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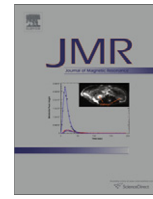

Repetitive sideband-selective double frequency sweeps for sensitivity enhancement of MAS NMR of half-integer quadrupolar nuclei

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ABSTRACT

A sensitivity enhancement scheme aiming at selective adiabatic inversion of a single set of satellite transition sidebands under magic angle spinning has been employed on samples of albite containing a single moderately distorted ^{27}Al site and zoisite containing two highly distorted octahedral ^{27}Al sites. Overall enhancements of ~2.5 for albite and ~3 for the two AlO_6 sites of zoisite are reported by applying this scheme at different spinning speeds reflecting the versatility of this enhancement scheme which achieves significant signal-to-noise enhancements for the systems with moderately high quadrupolar coupling and high quadrupolar coupling. Repeating the sensitivity enhancement scheme and signal read-out several times without allowing for spin-lattice relaxation leads to sensitivity enhancements of factors of ~4 for albite and ~5 for zoisite which substantially increases the detectability of the quadrupolar sites. The effectiveness of this scheme at high magnetic field under very fast magic angle spinning has been demonstrated. Finally, the possibility of performing spectral editing by selective enhancement of one of the quadrupolar sites in zoisite whilst keeping the other site unaffected has been explored.

1. Introduction

There is continuous interest in the investigation of quadrupolar nuclei in asymmetric chemical environments that give rise to broad NMR patterns. Quadrupolar nuclei, represent ~75% of the NMR-active nuclei in the periodic table and as a result constitute integral components of many industrially and biologically relevant substances which gives rise to the interest in studying these nuclei [1–8]. The high external magnetic field strengths that are currently available combined with small diameter magic angle spinning (MAS) rotors capable of reaching spinning speeds beyond 60 kHz have made it possible to acquire well-resolved quadrupolar NMR spectra even for very distorted sites with large quadrupolar interactions. However, the NMR sensitivity can be notoriously low for many quadrupolar nuclei due to low natural abundance, low gyromagnetic ratios, and large values of the quadrupolar interaction parameters. Despite great progress that has been made in this respect, designing efficient, versatile and robust sensitivity enhancement schemes for quadrupolar nuclei is still a crucial issue which can determine the success or failure of an experiment.

Building on the ideas of Vega and Naor [9], Double Frequency Sweeps (DFS) [10–13] have been used routinely to enhance the NMR central transition, CT, of half-integer spin quadrupolar nuclei in solid-state NMR experiments. In this scheme, the population of the nuclear spin states associated with the satellite transitions (STs) are manipulated in such a way that the population difference between the central $m_I = 1/2$ and $m_I = -1/2$ energy states is increased resulting in sensitivity enhancement when observing the CT. The strategy behind using the DFS as an enhancement technique in single crystals is to traverse adiabatically all the satellite transitions to invert their population and thereby maximizing the population difference between the $m_I = 1/2$ and $m_I = -1/2$ states before excitation of the CT [10]. This pulse sequence ensures the maximum theoretical enhancements. This protocol has been extended to stationary powder samples with considerable success where DFS with large sweep widths are used to cover the spread in ST's resulting from the orientation dependence of the quadrupolar interaction in powder. However for powder samples under MAS it proved to be difficult to consistently invert the ST's because of the combined frequency sweeping and time dependent resonance position of the ST's due to the reorientation of the powder particles with respect to the external magnetic field. As a result the satellite transitions are swept at different effective rates and in different order depending on the frequency trajectory of the satellite transitions of a particular powder orientation. The net effect is that the spin system is in a different state at the end of the frequency sweep for each crystallite resulting in randomly distributed effective enhancements for every crystallite [13]. This can be improved upon by applying much narrower adiabatic sweeps covering only

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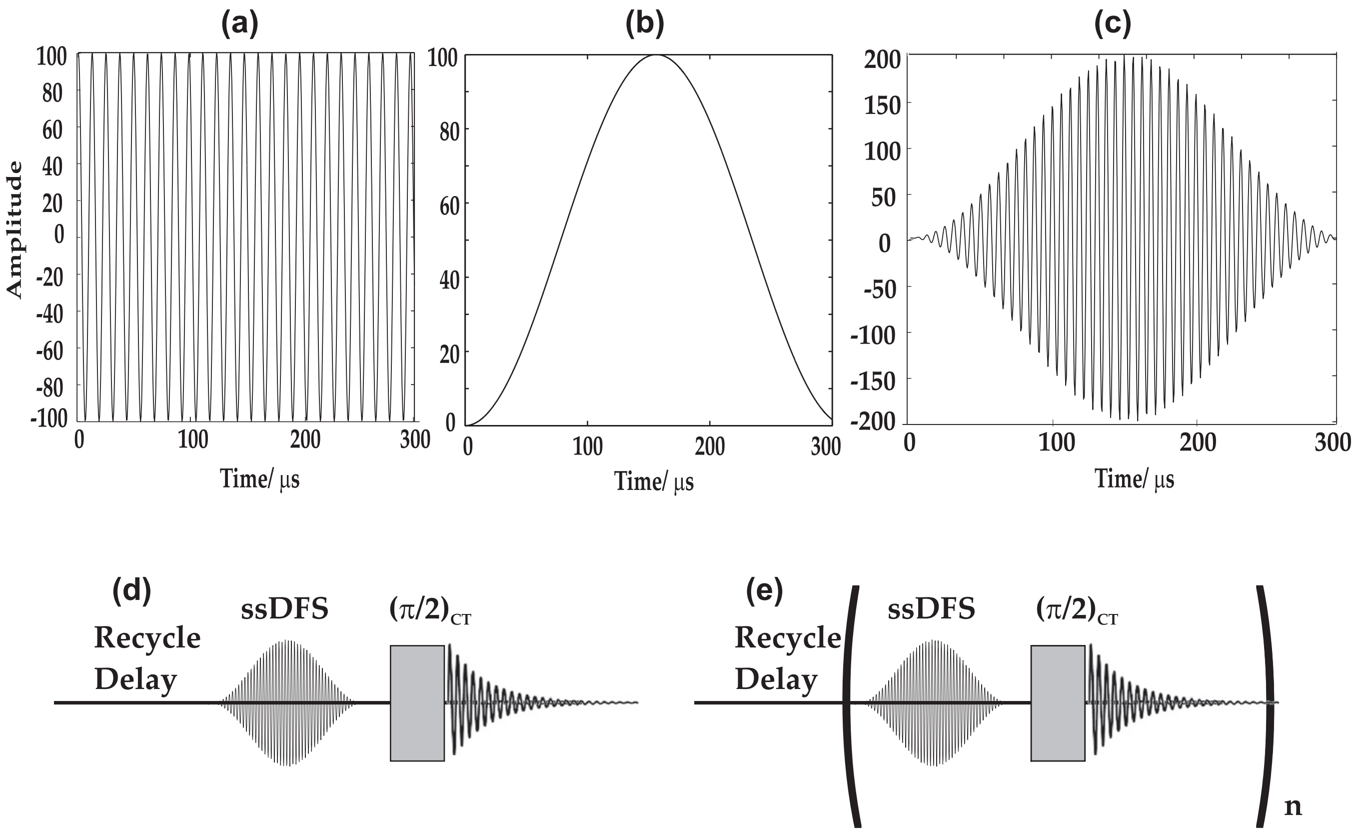

Fig. 1. (a) The RF amplitude profile of a 300 μs long narrow band double frequency sweep, (b) the $\sin^2 x$ shape function, (c) resultant RF amplitude profile of a 300 μs long ssDFS, (d) ssDFS – $(\pi/2)_{CT}$ sequence, (e) repetitive ssDFS – $(\pi/2)_{CT}$ sequence with n number of repetitions.

a single set of ST spinning sidebands (ssb) rather than sweeping the whole ssb manifold. Indeed it was shown by Wasylishen and co workers [14] while optimizing adiabatic Hyperbolic Secant pulses [14–17] and later by Dey et al. [18] that a narrow band adiabatic sweep over a single ST ssb performs much better than a wide band adiabatic sweep under MAS conditions. Recently Pell et al. [19] explored the conditions under which it is possible to obtain an efficient inversion of an entire sideband family, in the context of chemical shift anisotropy, using low-power, sideband-selective adiabatic pulses. This method shows that the most efficient inversion can be reached by sweeping the centerband which is not useful for the selective inversion of the ST's in a quadrupolar system, however. Nevertheless selective inversion of the ssb manifold is possible by sweeping any other sideband if this sideband has sufficient intensity and the rf field is chosen appropriately.

So under idealized conditions it will be possible to invert e.g. the inner satellite transitions by sweeping over a single sideband of the ssb manifold and thus achieve an enhancement of three for the central transition, whereas a consecutive inversion from the outer to the inner satellite transitions would give an enhancement by a factor 2I. However, in practice there are a number of factors that need to be considered for half-integer quadrupolar spin systems. First of all the two sideband manifolds of the $+m/2$; $+m/2-1$ and the $-m/2$; $-m/2+1$ satellite transitions overlap but have significantly different sideband amplitudes at either side of the central transition. Therefore the efficiency of the inversion will be different for each transition of the ST pair, especially when one of the sideband intensities falls below the critical value. This can be circumvented by applying a DFS acting symmetrically on a pair of sidebands around the central transition to equally affect both transitions within a pair. Secondly, for spins $I > 3/2$, the sidebands of the inner and outer satellites will generally be very close together and partially overlapping so that it is in most practical cases impossible to affect them selectively. By restricting the sweep width of the adiabatic pulse to the spinning speed one can make sure, however, that a set of sidebands of each ST pair is swept only once. Finally maintaining adiabaticity using a narrow band sweep, calls for an appropriate amplitude profile that avoids spurious excitation of the spin system when switching the sweep on or off. Thus by smoothly increasing and subsequently decreasing the amplitude of the sweep avoids *sudden* changes in the spin Hamiltonian. A pragmatic choice is a profile that does not demand experimental optimization depending on the sweep length.

Based on these considerations we demonstrated that a narrow band DFS performs much better than a broad band DFS under MAS [20]. We showed that a simple modification to a narrow band DFS scheme results in obtaining enhancement slightly favorable to that of the Hyperbolic Secant scheme in a sample of Albite, $NaSi_3AlO_8$. The new modified scheme, called sideband-selective double frequency sweep (ssDFS), is obtained by multiplying a narrow band DFS with a sine squared function to create a "well-behaved" [21] amplitude profile. This scheme showed impressive robustness to a variation of the experimental parameters such as the RF field strength used for the DFS, carrier offset, and sweep length. The appreciable robustness of this scheme means it requires very little optimization during actual experiments while giving significant signal enhancements.

Application of the ssDFS scheme to albite resulted in an enhancement of 2.44 in the signal-to-noise (S/N) ratio of the ^{27}Al MAS spectrum [20]. Although the enhancement is appreciable, it is far from the theoretical maximum of five. It has been shown however, that using different sensitivity enhancement schemes