

Characterization of local environments in crystalline borophosphates using single and double resonance NMR

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ABSTRACT

¹¹B and ³¹P magic-angle spinning as well as ¹¹B{³¹P} and ³¹P{¹¹B} rotational echo double resonance (REDOR) NMR have been applied to characterize the local environments in the crystalline borophosphates K₃[BP₃O₉(OH)₃], NH₄[ZnBP₂O₈] and Rb₃[B₂P₃O₁₁(OH)₂]. Dipolar second moment values extracted from the REDOR curves at short evolution times ($\Delta S/S_0 \leq 0.2$) are in reasonable agreement with those calculated from the internuclear distances in the corresponding crystal structures. In particular, the method is found to be useful for distinguishing between boron and phosphorus local environments with different numbers of B–O–P connectivities, making REDOR a well-suited tool for medium-range order investigations in glasses.

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1. Introduction

The interest in crystalline [1–15] and glassy or disordered [16–28] borophosphate compounds of the general composition $xM_2O-yB_2O_3-zP_2O_5(mH_2O)$ has increased dramatically in recent years due to the large structural diversity that can be found in these systems. Besides being of interest from the point of view of fundamental science, borophosphates have also attracted attention for a variety of technological applications in catalysis and ceramic engineering [11,12], as well as for fast ion-conducting materials [19–21]. While the structures of the crystalline borophosphates can be analyzed using single-crystal X-ray diffraction, the most valuable information regarding the structures of amorphous systems today comes from solid-state NMR investigations. While magic-angle spinning (MAS) has been used for characterizing local environments, a topic of much current interest is the elucidation of order/disorder phenomena at longer distance scales. In this context, advanced dipolar methods such as rotational echo double resonance (REDOR) [29–32] have been recently developed as a valuable source of information on second nearest-neighbor distributions (“network connectivities”) in glassy materials [33,34].

The structures of borophosphates are built up of BO₃, BO₄[−] and PO₄[−] units, which are interconnected to each other and can form complex networks with one-, two- and three-dimensional (1D)

topologies. From the viewpoint of the second nearest-neighbor environments, the local structures can be grouped into P_{mB}⁽ⁿ⁾ and B_{mP}⁽ⁿ⁾ units, where *n* specifies the number of bridging oxygen atoms and *m* denotes the number of heteroatomic linkages. Recent work has shown the promise of ¹¹B{³¹P} and ³¹P{¹¹B} REDOR experiments to reveal significant detail on the extent of boron–oxygen–phosphorus connectivity in borophosphate glasses [35,36]. However, such work requires careful validation (and/or calibration) studies on crystalline model compounds, in which the internuclear distance distributions are well-known. In this connection we present a systematic solid-state NMR investigation of the three crystalline model compounds K₃[BP₃O₉(OH)₃], NH₄[ZnBP₂O₈] and Rb₃[B₂P₃O₁₁(OH)₂]. Based on this work, we examine the potential of solid-state NMR spectroscopy for quantifying the number of B–O–P connectivities in unknown materials.

2. NMR methodology

REDOR has emerged as a powerful method for the analysis of short-range order in disordered materials and glasses [33–51]. REDOR in its original design is a heteronuclear recoupling technique applied under the MAS condition necessary to obtain well-resolved spectra. Fig. 1 illustrates the pulse sequence for the ¹¹B{³¹P} measurements reported in the present study. The NMR signal (*S*₀) is first recorded for observed nuclei *S* under the MAS condition using a rotor-synchronized spin echo. In a second step, the heteronuclear dipole–dipole coupling is recoupled by applying

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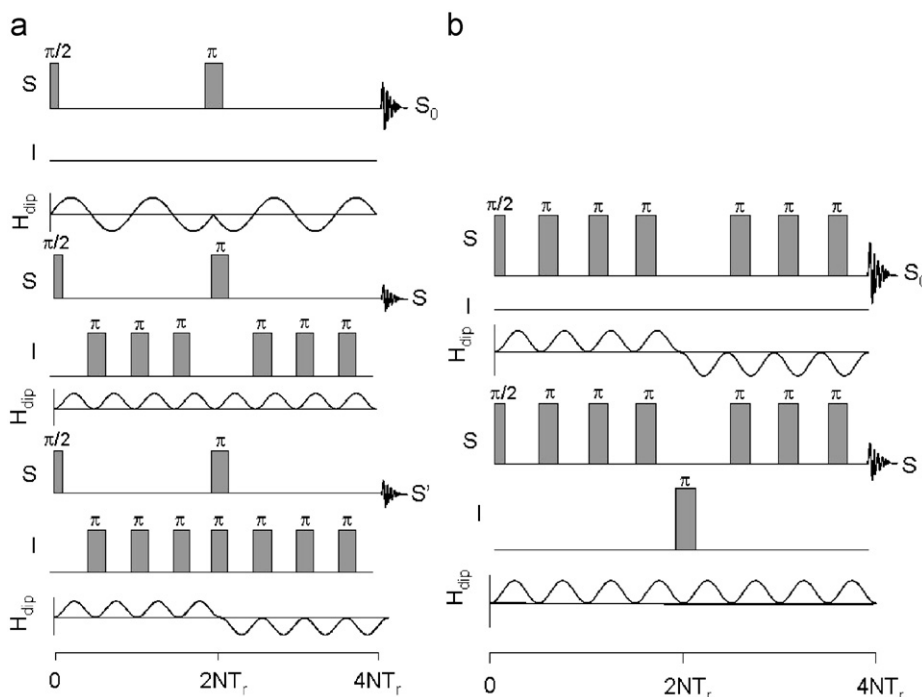


Fig. 1. Rotational echo double resonance pulse sequences used in the present study, shown for a dipolar evolution time of $4N$ rotor periods: In addition, the evolution of the heteronuclear dipolar Hamiltonian is shown. (a) Pulse sequence (compensated REDOR) used for the $^{11}\text{B}\{^{31}\text{P}\}$ REDOR experiments. (b) Pulse sequence used for the $^{31}\text{P}\{^{11}\text{B}\}$ REDOR experiments.

rotor-synchronized π pulses during the rotor cycles to the coupled nuclei I . As a result of this recoupling, the signal intensity S is reduced. For an isolated I - S two-spin system, the dipolar coupling constant D can be determined by fitting the normalized difference signal $\Delta S/S_0 = (S_0 - S)/S_0$ plotted against the dipolar evolution time NT_r (the duration of one rotor period multiplied by the number of rotor cycles) to the appropriate theoretical expression. In the case of most inorganic solids and glasses, however, the situation is more complicated because of multi-spin interactions, and the REDOR curves of such multi-spin systems are strongly dependent on the spin interaction geometries present. Furthermore, in the case of disordered systems and glasses, the order and geometry of the spin system is not known and is, in most cases, rather ill defined because internuclear distances and bond angles may be subject to wide distribution functions. Fortunately, both these aforementioned obstacles can be overcome by limiting the analysis of the REDOR data to the initial curvature, where $\Delta S/S_0 < 0.2$ [33,34]. In this limit of short dipolar evolution times, the REDOR curvatures are found to be geometry-independent and dominated by the van Vleck second moment (M_2), governed by the expression

$$\frac{\Delta S}{S_0} = \frac{S_0 - S}{S_0} = \frac{4}{3\pi^2} (NT_r)^2 M_2 \quad (1)$$

where M_2 is the van Vleck second moment [52] which is related to internuclear distance distributions according to

$$M_2 = \frac{4}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma_I^2 \gamma_S^2 I(I+1) \hbar^2 \sum_S r_{I-S}^{-6} \quad (2)$$

Thus, the M_2 value measured from REDOR data serves as an effective quantitative tool for characterizing the average dipole-dipole coupling strength, because it is proportional to the sum of the inverse sixth powers of the internuclear distances involved. Systematic errors arising from pulse imperfections and resonance offsets can be compensated, by adding a third (*dummy echo*)

component to the experiment [34]. By adding an extra π pulse on the I channel in the middle of the evolution period the sign of the heteronuclear dipole-dipole interaction will remain unchanged in the middle of the evolution period. As a consequence, the intensities of the spin echo (S_0) and the dummy echo (S') would be identical under perfect experimental conditions. Under imperfect conditions, however, the dummy echo signal is attenuated, providing a suitable correction to the original data set:

$$\frac{\Delta S}{S_0} = \frac{S_0 - S}{S_0} + \frac{S_0 - S'}{S_0} = \frac{4}{3\pi^2} (NT_r)^2 M_2 \quad (3)$$

If the dipolar dephasing of the observe-spins (here ^{31}P) occurs in the local field of $I > \frac{1}{2}$ nuclei (here ^{11}B), several complications enter. First, the different possible Zeeman states m_I for the I -nuclei differ in the respective sizes of their z-components and hence generate dipolar fields of different magnitudes at the observer spins [50,51]. Second, for large C_q values, the anisotropic broadening of the $|\frac{1}{2}\rangle \leftrightarrow |\frac{3}{2}\rangle$ "satellite transitions" produces large resonance offsets, which reduce the efficiency of the π pulses to effect population inversion. For strong quadrupolar interactions, only the central $|\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ coherences will be affected. In this limiting case only those S -spins that are coupled to I -nuclei in the Zeeman states with $|m_I| = \frac{1}{2}$ are expected to yield a REDOR response. Detailed simulations have shown that it is desirable in such cases to minimize the number of π -pulses applied to the quadrupolar nuclei, making the REDOR sequence of Fig. 1(b) the method of choice. For spin $I = \frac{3}{2}$ nuclei the initial curvature analysis approach discussed above can be extended by using the expression

$$\frac{\Delta S}{S_0} = \frac{1}{15\pi^2} (2 + 18f_1) (NT_r)^2 M_2^{I-S} \quad (4)$$

where the efficiency factor f_1 ($0 \leq f_1 \leq 1$) accounts for the extent to which the dipolar coupling of S -spins to I spins in their outer Zeeman states still influences the REDOR response [38]. Again, this approximation is only valid in the initial decay regime

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