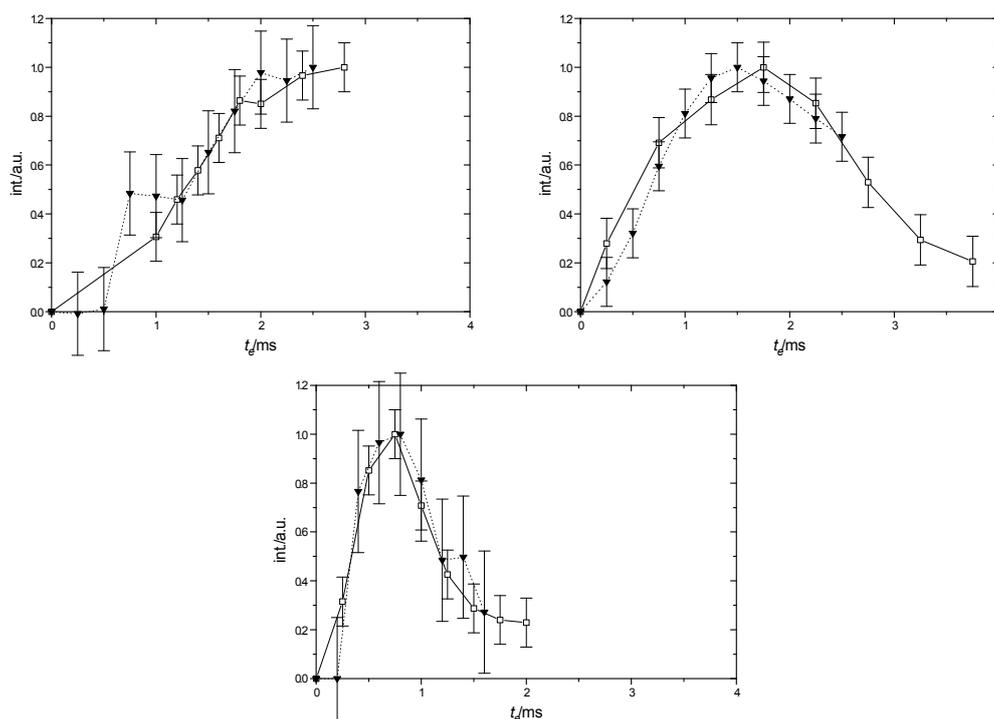


# Application of $^{31}\text{P}$ High-Resolution Double-Quantum NMR to Glassy and Crystalline Thiophosphates

**J. Schmedt auf der Günne, H. Eckert**

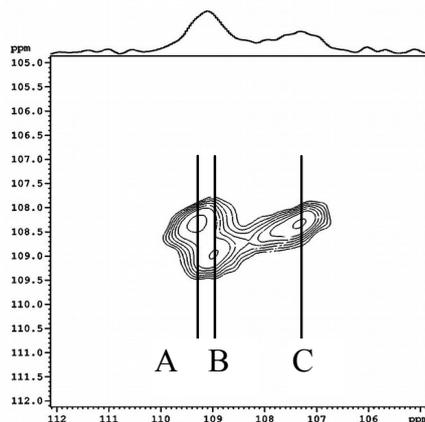
Institut für Physikalische Chemie  
Westfälische Wilhelms-Universität Münster  
D-48149 Münster

High resolution double-quantum  $^{31}\text{P}$  NMR spectroscopy is used to provide structural information in glassy and crystalline thiophosphates [1]. The homonuclear dipolar interaction is reintroduced under MAS-conditions to excite double quantum coherences. Among the various pulse schemes [2-6] available in the literature the C7-sequence [2,3] was found particularly useful. The development of the double quantum coherence as a function of the excitation time is determined by the strength of the homonuclear dipolar interaction. As shown in Figure 1 the thiophosphate anions  $\text{PS}_4^{3-}$ ,  $\text{P}_2\text{S}_7^{4-}$  and  $\text{P}_2\text{S}_6^{4-}$  can be identified unambiguously by characteristic excitation profiles.



**Figure 1** Double quantum excitation profiles for compounds bearing typical structural fragments in crystalline thiophosphates; Bottom:  $\text{P}_2\text{S}_6^{4-}$ -units in  $\text{Sn}_{1.008}\text{P}_2\text{S}_6$  (squares) and  $\text{Hg}_2\text{P}_2\text{S}_6$  (triangles); Top right:  $\text{P}_2\text{S}_7^{4-}$ -units in  $\text{Ag}_7\text{P}_3\text{S}_{11}$  (triangles) and  $\text{Hg}_2\text{P}_2\text{S}_7$  (squares); Top left:  $\text{PS}_4^{3-}$ -units in  $\text{Ag}_7\text{P}_3\text{S}_{11}$  (triangles) and  $\text{Li}_7\text{PS}_6$  (squares); Error bars are estimated from the signal-to-noise ratio.

Applications are presented for ionically conductive glasses in the system  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  and on thiophosphate crystals with incomplete and positionally disordered x-ray structures. For example, Figure 2 shows the DQ spectrum of  $\text{Li}_4\text{P}_2\text{S}_6$ . DQ-NMR in this case resolves three peaks and reveals, that peaks A and C belong to the same anion, while B is correlated with itself. The excitation profiles (not shown) of these three peaks are characteristic of  $\text{P}_2\text{S}_6^{4-}$ -groups. Thus the structure contains two distinct  $\text{P}_2\text{S}_6^{4-}$ -units, one with chemically equivalent  $^{31}\text{P}$  spins (peak B) and one with chemically inequivalent  $^{31}\text{P}$  spins (peaks A and C).



**Figure 2**  $^{31}\text{P}$ -NMR 2D-SQ(F2)-DQ(F1)-spectrum of  $\text{Li}_4\text{P}_2\text{S}_6$ , a positionally disordered crystal with only one phosphorus site in the published structure [7]; the one pulse spectrum is shown on top; the 2D-spectrum was acquired using the C7-sequence [2] with a length of the excitation period of  $600 \mu\text{s}$ , other details (see [1]).

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