Understanding the aqueous speciation of molecular metal oxides

Magda Pascual-Borràs and C. André Ohlin

Chemistry Department, Umeå University, 907 36 Umeå, Sweden
magdalena.pascual@umu.se

The behavior of metal oxides clusters at aqueous solution is dictated by numerous complex and interrelated phenomena. The most important features of metal-oxo clusters in solution are well understood and predictable while others are confounding, interdependent and variable. It is well known how polyoxometalates (POMs) of Mo, V and W are assembled and behaving in solution. On the other hand, formation mechanisms of Nb and Ta POMs are not well understood and described. Thus, there is a lack of knowledge of how Nb and Ta POMs behave in solution and this information is needed to understand the structural evolution among different POMs.[1]

The decaniobate ion ($[Nb_{10}O_{28}]^{6-}$, Nb_{10}) is unique in solution as it does not strongly protonate when dissolved in water and is stable at near neutral pH. However, it converts to hexaniobate ion ($[Nb_6O_{19}]^{8-}$, Nb_6) with pH increase. It is know that the conversion from Nb_{10} to Nb_6 proceeds via heptaniobate ion ($[Nb_7O_{22}]^{9-}$, Nb_7), which is detectable by ^{17}O NMR spectroscopy and ESIMS.[2] (Figure 1)

In that sense, we have used Density Functional Theory (DFT) to rationalize the observed species in solution, and develop an understanding of the solutions behaviors, in order to find a plausible reaction mechanism for the base-induced dissociation of Nb_{10}. The results show how important is to use computational chemistry to rationalize the experimental observations.
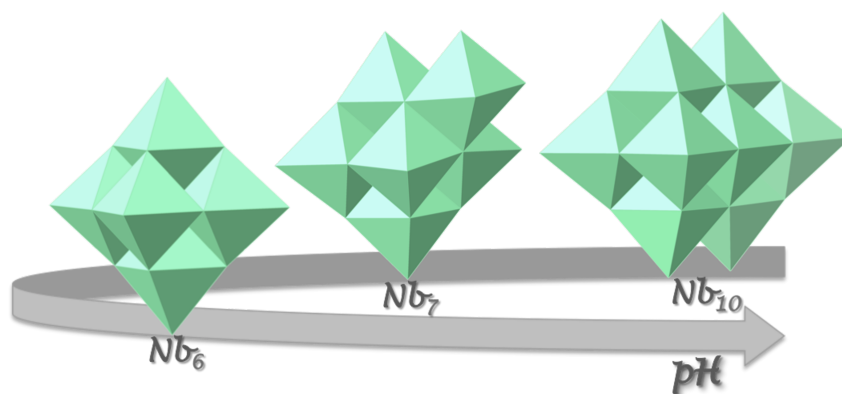

Figure 1: Representation of observed species in solution at different pH conditions.

References

1. D. Sures, M. Segado, C. Bo, M. Nyman, J. Am. Chem. Soc. **140**, (2018), 10803.

2. E. M. Villa, C. A. Ohlin, E. Balogh, T. M. Anderson, M. D. Nyman, W. H. Casey, *Angew. Chem. Int. Ed. 47*, (2008), 4844.