# A computational study of molybdates and polyoxomolybdates.

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Keywords: Ab Initio , Polyoxomolybdates and electronic structure.

## INTRODUCTION

In the last decade the Polyoxometalates (POMs) have attracted attention as building blocks for synthesizing advanced materials[1]. The polyoxomolybdates are the most studied POMs, which have been targeted for important technological applications in photocatalysis and nanotechnology[2]. Mostly of the giant polyoxomolybdates are octahedrally coordinated by 6 oxygens. However, square pyramidal (or trigonal bypiramidal) species with 5 coordinated oxygens and tetrahedral species with 4 coordinated oxygens are common. The POMs normally possess high negative charges and are dependent of the pH of the solution[1,2]. On the present work, the relative stability and the band gaps for the $Mo_xO_y^{6x-2y}$ (x=1, 2, 4, 6, 7, 8; y=3, 4, 7, 12, 13, 18, 19, 24, 26) have been calculated. The effects of the protonation of the different species have also been investigated.

## METHODS

Density functional method with GGA-PBE exchange-correlation functional has been used as implemented in the deMon-2K package[3]. The effective core potential (ECP) for the Mo atoms has been used and DZVP basis sets for the oxygen atoms. The geometries have been fully optimized with no symmetry constraint. The relative stability was calculated based on the atomization energy taking as reference the ground state of $Mo^{6+}$ and $O^{2-}$ atoms.

## RESULTS AND DISCUSSION

The main results are shown in the Table 1. The $[Mo_6O_{18}]$ species is the most stable. The neutral POMs are normally more stable than the charged structures. This is probably due to the fact that the solvent effects, was not taken into account in the present calculations. The band (BG) gap estimates are in the range between 1.81 eV for $[Mo_7O_{24}]^{6-}$ to 3.72 eV $[Mo2O7]^{2-}$. The structures investigated with more than 4 Mo present band gap between 1.81 – 3.0 eV.

**Table 1**. Relative Energy (RE) and Band Gap (BG) for the molybdate structures investigated.

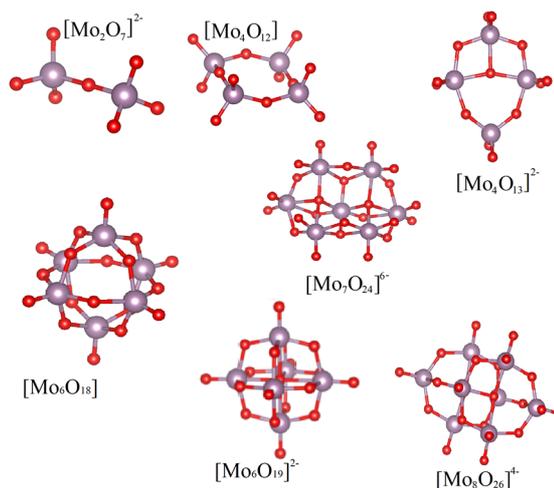| Structure | RE in eV/at | BG in eV |
|---|---|---|
| $[MoO_3]$ | 0.67 | 1.91 |
| $[MoO_4]^{2-}$ | 26.66 | 1.98 |
| $[Mo_2O_7]^{2-}$ | 16.68 | 3.72 |
| $[Mo_4O_{12}]$ | 0.01 | 3.07 |
| $[Mo_4O_{13}]^{2-}$ | 9.52 | 2.94 |
| $[Mo_6O_{18}]$ | 0.00 | 2.39 |
| $[Mo_6O_{19}]^{2-}$ | 1.84 | 2.64 |
| $[Mo_7O_{24}]^{6-}$ | 5.82 | 1.81 |
| $[Mo_8O_{26}]^{4-}$ | 1.28 | 2.87 |



**Figure 1**. Optimized geometries of molybdates.

## CONCLUSIONS

The multichannel reactions to form larger polyoxomolybdates have been calculated and will be discussed on detail. The effect on the protonation of the species to the BG, polarizabilities and hyperpolarizabilities will be presented.

## ACKNOWLEDGMENTS

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