above resonance to far below the resonance condition of the transition under consideration. During such a sweep the effective field in the rotating frame starts with an initial orientation along the z-axis and tilts down ending into a situation where it is antiparallel to the z-axis. If the changes in the rf-frequency are slow enough the spin system follows the effective field and the populations of the spin levels are exchanged. Double frequency sweeps (DFS) can be produced using a time-dependent cosine amplitude modulation [9–11]. In this case the sweeps are induced by the change in modulation frequency. An amplitude modulation generates sidebands [12] and thus has the advantage that symmetric frequency sweeps are induced simultaneously in both positive and negative parts of the spectrum. For half-integer quadrupolar nuclei this results in a simultaneous inversion of a pair satellite transitions. In this way the population of the outer energy levels can be brought into the central transition levels.

Frequency sweeps result in a complete inversion of a transition only when they are sufficiently adiabatic [8–11,13]. For normal values of the quadrupole frequency (0.1–3 MHz) inversion of the satellite transitions implies milliseconds sweeps, which is significantly larger that the normal time scale of pulsed excitation schemes employed in NMR experiments. This questions the applicability of frequency sweeps in MAS experiments. The complication arises from the modulation induced in the quadrupolar interaction by the sample spinning. This modulation is periodic with the inverse of the spinning frequency and periodically induces sign changes of the quadrupolar interaction for each orientation in the powder. The effect of this modulation during on-resonance rf-irradiation in terms of adiabatic phenomena have been studied extensively and have been put to good use in various MAS and MQMAS type experiments [9,10,14–17].

Experimentally enhancements of central transition spectra using DFS or FAM for spin 3/2 nuclei under MAS conditions have been reported [9,18]. Also enhancement of the polarization of the $|\pm 3/2\rangle$ energy levels for spin 5/2 nuclei under MAS has been observed [19]. In the latter case the polarization of the $|\pm 3/2\rangle$ energy levels has been monitored in a MQMAS experiment [20], the enhancement was achieved by affecting mainly the external satellites of the $I = 5/2$ spin system. The experimental results discussed so far have been obtained using relatively short amplitude modulated pulses. Yao et al. [18] used fast amplitude modulated pulses [16,17] lasting one full rotor period prior to the selective excitation of the central transition. An experimental gain close to a factor of 2 was reported for spin 3/2. This is half of the possible gain obtained when the satellite transitions are completely inverted. Therefore Yao et al. [18] claimed that they saturated the satellite transitions using only 100 μs irradiation. Iuga and Kentgens [19] used double frequency sweeps [9–11] of up to eight rotor periods and obtained an enhancement of 25% for the polarization of the $|\pm 3/2\rangle$ energy levels in MQMAS experiments, as compared to a 67% theoretically possible gain if the external satellites of a $I = 5/2$ spin system are inverted.

This paper analyzes the behavior of half-integer quadrupolar nuclei under two simultaneous modulations, the modulation of the quadrupolar interaction induced by magic angle spinning and the modulation of the rf-field leading to double frequency sweeps. The enhancement of the polarization of the central transition levels is explained. It is demonstrated that this gain is the result of a redistribution of the populations due to partially adiabatic passages of the satellite transitions. A statistical approach is used to analyze the behavior for all orientations in a powder. It is shown that the difference in adiabaticity for different orientations does not lead to distorted line shapes. Calculations are presented showing that the net enhancement and lineshape is similar for sweeps optimized for inverting the satellite transitions as compared to sweeps optimized to saturate the satellite transitions. The influence of spin–spin relaxation is discussed in terms of solutions for obtaining a true saturated state for the satellite transitions.

2. Multiple adiabatic passages

Frequency sweeps can adiabatically invert spin transitions. The efficiency of this process is expressed by the adiabaticity parameter [8,11,13]. For a linear sweep the adiabaticity parameter is defined as

$$A = \frac{\omega_{\text{eff}}^2}{\lambda}, \tag{1}$$

where ω_{eff} is the effective rf-field strength felt by the transition and λ gives the speed with which the frequency is swept

$$\Delta\omega(t) = \lambda t. \tag{2}$$

For practical applications an adiabaticity of 1 ensures that the adiabatic characteristics are predominant and the transition is completely inverted. If the adiabaticity parameter is smaller, the spin level populations are redistributed and simultaneously coherences between the spin states are created.

DFS obtained with a time-dependent cosine amplitude modulation of the rf-field can simultaneously invert two satellite transitions of a half-integer quadrupolar spin system. In the present context the effect of a DFS is identical to the passage of each satellite transition by a single frequency sweep. MAS interferes with this process, however and therefore the applicability of the DFS in MAS experiments must be analyzed carefully.

MAS modulates the quadrupolar interaction so that in a quarter of the rotor period many spins experience a variation of the quadrupolar interaction varying from a positive value to a negative value. Combined with an irradiation at a certain resonance-offset, this results in a frequency sweep through one (or more) transition(s) in the spin system with the adiabaticity controlled by the spinning speed [11,17]. If the irradiation is kept on for a longer period of time, each transition undergoes several passages and consecutive passages will be in opposite direction. As was discussed by Schäfer et al. [11] the adiabaticity of these transitions is determined by

$$A = \omega_{\text{eff}}^2 \Big/ \left(\frac{\mathrm{d}(\Omega_Q(t) - \omega_m(t))}{\mathrm{d}t} \right), \tag{3}$$

where $\Omega_Q(t)$ is the quadrupolar frequency and $\omega_m(t)$ is the resonance offset of the rf-irradiation.

In many practical cases this A is smaller than 1 rendering the transition only partly adiabatic. As a result a subsequent passage of the transition acts on a density matrix containing both populations and coherences, which will be "redistributed." In general such a passage, albeit in a different direction, does not revert the effect of a previous one. The end result of a long (modulated or unmodulated) rf-irradiation of a spinning crystallite will therefore depend on the number of passages experienced by a certain transition in the crystallite, and by their respective adiabaticity parameters.

When a DFS is applied to a spinning sample the two frequency sweeps described previously act simultaneously [11]. The variation in modulation frequency induces a time dependent off-resonance component in the spin Hamiltonian, whereas the MAS renders the quadrupolar frequency time-dependent. In an appropriate modulation frame [17], the I_z term in the Hamiltonian goes with the offset term $\Delta\omega_Q(t) = \Omega_Q(t) \pm \omega_m(t)$, where $\Omega_Q(t)$ is the value of the quadrupolar frequency during spinning and $\cos \int_0^t \omega_m(t')\mathrm{d}t'$ is the shape of the amplitude modulation [10,11,17]. For a linear DFS between an initial frequency ω_s and a final frequency ω_f and an irradiation time τ:

$$\omega_m(t) = \omega_s + \frac{\omega_f - \omega_s}{\tau} t. \tag{4}$$

One should notice that $\omega_m(t)$ is under the spectroscopists' control. Therefore it can be modified to decrease or increase the adiabaticity parameter of a specific transition. This is beneficial for single crystals, but for a powder each orientation has its own variation of $\Omega_Q(t)$ and one can modify $\omega_m(t)$ only in one way. Thus one should optimize $\omega_m(t)$ so that the optimum result is obtained for most of the orientations. The evolution of the population of the four energy levels of a spin 3/2 system during a DFS under 10 kHz MAS is presented in Fig. 1, along with the variation of $\Delta\omega_Q(t)$. From this picture it becomes clear that every time $\Delta\omega_Q(t) = 0$, population and coherence transfer occurs. The various $\Delta\omega_Q(t)$ zero crossings have different adiabaticity and act on different initial states. As a result of these successive crossings the populations of the $|1/2\rangle$ and $|3/2\rangle$ and of the $|-1/2\rangle$ and $|-3/2\rangle$ levels are progressively scrambled without simultaneous

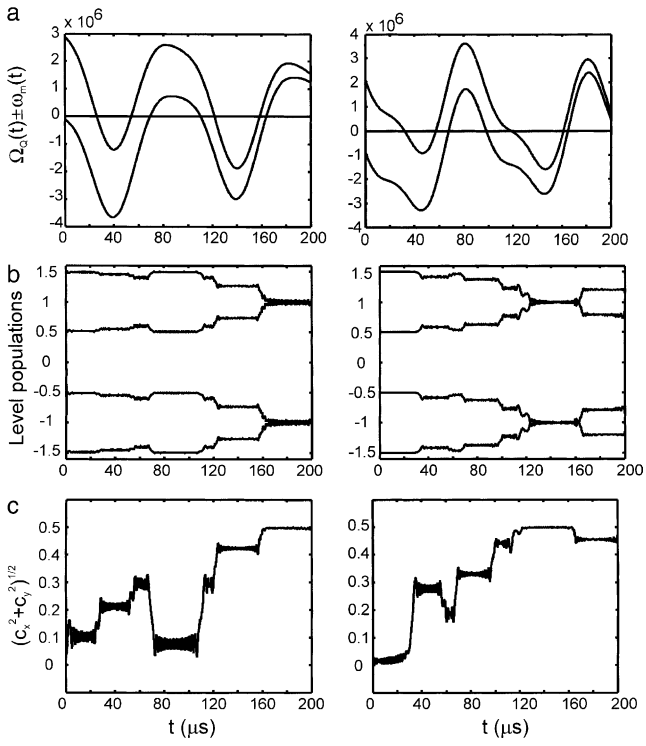

Fig. 1. The influence of a DFS and MAS for two random orientations of a 3/2 spin system. A 200 μs DFS from ±1.5 to ±150 kHz acts on a quadrupolar spin system with $C_{qcc} = 2.6$ MHz and $\eta = 0.5$. The sample is spun at 10 kHz and the DFS has an rf-field strength of $\nu_1 = 30$ kHz per sideband. (a) The off-resonance components of the effective field. Each time zero is crossed, population and coherence transfer occurs. (b) Evolution of the energy level populations. The energy levels are viewed from the laboratory frame. The initial density matrix is at thermal equilibrium. (c) Evolution of the coherences between $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ energy level during DFS irradiation. C_X and C_Y coherence represent the real and the imaginary parts of the coherence.

mixing of the positive and negative levels. The end result depends on the complete history of these passages and is different for each orientation. This difference is shown for two random orientations demonstrating the difficulties that are faced in optimizing $\omega_m(t)$.

In practice optimization is done by monitoring central transition spectra obtained by selectively exciting this transition after a DFS was applied in order to affect the $|1/2\rangle$ and $|-1/2\rangle$ level populations. As the line shape of the central transition is determined by the second order quadrupolar interaction one can not only monitor the overall effect of a DFS in a powder, but due to the anisotropic broadening, distortions in the lineshape could point out preferential enhancements of certain crystallite orientations. Using the analytical description of the transition frequency [1] Fig. 2a displays a regular MAS central-transition spectrum with different frequency regions encoded in gray scale [21]. Fig. 2b shows the corresponding crystallite orientations on a sphere using the same gray scale encoding.

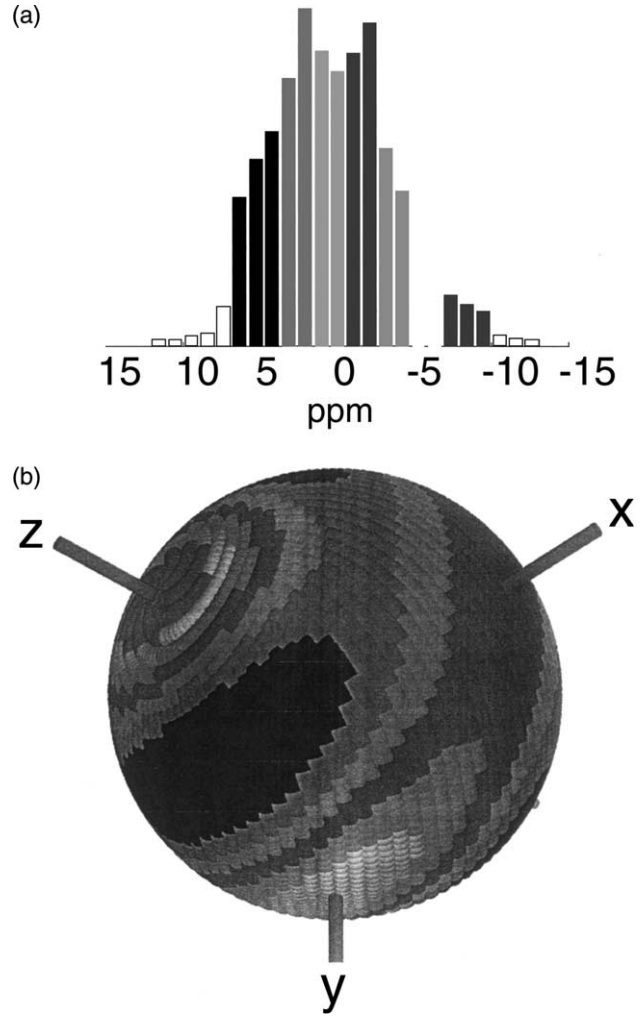

Fig. 2. The second-order quadrupolar lineshape for a powder sample with $C_{qcc} = 2.6$ MHz and $\eta = 0.5$. Different gray scales are used to identify the orientations that contribute to different frequency intervals of the lineshape.

To analyze the effect of a DFS on such a central transition spectrum, the combined influence of sweeping and spinning of each of the indicated orientations was analyzed. As was discussed previously, for each orientation, each level crossing has a different adiabaticity parameter. As a result the intensity gain for each crystallite is different and ranges between 1 and 3. Fig. 3 presents a distribution of gain factors calculated for two simultaneous double frequency sweeps over 150 kHz between ±100 and ±400 kHz. The y-axis represents the relative fraction of orientations that end up with a gain in the central transition intensity represented on the x-axis. Clearly, an even distribution of gain factors is obtained. Moreover, these gains are evenly distributed over all orientations on a sphere. Different gray scales were used to represent different orientations. No uniformly colored regions are visible on the sphere. Even after a short sweep of only 25 μs, implying that most of the orientations experienced only a single partially adiabatic passage, no correlation between the orientation parameters that have a similar gain was found. Unfortunately, in this case, the overall gain is smaller and proves that these individual passages are not very adiabatic.

As a result of the even orientational distribution of achieved gain factors, no obvious lineshape distortions are observed although the gain for each individual crystallite varies between 1 and 3. Each position in the frequency domain is an average over many crystallites experiencing the full range of gain factors, so that the intensity of each point in the frequency spectrum is enhanced by the average gain. This is demonstrated in Fig. 4 showing the calculated lineshapes with and without frequency sweeps as used in the calculation of Fig. 3. An overall enhancement of a factor of 2 is calculated.

3. Experimental results

Experimentally, one cannot follow the behavior of each orientation in a powder. But the previous description can be verified by its practical consequences, namely for spin 3/2 the intensity gain in the CT spectra should be around two and the line shapes should not be distorted. Enhancement of the central transition for different samples has been achieved using two simultaneous 400 μs long DFSs over 150 kHz between ±100 and ±400 kHz. For spin 3/2 the effects are illustrated in Fig. 5 showing the MAS spectra of $NaNO_3$ ($C_{qcc} = 337$ kHz) and Na_2SO_4 ($C_{qcc} = 2.6$ MHz). The samples were spun at 10 kHz. The measured gains are 1.7 for $NaNO_3$ and 1.9 for Na_2SO_4. In case of $NaNO_3$ the obtained gain is

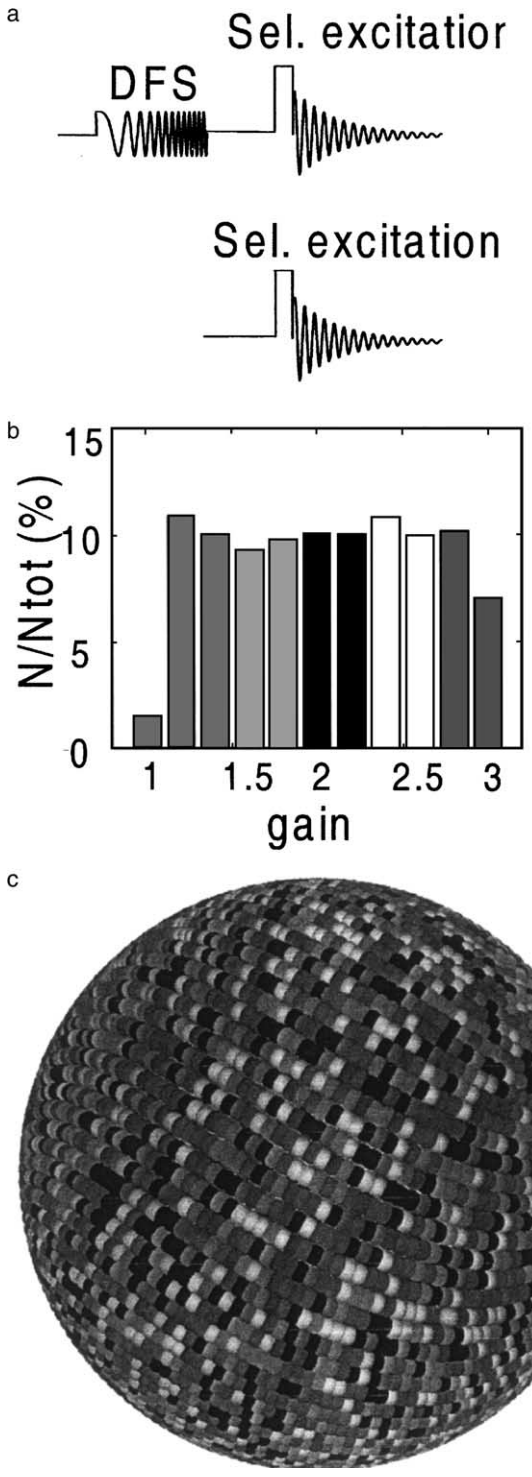

Fig. 3. (a) Pulse sequence to obtain sensitivity gains in MAS spectra of quadrupolar nuclei. Applying one or multiple DFSs prior to the selective excitation of the central transition an increased intensity is obtained as compared to a selective excitation without any preparation. (b) Fraction of the crystallites experiencing a certain gain for a sample with $C_{qcc} = 2.6$ MHz and $\eta = 0.5$. Two simultaneous (400 ms) double frequency sweeps, respectively, running from ± 100 to ± 250 kHz and ± 250 to ± 400 kHz, were employed. The rf-field strength was 34 kHz per sideband. The spinning speed was 10 kHz. (c) Orientational distribution of crystallites experiencing different gain factors. The gain factors are encoded in gray scale as indicated in (b).

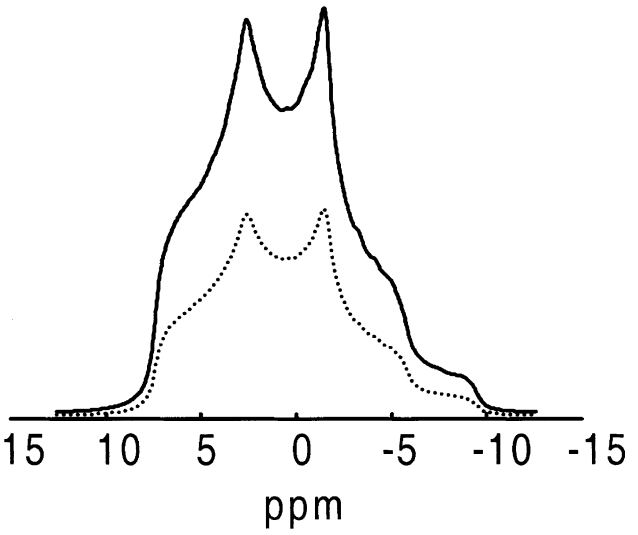

Fig. 4. Simulated lineshape for a powder sample with $C_{qcc} = 2.6$ MHz and $\eta = 0.5$ after a selective excitation $(\cdots)$ of the central transition. The solid line is obtained if prior to excitation a DFS as described in Fig. 3 is applied. Besides the overall gain no lineshape distortions are evident.

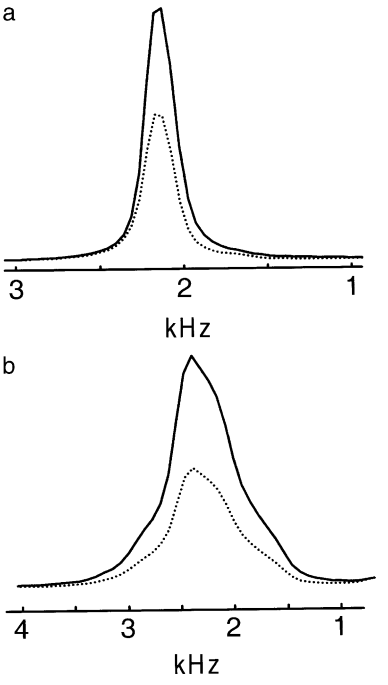

Fig. 5. MAS spectra ($\nu_r = 10$ kHz) of (a) $NaNO_3$ and (b) Na_2SO_4. The dotted lines represent the spectra obtained with a short hard pulse (tilting angle $<10°$). The solid lines represent the spectra obtained after two simultaneous double frequency sweeps (400 μs, $\nu_1 = 34$ kHz per sideband) over 150 kHz running from ± 100 to ± 250 kHz and from ± 250 to ± 400 kHz, respectively.

smaller as the C_{qcc} value is small. As a consequence some of the orientations will not be irradiated at all as the frequency sweep starts at ± 100 kHz. The frequency sweep starts at ± 100 kHz to avoid any influence of the sweep on the CT.

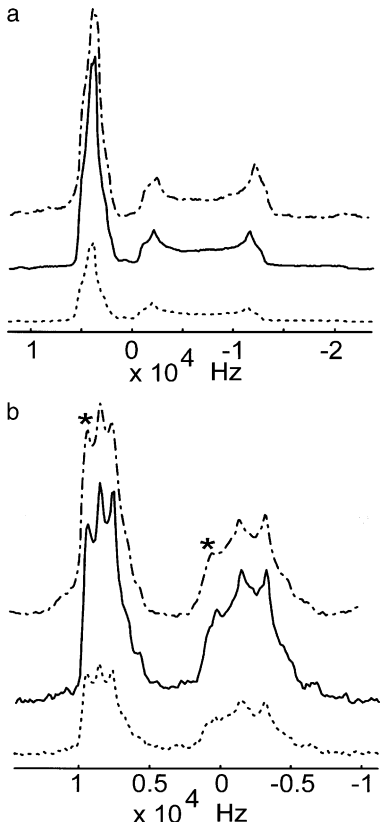

Fig. 6. MAS spectra of (a) andalusite ($\nu_r = 29.5$ kHz) and (b) sillimanite ($\nu_r = 25$ kHz). The dotted lines represent the spectra obtained with a short hard pulse (tilting angle $<10°$). The solid line represent the spectra obtained after (400 μs) two simultaneous double frequency sweeps ($\nu_1 = 34$ kHz per sideband) over 150 kHz running from ±100 to ±250 kHz and from ±250 to ±400 kHz, respectively. The dash-dotted top traces represent the spectra obtained applying a 12 ms DFS (sweep range ±1500 to ±100 kHz, $\nu_1 = 11$ kHz per sideband) prior to short pulse excitation using a spinning speed of 24 and 10 kHz for andalusite and sillimanite, respectively. * indicate an impurity in the sillimanite sample.

Similar considerations hold for spin 5/2, but in this case there are two pairs of satellite transitions, the internal ST between the $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ energy levels and the external ST between the $|\pm 5/2\rangle$ and $|\pm 3/2\rangle$ energy levels. By inverting first the external ST and then the internal ST the polarization of the CT is increased by a factor 5 [10,11]. Under multiple adiabatic passages with different adiabaticity parameters, for each individual crystallite the final gain varies between 1 and 5 and therefore for a powder an average gain of 3 should be obtained. This is demonstrated for ^{27}Al, an experimental gain of 2.5 in the intensity of the CT spectra was obtained using the same DFSs as the ones applied in the previous experiment. Spectra of the mineral andalusite with two crystallographically different sites ($C_{qcc} = 6.9$ MHz and $C_{qcc} = 15.7$ MHz) and the mineral sillimanite also with two crystallographic sites ($C_{qcc} = 6.77$ MHz and $C_{qcc} = 8.93$ MHz) are presented in Fig. 6. The sillimanite sample contains some impurities, which are enhanced as well, and the line shape is accurately reproduced. The andalusite spectra were measured using a spinning frequency of 29.5 kHz proving that this method is also valid for higher spinning speeds. The sillimanite sample was spun at 25 kHz.

In the previous measurements the sweeps influence the final results only by the polarization they induce in the central transition. Although the sweeps optimally only invert populations they also create coherences for the satellite transitions. In a powder these coherences are spread in frequency by the first-order quadrupolar interaction. Therefore, they do not influence the central transition spectra but can appear as spinning sidebands of the satellite transitions. During every level crossing that occurs in a sweep, exchange of population and coherences takes place (Fig. 1). Populations and coherences are differently affected by relaxation however. The population terms are subjected to T_1 processes (in the modulation frame $T_{1\rho}$) whereas coherences decay with $T_{2\rho}$. Although $T_{2\rho}$ is shorter than $T_{1\rho}$, in crystalline samples under MAS conditions it can still be quite long. It is expected that relaxation will play a minor role during the relatively short sweeps we used so far. For the samples in the present study, the T_2 was measured under MAS with a selective $\pi/2$–τ–π Hahn echo sequence on the central transition. The results indicate that the coherences between $|1/2\rangle$ and $|-1/2\rangle$ eigenfunctions are decaying with 0.8 ms for andalusite, 0.95 ms for sillimanite; 1.2 ms for Na_2SO_4; and 3 ms for $NaNO_3$.

Considering the fact that the experimental gain obtained for short-frequency sweeps in powders is half of the theoretical maximum (assuming an adiabatic inversion of the satellites of every crystallite in the powder) and the possible interference's from coherences generated with each (partially) adiabatic passage during a sweep, one might consider experimental conditions under which the satellite transitions become completely saturated, i.e., their populations are equalized and all coherences have decayed. As was argued by Yao et al. [16] in this case the possible gain in intensity is only half of that obtained for a full inversion of the satellites but possibly the saturation might be easier to achieve for all crystallites in a powder, so that the net effect is similar for both procedures. Yao et al. [16] applied an FAM sequence lasting one rotor period to achieve this goal. During such a modulation pulse only a few partially adiabatic passages of the satellite transitions occur, however. Even with rf-irradiation lasting up to 10 ms the number of passages is limited to a few hundred. It is the question whether this results in a truly saturated state for all crystallites in the powder or that still different states of population transfer is achieved for the separate crystallites. Furthermore, there is the question how one can distinguish these situation experimentally.

In order to gain some insight in this matter we did model calculations using a 12 ms DFS running from

± 1500 kHz to ± 100 kHz on a $I = 3/2$ spin system with a quadrupole coupling constant of 2.6 MHz spinning at 10 kHz. As is shown in Fig. 7a, even for such a long sweep a relatively flat distribution of gain factors covering the whole range from 1 to 3 is obtained if we ignore relaxation effects in our calculations. Decaying every m-quantum coherence with $T_{2\rho}/m$ changes the situation. Without going into the complicated theory of relaxation in quadrupolar spin systems under rf-irradiation we decided to decay the coherences generated during a level crossing using exponential decay rates scaled by m. As is shown in Fig. 7b and c the expected signal gain in the central transition gradually moves to a uniform factor of 2 for all crystallites in the powder if we allow for faster $T_{2\rho}$ relaxation of 5 ms and 1 ms, respectively. It should be noticed, however, that the average gain obtained for the whole powder remains equal. Using an identical decay rate $T_{2\rho}$ for every coherence leads to the same result. With the knowledge that the individual gain factors for each crystallite are randomly distributed over the sphere (Fig. 3), these results suggest that it is not possible to judge whether one has saturated the satellite transitions by studying the signal gain and lineshape of the central transition after a DFS or FAM irradiation of the spin system.

In order to verify these predictions experimentally, the ^{23}Na and ^{27}Al samples discussed earlier were subjected to a 12 ms long DFS prior to selective excitation of the central transition. In all cases similar results are obtained as compared to the much shorter sweeps discussed earlier. Indeed similar gain factors are obtained and only minor line shape distortions are observed as can be judged for the Al-spectra of the minerals andalusite and sillimanite in the top traces of Fig. 6.

This means that in terms of the desired enhancement of MAS spectra of half-integer quadrupolar spectra the use of amplitude-modulated pulses prior to excitation of the central transition is a robust method. The obtained effects do not vary strongly with sweep length. The discussion whether a saturation of the satellites was achieved is immaterial in this respect.

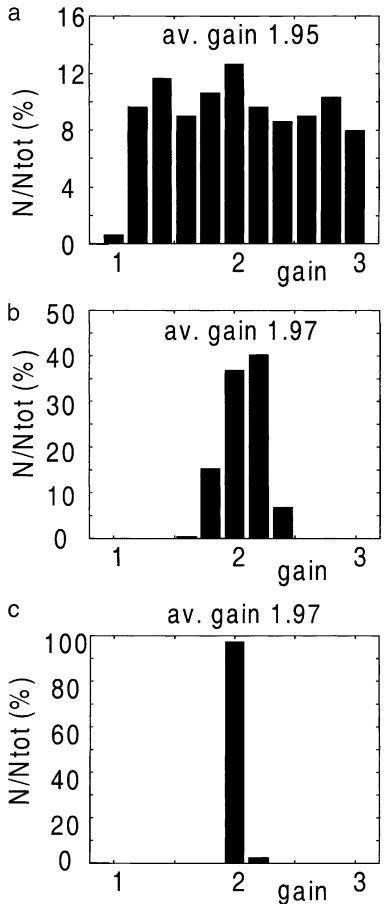

Fig. 7. Influence of $T_{2\rho}$ relaxation on the distribution of gain factors in a powder. A 12 ms DFS runing from ± 1500 to ± 100 kHz, with $\nu_1 = 10$ kHz per sideband was used. The sample is spun at $\nu_r = 10$ kHz and has $C_{qcc} = 2.6$ MHz and $\eta = 0.5$. (a) No relaxation considered, (b) $T_{2\rho} = 5$ ms, and (c) $T_{2\rho} = 1$ ms.

4. Conclusions

Double frequency sweeps can be used to enhance the polarization of central transition spectra of half-integer quadrupolar nuclei in MAS experiments. Experimentally, gains of 1.9 for Na and 2.5 for Al have been achieved. The gain comes from a population redistribution in the satellite transition levels, which is induced by the DFS in combination with MAS. During irradiation, the satellite transitions of different crystallites in a powder undergo several passages with different adiabaticity parameter. The final result varies for each orientation so that some achieve a complete inversion of the satellite transitions whereas other orientations remain completely unaffected. For the whole powder a flat distribution in gain factors ranging from 1 to $2I$ is obtained. Despite the strongly different effect induced for each crystallite orientation, undistorted line shapes are obtained. This is due to the fact that the gain depends on the path of the first-order quadrupolar interaction during spinning for each orientation, whereas the spectral lineshape is determined by the second-order quadrupolar interaction. The gains for different orientation are distributed randomly over the sphere and therefore the line shapes remain undistorted.

Relaxation effects can decay coherences generated during a sweep ultimately leading to a saturation of the satellite transitions and as a results a uniform gain factor for every crystallite in the powder distribution. This can be achieved by applying long frequency sweeps as compared to the spin–spin relaxation under MAS conditions. We found no experimental difference in the model compounds using either long or short sweeps. This is supported by model calculations. Therefore, in

practice, the only criterion for the choice of the sweep length should be to spin–lattice relaxation times T_1 as it will affect populations and thus have adverse effects for the obtainable signal gains.

4.1. Methods and experiments

All experiments were carried out on a Varian/Chemagnetics CMX Infinity 600 spectrometer, operating at 156.3 MHz for ^{27}Al and 158.6 MHz for ^{23}Na. A chemagnetics HX 2.5 mm MAS probes was used, employing spinning speeds up to 29.5 kHz. A PC based, arbitrary waveform generator from National Instruments (DAQArb PCI5411) generated the double frequency sweeps.

Simulations were performed using the GAMMA programming environment [22]. The powder distributions were simulated using up to 6044 orientations using the ZCW algorithm [23–25].

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