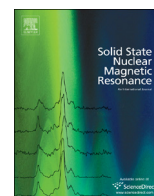




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Contents lists available at ScienceDirect

Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmr

Applications of DQ-DRENAR for the structural analysis of phosphate glasses

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ARTICLE INFO

Available online 21 October 2015

Keywords:

Dipolar coupling
Double-quantum excitation
Phosphate glasses

ABSTRACT

A new solid state NMR technique entitled DQ-DRENAR (Double-Quantum based Dipolar Recoupling Effects Nuclear Alignment Reduction) has been recently described for measuring homonuclear dipole–dipole interactions in multi-spin-1/2 systems under magic-angle spinning conditions. As in rotational echo double resonance (REDOR), the homonuclear dipole–dipole coupling constant can be extracted from a plot of a normalized difference signal $(S_0 - S')/S_0$ versus dipolar mixing time, where S is the signal amplitude with the DQ-Hamiltonian present, and S_0 is the signal amplitude in the absence of the DQ-Hamiltonian, which is used for normalization. Within the range of $(S_0 - S)/S_0 \leq 0.3$ – 0.5 such “homonuclear REDOR curves” can be approximated by simple parabolae, yielding effective squared dipole–dipole coupling constants $\sum b_{jk}^2$ summed over all the pairwise interactions present. The effect of glassy disorder has been studied by simulations, replacing singular-valued internuclear distances by Gaussian distance distributions with the same central value. This situation results in a systematic over-estimation effect, which tends to compensate the implicit under-estimation effect caused by the parabolic fitting approach. The present contribution describes applications to a number of phosphate-based glasses and glass ceramics. The method turns out to be well suited for the differentiation of the various $Q^{(n)}$ phosphate species, for characterizing the spatial distribution of isolated orthophosphate ions and for the detection of incipient nano-segregation and/or phase separation effects in glass ceramics.

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1. Background

Owing to the straightforward relationship between magnetic dipole–dipole coupling constants and internuclear distance distributions, the quantitative measurement of dipolar interactions is one of the principal goals of NMR experiments geared at structure elucidation [1]. In rare cases, where this interaction dominates the experimental lineshape, this information is directly accessible from the spectrum, as for the “Pake doublet” observed for isolated two-spin systems at low magnetic field strengths [2]. In the more common situation, where several internal interactions of comparable magnitude prevail, such information has to be extracted from the spectra with the help of selective averaging experiments, such

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as spin echo decay spectroscopy for homonuclear [3] and spin echo double resonance (SEDOR) techniques for heteronuclear dipolar coupling measurements [4]. The dipolar coupling information extracted from such measurements can be cast in the form of van-Vleck second moments [5], which lend themselves to quantitative comparisons with structural models [6,7]. Of course, given the limited spectroscopic resolution prevailing in static samples, this information represents an average over the entire ensemble of spins measured.

It is well-known that the spectroscopic resolution in solid state NMR can be dramatically increased by magic angle sample spinning, resulting in spectra in which nuclei in different chemical bonding situations give rise to spectroscopically separated signals. Furthermore, although the dipolar coupling is averaged to zero over the MAS rotor cycle, this information can be recovered with the help of suitable *re-coupling* methods. In this manner, dipole–dipole coupling measurements are possible in a site-selective fashion without any loss in resolution. For heteronuclear spin systems, the most effective and most widely applicable method has been the rotational echo double resonance (REDOR) technique pioneered by

Gullion and Schaefer [8]. In REDOR one measures a difference signal between a signal amplitude S_0 with the interaction absent and a reduced signal amplitude S' with the interaction re-coupled. This feat can be accomplished by coherent trains of inversion pulses

synchronized with the rotor period (REDOR) or, alternatively, continuous-wave irradiation during the rotor period (TRAPDOR [9], REAPDOR [10]). For two-spin systems, the REDOR response takes the form of a universal curve from which the internuclear distance

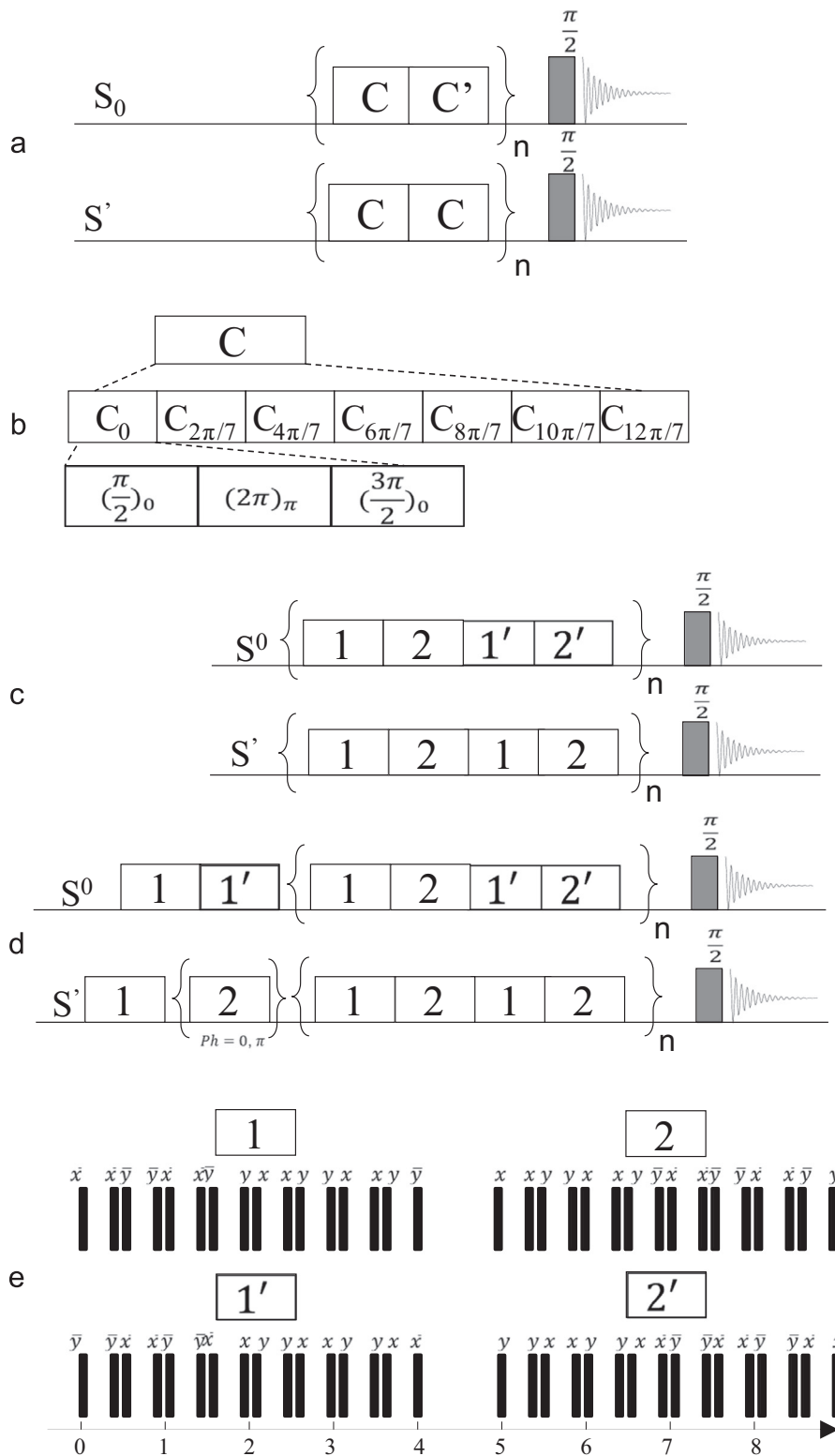


Fig. 1. (a) DQ-DRENAR pulse sequence using the POST-C7 excitation scheme of Hohwy and Jakobsen [40]; C' means all the phases of pulses in (b) are 90° shifted. (b) The pulse compositions of block C. (c) Standard DQ-DRENAR-BABA-xy16: the combination of pulse blocks 1 and 2 constitutes the BABA-xy-16 sequence; all the pulses within blocks 1' and 2' are 90° degree shifted relative to the blocks 1 and 2, respectively. The S^0 reference signals are obtained by combining the BABA-xy16 and 90° shifted BaBA-xy16 to average out the dipolar coupling effect. S' is obtained by repeating the unshifted BABA-xy16 block to recouple the dipolar interaction. (d) Modified sequence. (e) The construction of the pulse block, corresponding to phases 1, 2, 1' and 2'. Numbers at the bottom of the time axis indicate the rotor cycles.

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