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Letter

Quantum Chemical Study on the Multi-Electron Transfer of Keggin-Type Polyoxotungstate Anions: The Relation of Redox Potentials to the Bond Valence of μ_4-O-W

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By selectively investigating the effect of the bond valence using the hypothetical $[(PO_4)W_{12}O_{36}]^{3-}$ species having various bond valences, we could clearly reveal the origin of the linear dependence of the LUMO energy (or the redox potential) on the bond valence. The LUMO of the Keggin-type polyoxotungstates mainly consists of W 5d. The energy of W 5d as well as of the LUMO goes down as the bond valence becomes large (i.e., as the net electron population on W decreases due to the electron-withdrawing effect of the μ_4-O atoms). This is the origin of the linear dependence of LUMO energy on the bond valence.

Keywords: Multi-electron transfer, Polyoxometalate, Polyoxotungstate, DFT, LUMO

1 Introduction

Keggin-type polyoxometalates (POMs) are promising candidates for catalysts to promote proton coupled multi-electron-transfer reactions [1]. Their one-electron redox potentials (in neutral CH_3CN) linearly depend on the bond valence of μ_4-O–M (see Figure 1), and the occurrence of four-electron transfer (in acidified CH_3CN) has been found to be controlled with the bond valence [2,3]. Aiming at designing new Keggin-type POMs to act as a multi-electron transfer catalyst, we tried to elucidate the origin of the linear dependence of the redox potentials on the bond valence.

In a preceding study on Keggin-type tungsten POMs (Keggin-W-POMs) the linear dependence on the bond valence was reproduced by density functional theory (DFT) calculations and confirmed to be related with the changes in the lowest unoccupied molecular orbital (LUMO) energy level due to the electron-withdrawing effect of μ_4-O [4].

In this study, in order to reveal the detailed changes in the LUMO, we have performed DFT calculations of real α-Keggin-W-POM anions ($[(XO_4)W_{12}O_{36}]^z$, X = P, As, Si, Ge, B, Al, Ga) and hypothetical $[(PO_4)W_{12}O_{36}]^{3-}$ species having modified bond valences.

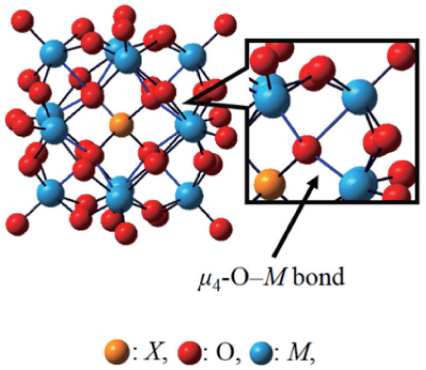

Figure 1. Structure of POM $[(XO_4)M_{12}O_{36}]^z$

Table 1. The calculation results of hypothetical $[(PO_4)W_{12}O_{36}]^{3-}$ species

Bond valence*	Percent components of the LUMO W5d%	Percent components of the LUMO μ_2-O2p%	LUMO level /Hartree	W5d level** /Hartree	μ_2-O 2p level** /Hartree	NEP*** on W
0.224	78.982	15.582	0.1854	−0.0708	0.0970	7.647
0.264	78.973	15.563	0.1848	−0.0739	0.0961	7.640
0.284	78.974	15.555	0.1845	−0.0753	0.0956	7.637
0.320	78.996	15.547	0.1840	−0.0776	0.0948	7.631
0.368	0.905	4.290	0.1477	−0.0803	0.0936	7.622
0.390	0.704	5.646	0.1274	−0.0813	0.0931	7.618

* The bond valence s of the μ_4-O–W bond was calculated using the relation:

$s = \exp[(d_0 - d)/B]$, where $d_0 = 1.917$, d = the μ_4-O–W bond length, and $B = 0.37$. (see Table S2)

** The atomic orbital energy levels were obtained as diagonal elements of Fock matrix.

*** NEP was evaluated as an average of twelve W atoms by subtracting bonding electron contributions from gross electron population.

2 Computational methods

DFT calculations of the above mentioned real and hypothetical Keggin-W-POMs in gas-phase were carried out with the quantum chemistry software NTChem [5]. For the real anions the geometry optimizations were performed without symmetry constraints (C_1 symmetry) using a program library DL-FIND [6]. All calculations were carried out using the ωB97XD functional. The basis set used for all atoms was Def2-SVP, and effective core potentials (ECP) were used for W atoms only. For natural population analysis (NPA) NBO 6.0 program was used.

3 Results and Discussion

The calculation results indicated that the LUMO of real Keggin-W-POM anions consists mainly of W 5d and μ_2-O 2p (Table S1) and that the energy levels of these atomic orbitals change depending on the bond valence, the ionic charge and the nature of the heteroatom X (Figure S1). To discuss the effect of the bond valence independently of the effects of the latter two, DFT calculations and NPA of the hypothetical $[(PO_4)W_{12}O_{36}]^{3-}$ anions with various μ_4-O–W bond lengths were performed. The results show that the contribution of W 5d in the LUMO for the hypothetical anions is around 79% and roughly comparable to that of W 5d in LUMO for the real ones (Table 1, note that the results for the bond valences = 0.368 and 0.390 show too small contributions of W 5d and μ_2-O 2p and thus are excluded from the discussion due to the abnormality, see Figure S3). The LUMO energy goes down as the bond valence becomes large, supporting the linear dependence of the LUMO on the bond valence (see Figure S3). The energy levels of μ_2-O 2p and especially W 5d also go down as the bond valence increases (Table 1). As the lowering in the energy level of W 5d is accompanied with a decrease in the net electron population (NEP) on W atoms, it is suggested that the linear dependence of the LUMO is mainly ascribed to the energy change of W 5d due to the electron depopulation on W atoms (derived by the electron-withdrawing effect of μ_4-O [4]).

4 Conclusion

First-principles DFT calculations of the Keggin-type polyoxotungstate anions were performed to investigate the origin of the linear dependence of the redox potentials on the bond valence. According to the results, the LUMO is mainly composed of W 5d and the atomic orbital is influenced by the bond valence and the ionic charge and the nature of the heteroatom. To isolate the effect of the bond valence from those of the heteroatom and the ionic charge, we have calculated the hypothetical $[(PO_4)W_{12}O_{36}]^{3-}$ species having various μ_4-O–W bond lengths. From the results about the energy level of W 5d and NEP on W, it was suggested that the linear dependence of the LUMO energy on the bond valence should be originated from the change in the energy of W 5d, derived by the electron-withdrawing effect of μ_4-O.

The computations were performed using the Research Center for Computational Science, Okazaki, Japan.

5 Supplementary Materials

Supporting_information.pdf (Table S2, Figures S1–S3)

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