Are the Solvent Effects Critical in the Modeling of Polyoxoanions?

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Abstract: DFT calculations were driven for a set of differently charged polyoxoanions in the gas phase and in solution. We have calculated and analyzed their geometries and orbital energies to trace simple rules of behavior regarding the modeling of anions in isolated form. We discuss the quality of the results depending on the molecular charge, $q$, and the size of the cluster in terms of the number of metal centers, $m$. When the $q/m$ ratio reaches a value of $\sim$0.8, DFT calculations for the isolated anion fail to describe the gap between the band of occupied oxo orbitals and the set of unoccupied orbitals delocalized among the metal atoms. In these cases the incorporation of the stabilizing external fields generated by the solvent through continuum models improves the geometries and orbital energies. © 2004 Wiley Periodicals, Inc. J Comput Chem 25: 1542–1549, 2004

Key words: density-functional theory calculation; polyoxoanion; gas-phase calculation; solvent; COSMO; highly charged anions

Introduction

Polyoxometalates (POMs), or polyoxoanions, are inorganic species that often display high charges and only exist in condensed phases, where the external field stabilizes the anions. However, due to technical limitations, most theoretical calculations driven on POMs assume molecules in the gas phase. Since the first high-level theoretical studies, greater accuracy in the description of POM’s properties, either by applying more exact functions or by introducing additional effects to the target systems, has been the main goal. The environment has been modeled in different ways to account for the external field generated by the solvent molecules and/or by counterions. In the last few years, some theoretical studies of several anions belonging to this family of compounds assumed that the external field generated on the anion is almost isotropic. Consequently, the presence of the solvent or the counterions hardly modifies the properties derived from the sequence of molecular orbitals. It is commonly accepted that many POM properties, such as the relative acid-base properties of the external oxygen sites, the magnetic properties, the encapsulation, etc., can be well described by considering the isolated anion—without including the secondary structure in the calculations. However, we have already noted that to study electron-transfer reactions between differently charged polyoxoanions one needs to incorporate the stabilizing external field into the calculations.

This note is motivated from a routine calculation of the isolated Lindqvist hexaniobate, $\text{Nb}_6\text{O}_{19}^{8^{-}}$, carried out by our group using the BP86 functional. In these conditions, two results were unexpected: the large discrepancy between computed and experimental Nb–O bond lengths (\(\sim\)0.15 Å for Nb–O\(_7\)) and the small gap obtained between HOMO and LUMO of 0.54 eV. The latter point is particularly important because niobates generally have similar electronic spectra (or are slightly shifted toward higher energies) than tungstates. Taking into account that the HOMO–LUMO (H-L) gap for the homologous tungstate $\text{W}_6\text{O}_{19}^{2^{-}}$ is larger than 3 eV, the electronic structure computed for the highly charged $\text{Nb}_6\text{O}_{19}^{8^{-}}$ anion is totally unrealistic. This failure to reproduce the

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Table 1. $q/m$ Ratio, Calculated Bond Lengths (in Å) and HOMO-LUMO Gaps (in eV) for the Series of $[\text{W}_{x}\text{M}_{m}\text{O}_{n}]^{y-}$ Lindqvist Anions ($x = 0–6$, $y = 7$, $m = 0–6$), $\text{W}_{x}\text{O}_{y}^{z-}$, $\text{XW}_{x}\text{O}_{y}^{z-}$ ($X = \text{P, Si}$), $\text{SiM}_{x}\text{W}_{y}\text{O}_{z}^{u-}$ ($X = \text{Nb, Ti}$), Computed in the Gas Phase and with Solvent.

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<th>$d$(M–O)$_y$</th>
<th>H-L gap</th>
<th>$d$(W–O)$_x$</th>
<th>$d$(M–O)$_y$</th>
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<td>1.76–1.77</td>
<td>3.76</td>
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</tr>
</tbody>
</table>

Heteropolyanions

| $\text{PW}_{12}\text{O}_{40}^{3-}$ | 0.25 | $T_{d}$ | 1.73 | — | 2.72 | 1.72 | — | 2.73 |
| $\text{SiW}_{12}\text{O}_{40}^{3-}$ | 0.33 | $T_{d}$ | 1.74 | — | 2.73 | 1.73 | — | 2.76 |
| $\text{NaP}_{7}\text{W}_{12}\text{O}_{40}^{7-}$ | 0.47 | $D_{2h}$ | 1.78–1.79 | 1.94 | 1.77–1.78 | — | — | 1.94 |
| $\text{SiNb}_{6}\text{W}_{7}\text{O}_{24}^{7-}$ | 0.58 | $C_{2v}$ | 1.77 | 1.80 | 2.84 | 1.75 | 1.79 | 2.95 |
| $\text{SiTi}_{3}\text{W}_{9}\text{O}_{40}^{7-}$ | 0.83 | $C_{2v}$ | 1.80–1.81 | 1.76 | 2.43 | 1.76 | 1.74 | 2.60 |

$^a$q/m indicates the (molecular charge)/(metal atoms) ratio.

$^b$M = Nb or Ti.

…

The importance of the negative charge of isolated clusters on their electronic properties may be crucial in some theoretical studies. We performed a series of calculations on a family of fully oxidized POMs to analyze a set of molecules with a variety of size and charge: (1) the relatively small isopolyanions $[\text{W}_{x}\text{M}_{m}\text{O}_{n}]^{y-}$ ($x = 0–6$ and $q = 2–8$) and $\text{W}_y\text{O}_{y}^{z-}$, some of which have high negative charges; (2) the medium-sized Keggin clusters $[\text{XW}_{x}\text{O}_{y}^{z-}]^n$ ($X = \text{P, Si}$ and $q = 3, 4$) and $[\text{SiM}_{x}\text{W}_{y}\text{O}_{z}^{u-}]^n$ ($X = \text{Nb, Ti}$ and $q = 7, 10$) and the large Preyssler anion, $\text{NaP}_{7}\text{W}_{12}\text{O}_{40}^{7-}$, a cluster with a high negative charge but also with a relatively large number of metal atoms. The data discussed arises from full geometry optimizations carried out for all the molecules. We used the ADF package to apply the DFT methodology. The calculations are based on the local density approximation characterized by the Xo model for exchange with Becke’s gradient-corrected functional, and the VWN parameterization for correlation, corrected with Perdew’s functional. We used TZP-quality basis sets and the ZORA approximation for the relativistic effects of the most inert (core) electrons. The calculations were made in the vacuum and including the solvent effects by means of the conductor-like screening model (COSMO) ($\varepsilon = 78$). Additional calculations based on the B3LYP functional with and without the Polarizable Continuum Model (PCM) for the solvent were also performed. For computing this series we used the Gaussian 98 package. The POM clusters presented here contain metal atoms free of valence electrons ($d^0$ electronic configuration), so the molecular orbitals sequence consists of two well-separated sets of energy levels: the occupied oxo orbitals and the virtual metal orbitals. Parameters related to the geometry and electronic structure of the molecules are listed in Table 1. In this series, the results for isolated anions are compared with those for anions in solution, where the solvent is modeled by a dielectric material simulating water. The central magnitude we refer to in this discussion is $q/m$. This represents the ratio between the total negative charge of the anion and the number of metal centers of the framework. The first section of the results concerns the relatively small Lindqvist structure and the heptatungstate anion, $\text{W}_7\text{O}_{24}^{6-}$. In the second section we discuss the results for Keggin and Preyssler heteropolyanions.

Isopolyanions

For the set of $\text{W}_{x}\text{M}_{m}\text{O}_{n}$ Lindqvist anions, it is known that formal substitution of W by Nb diminishes the electron affinity of the framework. This is a result of the larger H-L gaps in POM structures containing Nb, which decrease the oxidizing power compared to oxides of W VI. On the other hand, Ti-derivatives have slightly smaller H-L gaps than analogous tungstates, but fairly similar ones to isostructural tungstates. The $M$–O$_1$ bond lengths computed either in the gas phase or in solution were systematically...
Table 1 shows that, within the gas phase approximation, the quality of the geometry described with DFT decreased steadily in parallel with the overall charge of the molecule. Figure 1 shows the correction introduced to the metal-terminal oxygen distances after accounting for the solvent effects. Two sets of values are plotted: |Δd(M−O)| for M = W and M = Ti or Nb. For the hexatungstate anion, W$_6$O$_{19}^{2-}$, with q/m = 0.33 and a charge of −2, the description of the geometry was fairly accurate in the vacuum, with a deviation from the experimental value of 0.04 Å for d(W−O). Incorporating the solvent effects via the continuum dielectric did not improve the optimized distance. As the negative charge of the system increased, all the gas-phase M=O distances decreased fairly linearly. In the series of Lindqvist anions, the W−O distance was 1.73 Å for W$_6$. This converts into 1.82 Å in the WNb$_5$ structure, which is very poor. The trend was the same for d(Nb−O), but the deviation increased faster because we obtained d(Nb−O) = 1.78 Å for q/m = 0.5 and d(Nb−O) = 1.90 Å with q/m 1.33. The effects of the solvent shortened the M=O bonds by 0.1–0.7 Å, depending on the value of q/m. The other anions in Table 1 behaved similarly. We chose structures with q/m parameters ranging from 0.25 to 0.86. Although these values are not so large, there was also some improvement in the geometries.

Analysis of the electronic structure in the series of Lindqvist anions produces some very interesting results. Figure 2 illustrates the gas-phase energetics of the unoccupied (n−1)d and ns levels respective to the HOMO. For W$_6$, the first unoccupied levels were, as expected, the d(W) orbitals, 3.28 eV above the HOMO, whereas the s(W) set was located 7.4 eV from the oxo band. The W$_6$Nb element of the series behaved in a similar way, because the d orbitals (now a mixture of W and Nb) were again 3.3 eV from the HOMO and the s(Nb) orbitals, although below s(W), were still 5.5 eV higher than the oxo band. Figure 2 shows the drop in the relative energy of the ns orbitals as the q/m value increased. For larger values of q/m, this drop was clear and in WNb$_5$ and Nb$_6$, the s(Nb) levels were 1 and 2 eV below the d(M) band, respectively. The energy of the empty d(M) orbitals remained fairly constant in relation to the HOMO along the series computed in the gas phase without solvent (see Fig. 1). Considering that series W$_6$−Nb$_6$ is isoelectronic, the only change was the number of protons in the nuclei. Therefore, the more external (diffuse) orbitals were less destabilized when one proton was removed from the M$_6$O$_{19}$ framework. The more internal the orbital, the more sensitive to the nuclear charge. This explains the origin of the d/s crossing. This phenomenon is schematically shown in Figure 3. Introducing the solvent effects modified this behavior because each set of orbitals was affected differently by the solvent. The occupied orbitals with a high participation of oxo ligands were the most stabilized because they were the closest to the positively charged surface cavity. As Figure 4 shows, the gap between d(W) and oxo bands grew as the q/m value increased.

Figure 1. Absolute corrections introduced to the gas-phase bond lengths after accounting for the solvent, |Δd(M−O)|, in Å, vs. the q/m parameter for the series of Lindqvist anions, [W$_6$−Nb$_x$O$_{19}$]$^{9−}$, listed in Table 1. Two sets of values for W (filled) and M = Ti or Nb (empty) are represented.
increased. The largest difference occurred for Nb₆ with a relative destabilization of the d(Nb) orbitals by 0.40 eV. The energy of the s(M) orbitals was the least sensitive to the presence of the external field generated by the solvent (Fig. 3) and, in relative terms, the energy of the d(M) orbitals varied more than that of the s(M) band after solvation. For example, the d and s(Nb) bands in Nb₆, a molecule with a negative charge of \(-8\), appeared mixed \(-3.6\) from the oxo band because d(M) had destabilized more than s(Nb) in relation to the HOMO. However, the d(Nb) levels were not completely below the s band, though the blue species contained a dₓᵧ-like metal electron. This is again because of the anion’s large negative charge. For the least charged W₆ anion, the corresponding energies in solution of the d and s metal orbitals were 3.31 and 7.20 eV. The H-L gap agrees with the experimental lowest charge transfer band.

The last two elements of this series, Nb₁₀O₂₆⁻ and W₇O₂₄⁺, had \(q/m\) ratios of 0.60 and 0.86, respectively. The decaniobate anion, with an H-L gap of 3.42 eV in the vacuum, was fairly well described without the effect of the solvent. However, this orbital separation increased considerably when the COSMO was introduced. This gap in solution was 3.65 eV, which was fairly similar to that of the Nb₆ Lindqvist anion. Finally, for the heptatungstate, the H-L gap was 0.24 eV smaller in the isolated form than in solution. In this case, the LUMO mainly comprised d(W) orbitals. The first s(W) levels were found at higher energies, 4.2 eV above the HOMO. In solution this value was larger, following the trend found for the Lindqvist series. Moreover, the relative energy of the s(W) orbitals in the heptatungstate was similar to the 4.51 eV for this set in W₆Nb₃ [both had similar \(q/m\) ratios \((-0.85\)]. The packing in the W₇O₂₄ cluster was less compact than the other isopolyanions shown so far (Fig. 5), so the geometry was somewhat more affected by the solvent effects (see Table 2). X-ray data for W₇O₂₄⁺ was taken from ref. 30 and for Lindqvist anions from ref. 31. All the W—O distances improved after the solvent effects were accounted for. There was a decrease of 0.04 Å in d(W₂—O₂), which was almost identical to the X-ray measurement. There was a generalized shortening (improvement) of the interatomic distances caused by the external field. In the table, for comparison purposes, we also list the homologous M—O distances for the hexatungstate and -niobate. As we discussed above, the computation of W₆ in the gas phase produced very good results, whereas Nb₆, which carried a highly negative charge, was greatly affected by the solvent, and therefore, with a clear contraction of the framework, approached the distances obtained experimentally. However, it was the metal-bridging oxygen distances that remained nearly unchanged in the majority of cases exposed. The terminal and central oxo sites in Nb₆ dramatically approached the metals (by up to 0.08 Å for Nb—O₃) to which they were coordinated. Comparatively, the hexatungstate was almost unchanged by the effects of the solvent.

**Heteropolyanions**

A similar study was performed for several medium-sized and large heteropolyanions. For the simplest molecules of this set, the XW₁₂
(X = P, Si) clusters (with charges $-3$ and $-4$), respectively, the experimental distances were quite well reproduced in isolated form. This may be attributed to a small $q/m$ ratio (Table 1). The correction introduced to the geometries with the COSMO was $-0.01$ Å for W–O bonds. Both Keggin clusters roughly displayed the same H–L gap in the gas phase and in the solution. For larger values of $q/m$, say $\geq 0.5$, as in the Nb- and Ti-derivatives of the Keggin anion, the energy of the LUMO in the solution was somewhat different from the energy in the gas phase. The relative energy of this $d(W)$ orbital increased by 0.11 and 0.17 eV in SiNb$_3$ and SiTi$_3$, respectively. Despite the high charge of $-10$ carried by the SiTi$_3$W$_9$ cluster, the framework contained 12 metal centers ($q/m = 0.83$) and the gas-phase description was still accurate enough. Neither the XW$_{12}$ nor SiM$_3$W$_9$ anions suffered from $ns/(n-1)d$ crossing described for the Lindqvist series.

A great computational effort was done to obtain the gas phase- and solution-optimized structures of the Preyssler anion, NaP$_5$W$_{30}$O$_{110}^{14-}$. This case is especially interesting because it enables us to check anions with a high negative charge but a relatively small $q/m$ value of 0.47. The structure was optimized under the constraints of the $D_{5h}$ symmetry group. The X-ray geometry was well reproduced with the highest deviation in the M–O distances by 0.05–0.06 Å in isolated form. In agreement with this relatively small $q/m$ value, the calculations in aqueous solution hardly changed the geometry determined for the isolated anion. The energy of the $d(W)$ band was also unaltered after the effects of the solvent were included in the calculations. The formation of big (or giant) POMs is generally accompanied by an increase in the negative charge, but the values of $q/m$ remain quite small. Take, for example, Müller’s wheel, whose formula is [Mo$_{154}$(NO)$_{14}$O$_{420}$(OH)$_{28}$(H$_2$O)$_{70}$]$^{255+}$, where $q/m$ is less than

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**Figure 3.** Molecular orbitals scheme for two differently charged polyanions studied in the gas phase and in solution. The gray boxes and the empty boxes denote sets of occupied and unoccupied orbitals, respectively. The gas-phase $ns/(n-1)d$ orbital crossing is marked with dashed lines and discussed in the text. Notice that this is a simplified scheme and that there are also unoccupied $d$ orbitals above the $s$ block.
Figure 4. Energy of the first d(M)-like molecular orbital vs. the \( q/m \) parameter computed (1) in the gas phase (open diamonds) and (2) in solution (solid diamonds) for the series of \( W_{6-x}Nb_x \) anions studied. Notice that for clarity the energy scale in the y-axis is much shorter than that in Figure 2.

Figure 5. Ball-and-stick views for (A) the M6O19\(^{q/m} \) and (B) W7O24\(^{6-} \) anions, with filled spheres representing metal atoms. The point symmetry of the frameworks is \( O_h \) and \( C_{2v} \), respectively, and only the necessary positions are labeled.
This result is especially important because the COSMO treatment of the solvent did not involve a greater computational effort for small molecules. However, for a relatively large system, such as the Preyssler anion, the calculations in solution were ~5 times more demanding than for the isolated anion.

The results discussed up to this point were obtained by means of the BP86 functional and the COSMO method. Let us put to the test the conclusions drawn so far by changing the functional and the solvation model. The series of Lindqvist derivatives were recomputed, making use of the LDA and the B3LYP functionals. In the latter case, the PCM solvation method was used for comparison to the COSMO model. Table 3 contains selected interatomic distances and H-L gaps, computed using LDA and B3LYP functionals for the isolated anions and for the anions in a water solution. The reader may find that there are great similarities between the sets of data contained in Tables 1 and 3. In addition to the well-known behavior of the LDA distances, in general shorter than the BP86 or B3LYP ones, the only noticeable difference is that the H-L gaps are slightly larger with the B3LYP functional. This behavior was already reported by Bridgeman, and does not modify the conclusions emerged from the systematic study using the BP86 functional.

To sum up, independently of the functional, we find that the gas-phase results show that higher charges of the anion lead to (1) longer M-O distances, and (2) smaller H-L gaps. In absolute terms, this energy gap is characteristic of the functionals themselves, but the tendency is to be smaller as the charge increases in all cases. The incorporation of the solvent in the calculations

Table 2. Selected Interatomic Distances (in Å) for $W_7O_{24}^6/H_11002$, $W_6O_{19}^2/H_11002$, and $Nb_6O_{19}^8/H_11002$, Computed in the Gas Phase and in Solution, Together with X-ray Parameters.

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<th>Molecule</th>
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The labels in the left-hand column correspond to those shown in Figure 5.

Table 3. $q/m$ Ratio, Calculated Bond Lengths (in Å) and HOMO-LUMO Gaps (in eV) for the Series of $[W_6–Nb_6O_{19}]^{q/m}$ Lindqvist Anions ($x = 0–6$), Computed with the LDA and the B3LYP Methods in the Gas Phase and with Solvent.

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<th>d(Nb—O$_x$)</th>
<th>H-L gap</th>
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<td>0.67</td>
<td>$C_{2v}$</td>
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<td>$O_h$</td>
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<td>—</td>
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LDA calculations were performed with the ADF set of programs and the solvent was modeled by the COSMO procedure. Geometries were optimized in vacuum and in solution. For the B3LYP calculations the GAUSSIAN 98 package was used, and single-point water solution calculations were carried out with the PCM solvation method. The gas-phase geometries were not reoptimized in solution for the B3LYP/PCM calculations because the convergence procedure was extremely slow in GAUSSIAN 98 runs.
always leads to an enlargement of the H-L gap. This broadening is proportional to the charge of the anion.

Conclusions

In this article, we have compared the electronic properties of anions in isolated form and in solution. Bearing in mind that polyoxometalates (or polyoxoanions) only exist in condensed phases, their theoretical modeling must reproduce their behavior in solution. The gas-phase approximation may be satisfactory to study some chemical properties for low values of $q/m$; $q =$ charge and $m =$ number of metal centers. However, it is strictly necessary to incorporate the solvent effects in the calculations when $q/m \geq 0.8$. For example, the HOMO–LUMO gap improves simply by accounting for the external electrostatic effects generated by the solvent molecules. These theoretical results also show that the structures optimized in solution are always better than those for the isolated molecule. The iso- and heteropolyanions studied here follow the same trend irrespective of their shape. In addition, different computational methods and solvation models have been tested, always leading to the same trend.

Acknowledgments

The authors thank the reviewers’ comments.

References

16. The reader is warned that the use of the ZORA in the present calculations may change some DFT results published before by our groups.

26. The structural information on polyoxometalates containing Ti is scarce and unclear. X-ray diffraction data normally show disorder, and Ti=O distances are, in general, not accurately measured.
29. In the COSMO method, the solvent is modeled by a set of point charges distributed over a surface cavity surrounding the solute molecule.
32. The electronic structure of [XpW6O19]8− will be discussed in detail elsewhere.
35. Calculations characterized by the LDA functional (both in the gas phase and with the COSMO method for the solvent) were carried out with the ADF program. The B3LYP calculations were carried out with the Gaussian 98 package. In this case, the PCM solvent method was applied in single-point calculations, so no structural parameters are included for this case in the table.