

## A solid-state NMR study of dehydration of layered alpha-Niobium Phosphate

Jianfeng Zhu and Yining Huang

*Department of Chemistry, University of Western Ontario, London, Ontario*

[yhuang@uwo.ca](mailto:yhuang@uwo.ca)

The layered niobium phosphates (NbPs) are good candidates for catalysts. To better understand the applications and to design new NbP-based materials, detailed structure information on these layered materials is needed. In general, it is the dehydrated phases that are involved in catalysis while the hydrated materials are usually the precursors. In this study, the local environments of the niobium centers in layered alpha-niobium phosphate ( $\alpha$ -NbP) and its dehydrated phases were investigated by wide-line  $^{93}\text{Nb}$  NMR in combination with TGA and powder XRD. One of the goals of this work is to explore the sensitivity of  $^{93}\text{Nb}$  static spectra to the dehydration.

The  $^{93}\text{Nb}$  static NMR spectra of as-made  $\alpha$ -NbP and its dehydrated phases are shown in Figure 1. Since there is only one Nb site in  $\alpha$ -NbP, there should be only one  $^{93}\text{Nb}$  resonance in the spectrum of as made  $\alpha$ -NbP. However, the  $^{93}\text{Nb}$  NMR spectra at 14.1 and 21.1 T both clearly exhibit two signals. This confirms the TGA results (not shown) that the as-made NbP sample is a mixture of tri- and dihydrate phases. A comparison of the NMR intensity with the TGA weight loss ratio of the tri- and dihydrate phases allows one to assign the  $^{93}\text{Nb}$  resonance with an isotropic shift,  $\delta_{\text{iso}}$ , at -1160 ppm to the tri-hydrate phase and the signal with a  $\delta_{\text{iso}} = -1130$  ppm to the di-hydrate phase. The spectra are dominated by the CSA (the values of span are 1150 and 1100 ppm for tri- and di-hydrated phases, respectively). The skew  $\kappa$  values are 0.93 and 1.0 for di- and tri-hydrate phases, which indicates approximately axial CS tensors for both materials. The  $C_Q$  values of tri- and dehydrated phases are 45 and 30 MHz, respectively. The  $\eta_Q$  values for both phases are zero. The Euler angles of (0, 0, 0) suggest that the two axis systems describing the CS and the EFG tensors coincide with each other. The  $^{93}\text{Nb}$  static spectra of the sample dehydrated at 70 °C exhibit only one signal, consistent with the TGA result that this sample is a pure phase of monohydrate NbP. Simulating the

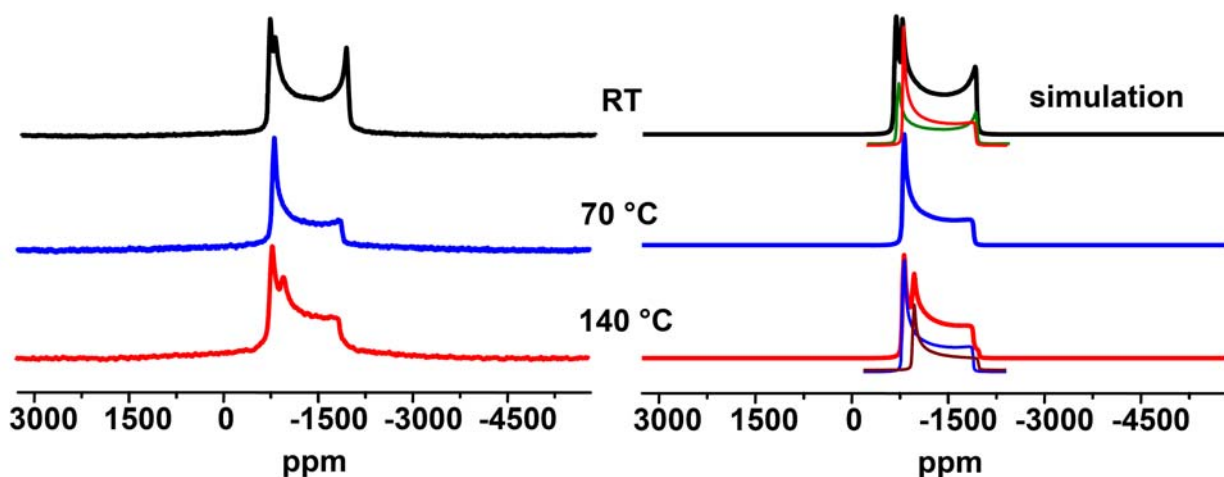
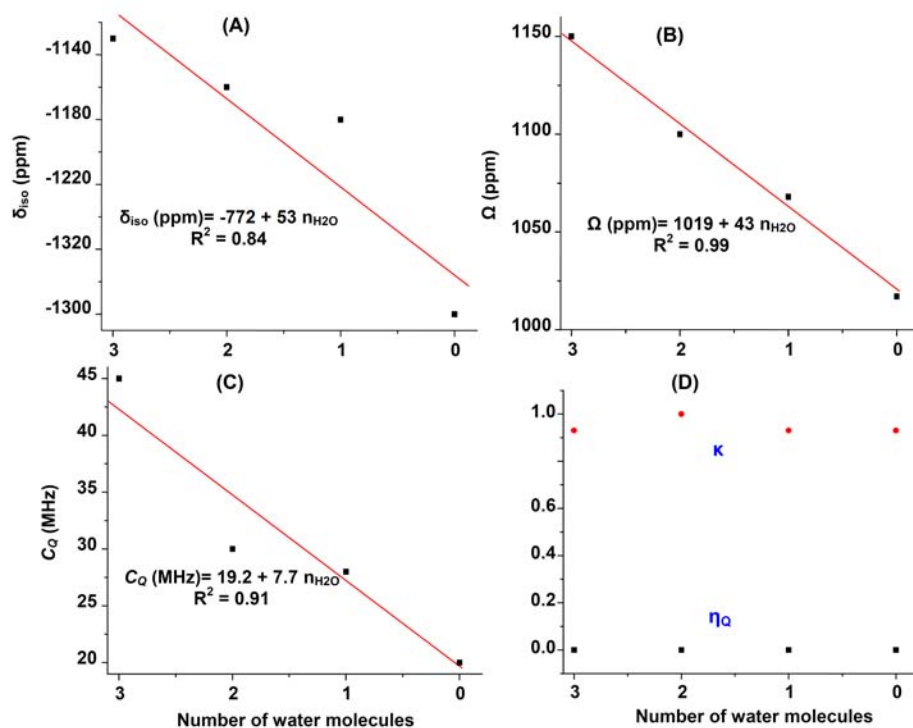


Figure 1:  $^{93}\text{Nb}$  static NMR spectra of as-made  $\alpha$ -NbP and its dehydrated phases recorded at 21.1 T.



**Figure 2:** The correlations of the number of water molecules in the lattice of  $\alpha$ -NbP with  $^{93}\text{Nb}$  NMR parameters: (A)  $\delta_{iso}$ , (B)  $\Omega$ , (C)  $C_Q$ , (D)  $\eta_Q$  and  $\kappa$ .

spectra yields the following CS and EFG parameters:  $\delta_{iso} = -1180$  ppm,  $\Omega = 1068$  ppm,  $\kappa = 0.93$ ,  $C_Q = 28$  MHz,  $\eta_Q = 0.00$ . The  $^{93}\text{Nb}$  static spectra of the sample dehydrated at  $140^\circ\text{C}$  show two signals: one is the same as that of the  $70^\circ\text{C}$  sample and the other one is slightly narrower but with a similar line-shape. The former can be assigned to the Nb in the monohydrate phase; the latter must be due to the Nb in the anhydrous material. The  $^{93}\text{Nb}$  static spectra of the sample dehydrated at  $250^\circ\text{C}$  can be well simulated with a single  $^{93}\text{Nb}$  resonance. The resulting CS and EFG parameters are  $\delta_{iso} = -1300$  ppm,  $\Omega = 1017$  ppm,  $\kappa = 0.93$ ,  $C_Q = 20$  MHz,  $\eta_Q = 0.00$ . The CS and EFG parameters extracted from simulation are identical to the second signal seen in the spectra of the  $140^\circ\text{C}$  sample discussed earlier, confirming the existence of anhydrous phase in the sample dehydrated at  $140^\circ\text{C}$ .

In summary, the dehydration induces a downfield chemical shift, a decrease in the CSA and a reduction of  $C_Q$ . These results indicate that the dehydration leads to a more symmetric Nb local environments in  $\text{NbO}_6$  octahedra due to (1) the water molecules are gradually removed from the lattice and (2) the Nb=O double bond is gradually lengthened and eventually transforms to a Nb-O single bond. Figure 2 shows approximate linear relationships between the  $^{93}\text{Nb}$  NMR parameters (including  $\delta_{iso}$ ,  $\Omega$  and  $C_Q$ ) and the number of water molecules in the lattice. These correlations indicate that the  $^{93}\text{Nb}$  NMR parameters are very sensitive to the dehydration. It is interesting to notice that the  $\eta_Q$  and skew  $\kappa$  remain essentially unchanged during the dehydration process, suggesting that during the dehydration the approximate  $C_4$  local symmetry is preserved.

[1] J. Zhu, Y. Huang, "A Solid-State NMR Study of Dehydration of Layered alpha-Niobium Phosphate," *Inorganic Chemistry* **48** (2009). <http://dx.doi.org/10.1021/ic9011668>