Molecular and Electronic Structures of the Super-Reduced State of a Polyoxometalate (POM), $[Mo_{12}O_{40}P]^{x}$ (x=-3, -27)

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The molecular and electronic structures of a POM cluster, $[Mo_{12}O_{40}P]^{x}$ (x = -3, -27), were investigated using density functional theory (DFT). In the super-reduced state, which is achieved by reduction of POM^{3-} by formally 24 electrons, we found in the X-ray absorption fine structure (XAFS) spectrum that the POM^{27-} cluster has characteristic short (about 2.5 Å) Mo-Mo bonds and suffers characteristic geometrical changes of Mo-O bond lengths [1]. This observation was practically reproduced by our theoretical calculations at the RI-BP86-D/def-SV(P) level of theory, using lithium atoms as countercations in order to stabilize the highly negative charge on the POM cluster. It was proven that the origin of observed short Mo-Mo bonds stems 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 POM^{3-} structure of X-ray result, we first added 35 Li atoms in random positions. In Figure 1, 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 500 Kelvin 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 straightforwardly optimized geometry.

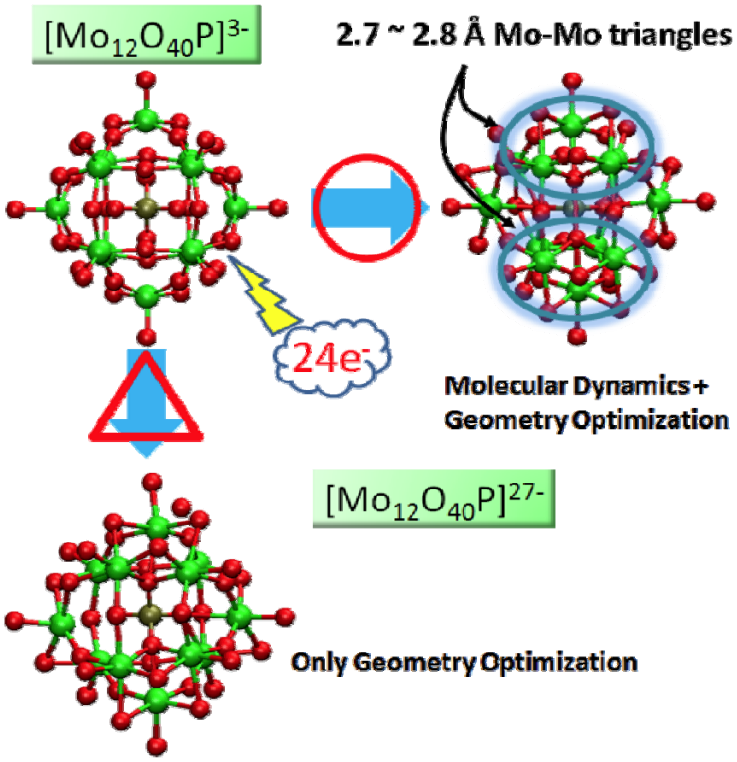

Figure 1. Optimized Structures of POM^{27-}.

Finally, another important character of the POM cluster, the reverse process (POM^{27-} →

POM^{3-}), was also verified. On depriving 24 electrons via removal of the 35 Li atoms from the super-reduced state, it was confirmed that the molecular structure was reverted to the POM^{3-} geometry in a straightforward geometry optimization.

References

[1] H. Wang, S. Hamanaka, Y. Nishimoto *et al.*, submitted.