

## Molecular and Electronic Structures of the Super Reduced State of a Polyoxometalate (POM), $[\text{Mo}_{12}\text{O}_{40}\text{P}]^x$ ( $x = -3, -27$ )

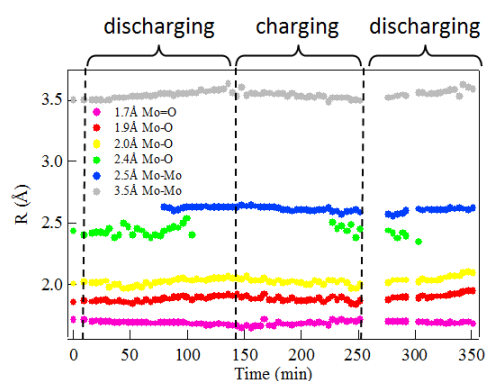
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Polyoxometalate (POM) clusters have a great potential as novel battery material with higher electronic capacity and stability. Its useful electrochemical properties in this regard were demonstrated by Kawasaki *et al.* [1], and its stability under solid-state electrochemical redox conditions is of great importance for practical application. Its wide range of charge states is of great interest to theoretical chemists.

In our contribution, the molecular and electronic structures of a negatively charged POM cluster,  $[\text{Mo}_{12}\text{O}_{40}\text{P}]^x$  ( $x = 3, 27$ ), were investigated using density functional theory (DFT). In the super-reduced state, which is achieved by reduction of  $\text{POM}^{3-}$  by formally 24 electrons, experimentalists found in the XAFS spectrum that the  $\text{POM}^{27-}$  cluster has characteristic short (about 2.5 Å) Mo-Mo bonds and suffers characteristic geometrical changes of Mo-O bond lengths [2] (Figure 1).

This observation was practically reproduced by our theoretical calculations at the RI-BP86-D/def-SVP level of theory, using lithium atoms as counter cations in order to stabilize the highly negative charge on the POM cluster. It was proven that the origin of observed short Mo-Mo bonds comes from the formation of triangular Mo-Mo sites, created under preservation of the original Mo skeleton via ‘squeezing out’ oxygen atoms from Mo-O-Mo bonds.

We note that our calculations were not only performed using ordinary geometry optimizations, but also employed the Born-Oppenheimer molecular dynamics (BOMD) technique. Starting with the structure of X-ray result, we first added 27 Li atoms in random positions. In Figure 2, the lower left structure was derived by an ordinary geometry optimization; on the other hand, the upper right structure was derived by quenching a BOMD NVT trajectory run at room temperature for 1.92 ps. Its resulting optimized geometry fits the experimental XAFS observations better, and is lower in energy by about 3 eV than the

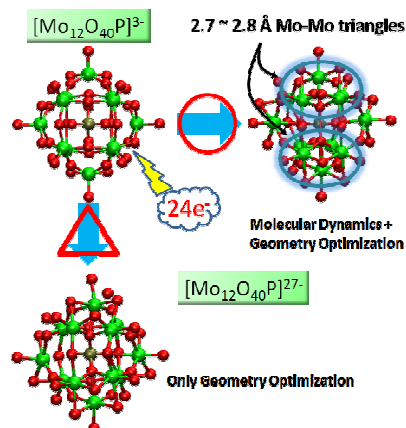


**Figure 1.** Bond distance changes during discharging and charging.

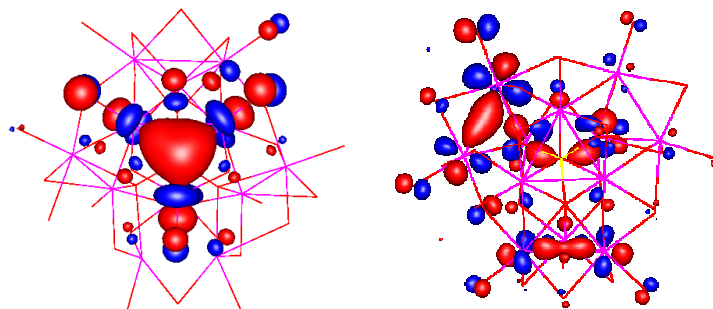
straightforwardly optimized geometry.

The optimized cluster has 3 isolated bonds (2 single and 1 double bonds) and two characteristic Mo-Mo triangles which were not seen in the 3- state. One of the interesting points of this Mo-Mo triangle bonds is to form a three centered bond in each site. A molecular orbital analysis shows that a strong  $\sigma$  interaction can be seen in the low lying state, in the left of Figure 3. We assume that one of the reasons of the stability at the super-reduced state

is the capability of localizing electrons in the Mo-Mo triangle sites. And also, we observed elongations of the outer Mo-O bonds from 1.7 Å to 1.9 Å or 2.0 Å. We found most outer Mo-O bonds are in the range from 1.9 Å to 2.1 Å, which agrees well with the experimental observation. Again, via molecular orbital analysis, this elongation was explained by the existence of anti-bonding orbitals between Mo and O atoms, shown on the right in Figure 3.



**Figure 2.** Optimized Structures of  $\text{POM}^{27-}$ .



**Figure 3.** Molecular orbitals of the optimized  $\text{POM}^{27-}$  structure. Shown are (left) a 3-center Mo-Mo bond (HOMO-12) and (right) an anti-bonding Mo-O orbital (HOMO-8).

Finally, another important character of the POM cluster, the reverse process ( $\text{POM}^{27-} \rightarrow \text{POM}^{3-}$ ), was also verified. On withdrawing 24 electrons via removal of the Li atoms from the super-reduced state, it was confirmed that the molecular structure was reverted to the geometry of the 3- state in a straightforward geometry optimization.

## References

- [1] N. Kawasaki *et al.*, *Angew. Chem.* **2011**, *123*, 3533.
- [2] H. Wang, H. Yoshikawa, K. Awaga *et al.*, in preparation.