



THEORETICAL STUDY OF POLYOXOVANADATES: ANALYSIS OF STRUCTURAL, MAGNETIC AND TRANSPORT PROPERTIES

Almudena Notario Estévez

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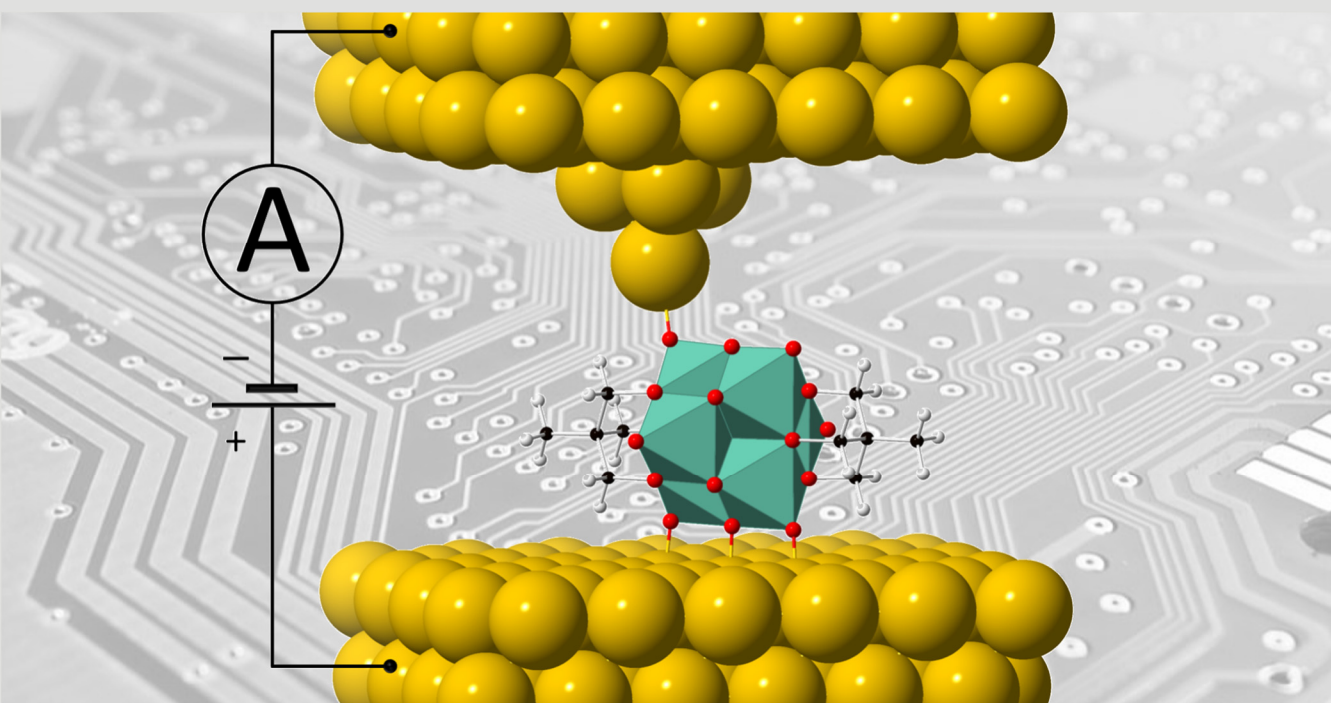
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UNIVERSITAT
ROVIRA I VIRGILI

Theoretical Study of Polyoxovanadates: Analysis of structural, magnetic and transport properties.

ALMUDENA NOTARIO ESTÉVEZ



DOCTORAL THESIS
2021

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DOCTORAL THESIS

Supervised by

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Departament de Química Física i Inorgànica
Grup de Química Quàntica



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Departament de Química Física i Inorgànica

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FEM CONSTAR QUE aquest treball, titulat

"Theoretical Study of Polyoxovanadates: Analysis of structural, magnetic and transport properties"

que presenta Almudena Notario Estévez per a l'obtenció del títol de Doctor, ha estat realitzada sota la nostra direcció al Departament de Química Física i Inorgànica d'aquesta universitat.

Tarragona, 12 de Febrer de 2021

Els directors de la tesi doctoral

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Collaborations

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List of Publications

The following scientific publications have been achieved during the Ph. D.

(1) Kozłowski, P.; Notario-Estévez, A.; de Graaf, C.; López, X.; Monakhov, K. Y. **Reconciling the Valence State with Magnetism in Mixed-Valent Polyoxometalates: The Case of a $\{VO_2F_2@V_{22}O_{54}\}$ Cluster.** *Phys. Chem. Chem. Phys.* **2017**, *19*, 29767.

(2) Notario-Estévez, A.; Kozłowski, P.; Linnenberg, O.; de Graaf, C.; López, X.; Monakhov, K. Y. **Decoding the Role of Encapsulated Ions in the Electronic and Magnetic Properties of Mixed-Valence Polyoxovanadate Capsules $\{X@V_{22}O_{54}\}$ ($X = ClO_4^-$, SCN^- , $VO_2F_2^-$): A Combined Theoretical Approach.** *Phys. Chem. Chem. Phys.* **2018**, *20*, 17847.

(3) Linnenberg, O.; Moors, M.; Notario-Estévez, A.; López, X.; De Graaf, C.; Peter, S.; Baeumer, C.; Waser, R.; Monakhov, K. Y. **Addressing Multiple Resistive States of Polyoxovanadates: Conductivity as a Function of Individual Molecular Redox States.** *J. Am. Chem. Soc.* **2018**, *140*, 16635.

(4) Albert Solé-Daura, Almudena Notario-Estévez, Jorge J. Carbó, Josep M. Poblet, Coen de Graaf, Kirill Yu. Monakhov and Xavier López. **How Does the Redox State of Polyoxovanadates Influence the Collective Behavior in Solution? A Case Study with $[I@V_{18}O_{42}]^q^-$ ($q = 3, 5, 7, 11$, and 13).** *Inorg. Chem.* **2019**, *58*, 3881.

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Overview of the Thesis

New technological applications for electronics are being investigated by a large and very active scientific community. These are aimed at covering new demands for smaller, more powerful electronic systems present in our daily lives, such as computers or mobile phones. Among the great variety of candidate materials being developed for these goals, polyoxovanadates (POVs) constitute a family that, because of their unique chemical and structural characteristics, has awoken interest in me. This Ph.D. thesis is first and foremost aimed at enlarging the knowledge on promising molecules and devices for cutting-edge technology. It is based on computational work done on a series of POV systems for which experimental data is available. What is more, a large part of the theoretical research herein presented, and the associated publications, has been carried out in collaboration with the experimental group of Prof. Monakhov (Aachen, Leipzig, Germany).

POVs constitute a promising subclass of polyoxometalates (POMs), a large family of molecular inorganic systems that have found their way into real-world applications in fields as medicine and catalysis, among others. The POVs are also finding potential applications in a range of areas such as materials engineering, information and energy storage, and molecular magnetism.

The first three chapters of the thesis are introductory. A historical perspective and the essentials of POV structures, properties and applications are described in Chapter 1, with allusion to the role of Computational Chemistry in the study of POMs. Chapter 2 starts with an overview of widely used surface science techniques followed by an introduction to the computational approach applied to study molecular conductivity, namely non-equilibrium Green's Function theory. Chapter 3 outlines the specific objectives of this thesis.

The next three chapters of the thesis present the research done in the last four years in the Quantum Chemistry Group at the URV. Chapters 4 and 5 put the focus on the conductivity of two POV types. One type is derived from the classical V_6O_{19} POM-like structure, with initially completely oxidized vanadium atoms (Chapter 4). The other systems under study are $V_{18}O_{42}$ arrangements, naturally

featuring unpaired valence metal electrons (Chapter 5). Lastly, Chapter 6 is devoted to the in-depth study of the electronic structure and complex magnetism of several host-guest systems based on the $V_{22}O_{54}$ architecture.

Chapter 4 can be divided in two main sections: The first part is dedicated to the adsorption of two functionalized POVs, $[V_6O_{13}\{(OCH_2)_3CCH_2SR\}_2]^{2-}$ ($R = Me, Ph$) on a gold surface, and in the second part we focus on their conductivity. Experimentalists showed that these compounds are adsorbed on gold with no particular ordering, both keeping their initial fully oxidized states when adsorbed. With this setup, conductivity measurements suggest several reduction processes taking place on the POV unit at different external voltages. Our computational structural analysis corroborates the observations by virtue of the several energetically degenerate adsorption positions and orientations that both V_6 systems present. Conductivity calculations support the experimentally observed connection between step-like increase of conductivity and the reduction of the POV as the external applied potential varies. With these calculations we have concluded also that the responsible for conductivity are the vanadium atoms of the POV.

Another very interesting POV system is $[I@VO_{42}]^{q-}$, by virtue of how accessible different redox states are. An extensive analysis of its properties is made in Chapter 5. Electronic structure calculations with $q = 3, 5, 7, 11$, and 13 show that the valence metal electrons tend to be delocalized over all the vanadium atoms of the POV cage. Initially, we loosely argued that the V_{18} system might have conductivity properties similar to V_6 . For this reason, we explore its adsorption on gold and its conductivity depending on the oxidation state. Calculations made on a variety of surface positions and orientations show that all adsorption energies are similar, suggesting a patternless adsorption for V_{18} , resembling that for V_6 . In terms of conductivity, we did not conduct a deep study, although, with the results obtained, we claim that V_{18} and V_6 behave differently. In particular, we do not expect a step-like behaviour of conductivity vs an applied potential for V_{18} . This fact is ascribed to the large number of transmittance peaks that V_{18} exhibits near the Fermi level in its resting state and that they do not vary much between the different degrees of reduction explored.

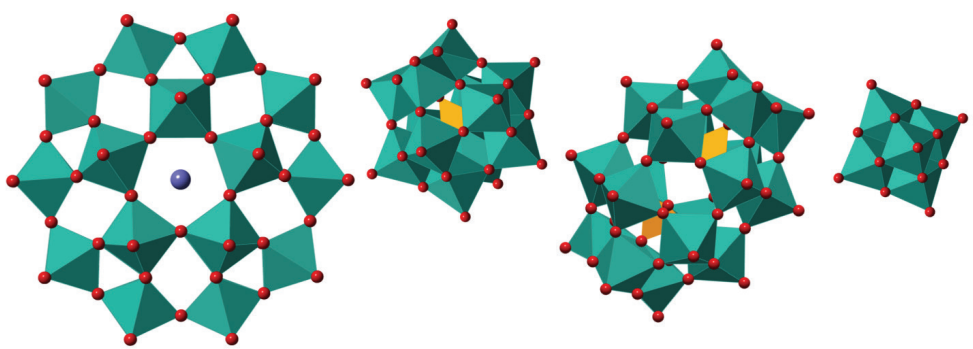
Chapter 6 analyses the electronic structure and magnetism of three mixed-

valent, host-guest $\{X@V^{IV/V}_{22}O_{54}\}$ POVs with diamagnetic template anions ($X = ClO_4^-$, SCN^- , and $VO_2F_2^-$). We apply density functional theory (DFT) and model Hamiltonian calculations. The form of the t-J like model Hamiltonian is dictated by the acquired DFT data and the valence state used in DFT calculations has been suggested by fittings to experimental magnetic data with the model Hamiltonian. This self-consistent approach breaks through the magnetochemical limitations of these compounds, giving results fully concordant with the experiment and allowing us to determine the valence state of the three different compounds. It is demonstrated that the guest anions weakly interacting with the molecular POV host-shell strongly influence the electronic and magnetic properties of the system, leading to various valence states of vanadium and modifying V–O–V exchange interactions.

Finally, the main conclusions and scientific progress made during this Ph.D. thesis are summarized in Chapter 7.

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D I S C O V E R



CHAPTER I

Discovering Polyoxovanadates

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CHAPTER 1

Discovering Polyoxovanadates

In this chapter we present an introduction to polyoxovanadates (POVs), describing their structure, main features and applications. First, we briefly define what polyoxometalates are to understand better the subfamily of polyoxovanadates. Then, the structure and synthesis of POVs are summarized. Later, their most important features and applications are shown. Finally, we take a look at the theoretical modeling of POMs during the last years.

1.1 Overview of Polyoxometalates

Polyoxovanadates —POVs for short— are a subclass of the polyoxometalate (POM) family, which constitute a large group of inorganic, generally anionic, molecular metal oxides. POMs have been investigated for many years, the first paper “Chemische Untersuchung über das Molybdänum oder Wasserbley” (Chemical studies on molybdenum or water lead)¹ being published in 1778 by Swedish chemist C. W. Sheedle, who characterized blue water solutions of “molybdenum blue” formed by oxidation of MoS₂ observed in some springs in Idaho Springs (Colorado) and in the Valley of Ten Thousand Smokes (Alaska). Around thirty years later, Berzelius reported the phosphomolybdic acid, H₃PMo₁₂O₄₀, as the product of the reaction between ammonium molybdate and phosphoric acid,² although its structure was not determined. Thirty-six years later, C. Marignac reported two structural forms of the silicotungstic acid, H₃SiW₁₂O₄₀, known nowadays as the α and β isomers.³ However, it was not until the 20th century when the structural features of POMs started to be revealed thanks to the improvement of spectroscopic techniques, like X-Ray diffraction. Scientists as Miolati and Pizzighelli, with the contribution of Pauling,^{4,5} Keggin,⁶ Bradley and Illingworth,⁷ Evans,⁸ and Dawson studied their structure.⁹ With some of these contributions, names as Keggin or Dawson became familiar in the POMs’ world.

4 | 1.2 Structure and Synthesis

During the last decades, the popularity of POMs has grown even more with the improvement of analytical and computational techniques.

POMs are inorganic compounds, typically anionic, made of oxygen and group-VI or -V transition metal atoms in their highest oxidation states, that is, with a d^0 or d^1 valence electronic configuration. Structurally, they can be viewed as aggregates of $\{MO_x\}$ units, where M (called the *addendum* atom by its position in the structure) is Mo, W or less commonly V, Nb and Ta, and $x = 4-7$, being the pseudo-octahedral coordination $\{MO_6\}$ the typical one (Figure 1.1 a). $\{MO_x\}$ units are linked to each other by sharing corners or edges (Figure 1.1 b), and less commonly faces (as in the $CeMo_{12}O_{42}^{8-}$ anion). The most common and stable POM structures reported are closed-shaped 3-dimensional frameworks.¹⁰⁻¹²

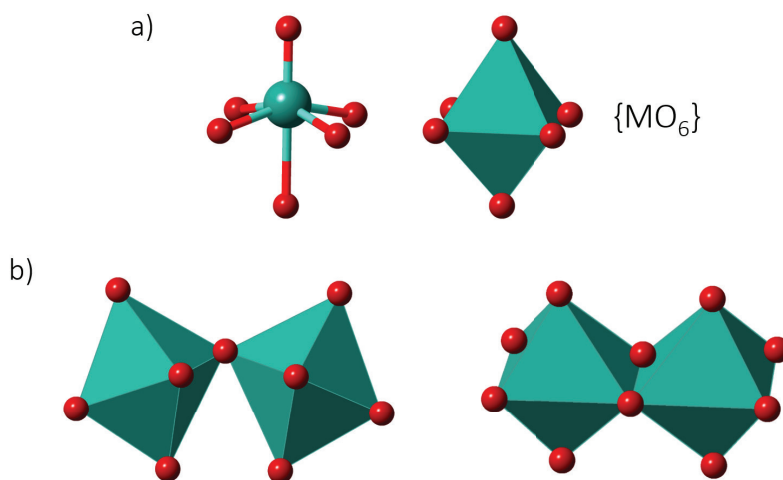


Figure 1.1 | a) Ball-and-stick and polyhedral representation of the $\{MO_6\}$ unit. b) Polyhedral representation of the main linkage patterns in POM structures.

In addition to the mentioned transition metals and oxygen, virtually any other element can be, in principle, incorporated to a POM structure, either in substitution of addenda metals (external framework) or occupying internal positions of the closed-shaped aggregate. In the latter case they receive the name of *heteroatoms*. Depending on the presence or not of heteroatoms, POMs can be structurally classified into two groups:¹³

- **Isopolyanions:** metal oxide frameworks without internal heteroatom or heteroanion with general formula $[M_nO_y]^{q-}$. They are often more unstable than their heteropoly- counterparts.¹⁴ The most well-known structure of this family is the Lindqvist structure, $[M_6O_{19}]^{q-}$ (Figure 1.2, left).

- **Heteropolyanions:** they include heteroanions such as SO_4^{2-} and PO_4^{3-} inside the structure. The general formula is $[X_2M_nO_y]^{q-}$ and examples of this class of POMs are Keggin, Wells-Dawson and Preyssler structures, shown in Figure 1.2.

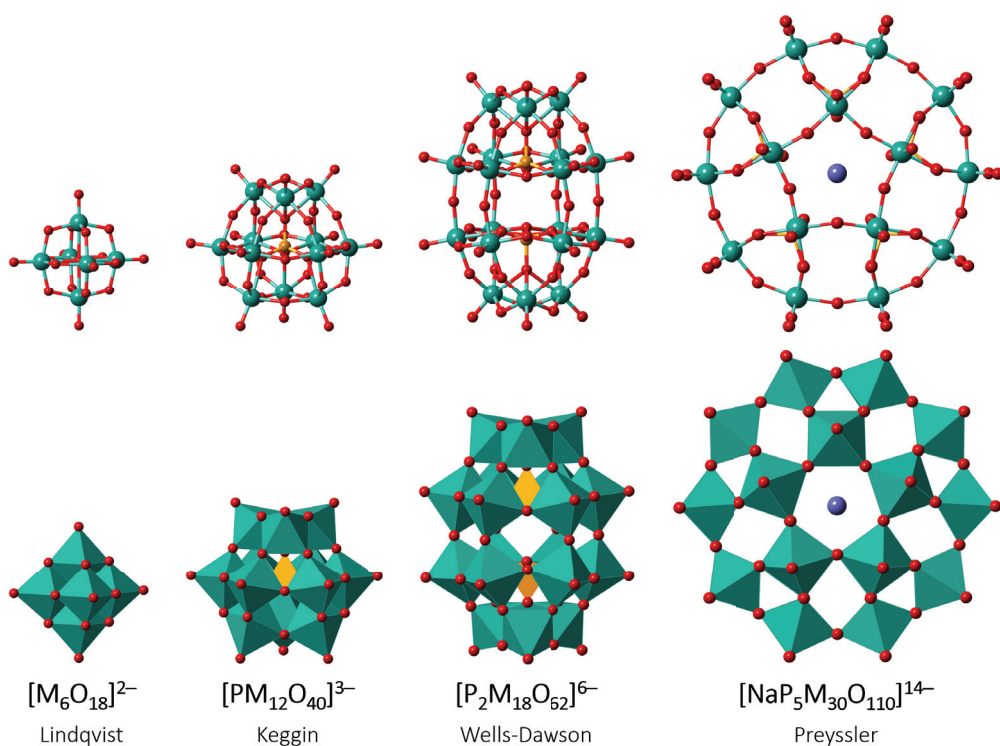


Figure 1.2 | Ball-and-stick and polyhedral representation for the most typical POMs. Orange polyhedra contain the heteroatom, turquoise octahedra represent MO_6 units.

The synthesis of these structures is quite simple, typically occurring via condensation reactions of the hydroxide complexes of molybdenum(VI), tungsten(VI) or vanadium(V) under acidic conditions. In general, the synthetic

6 | 1.2 Structure and Synthesis

routes of ordinary POMs have a few steps, or even just one in the so-called 'one-pot synthesis'. Nevertheless, the formation of POMs strongly depends on the experimental conditions. There can be several synthetic variables to be tuned for obtaining different POMs, such as pH, concentration, metal-oxide reactant anion, heteroatom, temperature, reaction solvent, presence of additional ligands or the presence of a reducing agent.¹³

Besides all these variables, POMs can be functionalized after formation to give additional characteristics. For example, the functionalization with organic ligands, as alkoxylation,^{17–24} but also their immobilization on surfaces as Au,^{24,25} Ag,²⁶ or HOPG (highly oriented pyrolytic graphite),^{27–29} among others, for future applications. As mentioned above, addenda atoms can be replaced by other transition metal atoms to change the properties of the POM. In addition, POMs can form supramolecular structures of metal-organic frameworks (MOFs) type, with cationic metal complexes or by themselves.³⁰

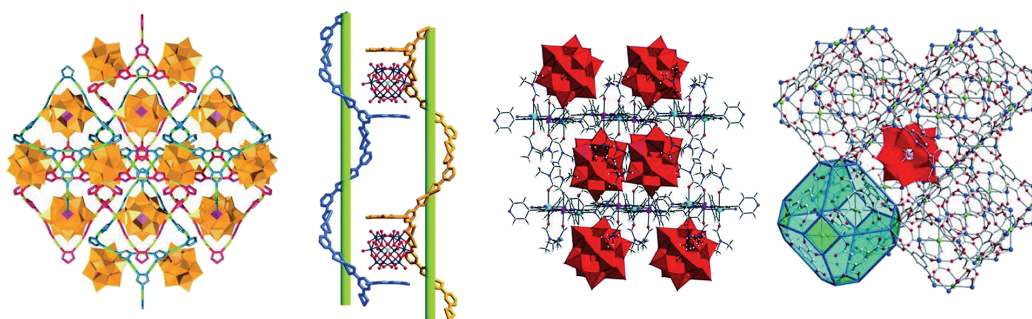


Figure 1.3 | Polyhedral and ball-and-stick representation of different POM@MOFs supramolecular structures. Figure taken from ref. 32.

So, these many variables can tune the structure and properties of POMs leading to a vast number of compounds and supramolecular arrangements with different potential technological applications.³¹

1.2 Structure and Synthesis

Polyoxovanadates, as explained before, are a subclass of POMs with vanadiums as principal metal atoms. While polyoxotungstates and -molybdates basically present MO_6 building blocks, vanadium as addendum atom is more versatile and can be present as tetrahedral $[\text{VO}_4]$, square pyramidal $[\text{VO}_5]$ or octahedral $[\text{VO}_6]$ building block. POVs presenting VO_6 units are structurally equivalent to classical POMs since the coordination is the same as for Mo and W. Besides that, vanadium shows common oxidation states between +2 and +5. The versatility of coordination environments and of vanadium oxidation states combined make POVs a rich subclass of compounds within the family of polyoxometalates.

On the other side, the lower oxidation state of vanadium compared to that of Mo or W can make POVs less stable than Mo- or W-based POMs. For example, for $[\text{Mo}_6\text{O}_{19}]^{2-}$ and $[\text{V}_6\text{O}_{19}]^{8-}$ Lindqvist structures, the molecular charge goes from -2 to -8 , a huge increase with implications in stability. Taking the Keggin framework, the charge difference is also large, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ vs $[\text{PV}_{12}\text{O}_{40}]^{15-}$. Organic functionalization of POVs constitutes a way to decrease the molecular negative charge, such as the Lindqvist-type case. Stabilization of the $[\text{PV}_{12}\text{O}_{40}]^{15-}$ framework can be achieved by formal incorporation of two $[\text{VO}]^{3+}$ units and subsequent protonation of the new cluster to obtain the $[\text{H}_6\text{PV}_{14}\text{O}_{42}]^{5-}$ structure. Then, using oxovanadate building units with less oxygens is a good alternative to get less charged POVs.^{32,33} Figure 1.4 represents some vanadate aggregates where different coordination spheres and linkage modes adopted by vanadium are distinguished: in the top row, all vanadium atoms present tetrahedral coordination, whereas $[\text{V}_{10}\text{O}_{28}]^{6-}$ formally has octahedral units in an isopolyanion-type arrangement, and the last two structures ($[\text{V}_{12}\text{O}_{32}]^{4-}$ and $[\text{V}_{16}\text{O}_{42}]^{4-}$) feature square pyramidal vanadium coordination.

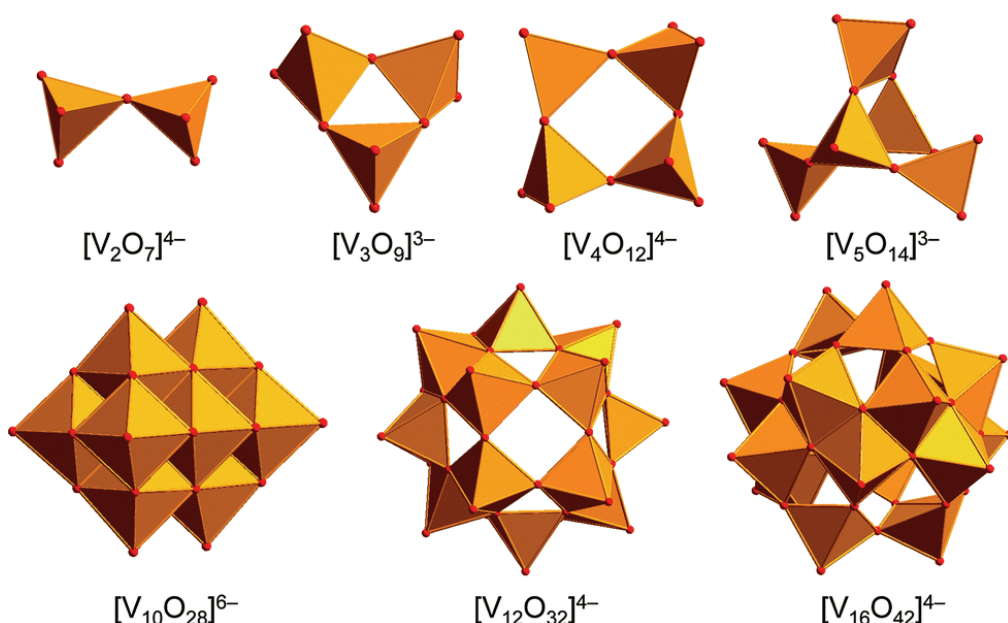


Figure 1.4 | Polyhedral representation of various polyoxovanadates where vanadium atoms present different coordination. Figure taken from ref. 34. Colour code: red balls: oxygen; orange polyhedral: V^VO_x .

Besides the flexibility of vanadium coordination in POVs, it is worth mentioning that some of these compounds present internal moieties such as anions or water, which are assumed to act as *templates* during POV formation. These can be classified in:

- Strongly interacting anionic units:** As we have explained before for POMs, some anions such as SO_4^{2-} and PO_4^{3-} can be found inside the structure. These units are $[XO_x]^{n-}$ tetrahedral or octahedral oxo-anions and are strongly electrostatically interacting with vanadium atoms of the cluster with O_x-V distances ca. 2.5–2.7 Å. An example of this unit is the $[H_6PV_{14}O_{42}]^{5-}$ structure, where a PO_4 is inside the POV with O_P-V distances ca. 2.35–2.40 Å. This kind of units are the ‘classical’ oxoanions. Nevertheless, there are also units as the oxomanganate or oxocobaltate,^{35,36} or other transition metals as Pd, Cu or Ni.³⁷
- Weakly interacting anionic or non-ionic units (host-guest chemistry):** The internal anions or non-ionic units can be halides, pseudohalides, inorganic or

organic guest. These templates interact via very weak electrostatic or van der Waals forces, with distances around 3.5–4.0 Å. Examples of these anionic units are: Cl^- , Br^- , I^- , SH^- , HCOO^- , CN^- , CO_3^{2-} , NO^- , NO_3^- , N_3^- , SCN^- , ClO_4^- or VO_2F_2^- , among others.^{38–44}

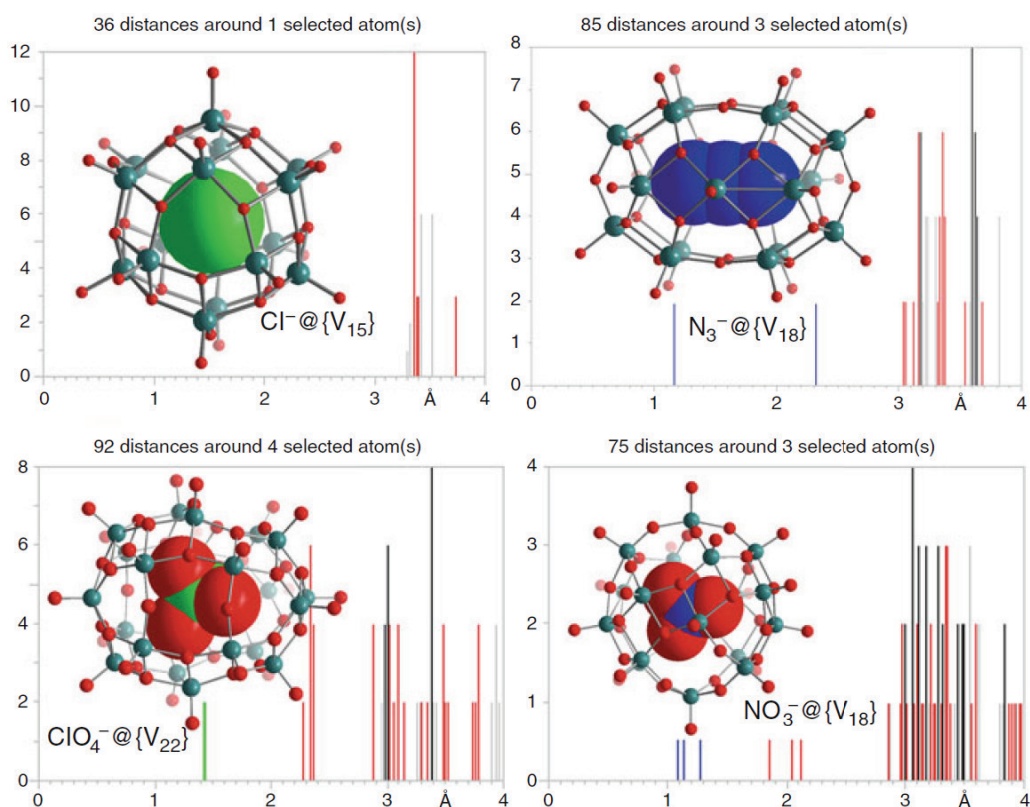


Figure 1.5 | Examples of weakly interacting internal anionic units. Histograms represent the atomic distances around the central template (red: oxygen distances; black/gray: vanadium distances). Figure taken from ref. 33.

Another classification that can be made to POVs refers to their structure:³⁰

- **POVs without organic groups:** these structures do not have any additional organic group or ligand. The most common isopolyoxovanadate (isoPOV) is the decavanadate, with general formula $[\text{H}_n\text{V}^{\text{V}}_{10}\text{O}_{28}]^{(6-n)-}$, shown in Figure 1.4. Other cases are $[\text{V}^{\text{V}}_3\text{O}_9]^{3-}$,⁴⁵ $[\text{V}^{\text{V}}_4\text{O}_{12}]^{4-}$,⁴⁶ $[\text{V}^{\text{IV}}_5\text{V}^{\text{V}}_{12}\text{O}_{42}]^{4-}$,⁴⁷ and $[\text{V}^{\text{IV}}_{16}\text{V}^{\text{V}}_{18}\text{O}_{82}]^{10-}$.⁴⁸ However,

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during the synthesis it is possible to obtain other types of POVs without organic groups but not being strictly isoPOVs. POVs can present mono- or multivacancies (lacunary POVs). Figure 1.6 shows three examples of lacunary POVs, where a) and b) represent related structures with one or three vacancies, respectively. Host-guest POVs also belong to this classification. POVs can also contain transition metal or lanthanide atoms. Apart from the latter elements, semimetals as Si(IV), Ge(IV), As(III), or Sb(III) can also decorate POVs, altering structural, electronic, and magnetic properties of this class of polyoxometalates.

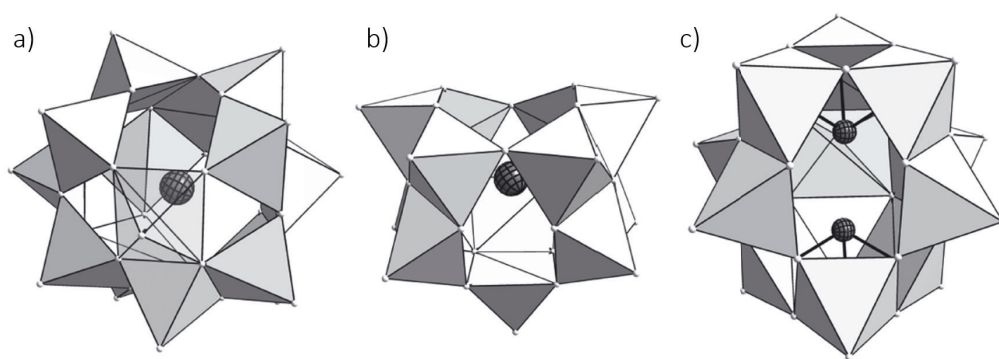


Figure 1.6 | Examples of lacunary POVs. a) $[\text{Cl}@\text{V}^{\text{IV}}_4\text{V}^{\text{V}}_{12}\text{O}_{36}]^{5-}$, b) $[\text{Cl}@\text{HV}^{\text{V}}_{12}\text{O}_{32}]^{5-}$, and c) $[\text{F}_2@\text{HV}^{\text{V}}_{11}\text{O}_{29}]^{5-}$. Colour code: $\text{V}^{\text{IV/V}}\text{O}_5$, grey and transparent polyhedral; O, white; Cl and F, hatched dark grey spheres. Hydrogens are omitted for clarity. Figure taken from ref. 49.

- **POVs with organic groups:** the first subgroup we can clearly define is that with the organic group covalently bonded to a vanadium center, or a semimetal when the cluster is a heteropolyoxovanadate (heteroPOV), as for example $[\text{V}^{\text{IV}}_{16}\text{Sb}^{\text{III}}_4\text{O}_{42}(\text{H}_2\text{O})\{\text{V}^{\text{IV}}\text{O}(\text{C}_6\text{H}_{14}\text{N}_2)_2\}_4]$, where four vanadium atoms are linked to an organic group, see Figure 1.7 a.⁵⁰ Another type is the Lindqvist-type hexavanadate, which it can only be isolated when stabilized with organic groups such as trisalkoxo ligands, see Figure 1.7 b).^{15,51} Finally, POVs can be part of MOFs but these are still rare. One example is $[(\text{V}^{\text{IV}}_4\text{V}^{\text{V}}\text{O}_9\text{Cl})_3(\text{TDA})_6]^{6-}$ (TDA = thiophene-2,5-dicarboxylate), which presents a triangular structure (Figure 1.7 c).⁵²

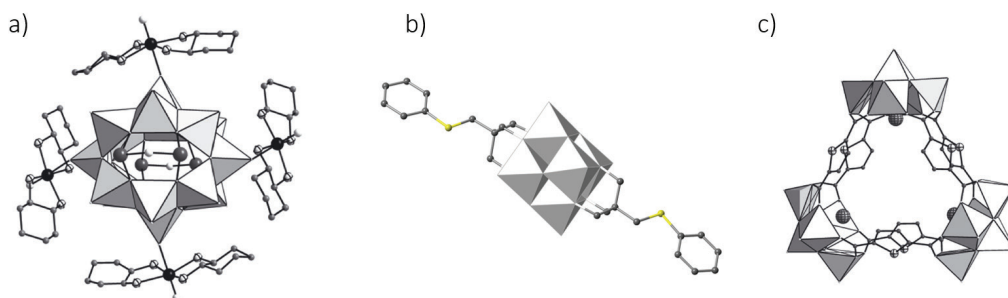


Figure 1.7 | Examples of POVs with organic groups. a) $[V^{IV}_{16}Sb^{III}_4O_{42}(H_2O)\{V^{IV}O(C_6H_{14}N_2)_2\}_4]$, b) Lindqvist-type $[V_6O_{13}\{(OCH_2)_3CCH_2SPh\}_2]^{2-}$ c) Example of POV-based metal organic assembly $[(V^{IV}_4V^{VO}_9Cl)_3(TDA)_6]^{6-}$. Colour code: VO_n , gray polyhedral; O, white; C, small gray, N, little hatched, V, black; Sb, gray; S, small yellow, Cl, hatched. Hydrogen atoms are omitted for clarity. Images a and c taken and adapted from ref. 49.

POVs can also be divided into four general families depending on their oxidation state. The first one is the **fully-oxidized** structure where all vanadium atoms in the structure are V^V (d^0); the **mixed-valent** (V^V/V^{IV} or V^{IV}/V^{III}); the **fully-reduced** (V^{IV} , d^1) and the **highly-reduced** where vanadium atoms are V^{III} (d^1).³⁴ A series of fully-oxidized POVs are shown in Figure 1.4. Mixed-valent POVs are $[V^{IV}_3V^{V}_{13}O_{42}]^{7-}$, $[V^{IV}_{16}V^{V}_2O_{42}]^{10-}$, $[V^{IV}_8V^{V}_{10}O_{42}]^{4-}$, and $[V^{IV}_8V^{V}_{14}O_{54}]^{6-}$.^{40,41,53} Mixed-valent V^{IV}/V^{III} and highly reduced POVs are mostly a variety of vanadium alkoxide structures and they are not discussed in this thesis.

The synthesis of POVs in aqueous solution is problematic since over a wide range of pH (2 to 6, approximately) the reaction product is $[H_xV_{10}O_{28}]^{(6-x)-}$ (Figure 1.4 and Figure 1.8) since it is thermodynamically the most stable POV in these conditions. Nevertheless, in basic media the result is obtaining these two species: VO_4^{3-} or VO_3^- . So, it is quite complicated to synthesize different POVs in aqueous solution. However, different routes to obtain a wide range of POVs is possible in other solvents, such as acetonitrile (MeCN), dimethyl sulfoxide (DMSO) or dimethyl formamide (DMF). The main difference between aqueous and organic solutions are changes in reaction intermediates.³³

12 | 1.2 Structure and Synthesis

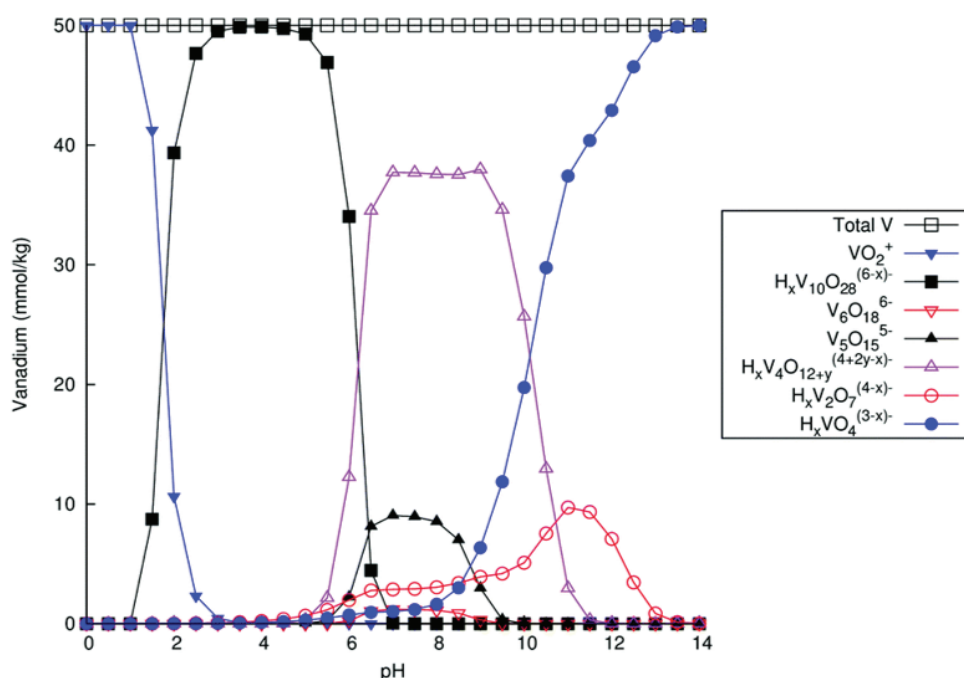


Figure 1.8 I. Diagram showing the amount of different POVs depending on the pH in aqueous solution. Figure taken and adapted from ref. 54.

Besides the solvent, the resulting structure can be tuned upon changes in the oxidation state of the vanadium atom. For example, using V^V in aqueous acidic conditions produces the decavanadate, but using the reduced form V^{IV} the resulting structure is $[V_{18}O_{42}]^{9-}$. Whereas the decavanadate contains octahedrally coordinated V^V atoms and the product is formally fully oxidized, the $[V_{18}O_{42}]^{9-}$ structure is based on VO_5 moieties and vanadium atoms are mixed-valent ($V^{IV/V}$). Also, these molecules are different in the V:O ratio, which is smaller in $[V_{18}O_{42}]^{9-}$, stabilizing the V^{IV} atom. In addition to the solvent, the pH and the oxidation state of vanadium atoms, other parameters such as temperature, heteroatom and the presence of ligands, among others, can also be modified as for POMs in general.

1.3 Features

The characteristics of POVs are, globally, similar to those of POMs, despite the fact that POVs are structurally more versatile because they present a major flexibility in the addenda coordination, as mentioned above. Some of these features are:³¹

- Anionic species
- Brønsted acids
- High solubility in water and in polar organic solvents
- Stable in water and air in a wide range of temperatures

Nonetheless, there are more properties characterizing them and making them very attractive for later applications in magnetism and catalysis, among others. The most important features of POVs are explained in more detailed below.

1.3.1 Host-guest chemistry

In the Structure and Synthesis section, a classification regarding the interaction of templates inside the POV has been made. One of the types refer to POVs with weakly interacting units. Many POV structures are sphere-like, typically with an internal cavity (see Figure 1.5) as a consequence of the square pyramidal coordination that vanadium atoms can present. This arrangement is related to POVs accommodating small species in their central voids forming host-guest systems through weak electrostatic and van der Waals forces.³³ This behaviour is reminiscent of, for example, fullerenes, which act as 'molecular containers'.^{34,49} POVs can host various species such as neutral or charged inorganic and organic moieties such as water, SCN^- , ClO_4^- , I^- , Br^- , and HCOO^- . Müller, Reuter, and Dillinger wrote in 1995: "In our opinion, isopolyoxovanadates currently present the most instructive examples for the inorganic chemistry of host-guest species".⁵⁵ This feature makes that a particular pseudo-spherical POV (the host: $\text{V}_{18}\text{O}_{42}$ or $\text{V}_{22}\text{O}_{54}$, for example) can present different electronic and chemical features depending on the guest species that, ultimately, define their potential properties and applications.

1.3.2 Mixed-valent compounds

We begin by defining what a mixed-valent compound is. Some molecules present 'mixed valency', also called 'mixed oxidation state' or 'nonintegral oxidation state'. Such an inorganic or metal-organic compound presents an element in more than one oxidation state.⁵⁶ In 1967, Robin and Day published a review on mixed-valence systems and proposed that the properties of such compounds could be classified according to their molecular or crystal structure.⁵⁷ Robin and Day differentiate between three different classes of mixed-valent compounds. Consider a metal appearing in two different oxidation states and occupying two distinguishable sites in the crystal. If the sites are very different the electrons will be completely trapped (class I). If, on the other hand, they are completely indistinguishable, the compound is class III, with a genuinely nonintegral valence. In between these two extremes lies class II, in which the sites are different but not too much. In vanadium oxides, like POVs, the V:O ratio for a mixed-valent compound between $V^{III/IV}$ is in the range of 1:1.5 and 1:2. Instead, for $V^{IV/V}$ is in the range of 1:2 and 1:2.5. Examples of the $V^{IV/V}$ case are the $V_{18}O_{42}$ cluster, where the ratio is of 1:2.33 and $V_{22}O_{54}$ with a ratio of 1:2.45.

1.3.3 Redox properties

One of the most important and widely studied features of POMs, and POVs, is their rich redox chemistry. In general, they are (strong) oxidizing agents, so they can accept electrons easily. POVs are formed by V^V (or some V^{IV}), usually with d^0 (or d^1) electronic configuration linked to O^{2-} ligands. The valence shell of metals (d orbitals) is formally empty, then POVs are capable to accept easily electrons without important structural changes. M. T. Pope classified POMs in two wide groups upon their redox properties:¹¹

- **Type I:** the metal atoms have only one terminal oxygen. They are easily reduced and reoxidized in a reversible process.
- **Type II:** the metal atoms have two terminal oxygen atoms. Reductions of these POMs are irreversible.

These extra added electrons in the reduction process can be partially or fully delocalized over the whole framework, giving rise to mixed-valent compounds. The degree of delocalization depends on: (i) the local structure of the M-O-M linkage, and (ii) structural and chemical equivalency of the M sites.

1.4 Applications

The properties of vanadium oxides make them potentially applicable in various fields, such as catalysis,^{58–63} photocatalysis,⁶⁴ magnetism,^{65–69} biochemistry,^{70–75} surface and nano science,^{76–78} and also as components for the fabrication of batteries.^{43,79,80} In this section we illustrate a few examples of some of them.

1.4.1 Catalysis

The principal interest for oxidation catalysis focuses on polyoxometalates of tungsten and molybdenum.^{33,81,82} Nevertheless, later, researchers realized that POVs are a promising alternative, particularly for oxidation catalysis, photoredox-catalysis^{83–86} and water oxidation.⁸⁷ The compounds that act as catalysts are normally POVs functionalized with other transition metals, namely Fe^{II}, Mn^{II}, Ni^{II} or Co^{II}.³⁴ As an example, in the selective catalytic reduction of nitrogen oxides into N₂ by propylene as a reductant using $[M_3(H_2O)_{12}V_{18}O_{42}(YO_4)] \cdot 24H_2O$ (M = Mn^{II}, Ni^{II}; Y = V, S) and $[M_3(H_2O)_{12}V_{18}O_{42}(YO_4)] \cdot 24H_2O$ (M = Fe^{II}, Co^{II}; Y = V, S) as precursors,⁸⁸ and also in the hydrogenation of propane by some of these mentioned POV-based compounds.^{89,90} There are also highly-reduced and mixed-valent POVs that act as catalysts, such as $\{(NH_4)_4[Zn_4(dach)_7(H_2O)_3[V^{III}_3V^{IV}_{18}P_6O_{60}(dach)_3]] \cdot 19H_2O$ (dach = (±)-trans-1,2-cyclohexanediamine = C₆H₁₄N₂,⁹¹ (N_nBu₄)₄[V^{IV}₇V^V₉O₃₈(Br)],⁹² and (N_nBu₄)₄[V^{IV}₅V^VO₇(OMe)₁₂].⁹³ So, these examples illustrate that the design of metal-functionalized vanadium oxides can be important and interesting for homogenous catalysis.

1.4.2 Magnetism

Mixed-valent $V^{IV/V}$ vanadium oxide clusters have aroused interest in molecular magnetism studies in POM chemistry.^{94,95} In POV structures, vanadium atoms are in a similar oxo coordination environment and, normally, in a very symmetric structure, so a high degree of electron delocalization is common. Magnetic properties in mixed-valent clusters with delocalized electrons are more complex to understand and model than in compounds with localized electrons. Electron transfer from one center to another in mixed-valent compounds is easier and it depends on the interplay between electron hopping and Coulomb repulsion.⁹⁵ A nice example of a mixed-valent POV with a complex magnetic behaviour is $[X@HV^{IV}_8V^{V}_{14}O_{54}]^{6-}$ with $X = ClO_4^-$, SCN^- or $VO_2F_2^-$ which, depending on the internal template, presents a different magnetic behaviour. Moreover, the magnetism of POVs can also be changed/tuned reducing or oxidizing the system since, depending on the oxidation state of vanadium atoms—as for example $\{V^{IV}O\}^{2+}$ (with spin 1/2, d^1 valence) or $\{V^{III}O\}^+$ (spin 1, d^2 valence)—, their magnetism changes.³⁴

1.5 POMs in Computational Chemistry

Since 1986, computational chemistry has been applied to the study of POMs, but it was not until 2002 that the number of publications increased considerably, mainly due to the massive use of Density Functional Theory, Figure 1.9. The theoretical modelling of POMs was unexplored until 1986, where N. Yamazoe and co-workers performed the first calculations applying the model potential $X\alpha$ method to study the electronic structure of the Keggin polyoxomolybdate, $[PMo_{12}O_{40}]^{3-}$.⁹⁶ This method was also used to study other polyoxometalates at that time.⁹⁷ The next works were carried out using semi-empirical methods such as the SCF-CNDO/2 approach.^{98–100} The first calculation using the Hartree-Fock Self-Consistent Field approximation (HF-SCF) was published in the early 1990s, where Bénard and co-workers analysed the electronic properties of a series of polyoxovanadates.^{101–104}

The first computational studies on POMs using the DFT methodology were reported in the late 1990s. At the beginning, the use of DFT was quite low for

some years, because of the large size of the systems and their high negative charge. But, with the improvement of the methodologies and the hardware, DFT nowadays is, by far, the most widely used methodology to study POMs. The success of DFT calculations is based on the inclusion of some electron correlation, which provides better results in terms of optimized geometries and electronic structure of POMs than HF-SCF at roughly the same computational cost.¹⁰⁵ Currently, solvation effects, large atomic basis sets and the use of hybrid functionals are supported in most DFT-based programs. Solvent effects are very important in POM modelling and are typically accounted for with continuum models like Conductor-like Screening Model (COSMO), Polarizable Continuum Model (PCM) or Solvent Model Density (SMD). Depending on the property studied and the degree of accuracy wanted in the calculations, a pure Generalized Gradient Approximation (GGA) or a hybrid functional can be used. Generally, for geometry optimizations and a general picture of the electronic structure, pure GGA functionals are sufficiently good. Alternatively, a single-point calculation can be performed using a hybrid functional on the GGA-optimized structure to obtain a more accurate electronic structure.

A different computational approach is Molecular Dynamics (MD), a widely used methodology accounting for the time evolution of a system. The system can be described by classical Newtonian equations (classical MD) or introducing quantum effects (Car-Parrinello MD, CPMD). Both of them have been applied to the theoretical study of POMs, the first publication of this type dating from 1995.¹⁰⁶ MD is usually applied to study the dynamic behaviour of POMs in solution using explicit solvent molecules and counteranions.^{107,108} CPMD has been applied, for example, to learn more about the time evolution of the nucleation process of fundamental metal oxide units into clusters.¹⁰⁹ These two last methodologies use periodic boundary conditions to reproduce infinity of a solution, and are also applicable to treat other periodic systems like solids and surfaces. Nonetheless, periodic boundary conditions can also be applied to static DFT. Typically, in periodic DFT and CPMD, common atomic basis sets are replaced by plane waves to make the calculation less time consuming. Correlated ab-initio methods are also used to study POMs when they have unpaired coupled electrons. Nevertheless, sometimes, these calculations are done on model

clusters and not in the complete POM because of the high computational cost of these methods.¹¹⁰

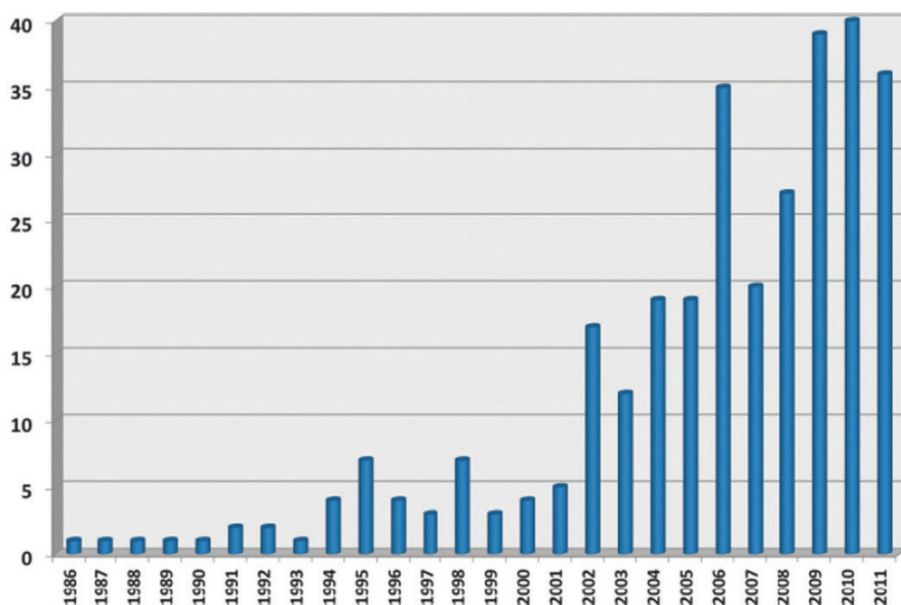


Figure 1.9 I. Number of articles about POMs where some theoretical results are involved. Figure taken from ref. 111.

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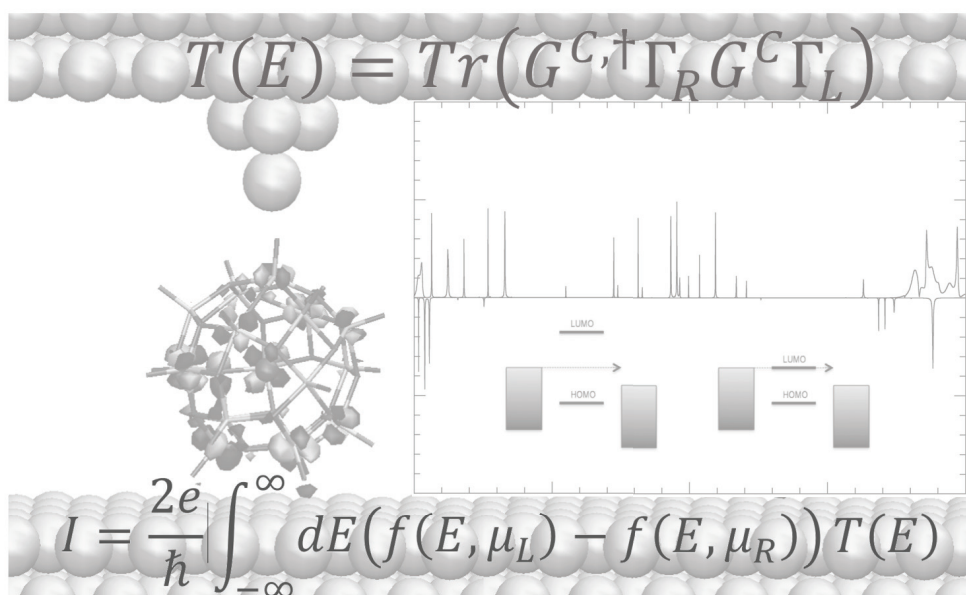
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THEORETICAL STUDY OF POLYOXOVANADATES: ANALYSIS OF STRUCTURAL, MAGNETIC AND TRANSPORT PROPERTIES
Almudena Notario Estévez



CHAPTER 2

Single-molecule Electrical Conductivity

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CHAPTER 2

Single-molecule Electrical Conductivity

In this section, the reader is introduced to the world of single-molecule electrical conductivity. For this purpose, we describe the most important experimental techniques used for studying molecular electrical conductivity and also the different types of molecular electron transport. Furthermore, we take a look at the basic theoretical aspects of electron transport theory. For a more complete account on this topic, the references cited throughout the chapter can be consulted.

Other routine computational methods applied in the thesis, such as density functional theory and the theoretical foundations of periodic electronic structure calculations are not described in this chapter. Extensive information about these and other methodologies can be found in ref. 1.

2.1 Experimental Techniques

One of the main challenges in single-molecule electronic devices is mastering the formation and control of metal-molecule-metal (MMM) junctions.² A variety of techniques have been developed to fabricate them, such as mechanical break junction,³ electrochemical deposition⁴ or scanning probe techniques,⁵ among others. The determination of single-molecule electrical conductivity must be flawless to ensure that the measurement is actually 'single-molecule'. In addition, the target molecular entity must be properly attached to the two probing electrodes and the measurement must be performed in a controlled, well-defined environment.⁶ This section presents the most widely used techniques to measure single-molecule electrical conductivity.

2.1.1 Scanning probe microscopy (SPM)

SPM-based techniques have been used to investigate single-molecule electrical conductivity.⁷ They are based on the exponential dependence of the quantum tunneling current with the distance between the probe and the substrate (for example a molecule adsorbed on a metallic surface).⁸ Scanning tunneling microscopy break junction (STM-BJ) allows direct observation of the system (individual molecules adsorbed on the surface of some conductive substrate) with submolecular resolution. It also permits studying electron transport of the adsorbed molecule by placing a scanning-tunneling-microscopy tip on top of it (Figure 2.1 a).⁶ The working principle is based on the application of constant bias voltage while the tip is retracted from the surface at constant speed until the junction metal-molecule-tip junction breaks and conductivity drops to zero. Furthermore, the atoms' and molecules' positions on the surface can be manipulated by means of the tip. A closely related technique is the conducting probe atomic force break junction (C-AFM-BJ). It has lower resolution than STM, but C-AFM-BJ can measure both mechanical and electrical properties of molecules when a conductive tip is used. C-AFM-BJ uses a metal-coated AFM tip as electrode and involves a laser-reflection controlled force signal detector, which enables conductance and force measurements in parallel (Figure 2.1 b). Both techniques simultaneously allow the direct observation of the system under investigation and the study of electron transport.

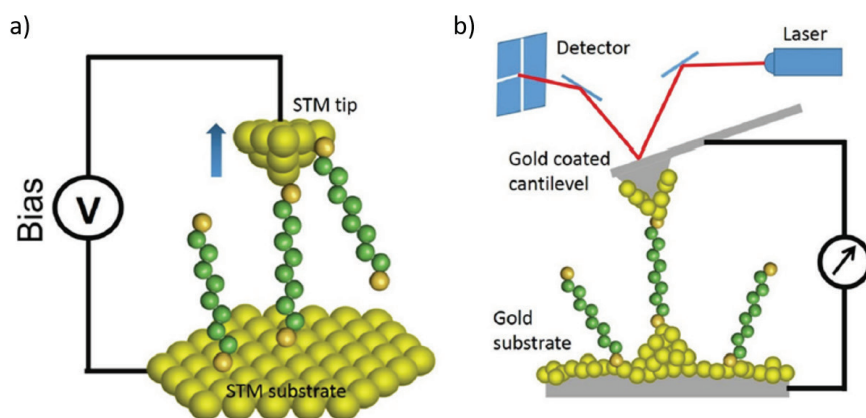


Figure 2.1 | Schematic representations of a) STM-BJ and b) C-AFM-BJ. Figure taken from ref. 9.

2.1.2 Mechanically controlled break-junction (MCBJ)

MCBJ provides another possibility to measure single-molecule electron transport, allowing to study statistically the electron transport of the molecule depending on the molecule-metal geometry and interaction. Figure. 2.2 shows that MCBJ works with a small piece of a metallic wire fixed at two points of a flexible substrate. The cross section of the wire is reduced between two fixed points by making a notch near the middle of the wire. A vertical movement of the push rod will exert a force to the bending beam. As the beam is bent, the sample wire starts to elongate between the two fixed points, resulting in the reduction of the cross section at the notch until rupture of the wire (black frame in Figure 2.2). At the moment of the rupture, two clean facing nano-electrodes are generated. The gap between both electrodes can be controlled by further bending or relaxing the substrate. After incorporating the molecules into that gap, they may bridge the two electrodes and the electronic properties of such molecules can be determined. The molecules can be introduced before and after the formation of the electrodes what further increases the statistical variation of M-molecule-M interaction.

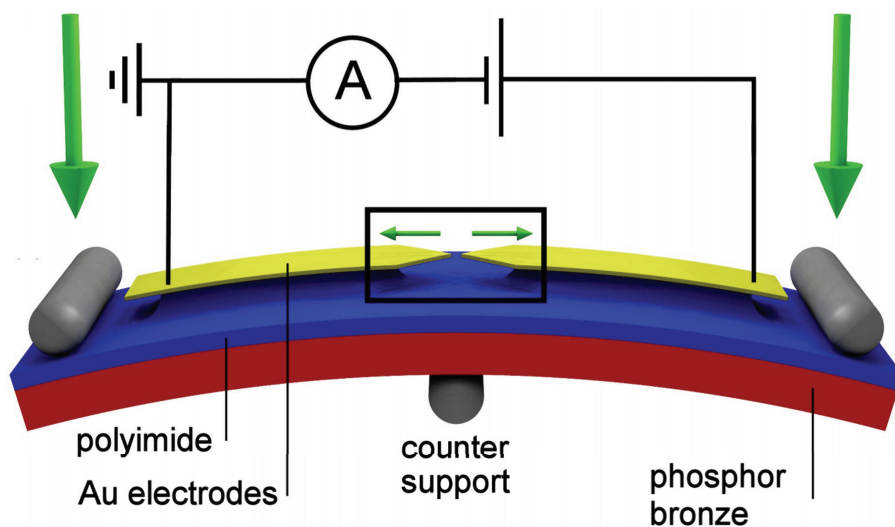


Figure 2.2 | Schematic representations of MCBJ. Figure taken from ref. 10.

2.1.3 Electromigration break-junction (EBJ)

EBJ is an advantageous method to fabricate a three-electrode molecular device (see Figure 2.3). These junctions are formed when a voltage is ramped across a metallic wire with a small cross section until breakage, resulting in the formation of a nanometer-sized gap between the electrodes. It is possible, as with MCBJ, to control the gap width. Moreover, the junctions can be directly fabricated on a gate dielectric. However, formation yields are typically as low as 10%. The disadvantage of EBJ compared to MCBJ is the difficulty to obtain a large number of metal-molecule geometries with the same junction characteristics. Consequently, many devices are required to measure a large number of single-molecule junctions, hence making the study of the statistical behavior of molecules less simple than with MCBJ.

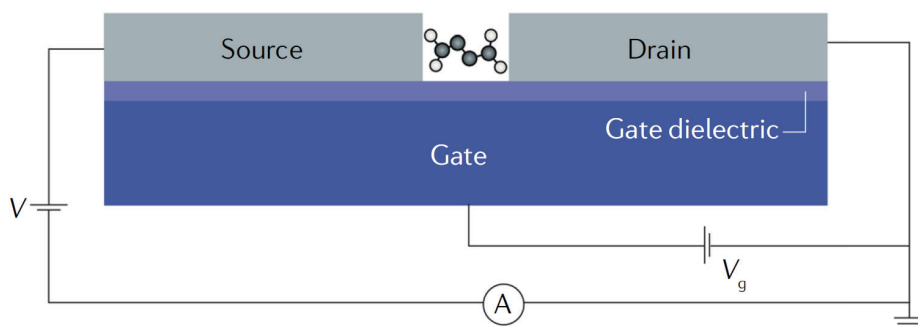


Figure 2.3 | Schematic representations of EBJ. Figure adapted from ref. 11.

2.2 Electron Transport in Molecules

Before studying electron transport in molecules, it is convenient to look into the elements of a molecular junction. A MMM junction contains the central molecule connected to the conducting 'contacts'. In most cases there is a significant mismatch between the electronic levels of the different components and the existence of important potential energy barriers is also frequent. Depending on these two factors different types of molecular electron transport can be observed. The next sections shortly describe these different molecular conduction mechanisms.

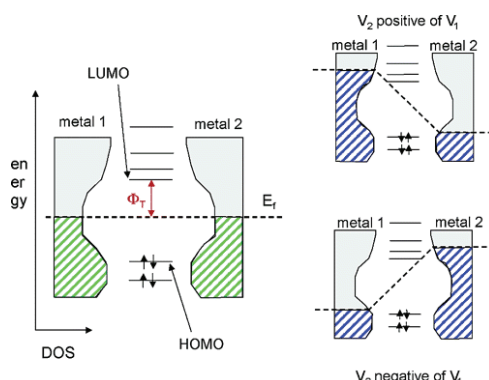


Figure 2.4 | Schematic energy levels of a MMM junction at 0 bias (left) and a $V \neq 0$ (right). Figure taken from ref. 12.

2.2.1 Coherent tunneling

Classical, or coherent, tunneling is the quantum mechanical phenomenon of a wavefunction propagating through a potential barrier of a certain thickness and height with finite probability (Figure 2.5).

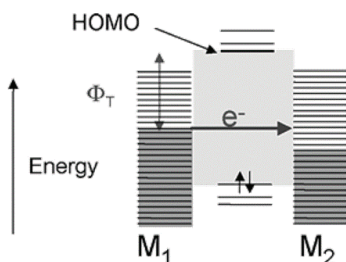


Figure 2.5 | Schematic representation of the energy levels for coherent tunneling of a MMM molecular junction. Figure adapted from ref. 12.

The rate of coherent tunnelling depends exponentially on the barrier thickness and height, as shown by the Simmons relation (equation 2.1) for tunnelling through a rectangular barrier:

$$J = \frac{q^2 V}{h^2 d} (2m\Phi)^{\frac{1}{2}} e^{\left[\frac{-4\pi d}{h} (2m\Phi)^{\frac{1}{2}} \right]} \quad (2.1)$$

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where J is the current density (A/cm^2), q the electron charge, V the applied voltage, h Planck's constant, m the electron mass, Φ the barrier height, and d the barrier thickness. In the case of a molecular junction, d is the distance between conductors. In coherent tunneling, the phase of the wave function of electron is preserved during the tunneling process. It is a temperature-independent phenomenon but depends on the molecular conformation, that is, molecular vibrations and rotations can give rise to changes in the energy barrier that can affect the transport efficiency. So, although coherent tunneling is temperature-independent, it can be altered by the thermal conformational changes in the molecule. Normally, the rate for coherent tunneling is very small for metals and even less for molecules, though for 'faster-than-expected' tunneling, a widely accepted explanation is 'superexchange'. Interactions between the metal contacts' electrons and the molecular orbitals of the bridging molecule in a MMM enhance the tunneling rate, making 'through bond' tunneling more efficient than 'through space' tunneling.

The highest occupied molecular orbital (HOMO) and/or the lowest unoccupied molecular orbital (LUMO) can aid the tunneling process. When either of these orbitals lie close to the Fermi level (E_F) of the metal contacts, electron transfer can take place through one of them and, then, the process is called coherent resonant tunneling (Figure 2.6). This 'through bond' tunneling is more efficient than 'through space'.

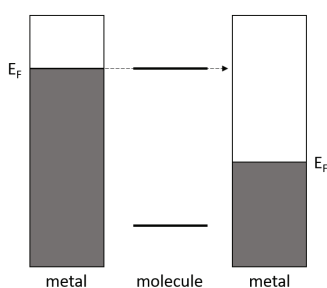


Figure 2.6 | Schematic representation of coherent resonant tunneling of a MMM molecular junction.

The tunneling rate can also be influenced by the application of an external electric field. If this field exceeds the barrier height, so-called Fowler-

Nordheimer tunneling becomes operative.¹³ It is an interfacial effect and, in addition, is also temperature-independent but decreases exponentially with contact-contact distance.

2.2.2 Incoherent tunneling

Incoherent tunneling is a phenomenon in which an electron tunnels coherently through a series of barriers and sites, as shown in Figure 2.7. In incoherent tunneling, the residence time of the electron in a potential well is long enough to disturb its phase. This process is, in principle, also temperature-independent since it can be viewed as a series of discrete temperature-independent steps.

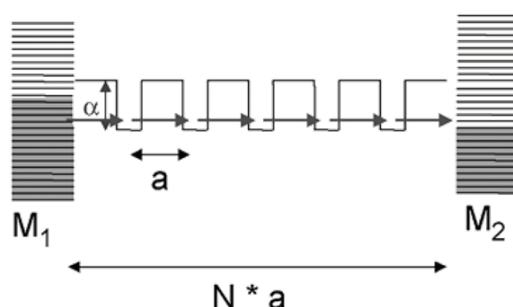


Figure 2.7 | Schematic representation of the energy levels for incoherent tunneling of a MMM molecular junction. Figure adapted from ref. 12.

2.2.3 Hopping mechanism

Hopping is an incoherent, thermally activated electron transfer process in which an electron moves from one site to another losing all the information about its phase. The hopping probability is a negative exponential of the energy barrier between sites, and follows a classical Arrhenius-like relation (see equation 2.2). k_{ET}^0 can be determined from a probability distribution of the electron, and hence, no explicit wave function representation is required.

$$k_{ET} = k_{ET}^0 e^{\left(\frac{-E_a}{kT}\right)} \quad (2.2)$$

2.3 Transport Theory

2.3.1 General aspects about MMM junctions

As explained in section 2.2, a MMM junction contains a molecule between two leads/contacts (left L and right R), which are treated as free electron reservoirs with nearly continuous energy spectra. The molecule in the junction does not present the same behavior as in the gas-phase. In fact, its discrete energy levels are broadened by an energy amount Γ due to the contacts with the left and right leads, (Figure 2.8), which will vary depending on the energy levels. Such level broadening can be taken into account by replacing the discrete level with energy E_0 by a Lorentzian density of states, $D(E)$, depending on energy E :

$$D(E) = \frac{1}{2\pi} \frac{\Gamma}{(E - E_0)^2 + (\Gamma/2)^2} \quad (2.3)$$

where $\Gamma = \Gamma_L + \Gamma_R$, and $\Gamma_{L,R}$ are the parameters characterizing the coupling between the molecule and the left (L) and right (R) contacts.

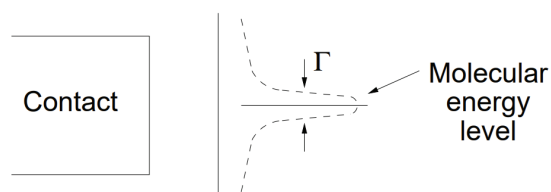


Figure 2.8 | Energy level broadening. Figure taken from ref. 14.

Moreover, the absolute value of electronic energy levels of a molecule coupled to the leads in a MMM junction can also differ from those of the isolated molecule. The differences originate in the electrostatic potential changes generated inside the molecule as a result of the charge polarization/transfer between the molecule and the leads. These notably depend on the coupling strength, that is, when a molecule is weakly coupled to the leads, the charge transfer is insignificant, and the molecular orbitals remain

practically unchanged. The stronger the coupling is, the more obvious the energy level shift and broadening is from the initial position.

In absence of an applied voltage, the MMM remains in equilibrium and the number of states with $E < E_F$ is equal to the number of electrons in the molecule. E_F is located somewhere in between the HOMO and LUMO. But, its precise location is difficult to determine because of its high sensitivity to changes in the transferred charge.

If a potential difference between the leads is applied, the electrochemical potentials of the left (μ_L) and right (μ_R) contacts are no longer equal and, thus, electrical current can appear in the junction as a response. The energy levels located between those differing electrochemical potentials (see Figure 2.4, right) are essential elements for electrical current to exist, that is, molecular orbitals work as channels for electron transmission. Obviously, the magnitude of the electrical current depends on the quality and intensity of the coupling in the molecule-leads contacts.

2.3.2 Landauer expression for the current through a MMM junction

The electrical current for a phase-coherent conductor connected to two metal contacts (a source and a drain) can be obtained calculating the total probability for an electron to travel between two electrodes at a certain tunneling energy (E) and integrating the resulting probability over the whole energy range. The expression of the current is defined by the Landauer formula, where the elastic conductance through a molecule can be conceived as a transmission problem:¹³

$$I = \frac{e}{\pi\hbar} \int T(E) [f_L(E) - f_R(E)] dE \quad (2.4)$$

where

$$f_\beta(E) = \left(1 + e^{\left[\frac{E - \mu_\beta}{kT} \right]} \right)^{-1} \quad (2.5)$$

is the Fermi distribution function for the β lead ($\beta \in L, R$) at its respective potential, μ_β . $T(E)$ is the electron transmission function, or transmission coefficient, a property of the whole system comprising the leads, the molecule and their contacts. Using a simple model, where the molecular bridge is simulated by a single spin-degenerate energy level with energy E_0 , $T(E)$ is defined as:¹⁵

$$T(E) = \frac{\Gamma_L \Gamma_R}{(E - E_0)^2 + (\Gamma/2)^2} \quad (2.6)$$

where the Lorentzian expression has been used to describe the level broadening. Figure 2.9 shows how the transmission varies as function of the energy. It is readily seen that for an optimal transmission the levels of the molecule (E_0) must coincide (or at least be comparable) with E . Comparing the left and right panels, we see how the coupling with the electrodes influences the transmission probability; strong coupling makes the transmission extend over a wider energy interval, while for weak coupling an exact match is required for sizeable transmission.

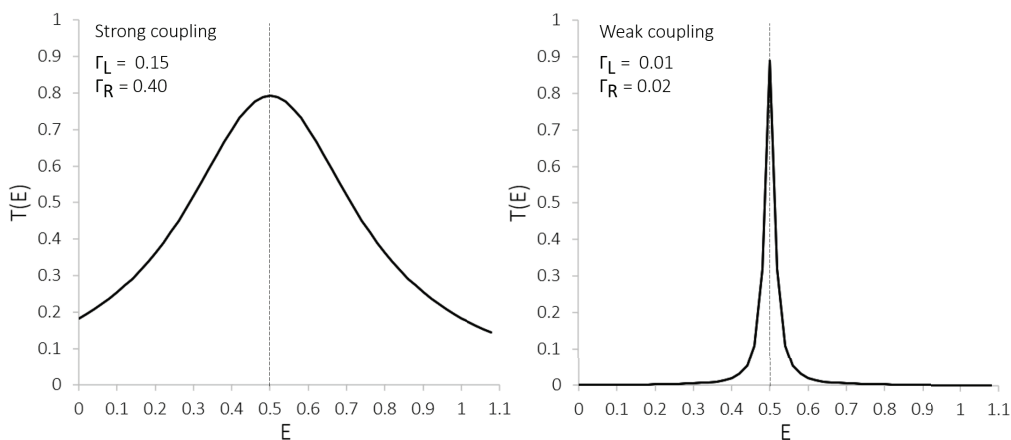


Figure 2.9 | Variation of the transmission as function of the tunnelling energy E . E_0 is 0.5 eV in both graphs.

Therefore, when the electrode potentials differ, a current can appear in the junction with the energy level of the bridge (E_0) taking a value in between the

electrodes' potentials. Otherwise, the difference in the Fermi functions would vanish, the current through the junction being zero. A more complete expression of the transmission function, going beyond the simple one-level approximation made above, relies on the application of non-equilibrium Green's function. This leads to the following expression for $T(E)$:

$$T(E) = \text{Tr}\{\Gamma_L G(E) \Gamma_R G^\dagger(E)\} \quad (2.6)$$

where Γ_L and Γ_R are no longer simple numbers but matrices. The same happens for $G(E)$ and $G^\dagger(E)$, which are the retarded and advanced Green's functions for the Hamiltonian of the molecule coupled to the leads ($H = H_M + H_T$), since the junction is described by the Anderson Hamiltonian: $H = H_L + H_R + H_M + H_T$, where $H_{L,R}$ correspond to the left and right leads, H_M to the molecule and H_T accounts for the coupling between the leads and the molecule of the MMM junction.

Green's functions matrices are determined by:

$$G(E) = [(E+i\eta)S - F - \Sigma_L - \Sigma_R]^{-1} \quad (2.6)$$

where S and F are the overlap and Fock matrices of the molecule and η is a positive infinitesimal parameter. Σ_β is the self-energy of the leads, which considers the coupling between the molecule and the electrodes (Γ_β) and contains all the information about the electrodes.¹⁶

Because of the wave-like nature of the electron, quantum interference (QI) must be taken into account in the theoretical description of electron transport processes.¹¹ The isolated molecule is a closed system characterized by constructive QI leading to molecular orbitals and a discrete energy spectrum. This changes dramatically when the molecule is connected to electrodes. The system is now open and the energies of the electrons that enter the molecule form a continuum. In this case, we are interested in calculating the $T(E)$ of the molecule, which can lead to both constructive and destructive interferences. So, in this case, QI should be described in terms of the interference pattern of the

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de Broglie waves due to electrons traversing a molecule from one electrode to the other. In a tutorial review by Lambert,¹⁷ Green's functions are described as the technical term for such an interference pattern. A simple analogy is proposed to try interpreting that: "imagine a singer at the entrance to an auditorium, emitting a note of constant frequency. If the note is sustained for long enough this will set up a standing wave within the auditorium, with a complex pattern of nodes and antinodes. When the singer is located at position i , then the amplitude of the standing wave at position j is proportional to the Greens function $G(j,i)$. If a window is opened at position j and the location of the window coincides with an antinode of the standing wave $G(j,i)$, a loud sound will exit from the window. This is an example of constructive interference. On the other hand, if the window is located at a node, no sound will exit and destructive interference is said to occur. In this analogy, the auditorium and the sound wave are analogues of a molecule and a de Broglie wave, respectively, and in a model based on atomic orbitals, i and j label atomic orbitals at specific locations within a molecule. In this case, $G(j,i)$ is the amplitude of a de Broglie wave at j , due to a source at i and is a property of the isolated molecule. If an electrode is attached to $i = 1$ and a second electrode attached to $j = 2$, then the transmission coefficient $T(E)$ will vanish when $G(2,1) = 0$; i.e. when atomic orbital 2 coincides with a node."

The next section summarizes the non-equilibrium Green's functions (NEGF) applied to the calculation of electron transport properties.

2.3.3 Non-equilibrium Green's functions (NEGF) formalism

The one-level model used in the previous section cannot be applied to calculate real systems like molecules, with multiple levels that often broaden and overlap in energy. The mathematical functions needed to the calculation of electron transmission through a molecule with multiple levels with arbitrary broadening and overlap are provided by the NEGF formalism. These functions take the role of propagators.^{14,15}

Let's consider an electron. Its Green's function matrix elements $G_{ij}(\tau, \tau')$ are defined as:

$$G_{ij}(\tau, \tau') = -i \langle T_c c_i(\tau) c_j^\dagger(\tau') \rangle \quad (2.7)$$

conveniently written in the so-called Keldysh formalism^{18,19} in which the explicit time evolution operators are replaced by contour operators parametrized by contours paths on the time axis. τ evolves along these closed contours starting at $t = -\infty$ going through $t = 0$ and closing the contour again at $t = -\infty$.²⁰ $c_i(\tau)$, $c_j^\dagger(\tau')$ are the annihilation and creation operators for the electrons taken at corresponding times τ and τ' . The Keldysh formalism provides a way to study non-equilibrium systems.

Now, let's consider a metal-molecule junction, whose Green's function satisfies the integral

$$G_{ij}(\tau, \tau') = G_{ij}^0(\tau, \tau') + \sum_{k,l} \int d\tau_1 \int d\tau_2 G_{ik}^0(\tau, \tau_1) \Sigma_{kl}(\tau_1, \tau_2) G_{lj}(\tau_2, \tau') \quad (2.8)$$

The integration over τ_1 and τ_2 is carried out over the Keldysh contour. $G_{ij}^0(\tau, \tau')$ is associated with the molecule detached from the leads and phonons and hence only describes the time-evolution of the quantum interference inside the molecule due to the electrons entering it. $\Sigma(\tau_1, \tau_2)$ is the electron self-energy which by definition describes the electrons of the electrodes and the interaction with the molecule.

Considering a steady state process, we can project the Green's functions onto the real time axis. Then one may use the fact that, under steady state conditions, all two-time quantities actually depend only on time differences, so one may turn to Fourier-transform functions in the energy space ($t - t' \rightarrow E$). The relevant projections are commonly denoted as retarded, advanced ($\dagger$), lesser ($<$) and greater ($>$) Green's functions. The retarded electron Green's function Fourier transform is introduced by:

$$G_{ij}(E) = -i \int_0^\infty [c_i(t), c_j^\dagger] e^{i(E + i\eta)t} dt \quad (2.9)$$

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where η is a positive infinitesimal parameter. The advanced electron Green's function is a Hermitian conjugate of the retarded one: $G^{\dagger}(E) = [G(E)]^{\dagger}$. The functions $G^{>}(E)$, $G^{<}(E)$ are determined by the Keldysh equations. In matrix form, these equations can be written as:

$$G^{>}(E) = G(E)\Sigma^{>}(E)G^{\dagger}(E) \quad (2.10)$$

$$G^{<}(E) = G(E)\Sigma^{<}(E)G^{\dagger}(E) \quad (2.11)$$

And rewriting equation 2.9 with the lesser and greater Green's functions, we obtain equation 2.12, an equivalent equation for its advanced counterpart.

$$G(E) = G_0(E) + G(E)\Sigma(E)G_0(E) \quad (2.12)$$

The significance of Green's functions and self-energies for transport theory is based on the fact that they can be used to calculate important observable transport characteristics. The relaxation rates for electrons $\Gamma(E)$ have the form:

$$\Gamma(E) = i[\Sigma(E) - \Sigma^{\dagger}(E)] \quad (2.13)$$

where $\Sigma(E)$ ($\Sigma^{\dagger}(E)$) is the retarded (advanced) electron self-energy.

Assuming that the interaction of the molecule with the electrodes does not depend on the interaction of the molecule with the rest of the environment, and only elastic transport is of importance, we have:

$$\Sigma(E) = \Sigma_L(E) + \Sigma_R(E) \quad (2.14)$$

and in the same form for $\Sigma^{\dagger}(E)$, where $\Sigma_L(E)$ and $\Sigma_R(E)$ are the couplings of the molecule to the leads. This term may be written as:

$$\Sigma_{\beta}(E) = \Sigma_{\beta}^{\dagger}(E) \equiv \Sigma_{0\beta}(E) \quad (2.15)$$

$$\Sigma_{0\beta}^{ij}(E) = \sum_{r,\sigma} \frac{T_{ir\beta\sigma}^* T_{jr\beta\sigma}}{E - \epsilon_{r\beta\sigma} + i\eta} \quad (2.16)$$

where $\epsilon_{r\beta\sigma}$ are the single-electron energies in electrode β for electron states r , σ , and $T_{jr\beta\sigma}$ describes the couplings of the r , σ electron states belonging to lead β to the j , σ energy level of the molecule. The imaginary part of $\Sigma_{0\beta}^{ij}(E)$ determines the matrix elements of the Γ matrices describing molecular level broadenings due to the coupling of the molecule to the leads:

$$\Gamma_{\beta}^{ij}(E) = \pi \sum_{r,\sigma} T_{ir\beta\sigma}^* T_{jr\beta\sigma} \delta(E - \epsilon_{r\beta\sigma}) \quad (2.17)$$

Assuming that intramolecular electron-electron interactions do not affect its coupling to the leads, $\Sigma^{<}$ and $\Sigma^{>}$ can be written as:

$$(\Sigma_{\beta}^{<})^{ij} = i f_{\beta}(E) \Gamma_{\beta}^{ij}(E) \quad (2.18)$$

$$(\Sigma_{\beta}^{>})^{ij} = -i \{1 - f_{\beta}(E)\} \Gamma_{\beta}^{ij}(E) \quad (2.19)$$

where $f_{\beta}(E)$ is the Fermi distribution function for lead β . If the transport through the junction is elastic, we can use equations 2.10 and 2.11 to rewrite the current as:

$$I = \frac{e}{\pi\hbar} \int dE \text{Tr} \{ \Sigma_L^{<}(E) G(E) [\Sigma_L^{>}(E) + \Sigma_R^{>}(E)] G^{\dagger}(E) - \Sigma_R^{>}(E) G(E) [\Sigma_L^{<}(E) + \Sigma_R^{<}(E)] G^{\dagger}(E) \} \quad (2.20)$$

Then, substituting into this formula the expressions 2.18 and 2.19 one may reduce the last expression to the Landauer form given by equation 2.4.

2.3.4 DFT + NEGF methodology

For the calculation of the current through a MMM junction, the junction is partitioned in three subsystems: the left electrode, the central region (or device region) and the right electrode, see Figure 2.10. The central region contains the molecule and the portion of the electrodes that are considered to be affected by the contact and for which the Hamiltonian differs from that of the bulk metal.

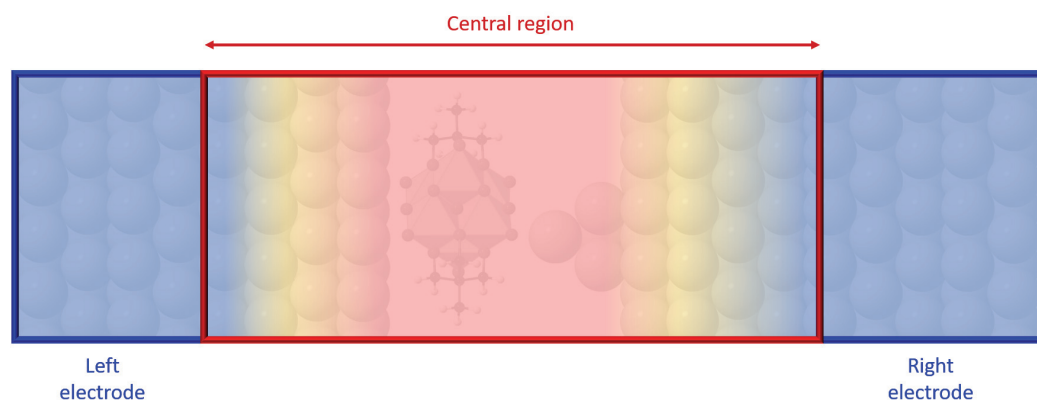


Figure 2.10 | Schematic representation of device partitioning in the NEGF scheme.

This arrangement is used as the unit cell in a periodic DFT calculation to get its Hamiltonian and overlap matrix. For the electrodes, the Hamiltonian and the overlap matrices are obtained in a separate calculation of the bulk metal. With this setup, the Green's function of the device system is calculated through equation 2.6 with no periodic boundary conditions in the direction of the current flow. Finally, applying equations 2.6 and 2.4 the current through the junction is calculated.

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CHAPTER 3

Goals of the Thesis

UNIVERSITAT ROVIRA I VIRGILI
THEORETICAL STUDY OF POLYOXOVANADATES: ANALYSIS OF STRUCTURAL, MAGNETIC AND TRANSPORT PROPERTIES
Almudena Notario Estévez

CHAPTER 3

Goals of the Thesis

Herein we summarize the main goals of the thesis by chapters. The majority of the projects described in this thesis are collaborations with experimental groups. Combining the experimental and theoretical viewpoints allows us to reach a more complete understanding of the properties of the POM family of compounds. During these years of research, we have studied (and clarified) many aspects of the molecular conductivity of POMs and POVs, their adsorption on gold, and also their magnetic properties. The first two chapters focus on the molecular conductivity of one type of POM ($[V_6O_{13}\{(OCH_2)_3CCH_2SR\}_2]^{2-}$, with $R = Me$ or Ph , in Chapter 4) and POV ($[V_{18}O_{42}]$, in Chapter 5). Chapter 6 describes the magnetic properties of $\{X@V^{IV/V}_{22}O_{54}\}$ $X = ClO_4^-$, SCN^- , and $VO_2F_2^-$) and resolves the so-far unknown oxidation state of the complex as function of X .

Chapter 4: Conductivity of a Functionalized V_6O_{19} structure and its link with Molecular Redox States

The experimental groups of Dr. Monakhov and Dr. Waser have recently obtained promising results about two functionalized derivatives of the V_6O_{19} POM: $[V_6O_{13}\{(OCH_2)_3CCH_2SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCH_2SPh\}_2]^{2-}$. The experimental data suggest that the POMs are adsorbed on a Au surface with no order. Moreover, the most promising result is the step-like molecular conductivity of the two complexes. To explain this surprising behaviour, it was assumed that the POMs are reduced upon increasing voltage during the conductivity measurements. To check this reduction hypothesis, the objectives for this project are:

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- Characterize the adsorption on Au(111) surface of two functionalized V_6O_{19} structures: $[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$.
- Study the stability of both POMs on Au(111) surface.
- Evaluate the behaviour of the functionalized V_6O_{19} adsorbed on Au(111) surface upon applying an external electric field.
- Identify where the reduction on the POM-Au(111) system takes place.
- Investigate the importance of the position of the POM on the surface and the position of the tip in the POM in molecular conductivity calculations.
- Verify that the stepped conductivity for $[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$ is coupled to reduction processes.
- Investigate which atoms are responsible for the conductivity properties of $[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$.

Chapter 5: Multi-electron Redox Activity of $I@V_{18}O_{42}$

After the discovery of the step-like I-V behaviour of two functionalized V_6O_{19} , and knowing the exceptional facility of $I@V_{18}O_{42}$ to undergo oxidations and reductions, we investigated the possibility of $I@V_{18}O_{42}$ to present the same behaviour as the functionalized V_6O_{19} but with more accessible reduction states. For this reason, we have decided to study its electronic structure, adsorption and conduction properties. In more detail, the objectives for this chapter are:

- Study the isolated $[I@V_{18}O_{42}]^{q-}$ with $q = 3, 5, 7, 11$, and 13 by DFT calculations and combined the results with MD and CPMD calculations done by Dr. Solé-Daura.

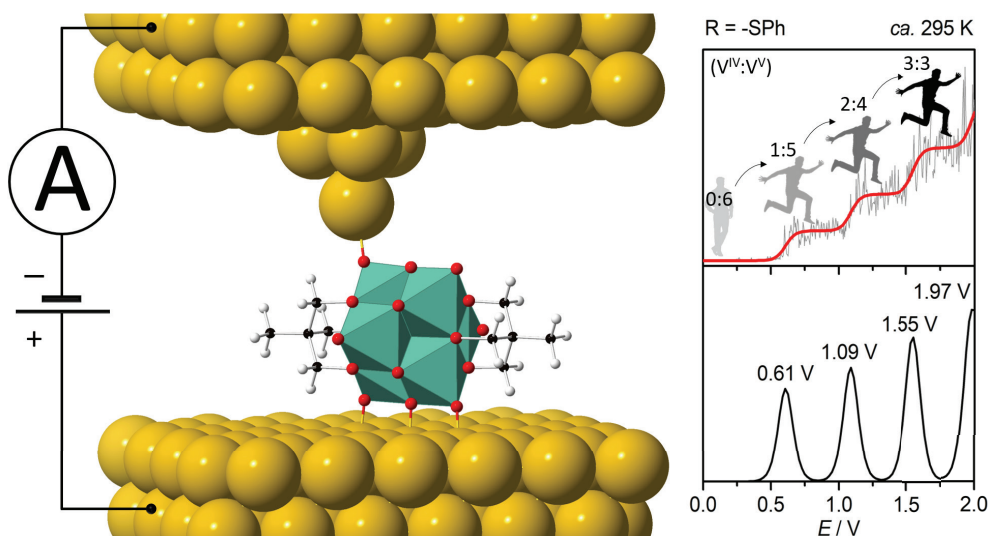
- Characterize the adsorption of $[\text{I}@\text{V}_{18}\text{O}_{42}]^{5-}$ on Au(111).
- Study the stability of $[\text{I}@\text{V}_{18}\text{O}_{42}]^{5-}$ on Au(111).
- Establish a possible relation between oxidation state and molecular conductivity in $[\text{I}@\text{V}_{18}\text{O}_{42}]^{3-}$, $[\text{I}@\text{V}_{18}\text{O}_{42}]^{5-}$ and $[\text{I}@\text{V}_{18}\text{O}_{42}]^{7-}$.

Chapter 6: Connection between Valence State and Magnetism in Mixed-Valent $\{\text{X}@\text{V}_{22}^{\text{IV/V}}\text{O}_{54}\}$

$\{\text{X}@\text{V}_{22}^{\text{IV/V}}\text{O}_{54}\}$, with $\text{X} = \text{VO}_2\text{F}_2^-$, presents a markedly different magnetic behaviour than $\text{X} = \text{ClO}_4^-$ or SCN^- . To study their magnetic properties and model properly these compounds it is necessary to know their oxidation state. Identifying the oxidation state of polyoxometalates is not always easy. Sometimes, experimental techniques fail to determine it, either because of the poor solubility of the compound or because the results are not entirely clear, since this class of compounds may be protonated. Hence, the main objectives of this project are:

- Study the geometric and electronic structure of this family of POVs ($\{\text{X}@\text{V}_{22}^{\text{IV/V}}\text{O}_{54}\}$ with $\text{X} = \text{ClO}_4^-$, SCN^- , and VO_2F_2^-) with three different oxidation states: holding 7, 8 or 9 d electrons.
- Characterize the degree of protonation of these compounds.
- Find the correct valence state for each compound.
- Compare the calculated magnetic properties with experimental observations to ascertain the calculated results and establish the origin of the difference between the three compounds.

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CHAPTER 4

Conductivity of a Functionalized V_6O_{19} and its Link with Molecular Redox States

Related Publications:

Linnenberg, O.; Moors, M.; Notario-Estévez, A.; López, X.; De Graaf, C.; Peter, S.; Baeumer, C.; Waser, R.; Monakhov, K. Y. Addressing Multiple Resistive States of Polyoxovanadates: Conductivity as a Function of Individual Molecular Redox States. *J. Am. Chem. Soc.* **2018**, *140*, 16635.

CHAPTER 4

Conductivity of a Functionalized V_6O_{19} structure and its Link with Molecular Redox States

In this chapter we study the conduction properties of single polyoxometalate (POM) molecules, which have been targeted as possible successors of the materials that are currently used in complementary metal-oxide semiconductor (CMOS) technology. Lindqvist-type POMs physisorbed on the Au(111) surface, preserve their structural and electronic characteristics. By applying an external voltage at room temperature, the valence state of the single POM molecule changes multiple times through the injection of up to 4 electrons. The molecular electrical conductivity is dependent on the number of vanadium 3d electrons, resulting in several discrete conduction states with increasing conductivity. This fundamentally important finding illustrates the far-reaching opportunities for POM molecules in the area of multiple-state resistive (memristive) switching.

This work was carried out in collaboration with the experimental group of Dr. Kirill Yu Monakhov from RWTH Aachen University, with the group of Dr. Rainer Waser from RWTH Aachen University and with the group of Dr. Christoph Baeumer from Peter Grünberg Institute, all of them in Germany.

4.1 Background

The common architecture of current computer systems is based on the classical von Neumann principle —also known as the von Neumann model or Princeton architecture—, in which the Central Processing Unit (CPU) and the memory unit or Random Access Memory (RAM) are separated parts and work as two independent units,¹ see Figure 4.1. The main disadvantage of this setup, besides the size due to the differentiation between units, is the constant transfer of data between both. One of the promising solutions to address this problem is to implement memristive devices combining data processing and storage in the

same unit. A memristor —short for memory resistor— was introduced in 1971 by Professor Chua, as a device that acts, in some way, as a resistor with memory.² However, it was not until 2008 when the first memristor was built in the Hewlett-Packard laboratories.^{3,4} Working in this direction, the size and the power dissipation in future computers will be dramatically diminished. Among the emerging memories, the Resistive Random Access Memory (ReRAM) —also known as resistive switching memory— raises strong interest as memristive device due to its simple structure consisting in a simple “electrode/insulator/electrode”-cell setup in which, commonly, a metal oxide is placed between electrodes.

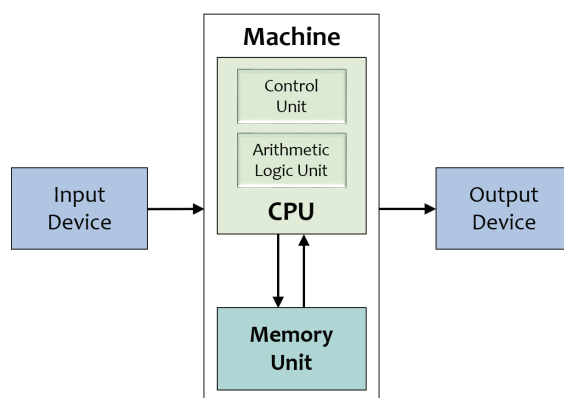


Figure 4.1 | Schematic representation of the von Neumann architecture.

As shown in Chapter 1, one of the most attractive features of vanadium-containing classical POMs and of POVs is their fascinating reduction-oxidation activity^{5–9} allowing them to meet the physicochemical requirements for their potential implementation into ReRAM. The experimental groups of Dr. Monakhov, Dr. Baeumer and Dr. Waser have replicated a ReRAM cell by embedding the fully-oxidized Lindqvist-type hexavanadate molecules, $[V_6O_{13}\{(OCH_2)_3CCHR'SR\}_2]^{2-}$ (**1–7**), where R = Me (**L1**, **L2**), Pr (**L3**), C₅H₉ (**L4**), Ph (**L5**), 2-C₁₀H₇ (**L6**), CF₃ (**L7**), R' = H (**L1**, **L3–L7**), Me (**L2**), see Figure 4.2, into a model setup, in which the bottom electrode is a Au(111) surface substrate and the top electrode is a STM platinum tip. The choice of these Lindqvist-type hexavanadate derivatives (**1–7**) was prompted by a low molecular charge (2–), a counteraction-dependent solubility in organic solvents and thermodynamic stability in air, all of them advantageous for immobilization on electrode surfaces.

The Lindqvist hexavanadate has a high charge (8-) when it is completely oxidized. Nevertheless, functionalization with some organic ligands decreases its charge. The idea of reducing the charge circumvents the serious problem of agglomeration illustrated, for example, for $[I@V^{IV}_{10}V^V_8O_{54}]^{5-}$ on Au(111).⁸

Therefore, the experimental group of Dr. Monakhov synthesized seven Lindqvist-type hexavanadates (**1-7**) with different side groups (see Figure 4.2). The bond valence sum analysis and the ^{51}V NMR (signal at ca. -495 ppm¹⁰) show that the hexavanadate unit is fully oxidized $\{V^{IV}_6O_6\}$.¹¹ Furthermore, when monolayers of compounds **1** and **5** were attached to the gold surface, their structural and fundamental electronic integrity were retained, as infrared reflection absorption spectroscopy (IRRAS) and X-ray photoelectron spectroscopy (XPS) measurements suggest.

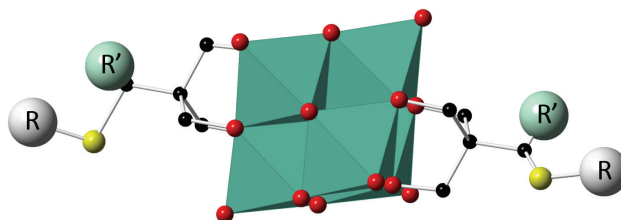


Figure 4.2 | Schematic representation of the different Lindqvist-type hexavanadate molecules used for the ReRAM cell, where R = Me (L1, L2), Pr (L3), C₅H₉ (L4), Ph (L5), 2-C₁₀H₇ (L6), CF₃ (L7), R' = H (L1, L3– L7), Me (L2). Hydrogen atoms are omitted for clarity.

The experimental groups also performed STM analyses on **1** and **5** adsorbed on Au(111). The electron densities obtained for the discrete hexavanadates showed a homogeneous distribution of the substrate with no long-range ordering effects and a measured height of both deposited hexavanadates of 0.80 ± 0.05 nm, see Figure 4.3. The stable scanning with positive bias voltage and the convenient STM depiction of single hexavanadate units of **1** and **5** allowed to assess their current–voltage (I–V) characteristics via single-point scanning tunneling spectroscopy at room temperature (~ 295 K), which is a favorable measurement condition in the field of molecular electronics and spintronics. The I–V curves presented in Figure 4.3 e) show a staircase-like dependency of the current with the applied potential with clearly distinct current steps for **1** at 0.66 V, 1.08 V, 1.48 V and 1.90 V and for **5** at E = 0.61 V, 1.09 V, 1.55 V and 1.97 V.

To elucidate the distinct resistive states, the derivative of the fitted I-V data (dE/dI) were calculated resulting in four electron transitions for **1** and **5**. As no changes in the oxidation state of the fully-oxidized systems were observed when attached to gold, each step in the recorded I-V curves could be attributed to a single-electron reduction of the hexavanadate core ($\{V^{IV}_0V^V_6\} \rightarrow \{V^{IV}_1V^V_5\} \rightarrow \{V^{IV}_2V^V_4\} \rightarrow \dots$), thus being the vanadium atoms responsible for the conductivity between the electrodes.

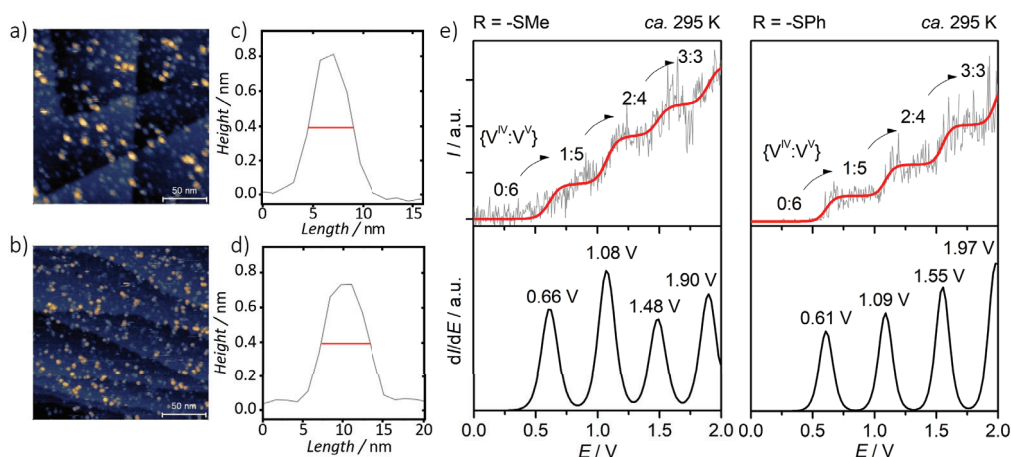


Figure 4.3 | STM images (200x200 nm) of drop-coated ($7.5 \cdot 10^{-3}$ mM) a) **1** and b) **5** recorded on Au(111) with $E_{BIAS} = 1.0$ V at room temperature and averaged corresponding line profiles for c) **1** and d) **5**. e) Experimental scanning tunnelling single-point spectroscopy data of single scans at room temperature (black) of **1** and **5** with corresponding electron population for each step, red: fitted experimental data (tetra Dose-Response function) and dI/dE of the I-V curve of fitted data. Figure adapted from ref. 10.

In order to corroborate the experimental assumptions and to get a better understanding about these systems we computationally explore the adsorption mode of **1** and **5** and analyze their electronic structures when adsorbed on gold. We also apply an external electric field to the substrate-gold system to grasp the possible reduction of the structure, as experimentalists consider. Additionally, we perform molecular conductivity calculations of this setup including oxidation state variations in the hexavanadate to confirm that each step in the recorded I-V curves might be attributed to a single-electron reduction of the inorganic core of the substrate and, moreover, to know if vanadium atoms govern the conductivity.

4.2 Computational Details

4.2.1 Adsorption on gold

The computational model consists of a unit cell containing a slab of five 10×8 layers representing an infinite Au(111) surface, the vanadium POM adsorbate and potassium counterions to ensure charge neutrality of the system. Density Functional Theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP5.3.5).^{12–15} On the basis of previous studies of closely related systems,^{16–18} we applied the generalized gradient approximation-type exchange-correlation functional by Perdew and Wang (PW91),¹⁹ which suffices to describe not too strong electron correlations, such as fully oxidized POMs, and a basis set of plane waves with a 500 eV kinetic energy cutoff. For the 1e-, 2e- or 3e-reduced V_6 system, the assumed delocalized nature of the extra electrons at room temperature ensures that each vanadium holds an average of 1/6, 1/3 or 1/2 electrons in the 3d-shell, respectively, which are sufficiently low electron populations to not consider adding the U effective local parameter to the calculations. We considered the following atomic valence electrons: Au: $5d^{10}6s^1$, C: $2s^22p^2$, H: $1s^1$, O: $2s^22p^4$, S: $3s^23p^4$, V: $3d^34s^2$ and K: $3s^23p^64s^1$, where the core electrons were represented by the Projector Augmented Wave (PAW) method.^{20,21} This computational setup results in a lattice parameter for the gold bulk of 4.17 Å, which is in reasonable agreement with the experimental value (4.07 Å).^{22,23} Accordingly, the dimensions of the unit cell are $a = 29.52$ Å and $b = 23.62$ Å (where $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$). The length along the c direction was set to 30 Å including a vacuum region of thickness slightly larger than 17 Å, which was proven to be sufficient to avoid interactions between cell replicas. The isolated molecules were calculated with the same box but removing the surface. Solvent effects were not considered.

We modeled a low-coverage regime for the POM–Au system with non-interacting adsorbed molecules (POM–POM distance > 7.5 Å). The POM–Au models were relaxed fixing the three gold layers at the bottom of the slab to the geometry obtained in the bulk calculation. The optimizations were performed until self-consistency, with thresholds of 10^{-5} eV and 0.02 eV·Å⁻¹ for electronic and ionic convergence, respectively. The Brillouin zone was sampled with the

Monkhorst-Pack grid.²⁴ A 9×9×9 Monkhorst-Pack mesh of k-points was applied to run geometry optimizations of the bulk, and for the surface optimizations we used a 7×7×1 mesh. Nevertheless, only the Γ -point was taken into account for the optimization of the POM–Au system due to the large size of the unit cell used. Discussion of atomic charges and spins is based on Bader’s AIM (Atoms in Molecules) method²⁵ using the Henkelmann algorithm.²⁶

4.2.2 Molecular conductivity

Transport calculations were performed on the optimized POM-Au systems, using version 4.1 of the SIESTA/TRANSIESTA code and the post-processing TBtrans package.^{30,31} PW91¹⁹ has been used as exchange-correlation functional. For all the atoms, except for gold, the valence electrons have been described using a double-zeta basis set and the core electrons by norm-conserving Troullier-Martin pseudopotentials.^{32,33} For gold atoms, a single-zeta basis set was used in combination with a pseudopotential which accounts only for 1 valence electron. This apparently crude description gives reasonable transport properties in single-point calculations.^{34,35} We gradually increased the number of k-points until convergence of the DOS for gold electrodes firstly and, secondly, of the transmission function of the device. These calculations gave us a grid of 13×13×17 for TRANSIESTA calculations and 27×27×21 for TBtrans. For electron-reduced systems only the counteranions were optimized in the complete POM-Au(111) system, keeping the POM-Au(111) structure of the completely oxidized system.

4.3 $[V_6O_{13}\{(OCH_2)_3CCH_2SR\}_2]^{2-}$ (R = Me, Ph) on Au(111) Surface

4.3.1 Adsorption sites and orientations: stability and structure

DFT geometry optimizations were performed for **1** and **5**, where R' = H and R = Me, Ph respectively, on Au(111). The adsorption of the POM was tested for face and edge adsorption modes, characterized by six and three Au-O_{POM} contacts, respectively. The oxygen atoms of the substrate in contact with the gold surface are shown as red spheres Figure 4.4 b) and c) for face and edge

orientations. These atoms can make contact with the surface through top, hcp, fcc, and bridge positions of the Au(111) surface. For the face orientation, only the fcc position was calculated (F_{fcc}), being the most favorable one in previous calculations on the analogous $Mo_6O_{19}^{2-}$ Lindqvist structure.²⁷ Less is known about the edge orientation and, therefore, we have tested the four positions and, in addition, two different directions on the gold surface for the optimization of **5**, which are described in Figure 4.4 d). For the nomenclature of the adsorption sites and directions for the edge orientation we have used the following form: **Site**_{**Direction**}, being the **Site** the position of the O_t (in blue in Figure 4.4) with respect to the gold surface —top, hcp, fcc or bridge— and **Direction 1** or **2** depending on the angle in the unit cell —dashed or dotted line—. All the structures are represented in Figure 4.4.

Only fully oxidized POMs, with charge -2 , have been considered. The potassium counter cations that ensure the charge neutrality of the unit cell were placed at a distance larger than 10 Å from the POM. Without taking into account the dispersion interactions and fixing the position of potassium cations, the relative energies of the different adsorption modes and directions of **5** on Au(111) are ranged within 0.34 eV, being F_{fcc} and T_1 the most stable ones and practically degenerate in energy ($\Delta E = 0.03$ eV, see Table 4.1). Subsequently, the energetically most favourable structure of each orientation for **5** have been optimized for compounds **1** and **5** without constraining the position of potassium atoms. From these new optimizations, the T_1 orientation is more stable than the F_{fcc} one by 0.23 eV and 0.15 eV for **5** and **1**, respectively. Considering dispersion, the T_1 orientation for **5** is still the most stable but the energy is 0.12 eV closer to F_{fcc} .

In the optimal geometries of **5** on Au(111) — F_{fcc} and T_1 — the top of the adsorbed POV is found 7.62 and 7.63 Å above the gold surface, respectively, in good agreement with the experiment (7.5 ± 0.05 Å). These values take into account the van der Waals atomic radii of 1.52 for O and 1.66 Å for Au atoms (see Figure 4.5).^{28,29} For compound **1**, the computed heights are 7.66 Å (T_1) and 7.63 Å (F_{fcc}). Including the dispersion effects for **5**, the height decreases about 0.4 Å for T_1 , which we attribute to a notable increase in the phenyl-Au interactions that drags the phenyl rings towards the Au surface. On the other hand, the decrease is only 0.17 Å for F_{fcc} , because one phenyl ring is already in close contact

66 | 4.3 $[V_6O_{13}\{(OCH_2)_3CCH_2SR\}_2]^{2-}$ (R = Me, Ph) on Au(111) Surface

with the Au surface without taking into account the dispersion, see Figure 4.5. The O-Au contacts can be via O_b and O_t . T_1 adsorption presents three O-Au contacts, one of them O_b type and two O_t , see Figure 4.5. On the other hand, F_{fcc} presents five contacts, three O_b and 3 O_t . The O-Au distances in the T_1 mode range within 2.32-2.40 Å and 2.31-2.37 Å for **1** and **5** respectively, and for F_{fcc} it is 2.34-3.25 Å for both compounds. The complete list of distances is shown in Table 4.2.

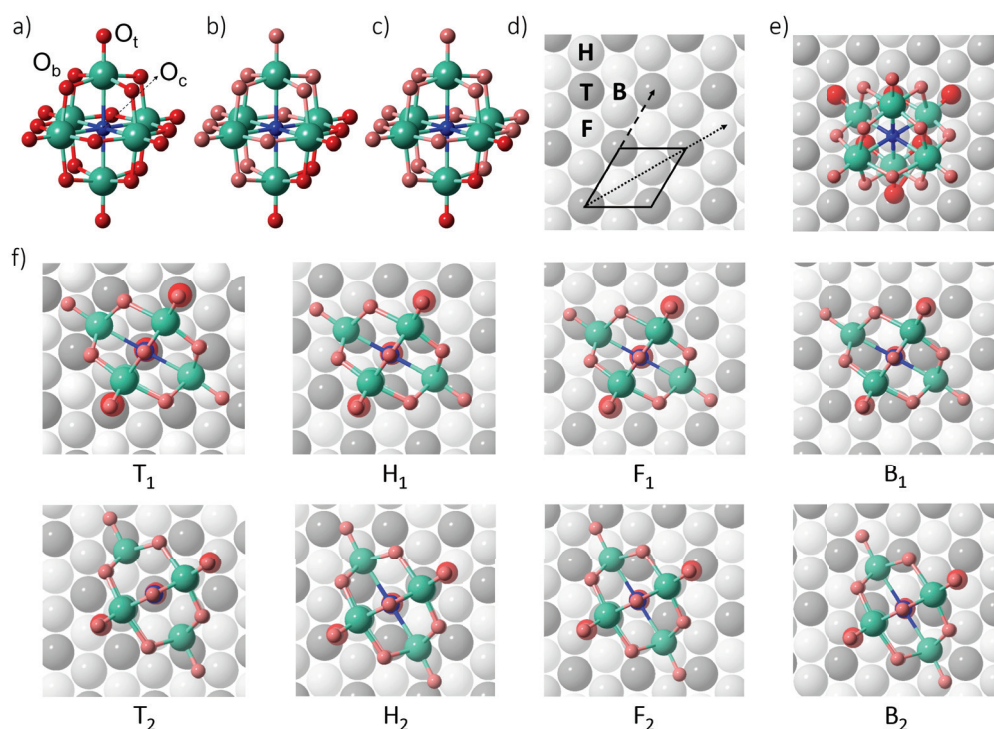


Figure 4.4 | a) Ball and stick representation with oxygen labelling for Lindqvist $[V_6O_{19}]^{8-}$. The central oxygen (O_c , in blue) is the reference for the nomenclature of adsorptions.²⁷ Adsorption of the POM on Au(111): b) Representation with red balls representing oxygen atoms in contact with the surface for the face and c) edge orientations. d) The Au(111) surface with the unit cell shown in black. Arrows represent the two different directions studied for the adsorption of **5** on Au(111), being the dashed line the direction 1 and the dotted one direction 2; T: top, H: hcp, F: fcc and, B: bridge adsorption sites. e) Top view of $[V_6O_{19}]^{8-}$ adsorbed on Au(111) for face orientations. f) Adsorption tested sites for edge orientation. Structures **1** and **5** are represented by the $[V_6O_{19}]^{8-}$ part only for clarity. Colour code: red, pale red and blue for oxygen; turquoise for vanadium; deep grey, medium grey and light grey for gold of the 1st, 2nd and, 3rd layer, respectively.

Table 4.1 | Relative energy of different adsorption modes for **5** with fixed counterions.

Orientation	Adsorption mode	Relative energy (eV)
Face	Fcc	0.03
Edge	T ₁	0.00
	H ₁	0.13
	F ₁	0.13
	B ₁	0.34
	T ₂	0.19
	H ₂	0.20
	F ₂	0.20
	B ₂	0.13

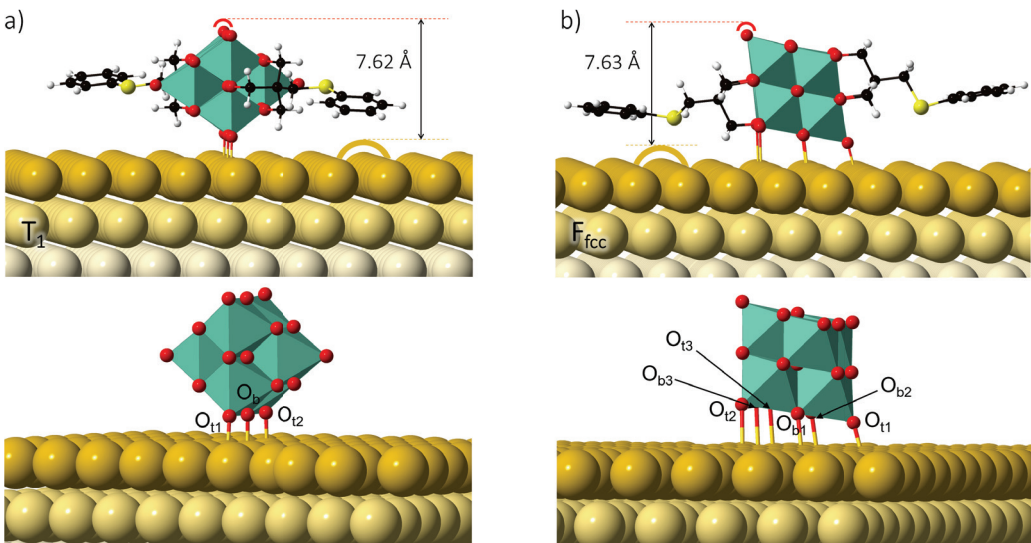


Figure 4.5 | Above: the most stable optimized adsorption geometries of **5** on Au(111), a) **T₁** and b) **F_{fcc}**. Below: oxygen types for distances shown in Table 4.2 for each optimized structure. Turquoise: V, red: O, yellow: S, black: C, white: H, and golden, pale golden and beige: Au. Counterions are omitted for clarity.

Table 4.2 | O-Au distances for adsorbed **1** and **5** compounds on Au(111) surface in the most stable orientations. All the distances are shown in Å. Oxygen types are specified in Figure 4.5.

Type of contact	1		5	
	T ₁	F _{fcc}	T ₁	F _{fcc}
O _{t1} -Au	2.32	2.34	2.31	2.34
O _{t2} - Au	2.40	3.02	2.37	3.02
O _{t3} - Au	-	3.14	-	3.12
O _{b1} - Au	2.38	2.67	2.36	2.67
O _{b2} - Au	-	2.74	-	2.73
O _{b3} - Au	-	3.25	-	3.25

The relative energies discussed above allow us to assess the various adsorption sites and orientations of **1** and **5** on Au(111). To analyse the POM-surface interaction we have computed the adsorption energies (E_{ads}) for the different models as

$$E_{ads} = E_{tot} - E_{surf} - E_{KPOM}$$

(4.1)

where E_{ads} is the energy of the whole system, E_{surf} is the energy of the clean surface, and E_{KPOM} is the energy of the isolated POM surrounded by the counteractions in its optimal distribution. The computed E_{ads} are −0.41 eV (F_{fcc}) and −0.64 eV (T₁) for **5**, and −0.51 eV (F_{fcc}) and −0.66 eV (T₁) for **1**, revealing that both compounds prefer the T₁ mode, a behaviour that is preserved including the dispersion effects. Nevertheless, these effects make the calculated adsorption energies to increase dramatically to −35 eV. To study the effect of dispersion due to the phenyl rings in **5**, we optimized adsorption mode T₁ for **5** for a model where the ligand is cut before the sulphur atom (**model 1**, see Figure 4.9) to avoid dispersion interactions between the gold surface and the sulphur atom or the phenyl group. The calculated E_{ads} for **5** and **model** are −36.54 and −33.04 eV, respectively. In a previous work from our group it has been perceived that DFT-D2 may not be enough for our system, since the default van der Waals values provided by VASP are based on neutral atoms and not on ions (V^{IV}, V^V, O²⁻), resulting in incorrect values for adsorption energies for our systems.²⁷ Therefore, adsorption energies for this kind of system must be used only for comparison between the different adsorption modes in order to decide on the most probable

adsorption orientation. However, these E_{ads} must not be used to associate the adsorption to a physical or a chemical type.

4.3.2 Electronic structure: density of states and Bader analysis

The projected density of states (PDOS) of **1** and **5** in the isolated and the most stable adsorbed forms are depicted in Figure 4.6 and Figure 4.7. From Figure 4.7, it is readily seen that the orientation of the POV with respect to the Au surface does not affect the electronic structure —very similar PDOS are observed. The highest occupied band corresponds to S and C atoms and is located between -0.5 and 0.0 eV below the Fermi level (E_F). The oxo band lies at slightly lower energies, below -1.0 eV. At $E > E_F$ we find the vanadium d-bands, which are likely to play an important role in electron conduction, especially the one closer to E_F . Comparing the PDOS of the isolated and adsorbed compounds it can be confirmed that the POMs retain their nature upon adsorption on Au(111). The only apparent difference concerns the adsorbed compound **5** in the T_1 adsorption orientation, as the C/S band is upshifted, nearly hitting E_F . This relative high energy can be ascribed to the poor contact between ligands and the gold surface in this orientation compared with F_{fcc} . Besides, from the calculations, it should be stressed that **1** and **5** remain chemically intact when adsorbed on Au(111), keeping their initial redox state as the Bader atomic charge analysis shows, see Table 4.3. The molecular charges of the adsorbed POVs are -1.90 (**1**) and -1.93 (**5**), being virtually the same as in isolated form (-2). The PDOS also indicate that the organic ligand (Me or Ph for **1** and **5** respectively) does not affect the vanadium d-band.

Table 4.3 | Bader charges per fragment for different adsorption modes for **1** and **5** on Au(111).

	Site	Σ POM atoms	Σ counteranions	Σ Au atoms
1	T_1	-1.92	1.83	0.09
	F_{fcc}	-1.90	1.83	0.07
5	T_1	-1.90	1.83	0.07
	F_{fcc}	-1.93	1.83	0.10

70 | 4.3 $[V_6O_{13}\{(OCH_2)_3CCH_2SR\}_2]^{2-}$ (R = Me, Ph) on Au(111) Surface

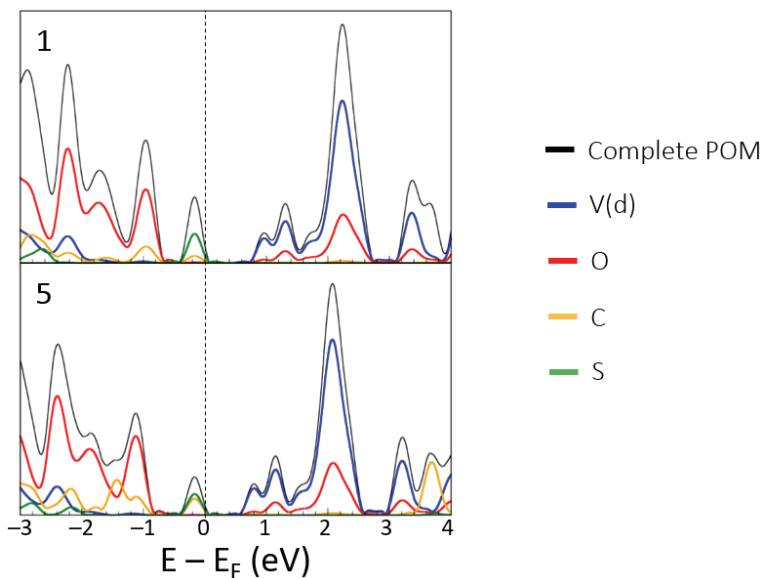


Figure 4.6 | Density of states and Projected density of states for isolated molecules **1** and **5**. All energies refer to the Fermi level (E_F). Accordingly, the bands located at negative energies are occupied.

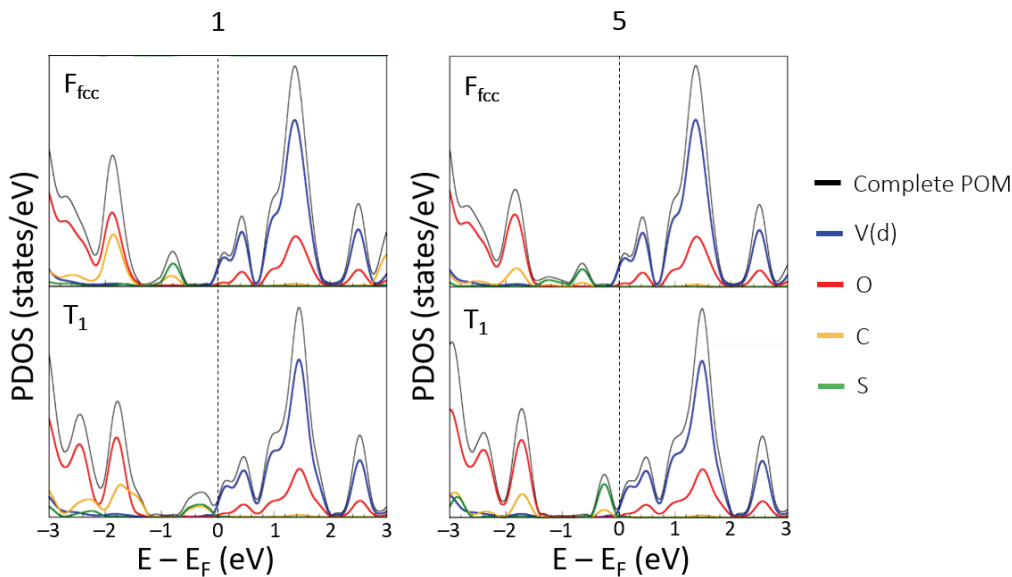


Figure 4.7 | Projected density of states for **1** and **5** adsorbed on Au(111). All energies refer to the Fermi level (E_F). Accordingly, the bands located at negative energies are occupied.

To gain additional insight into the nature of the adsorption we have considered the gold surface and the POM adsorbate as two interacting fragments. In isolated form, their corresponding electron density distribution functions are $\rho(\text{Au})$ and $\rho(\text{POM})$. When both fragments are put together at adsorption geometry, these ρ evolve to become $\rho(\text{Au} + \text{POM})$, which is not equal to the sum of the initial densities. The charge density difference ($\Delta\rho$) refers to the change experienced by the total electron density distribution of surface and adsorbate upon mutual interaction:

$$\Delta\rho = \rho(\text{Au} + \text{POM}) - (\rho(\text{Au}) + \rho(\text{POM})) \quad (4.2)$$

At variance with ρ , $\Delta\rho$ can take positive (accumulation of ρ) or negative (depletion of ρ) values at any point in space. The most intuitive way of interpreting $\Delta\rho$ is to represent a surface connecting points of the same value and sign, thus identifying regions of accumulation or depletion of ρ . As represented in Figure 4.8 for **5** in both adsorption modes, a region of electron density depletion ($\Delta\rho < 0$, blue colour) is located in between the two fragments, indicative of a non-covalent interaction. This feature, distinctive of weakly or moderately interacting fragments, denotes minor changes in their respective electronic structures and implies that the chemical integrity of the fragments is mostly maintained.

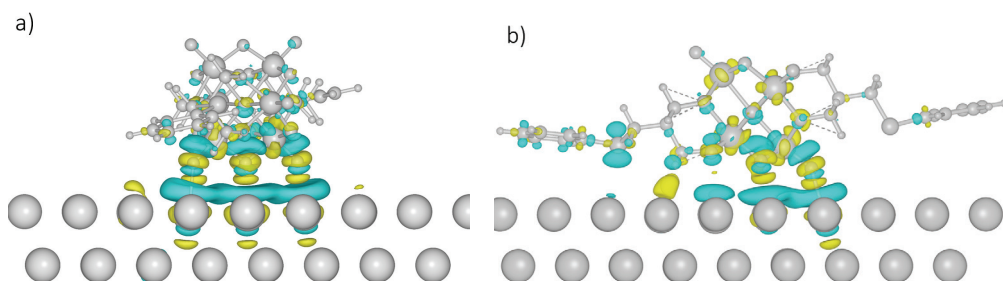


Figure 4.8 | Charge density difference ($\Delta\rho$) computed for **5** in a) T_1 and b) F_{fcc} adsorption modes. Yellow and blue regions represent accumulation and depletion of electron density, respectively. The surface isosurface is set to 0.001 e/Bohr³.

4.3.3 Introduction of an electric field and system reduction

To predict the possibility of the POM to be reduced by an external potential (as experimentalists consider), we modelled an electric field in our calculations. The effect of applying $E_{\text{ext}} = 0.5 \text{ eV } \text{\AA}^{-1}$ has been analysed for **1** and **5** adsorbed on Au(111). The Bader analysis evidences that the adsorbed molecules are reduced under such an electrical field, with a calculated molecular charge increase of almost one unit, up to -2.72 for **5** in $\mathbf{F}_{\text{fcc}}$. Concomitantly, the gold slab is oxidised by 0.90 e . In line with these results, the energy of the lowest vanadium d-band is downshifted by the effect of the electric field, fully hitting the Fermi level and accepting electron density from gold (Figure 4.9 a)). Focusing on the PDOS and the Mulliken atomic spin densities (MASD) (Table 4.4) of the system when an electric field is applied, we can easily figure out that the extra electron is accepted by the vanadium atoms.

To complete the picture, we have studied the one-, two- and three-electron reduced system. Upon one-electron reduction, the α -PDOS reveals that the vanadium d-band crosses E_{F} indicating filling of this band, whereas the β -PDOS does not suffer significant changes, Figure 4.9 b). The partial filling of the vanadium d-levels is corroborated by the Mulliken atomic spin densities (see Table 4.5). For the 2e-reduced compound we considered the lowest triplet state, although it is actually a singlet by virtue of the well-known strong antiferromagnetic coupling occurring in many 2e-reduced POMs. The coupling of the unpaired electrons is actually so strong that these 2e-reduced POMs behave as diamagnetic species. Both solutions have, though, very similar electronic spatial distributions and, for the sake of an easier electron count of delocalized d electrons per vanadium, in Table 4.5 we have listed the MASDs taken from the triplet calculation. Confirming that both solutions are practically identical, the total charge of the singlet closed-shell for the POM has been computed to be extremely close to the one found in the high-spin solution. Successive reductions associated to an applied electric field involve a steady filling of the vanadium d-band in the V₆O₁₉ unit and a concomitant increase in the MASD of V atoms.

Table 4.4 | Bader charges and MASD for **5** in isolated and adsorbed forms without and with an electric field.

	Isolated 5	5 on Au(111)		
	no E field	no E field	E = 0.5 eV/Å	
	Bader	Bader	Bader	MASD
V	1.90	1.89	1.88	0.12
	1.89	1.90	1.88	0.23
	1.89	1.88	1.88	0.09
	1.92	1.89	1.87	0.26
	1.89	1.90	1.88	0.13
	1.90	1.89	1.88	0.25
O	-0.67	-0.69	-0.70	-0.01
	-0.67	-0.67	-0.74	-0.02
	-0.79	-0.89	-0.90	-0.02
	-0.89	-0.89	-0.93	-0.03
	-0.89	-0.83	-0.84	-0.02
	-0.67	-0.70	-0.71	-0.01
	-0.89	-0.83	-0.83	-0.02
	-0.89	-0.88	-0.93	-0.03
	-0.69	-0.69	-0.78	-0.02
	-0.67	-0.69	-0.70	-0.01
	-0.79	-0.89	-0.90	-0.02
	-0.67	-0.66	-0.74	-0.02
	-0.99	-1.06	-1.09	0.00
	-1.06	-1.04	-1.01	0.00
	-0.99	-1.08	-1.07	0.01
	-1.19	-1.20	-1.20	0.00
	-1.00	-1.03	-1.01	0.01
	-1.06	-1.00	-1.05	0.01
	-0.98	-0.99	-0.99	0.01

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4.3 [V₆O₁₃[(OCH₂)₃CCH₂SR]₂]²⁻ (R = Me, Ph) on Au(111) Surface

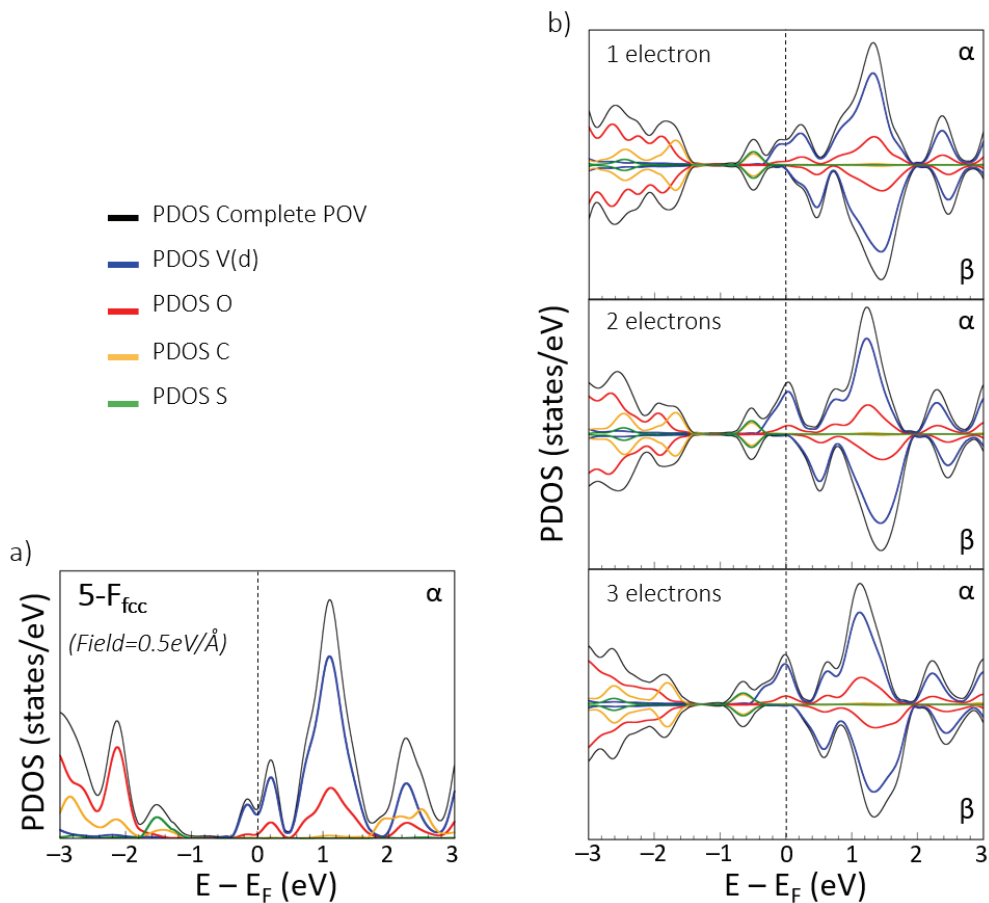


Figure 4.9 | Projected density of states (PDOS). a) Adsorbed molecule **5** under $E_{\text{ext}} = 0.5 \text{ eV \AA}^{-1}$.
1. b) One-, two-, and three-electron reduced molecule **5** adsorbed in T_1 mode.

Table 4.5 | MASD for vanadium atoms in **5** with different number of extra electrons.

1e-reduced	2e-reduced	3e-reduced
0.08	0.31	0.30
0.25	0.31	0.31
0.06	0.38	0.54
0.37	0.38	0.40
0.10	0.28	0.43
0.23	0.29	0.45

4.4 Molecular Conductivity

The second part of the study focuses on the molecular conductivity of the POM-Au system, specifically whether the vanadium atoms of the POM are the main responsible for this phenomenon, as experimentalists propose. Furthermore, another assumption must be confirmed: each stage in the stepped I-V plot is due to a 1e-reduction of the POM. To take into account the experimental reduction phenomenon, we have calculated the conductivity of four different systems: the completely oxidized and the one-, two- and three-electron reduced systems. These results allow us to compare the electrical conduction as a function of the oxidation state of the system with the experimental I-V data.

4.4.1 Device model

It is well known that conductivity calculations are computationally very expensive. Observing that the I-V behavior for **1** and **5** is practically the same, we can assume that the last part of the ligands (R') is not essential for conductivity. Moreover, assuming that vanadium atoms are the main responsible for conductivity, it is not necessary to consider the ligands in the conductivity calculations. Thus, by removing the outer part of the organic ligands connected to the POM, we can significantly reduce the size of the model and, thus, a smaller gold slab suffices to ensure non-interacting POMs from different unit cells. We have tested the two models shown in Figure 4.10 to reduce the system size. Their PDOS are very similar to that of **5** and, thus, they represent correctly the main electronic features of the full system. Nevertheless, we have chosen **Model 1** (hereafter called **model**) as the most representative one for the conductivity study, inasmuch as its vanadium PDOS is practically that of **5**, which we have assumed to be responsible for the system conductivity.

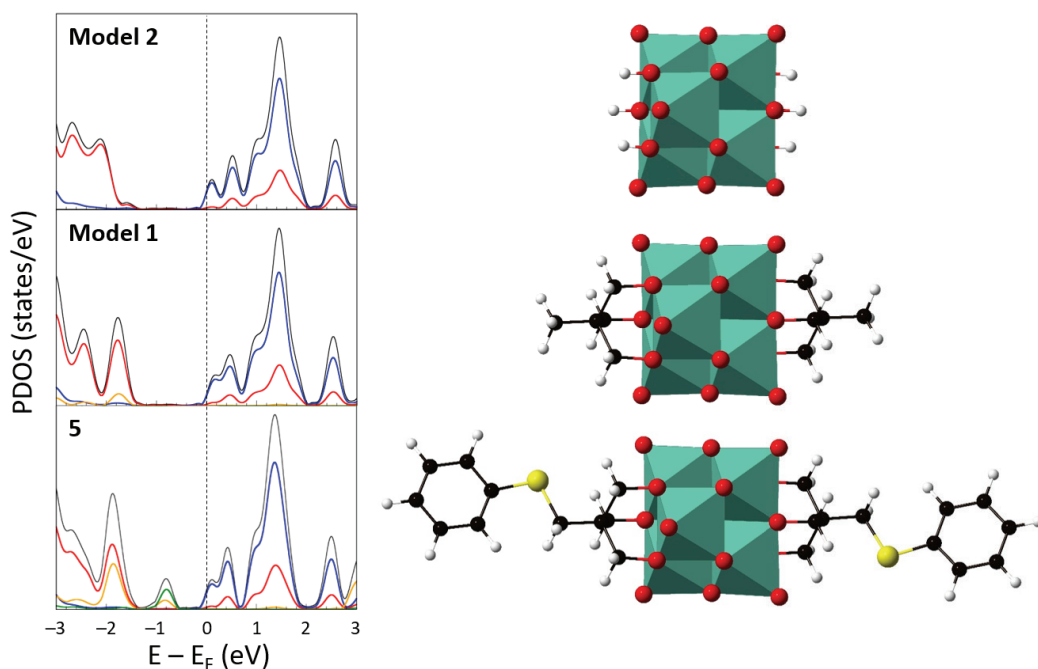


Figure 4.10 | Projected density of states (PDOS) for **5** and two different models (**Model 1** and **Model 2**) adsorbed on Au(111). Color code for PDOS as Figure 4.8.

To build the device we have decided to use gold for both electrodes. The optimized structures of **5** have been used for the calculations, replacing the POM by the corresponding model and reducing the Au(111) surface until an inter-cell POM-POM distance of 7 Å is reached. Then, one of the electrodes is a 8-layer gold surface where the POM is adsorbed, and the other electrode is made of an optimized 8-layer gold surface with the smallest tip possible, formed by 4 atoms. The chosen O-Au distance between the tip and the model was fixed to 2.32 Å, the smallest Au-O distance obtained in a POM-Au(111) optimization. The models have been studied for F_{fcc} and T_1 adsorptions. However, for T_1 , two options are possible: the tip on top of a terminal (T_{1a}) or of a bridging (T_{1b}) oxygen (Figure 4.11).

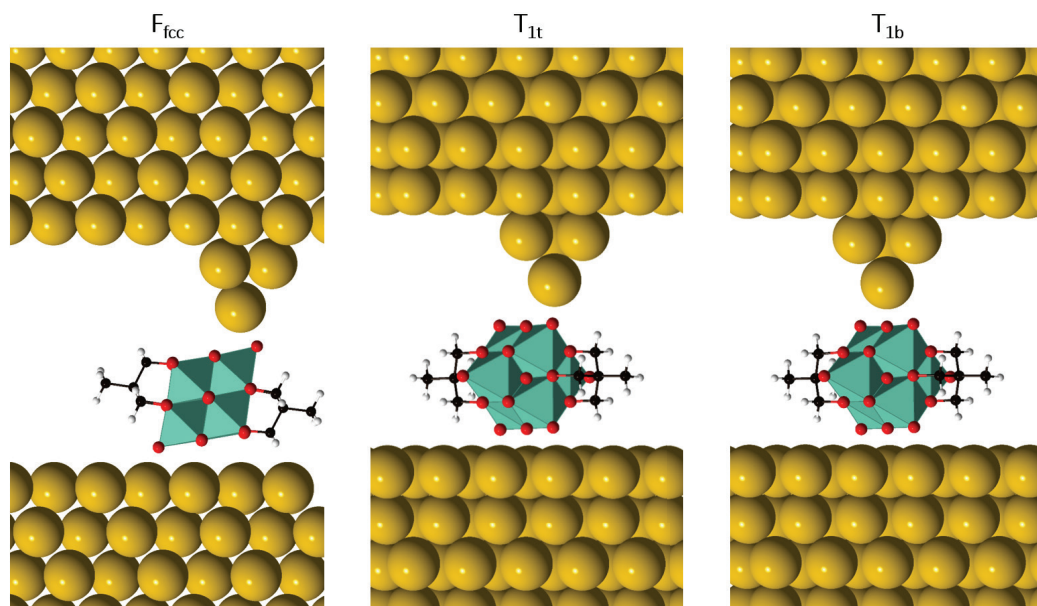


Figure 4.11 | Three different devices used for conductivity calculations. Counteranions are omitted for clarity. Turquoise polyhedral: V, red: O, yellow: S, black: C, white: H, and golden: Au.

4.4.2 Completely oxidized system: comparison between different devices

The first step of the study is to compare the three different model systems describing the device: F_{fcc} , T_{1t} and T_{1b} , as shown in Figure 4.10. As a first approach, we consider the behavior of the transmission spectra of our model (Figure 4.12), with peaks at different energies, those near the Fermi level being potential sources of conductivity. Larger and broader peaks are typically related to more pronounced conductivity. Starting the comparison between the transmission spectra for models T_{1t} and T_{1b} , where the only difference is the position of the tip, it is clear that T_{1t} shows a transmission peak near E_F that is more intense than for T_{1b} . Then, the position of the tip on top of a terminal oxygen has a better response and, therefore, it must have larger conductivity. From the comparison between T_{1t} and F_{fcc} , with different POM orientations of the POM on the surface, the transmission obtained is nearly identical. These calculations, performed with the PW91 functional, and analogous ones obtained

with the PBE functional, give practically the same results, see Figure 4.13, confirming the robustness of the conclusions obtained.

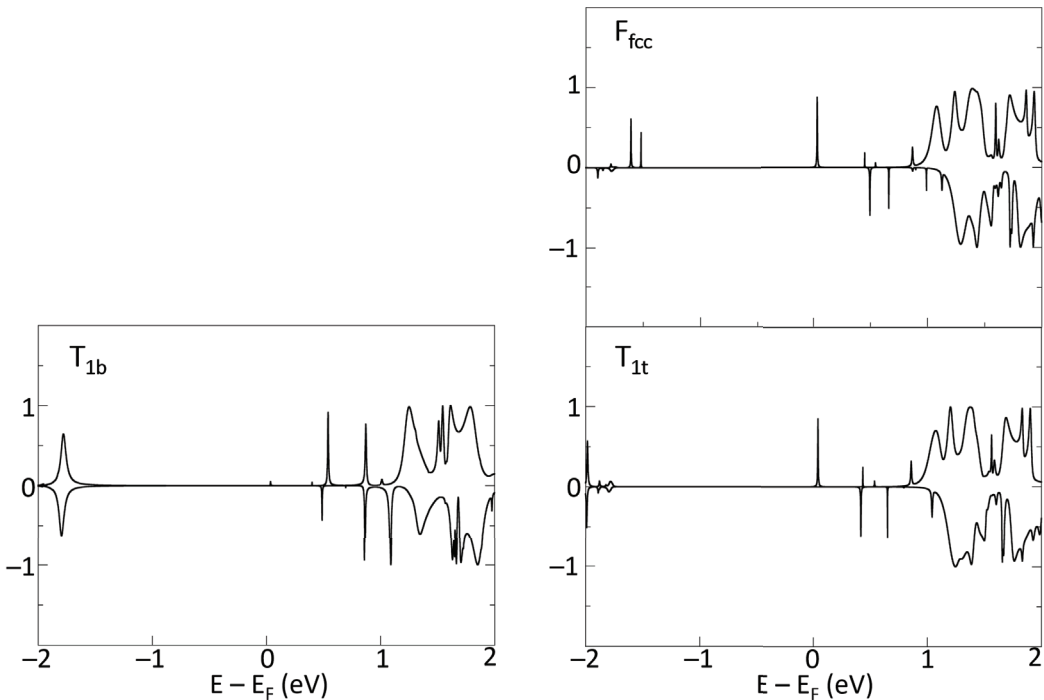


Figure 4.12 | Zero bias transmission spectra for the three devices studied: T_{1b} , T_{1t} , and F_{fcc} . Positive and negative transmission values correspond to α and β spin-orbital contributions.

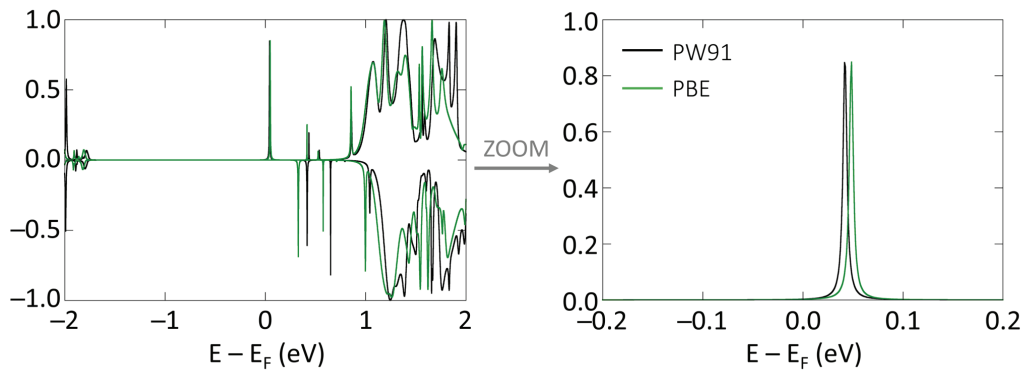


Figure 4.13 | Zero bias transmission spectrum of T_{1b} obtained with PW91 and PBE density functionals. Positive and negative transmission values correspond to α and β spin-orbital contributions.

Considering these results, we performed conductivity calculations for systems T_{1t} and F_{fcc} and compared them at different applied voltages to analyze their respective behaviors. In Figure 4.14, transmission spectra at different applied potentials are shown, with a α transmission peak near E_F hitting the bias window with increasing applied potential. This fact suggests to a current increase as the applied voltage increases, as shown in the I-V graph in Figure 4.14 b). On the other hand, the β spin contribution to the electrical current is practically zero (approx. 10.5 nA), in agreement with the absence of β spin-orbital peak near E_F in the transmission spectrum. Nevertheless, this dissimilar behavior in the α and β spin contributions cannot be attributed to spin-filtering properties. This α peak could also appear in the β region since it is due to polarization. The program imposes the polarization in α and, so a in the α region is shown. However, we have to consider the other half, the β , as if the program had considered β polarization. So, this false spin-filtering behaviour is an artifact imposed by the program and we do not have to consider this property. Moreover, we could not identify relevant differences between T_{1t} and F_{fcc} , confirming that the main properties of the adsorbed POM are not strongly influenced by its position and direction on top of the surface, in agreement with previous findings in our group.^{16,17}

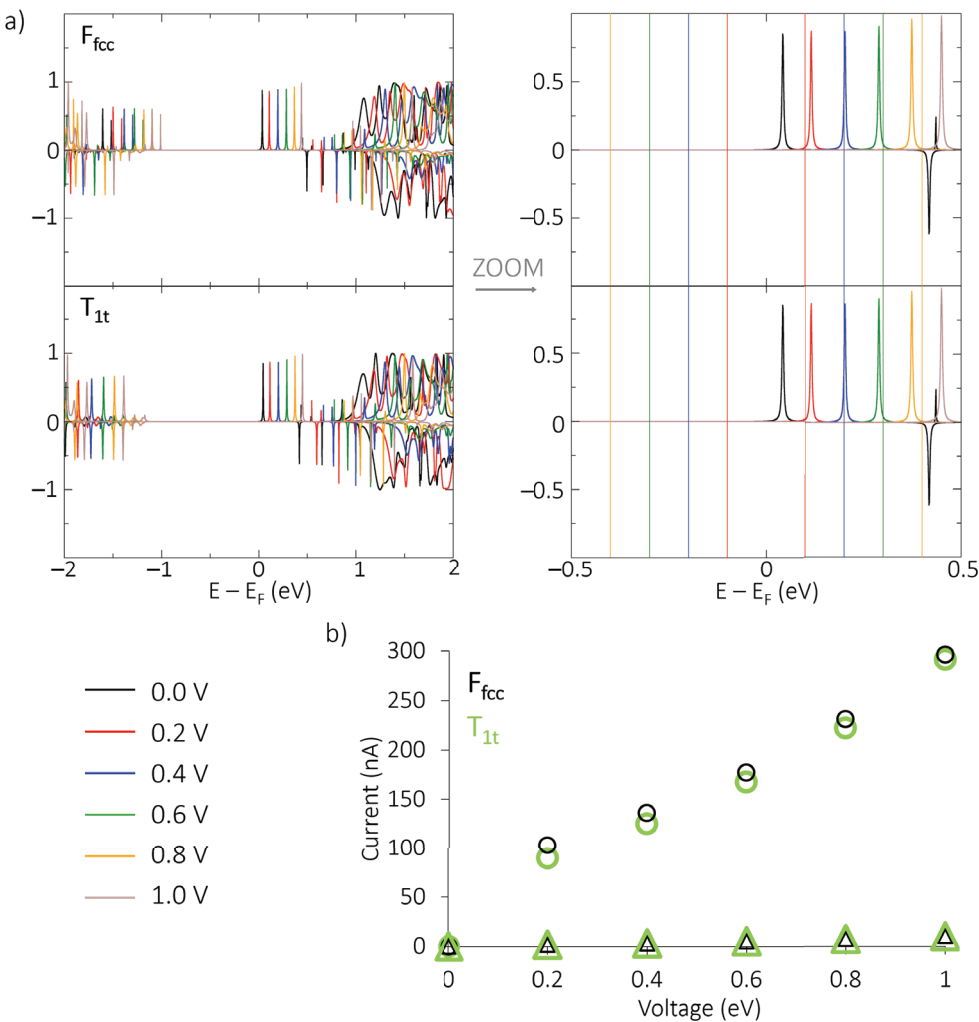


Figure 4.14 | a) Transmission spectra at different applied voltages for T_{1t} and F_{fcc} . Vertical lines in the ZOOM spectra define the bias window for each applied potential. Positive and negative values of transmission correspond to α and β spin-orbital contributions. b) I-V graph for both devices, with α (circles) β (triangles) contributions to the electrical current.

4.4.3 Zero-, one-, and two-electron reduced systems

Only the T_{1t} model was considered in this study since it shows the largest conductivity and also the same transmission and conductivity as F_{fcc} . The increase in the number of electrons have been modeled adding the corresponding counteranions but keeping the initial optimal structure. Figure 4.15 shows the

transmission spectra for zero- (black), one- (orange) and two- (red) electron reduced T_{1t} at 0 V. An increase in the number of transmission peaks near E_F as the system gains electrons is evident, which can potentially hit the bias window when the potential increases. The device features one, two and three transmission peaks for the zero-, one-, and two-electron reduced forms, respectively. Consequently, a rise of the electrical current is anticipated as the device gains electrons due a progressive filling of the vanadium d-band, which produces more states near E_F accessible for transmission.

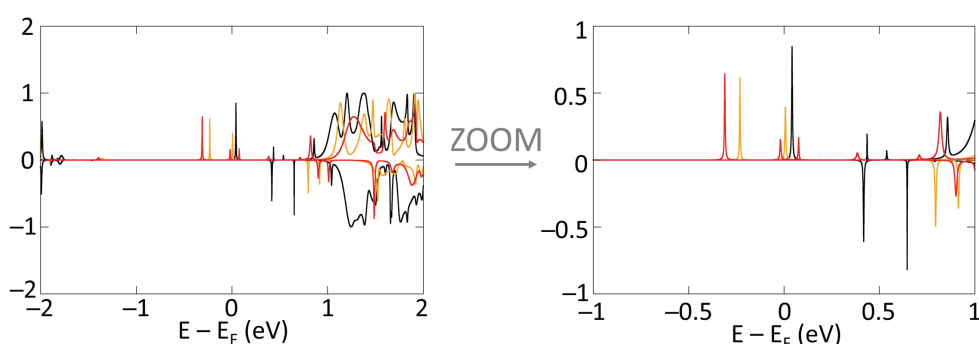


Figure 4.15 | Transmission spectra for zero- (black), one- (orange) and two- (red) electron reduced T_{1t} at 0 V. Positive and negative values of transmission correspond to α and β spin-orbital contributions, respectively.

Next to the analysis of transmission spectra at 0 V, calculations including a potential $V \neq 0$ have been performed. As shown in Figure 4.16 a), all the systems feature more electrical current as the applied potential increases. However, it is not totally clear whether more extra electrons in the POM enhance the electrical current. It is expected that increasing the potential helps adding electrons to the system. Bearing in mind the assumption of the experimentalists that each step in the I-V plot is associated to a different reduction state of the system, we draw a new I-V plot considering the actual reduction state at each potential accordingly (Figure 4.16 b)). In other words, for $V = 0$ – 0.6 V we have used the results of the oxidized system, for $V = 0.7$ – 1.0 V of the one-electron reduced, and for $V = 1.1$ – 1.5 V of the two-electron reduced one. A stepped behavior can be guessed in the theoretical I-V plot associated to an increasing number of electrons in the system, in agreement with the observations (overlapping the experimental and

the calculated I-V graphs, a similar behavior can be perceived, Figure 4.16 c)). Even though, at variance with experiments, increasing the potential for a given reduction state gives a varying current, thus the theoretical plot not being exactly stair like. In addition, comparing the experimental and the calculated dI/dV vs. V plots (Figure 4.16 d)), a similar behavior arises, the only difference being the peak at 0.2 V present in the calculated plot only. This peak is most probably an artifact of the way the derivative of the calculated current is determined. The simple two-point estimate for the gradient at each calculated point breaks down for 0.2 V as the current at 0 V is zero by definition. More sophisticated estimates of the gradient with three- or five- point estimates would require much more data points. This is unfortunately not realistic at this point given the large computational cost of these calculations. So, currently, we confirm that each step is due to a different reduction state of the Lindqvist-type hexavanadate, since we have demonstrated that the POM is reduced when an external potential is applied and also observed a different behavior in conductivity for the different reduced systems, see Table 4.6.

Table 4.6 | Total spin polarization ($Q_{\alpha} - Q_{\beta}$) of the different devices when a voltage is applied.

Voltage (eV)	Device			
	Oxidized	1e-reduced	2e-reduced	3e-reduced
0.0	0.18	1.47	2.62	3.28
0.2	0.25	1.50	2.66	3.33
0.4	0.33	1.51	2.68	3.38
0.6	0.39	1.55	2.72	3.41
0.7	-	1.56	-	-
0.8	0.44	1.58	2.76	3.44
0.9	-	1.60	-	-
1.0	0.49	1.61	2.81	3.47
1.1	-	-	2.83	-
1.2	0.50	1.63	2.85	3.49
1.3	-	-	2.88	-
1.4	0.48	1.64	2.90	3.52
1.5	-	-	-	3.53
1.6	0.44	1.71	2.96	3.55
1.7	-	-	-	3.57
1.8	0.40	1.77	3.01	3.59

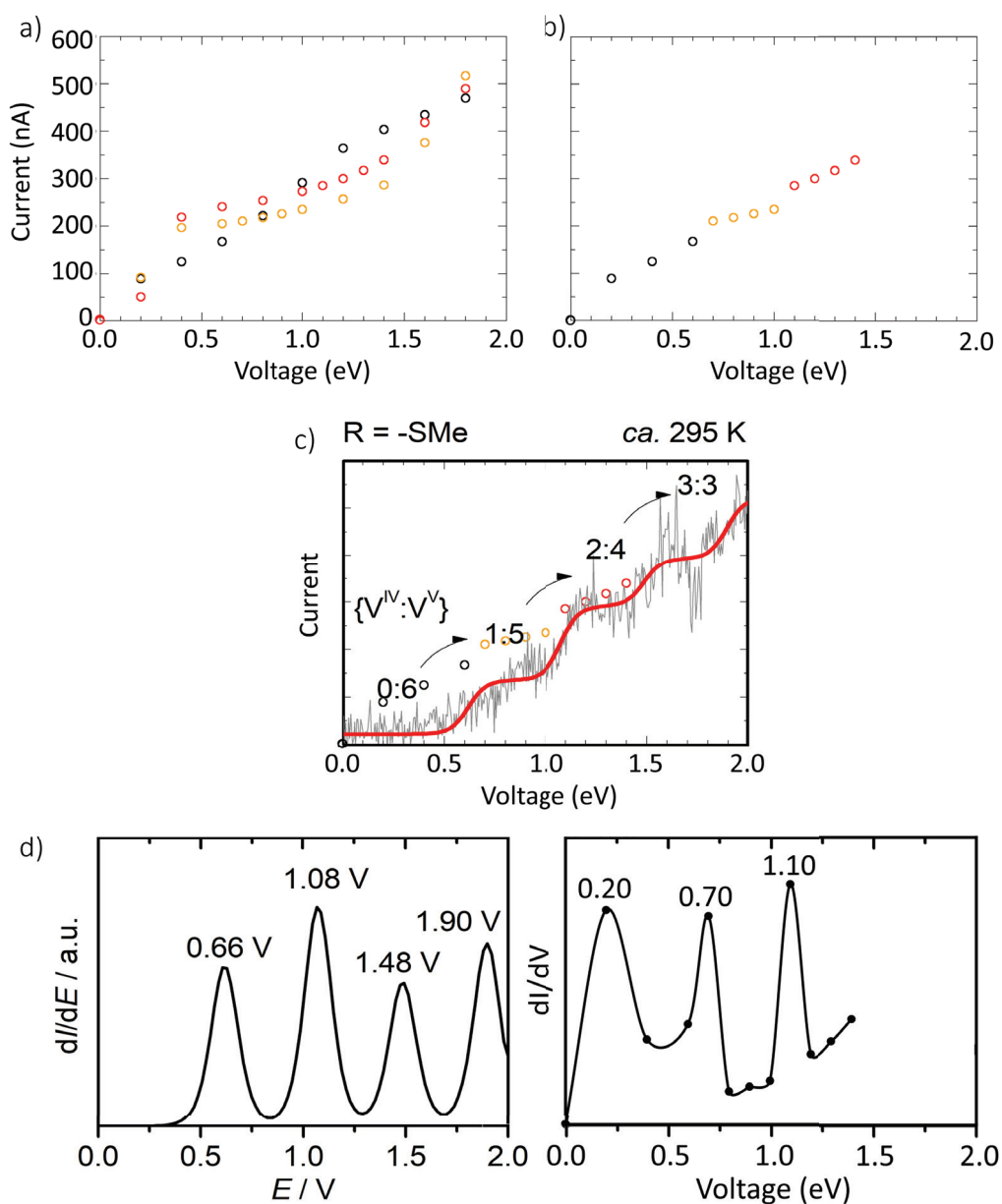


Figure 4.16 | a) I-V plot for zero- (black), one- (orange) and two- (red) electron reduced T_{1t} . b) I-V graph for zero- (black), one- (orange) and two- (red) electron reduced T_{1t} but only taking into account the resting state at each applied potential. c) Schematic superposition of both experimental and calculated I-V graphs. Only α spin-orbital contributions are shown. d) Experimental (left) and calculated (right) dI/dV vs. V plot.

4.4.4 Vanadium atoms: responsible for conductivity

The last question that must be solved is: are vanadium atoms responsible for the system's conductivity? To answer this question, we have to take into account different aspects. A first indication comes from the fact that the vanadium d-band is very close to the Fermi level for the fully oxidized system, but it completely hits the Fermi level in reduced form. Consequently, we can guess that vanadium atoms are involved in the conductivity. The eigenchannel scattering states of the different devices with different oxidation states at E_F can answer this inquiry.^{36,37} Focusing on the most transmitting eigenchannel scattering states (shown in Figure 4.17), we can observe that the main orbitals involved in the transmission are vanadium d orbitals. In some of the eigenchannels a contribution appears from the cations (Mg) that keep the electroneutrality of the cell. However, they do not significantly contribute to the transmission and, thus, they are not relevant.

We performed an additional calculation replacing Mg by Ca atoms and the main eigenchannels of the second device do not have any contribution of Mg atoms because the Ca orbitals lie higher in energy than Mg ones (Figure 4.18). With this extra calculation we have been able to observe that molecular conductivity calculations are very sensitive to changes, since a little change in the counteranions produces a variation in the main transmitting eigenchannels.

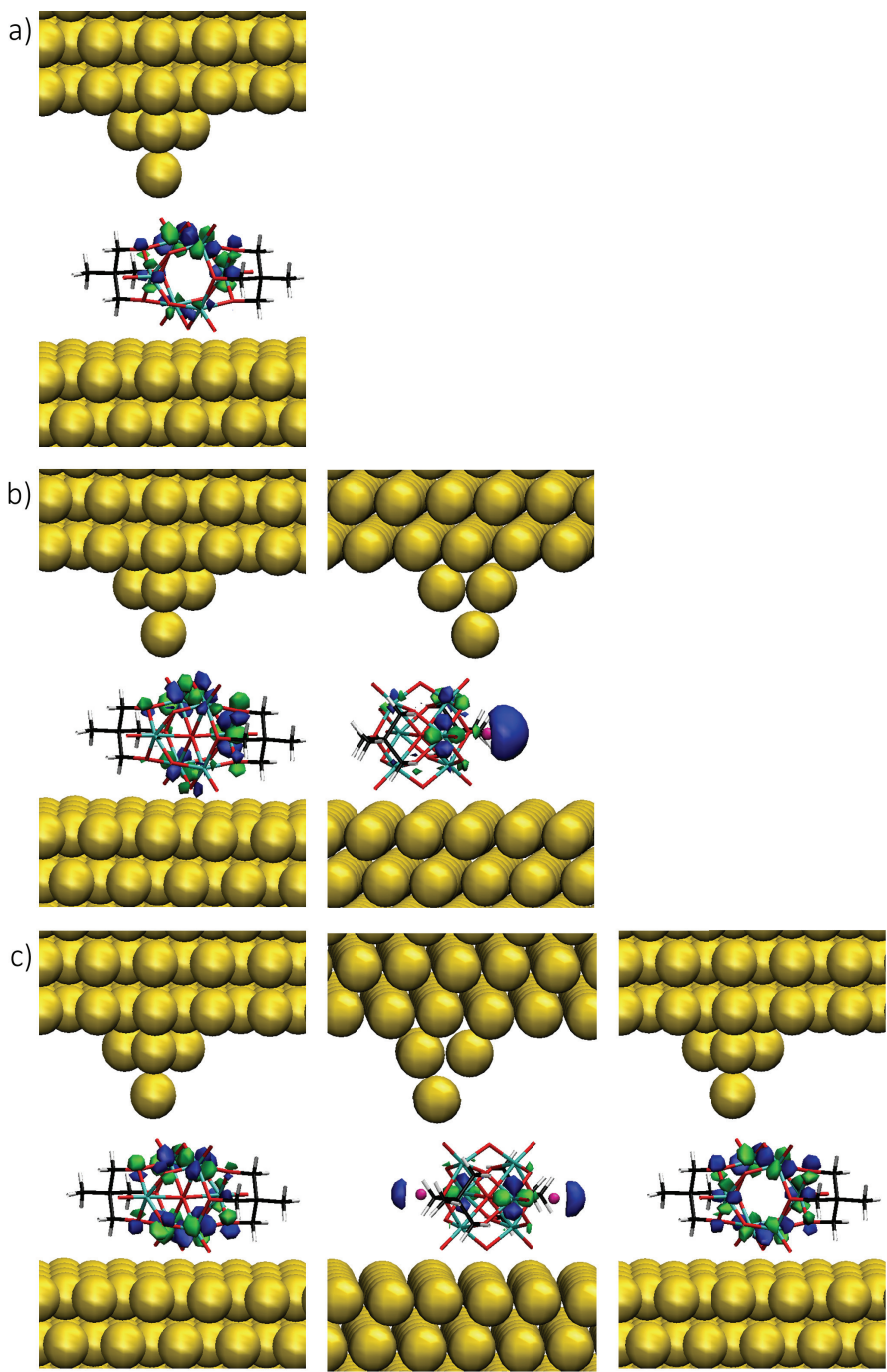


Figure 4.17 | Isosurface plots of the real part of the most transmitting eigenchannel scattering states of the a) zero-, b) one- (from left to right, at -0.23 eV and -0.01 eV) and, c) two- (from left to right, at -0.31 eV, -0.02 eV, and 0.08 eV) electron reduced systems.

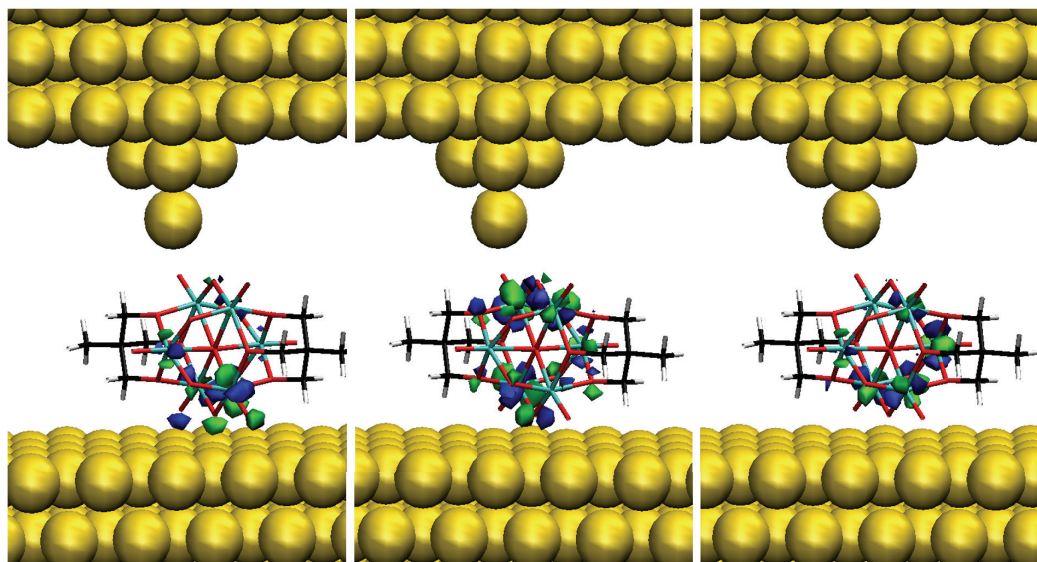


Figure 4.18 | Isosurface plots of the real part of the most transmitting eigenchannel scattering states for the one-electron reduced system after replacement of Mg by Ca. Cations are omitted for clarity. From left to right, at -0.40 eV, 0.04, and 0.29 eV.

4.4.5 Three-electron reduced system

In the study of the one- and two-electron reduced system, we successfully used the model defined for the oxidized form. That is, we applied the same POM, Au(111) and tip geometries, only varying the counteranions necessary to keep the electroneutrality of the unit cell.

The transmission spectrum of the three-electron reduced system is shown in brown in Figure 4.19. It is clear that near the Fermi level, it is the oxidation state with the highest number of transmission peaks. The trend we obtained with zero-, one- and two-electron systems is maintained for three-electron reduced system. The number of transmission peaks near the Fermi level increases with the number of electrons. Nevertheless, looking at the current vs. voltage graph (Figure 4.20) we can perceive how the 3-electron reduced system deviates considerably from the behaviour of the other oxidation states. The tendency is the same for all the reduction states: the more voltage, the more current. But, from approximately 0.8 eV of voltage the increase is much more abrupt for the three-electron reduced system. It is because at 0.8 eV an intense peak appears in the bias

window. In Figure 4.21, two transmission spectra are shown for comparison (at 0.4 V and 0.8 V), where we can clearly observe this change.

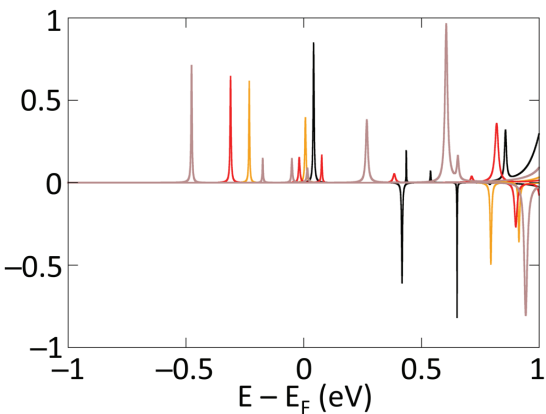


Figure 4.19 | Transmission spectra for zero- (black), one- (orange), two- (red) and three- (brown) electron reduced T_{1t} at 0 V. Positive and negative values of transmission correspond to α and β spin-orbital contributions, respectively.

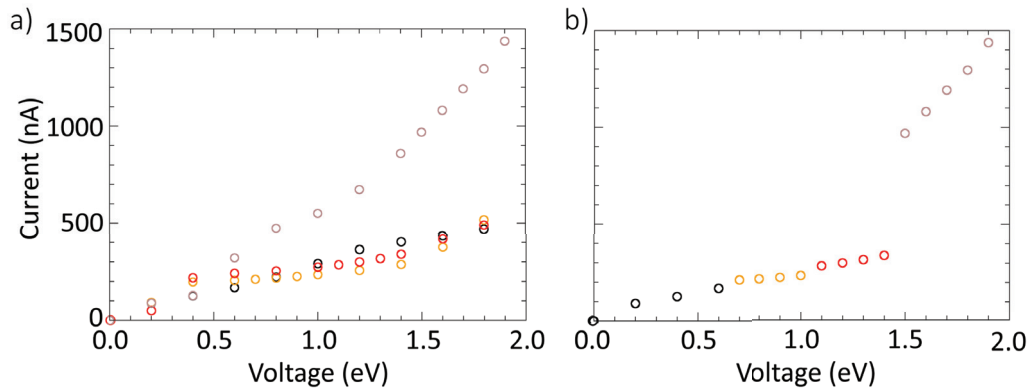


Figure 4.20 | a) I-V plot for zero- (black), one- (orange), two- (red), and three- (brown) electron reduced T_{1t} . b) I-V graph for zero- (black), one- (orange), two- (red), and three- (brown) electron reduced T_{1t} but only taking into account the system is present at each applied potential.

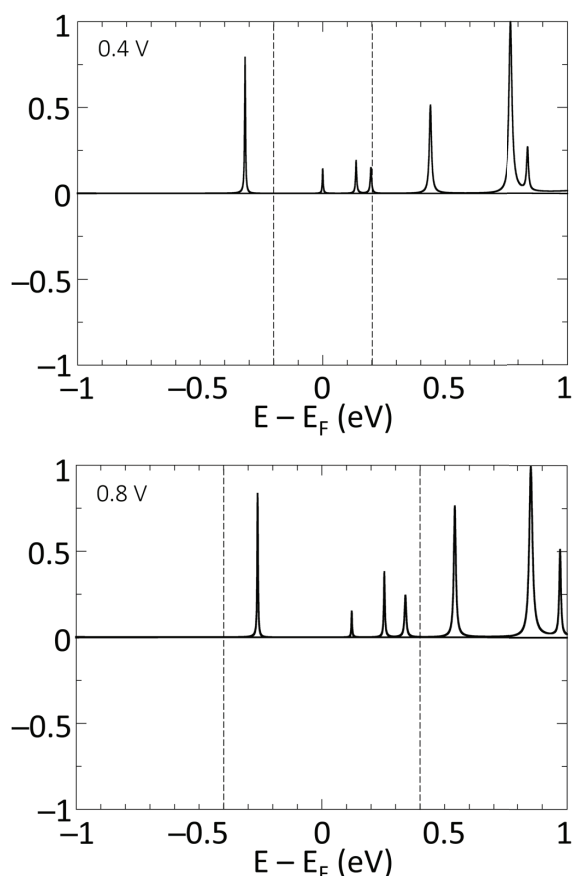


Figure 4.21 | Transmission spectra for three-electron reduced T_{1t} at 0.4 and 0.8 V. Dotted lines define the bias window for each applied potential.

This abrupt change in the intensity increase compared to the other reduction states is not observed experimentally. To explain this result, we focus on the details of the highly-reduced system, that is, any geometrical variations that we may have overlooked. The geometry optimization of compound **5** in the T_1 adsorption mode reveals structural expansion, as shown in Tables 4.7 and 4.8. This expansion is more noticeable in the vanadium atoms furthest from the surface, that is, those closest to the tip (V_2 and V_3). Furthermore, an increase in the Au- O_{POM} distance is also with differences of up to 0.13 Å between the oxidized and the three-electron reduced system. An increase in the charge of the POM (from -2 to -5) produces a repulsive interaction with the surface increasing the Au- O_{POM} distance. This also generates a repulsive interaction with the tip,

pushing it away to a total distance of 0.26 Å. Thus, at this point, we hypothesize that the expansion of the POM combined with the larger separation of it to the Au surface and to the tip be at the origin of the computational overestimation of the conductivity for the 3e-reduced system. This possibility needs to be verified by additional conductivity calculations.

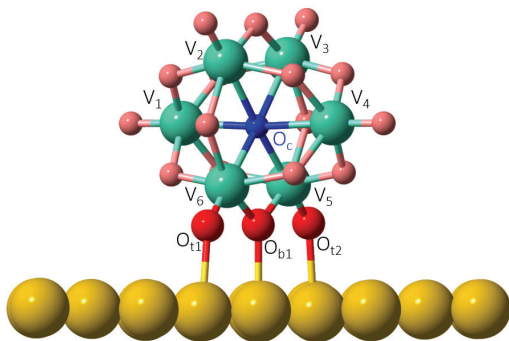


Figure 4.22 | Atom labelling and geometrical arrangement corresponding to Table 4.7 and Table 4.8. Colour code: Turquoise: V, red, pale red, and blue: O, and golden: Au. Counterions and ligands are omitted for clarity.

Table 4.7 | O-Au distances for adsorbed **5** on Au(111) surface. All the distances are shown in Å. Vanadium atoms are specified in Figure 4.22.

Oc-V distance	Oxidized	1e-reduced	2e-reduced	3e-reduced
Oc-V ₁	2.26	2.27	2.25	2.25
Oc-V ₂	2.34	2.35	2.41	2.41
Oc-V ₃	2.35	2.41	2.42	2.41
Oc-V ₄	2.26	2.21	2.25	2.29
Oc-V ₅	2.18	2.23	2.19	2.18
Oc-V ₆	2.15	2.17	2.22	2.23

Table 4.8 | O-Au distances for adsorbed **5** on Au(111) surface. All the distances are shown in Å. Oxygen types are specified in Figure 4.22.

Distance type	Oxidized	1e-reduced	2e-reduced	3e-reduced
O _{t1} -Au	2.31	2.37	2.38	2.40
O _{b1} - Au	2.36	2.43	2.44	2.46
O _{t2} - Au	2.37	2.43	2.48	2.50

4.5 Concluding Remarks

In this chapter we have explored the adsorption on gold of two hexavanadates: $[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$ and analyzed their electronic structure, since the position on the surface can be important for the conductivity response. Additionally, we perform molecular conductivity calculations of this setup including oxidation state variations in the hexavanadate.

The adsorption of $[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$ on Au(111) is random, most probably disordered with no particular packing preference for a particular geometry, since E_{ads} of all the adsorption modes analysed are energetically very similar. Neither POM gets reduced upon adsorption, with the DOS of the isolated and adsorbed forms showing that their chemical integrity is preserved when they are in contact with Au(111). Calculations show that the POM gains electron density when an external electric field is applied to it, in line with experimental measurements.

Regarding molecular conductivity, it does not significantly change with the adsorption orientation, but it does with the tip position with respect to the POM. In fact, a terminal POM oxygen in contact with the tip reveals enhanced transmission near the Fermi level in comparison with the bridging oxygen case. The more voltage, the more conductivity the system presents. The POM presents stepped conductivity associated to reduction processes. Additionally, the vanadium atoms are responsible for this conductivity as we have been able to observe in the most transmitting eigenchannels of the system, where vanadium d-orbitals are present. Molecular conductivity calculations are very sensitive and the analysis of the results has to be done with caution.

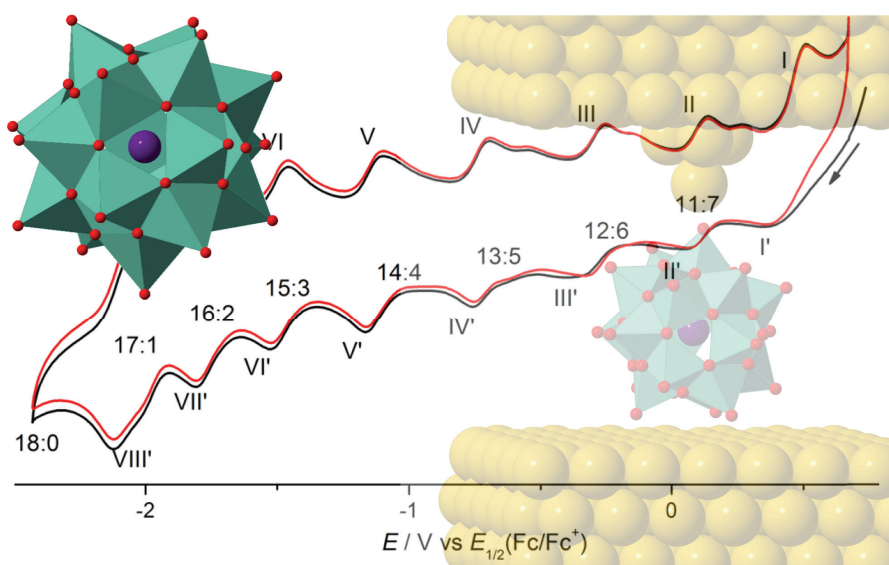
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CHAPTER 5

Multi-electron Redox Activity of I@V₁₈O₄₂

Related Publications:

Albert Solé-Daura, Almudena Notario-Estévez, Jorge J. Carbó, Josep M. Poblet, Coen de Graaf, Kirill Yu. Monakhov and Xavier López. How Does the Redox State of Polyoxovanadates Influence the Collective Behavior in Solution? A Case Study with $[I@V_{18}O_{42}]^{q-}$ ($q = 3, 5, 7, 11$, and 13) *Inorg. Chem.* **2019**, 58, 3881.

CHAPTER 5

Multi-electron Activity of $I@V_{18}O_{42}$

A series of stable reduction-oxidation states of the cagelike $[I@V_{18}O_{42}]^{q-}$ polyoxovanadate with $q = 3, 5, 7, 11$, and 13 was studied with density functional theory. The relative stability and electronic structure of the states are analyzed, with the possibility in mind that this V_{18} -cage may have similar conductivity properties as the V_6 complexes studied in the previous chapter. The calculations show that electrons tend to be delocalized over all vanadium atoms. $[I@V_{18}O_{42}]^{5-}$ is adsorbed on Au(111) surface with no topological preference. Conductivity calculations suggest that $[I@V_{18}O_{42}]^{q-}$ will not behave like $[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ or $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$ and will not have a step-like I-V behaviour.

This work was carried out in collaboration with the experimental group of Dr. Kirill Yu Monakhov from RWTH Aachen University in Aachen (Germany).

5.1 Background

In the previous chapter we have discussed the far-reaching opportunities for POM molecules in the area of multiple-state resistive (memristive) switching, based on their special reduction-oxidation properties. Following this discussion, we hypothesize that POVs would be equal or even better candidates than POMs for this kind of devices because of their inherent mixed-valent character. Typically, POVs present more accessible redox states than 'classical' POMs, which results in easier redox processes. In 2017, Linnenberg and coworkers reported a comprehensive study of the host-guest vanadium-oxo cluster $[I@V_{10}^{IV}V_8^{V}O_{42}]^{5-}$.¹ Molecular characteristics were investigated in solution and adsorbed on gold, combining MD simulations and several experimental techniques as ultraviolet-visible spectroscopy (UV/vis), cyclic voltammetry (CV), small-angle X-ray scattering (SAXS), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). One of the most striking observations this

compound—synthesized for the first time for Müller and coworkers in 1997²— is its CV, shown in Figure 5.1. The CV revealed a Coulomb staircase of eight reduction waves, which means that $(\text{NEt}_4)_5[\text{I}@\text{V}^{\text{IV}}_{10}\text{V}^{\text{V}}_8\text{O}_{42}]$ can be reduced up to 8 times, until getting its fully reduced form. This behaviour could be an indication that this compound possibly behaves like the V_6 -type complexes, discussed in the previous chapter, but with many more accesible reduction states.

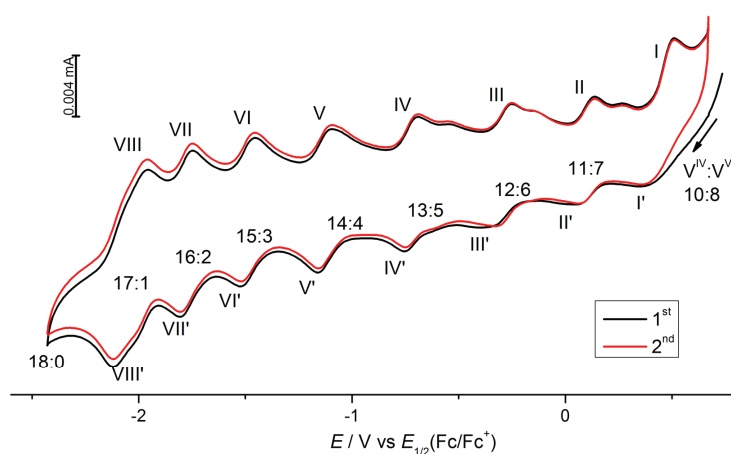


Figure 5.1 | Cyclic voltammogram (1st and 2nd cycles) of $(\text{NEt}_4)_5[\text{I}@\text{V}^{\text{IV}}_{10}\text{V}^{\text{V}}_8\text{O}_{42}]$. Figure taken from ref. 1.

Furthermore, carrying on with the studies of Linnenberg and coworkers, the ability of the mixed-valence host-guest $(\text{NEt}_4)_5[\text{I}@\text{V}^{\text{IV}}_{10}\text{V}^{\text{V}}_8\text{O}_{42}]$ was probed to form agglomerates both in aqueous and in acetonitrile (MeCN) solutions and it was shown that this agglomeration is strongly dependent on the solvent used. Moreover, the deposition of $(\text{NEt}_4)_5[\text{I}@\text{V}^{\text{IV}}_{10}\text{V}^{\text{V}}_8\text{O}_{42}]$ from MeCN or DMF onto Au(111) surface produces the formation of round-shaped particles; bigger in DMF than in MeCN, showing the importance of the solvent used also in the formation of agglomerates on the surface. Another aspect to control the deposition of $(\text{NEt}_4)_5[\text{I}@\text{V}^{\text{IV}}_{10}\text{V}^{\text{V}}_8\text{O}_{42}]$ on Au(111) surface is the concentration of the compound in the solution. Higher concentration of $(\text{NEt}_4)_5[\text{I}@\text{V}^{\text{IV}}_{10}\text{V}^{\text{V}}_8\text{O}_{42}]$ leads to a multilayer coverage, lower concentrations give rise to a monolayer situation. XPS measurements show that the complex is slightly oxidized by the gold surface when deposited in a monolayer.

This chapter continues the theoretical study of the $\text{I@V}_{18}\text{O}_{42}$ structure (hereafter called V_{18} for short) and describes in detail the stability, geometric and electronic structure, adsorption on gold and also a first insight into the possible molecular conductivity of the POV. In parallel, a member of the group (Dr. Albert Solé-Daura) studied the interactions of the compound with other species in solution using Car-Parrinello molecular dynamics (CPMD) and MD methodologies. In this chapter, we will mention some of his results to complete the picture of this system.

5.2 Computational Details

5.2.1 Isolated species

For the non-adsorbed molecule, DFT calculations, as implemented in the Amsterdam Density Functional (ADF 2013.01³⁻⁵) package, were carried out for geometry optimizations of all compounds by means of the BP86⁶⁻⁹ exchange-correlation functional. The total energy and the electron density (and properties derived from them, such as orbital energies, atomic populations, etc.) were obtained from single point calculations with the B3LYP¹⁰⁻¹² hybrid functional. Grimme's dispersion corrections¹³⁻¹⁶ were included, as well as the relativistic effects via the zeroth-order regular approximation (ZORA).¹⁷⁻²⁰ We used all-electron triple- ζ quality basis sets with double polarization functions (TZ2P) for all atoms. The solvent effects were treated by the conductor-like screening model (COSMO)²¹⁻²³ with $\epsilon = 78.4$ for water and $\epsilon = 37.5$ for MeCN. Point-group symmetries were applied as discussed in the text. For the open-shell electronic configurations, the spin-unrestricted formalism was applied. Atomic spin populations (ASPs) were obtained with Bader's electron density partition.²⁴ Based on the work of Müller et al., we considered for $[\text{I@V}_{18-x}^{\text{IV}}\text{V}_{18-x}^{\text{V}}\text{O}_{42}]^{5-x}$ the redox states characterized by $x = 8, 10, 12, 16$, and 18 with overall charges $q = 3-, 5-, 7-, 11-$, and $13-$, respectively. These states are labelled $(\text{V}^{\text{IV}}:\text{V}^{\text{V}})$ that is, **(8:10)**, **(10:8)**, **(12:6)**, **(16:2)**, and **(18:0)**.

5.2.2 Adsorbed species

The computational model to study the adsorbed species consists of a unit cell containing a slab of five 10×8 rectangular layers representing an infinite Au(111) surface, the POV adsorbate and magnesium and sodium counterions to ensure charge neutrality of the system. DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP5.3.5)^{25–28} which works with periodic boundary conditions. On the basis of previous studies of closely related systems,^{29–31} we applied the generalized gradient approximation-type exchange-correlation functional by Perdew and Wang (PW91),³² which suffices to describe not too strongly correlated electronic structures such as those of the (fully) oxidized POMs, and a basis set of plane waves with a 500 eV kinetic energy cutoff. As for V_6 -type in Chapter 4, we have not included the on-site repulsion parameter U in the calculations. We considered the following atomic valence electrons: Au: $5d^{10}6s^1$, C: $2s^22p^2$, H: $1s^1$, O: $2s^22p^4$, S: $3s^23p^4$, V: $3d^34s^2$, I: $5s^25p^5$, Mg: $3s^2$, and Na: $2p^63s^1$ where the core electrons were represented by the Projector Augmented Wave (PAW) method.^{33,34} This computational setup results in a lattice parameter for the gold bulk of 4.17 Å, which is in reasonable agreement with the experimental value (4.07 Å).^{35,36} Accordingly, the dimensions of the unit cell for the POV-Au are $a = 20.67$ Å and $b = 20.44$ Å (where $\alpha = \beta = \gamma = 90^\circ$). The length along the c direction was set to 35 Å including a vacuum region of thickness about 13.5 Å, which was proven to be sufficient to avoid interactions between cell replicas. The isolated molecules were calculated with the same surface-free box. Solvent effects were not considered.

We modeled a low-coverage regime for the POV–Au system with non-interacting adsorbed molecules (POV–POV distance > 12 Å) to have a first look of the system on gold, without considering agglomeration processes. The POV–Au models were relaxed freezing the three gold layers at the bottom of the slab to the geometry obtained of the bulk calculation. The optimizations of the bulk and surface were performed until self-consistency, with thresholds of 10^{-5} eV and $0.02 \text{ eV} \cdot \text{Å}^{-1}$ for electronic and ionic convergence, respectively. Nevertheless, only $0.06 \text{ eV} \cdot \text{Å}^{-1}$ for ionic convergence were fixed for the optimization of the POV–Au system. The Brillouin zone was sampled with a $9 \times 9 \times 9$ Monkhorst-Pack grid³⁷ of k -points to run geometry optimizations of the bulk, for the surface optimizations we used a $7 \times 7 \times 1$ mesh, and $3 \times 3 \times 1$ was taken into account for the optimization

of the POM–Au system. Discussion of atomic charges and spins is based on Bader's AIM (Atoms in Molecules) method³⁸ using the Henkelmann algorithm.³⁹

5.2.3 Molecular Conductivity

Transport calculations were performed on the optimized POV–Au systems, using version 4.1 of the SIESTA/TRANSIESTA code and the post-processing TBtrans package.^{40,41} PW91³² has been used as exchange-correlation functional. For all the atoms, except gold, the valence electrons have been described using double-zeta basis set and the core electrons by norm-conserving Troullier-Martin pseudopotentials.^{42,43} For gold atoms, a single-zeta basis set was used in combination with a pseudopotential which accounts only for 1 valence electron, this apparently rather crude description gives reasonable transport properties in single-point calculations.^{44,45} We gradually increased the number of k-points from the converged grid for V_6 until convergence of the DOS for gold electrodes firstly, and secondly of the transmission of the device. The grid used for V_6 (in the previous chapter) is enough to describe correctly the current system: a grid of $13 \times 13 \times 17$ for TRANSIESTA calculations and $27 \times 27 \times 21$ for TBtrans.

5.3 Study of its Stability, Geometric and Electronic Structure

5.3.1 Geometric and electronic structure

The $[\text{I@V}_{18}\text{O}_{42}]^{5-}$ structure presents two isomers characterized by the T_d and D_{4d} point group symmetries that are related by a 45° rotation of one of the V_5 hemispheres about the S_4 axis, as shown by Müller et al.² The 18 vanadium centres follow the arrangement $\text{V}_1:\text{V}_4:\text{V}_8:\text{V}_4:\text{V}_1$, with three structural types of V: Apical ($2 \times \text{V}_1$), outer ring ($2 \times \text{V}_4$) and inner ring ($1 \times \text{V}_8$), as shown in Figure 5.2 for the D_{4d} arrangement. We firstly quantified the relative stabilities of both cages (T_d and D_{4d}). Taking the empty structures, $\text{V}_{18}\text{O}_{42}$, the fully oxidized forms $[\text{V}_{18}\text{O}_{42}]^{6+}$ differ by 1.27 eV (29 kcal mol⁻¹), and the 10-electron forms by 0.95 eV (22 kcal mol⁻¹), being the D_{4d} arrangement the most stable in both cases. For the encapsulated iodine case in reduced form, $[\text{I@V}_{18}\text{O}_{42}]^{5-}$, the energy difference

between both isomers was estimated to be 1.03 eV (24 kcal mol⁻¹). Such large differences suggest that the T_d form does not compete with the other isomer at room temperature as long as the encapsulated guest is not bulky (case of VO₄³⁻, structure 8 in ref. 2). In the following sections, we therefore limit our discussion to the D_{4d} arrangement.

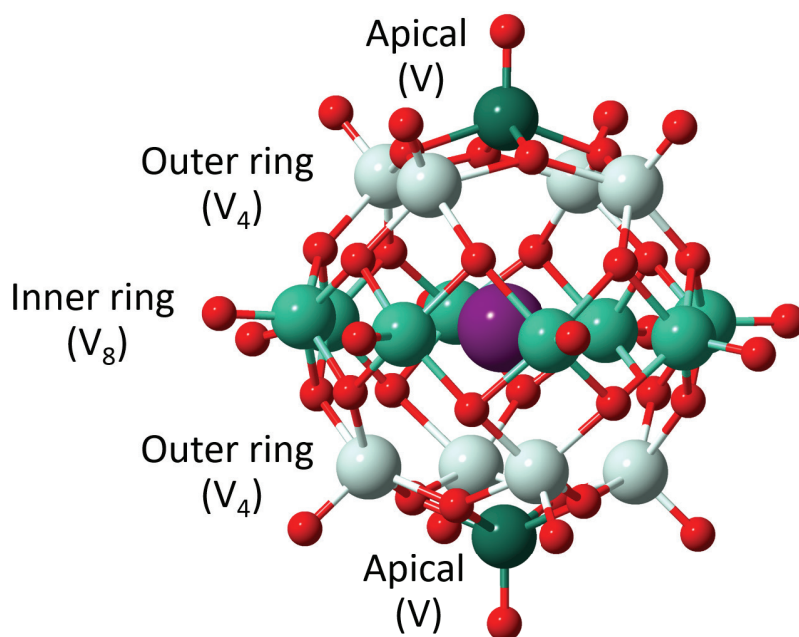


Figure 5.2 | Ball-and-stick representation of the ideal D_{4d} arrangement of V₁₈. The different regions are indicated. Color code: V, green, deep and light green; O, red; I, purple.

Several imaginary vibrational frequencies, in the geometry optimizations applying symmetry constraints, have been identified revealing that the idealized maximal D_{4d} symmetry is not the absolute minimum. Therefore, atomic displacements following the imaginary normal modes and re-optimizations with less symmetry constraints were applied until a minimum was achieved. The real minimum found has C₁ symmetry due to a pseudo Jahn-Teller effect, as observed in other POMs.^{46–48} The associated energy stabilization caused by the symmetry descent is 0.21 eV (4.92 kcal mol⁻¹). Averaged geometrical parameters obtained from DFT calculations for V-O(term), I-V and V-V distances are 1.622/1.622, 3.787/3.785 and 3.150/3.149 Å, respectively for D_{4d}/C₁ symmetry, rather close to

those determined by X-ray diffraction (1.605, 3.788, and 2.910 Å). Herein the main focus is placed on the distorted form of the most stable arrangement.

Calculation of the fully oxidized system $[\text{I@V}_{18}\text{O}_{42}]^{5+}$ reveals very deep HOMO (−10.37 eV) and LUMO (−7.41 eV) levels. This feature is common to other POMs based on vanadium, naturally electron-rich, a fact deriving of the strong oxidant nature of V^{V} centers. For the distorted resting state $[\text{I@V}_{18}\text{O}_{42}]^{5-}$, the HOMO-LUMO gap is much smaller than in the fully oxidized complex, but still rather large, 1.12 eV, and the singly occupied orbitals containing the 10 metallic electrons are found in the −6.44 to −5.77 eV range. Bader ASDs derived from our optimized C_1 structure indicate that these 10 electrons are largely spread over 16 vanadium atoms (see values for **(10:8)** in Table 5.1), suggesting minor differences between V centers. For comparison, we re-computed the electronic structure for the more disordered X-ray structure. This structure, shows notable differences in the ASDs compared to the optimized structure as the 10 electrons are mostly localized on 10 vanadium centers throughout the molecule. The different electron distribution is attributed to the packing effects existing in the crystalline phase, which make formally identical positions to behave differently. That is, in the crystallographic structure electrons tend to be more localized than in the more regular optimized geometries, more representative of the liquid phase or the vacuum. Importantly, these results may also be indicative that a small structural reorganization might induce notable changes in the vanadium valence d electron density. We also deduce that if the anion is found in an isotropic environment, the average electron distribution may resemble that of the highest symmetry structure. Regarding the low symmetry structure, the electrons are highly dispersed over the whole system, as has been observed in other POVs.^{47,48}

Variants of the resting state **(10:8)** with different number of metal electrons show that oxidation, and the associated decrease in the total negative charge, produces a lowering of all the orbital energies, see Figure 5.3. The LUMO for **(8:10)** is downshifted to −5.01 eV and the HOMO-LUMO gap is 1.14 eV in water. In conditions of no protonation, the increase of charge upon reduction upshifts all the orbitals, for instance, adding two electrons we obtain **(12:6)**, with a LUMO energy of −3.95 eV and a HOMO-LUMO gap of 1.36 eV. In MeCN, the frontier orbitals are around 0.13 eV higher for **(10:8)** in average, but only 0.03 eV in **(8:10)**,

whereas for **(12:6)** the upshift amounts 0.24 eV. So, the orbital upshift when water is replaced by MeCN is more pronounced for the more anionic POV species. As expected, the electron distribution among the V centers and the HOMO-LUMO gaps remain unaltered.

Table 5.1 | Bader atomic and region spin densities (in *italics*) of the vanadium atoms in V₁₈O₄₂ in different (**V^{IV}:V^V**) reduction states.

(V^{IV}:V^V)	(8:10)		(10:8)		(12:6)		(16:2)		(18:0)	
Apical	0.36		0.36		0.12		0.21		0.99	
	0.55		0.93		0.97		1.00		1.00	
Outer ring (V ₄)	0.16	1.75	0.21	2.71	0.93	3.80	0.93	3.85	1.00	3.98
	0.89		0.90		0.97		1.00		1.00	
	0.14		0.67		0.93		0.93		1.00	
	0.68		0.46		0.50		0.98		1.00	
	0.32		0.46		0.62		0.99		1.00	
	0.52		0.63		0.62		0.99		1.00	
Inner ring (V ₈)	0.52	4.08	0.55	4.31	0.50	4.48	0.98	7.89	1.00	7.97
	0.52		0.52		0.50		0.98		1.00	
	0.52		0.52		0.62		0.99		1.00	
	0.32		0.55		0.62		0.99		1.00	
	0.68		0.63		0.50		0.98		1.00	
	0.14		0.93		0.93		0.93		1.00	
Outer ring (V ₄)	0.89	1.75	0.69	2.73	0.97	3.80	1.00	3.85	1.00	4.02
	0.16		0.90		0.93		0.93		1.00	
	0.55		0.22		0.97		1.00		1.00	
Apical	0.36		0.35		0.12		0.21		0.99	

The doubly oxidized **(8:10)** system has two electrons less in the outer rings compared to the **(10:8)** resting state. The electron distribution on the inner ring is basically the same with eight vanadium atoms sharing four electrons and the remaining four electrons are shared by the apex and outer rings: 2 times four mostly delocalized electrons. The situation changes significantly when the resting state is reduced by two electrons. In the resulting **(12:6)** complex, all vanadium centers on the outer rings become V^{IV} (ASD close to one), and the apex vanadiums can be best considered as V^V. The inner ring is the only region where

the vanadium atoms are still of mixed valence character, sharing four electrons over 8 centers, almost identical as in the resting state. Further reduction first saturates the inner ring (**16:2**) before the apex vanadiums also become V^{IV} in (**18:0**).

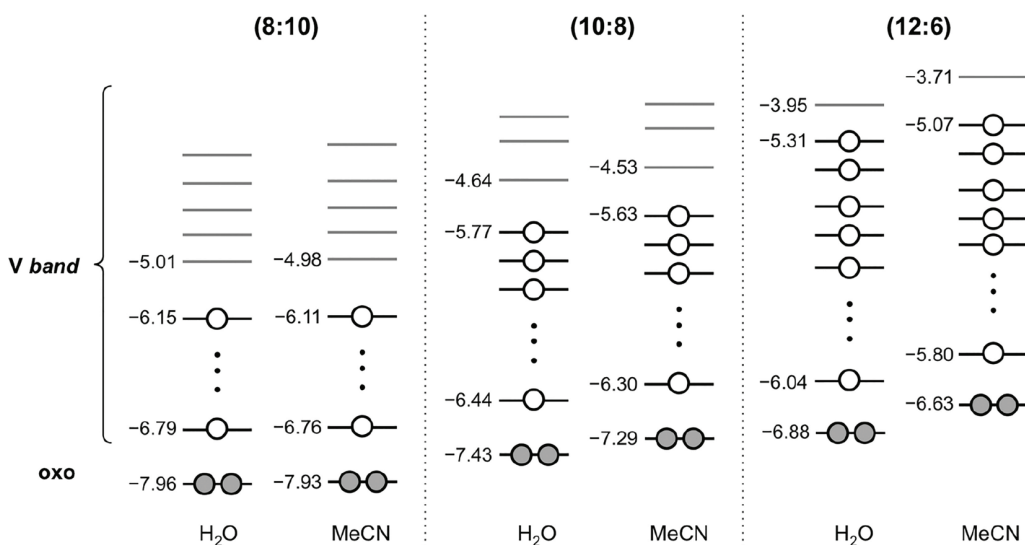


Figure 5.3 | Scheme of the frontier molecular orbitals for V_{18} with different oxidation states and solvent. Molecular orbital energies are shown in eV.

The highly delocalized valence electrons are presumed to be susceptible of relocation when some external stimulus is applied. We evaluated the effect of applying a homogeneous electric field of 0.01 a.u. ($5.2 \cdot 10^7 \text{ V cm}^{-1}$) parallel to the axis containing the two apical vanadium centers (see Table 5.2 and Figure 5.4) of the (**10:8**) species. As a result, a notable concentration of spin density into one of the hemispheres takes place, from 3.09 to 4.84 e (thus, roughly one electron per V center), and a concomitant electron depopulation in the other region of the molecule, from 3.06 to 1.19 e. The inner ring does not change its spin population.

Table 5.2 | Vanadium atomic and region spin densities (in italics) computed for V₁₈O₄₂ **(10:8)** without and with an external electric field of 0.01 a.u. applied in the direction containing the two apical centers.

	No external field		External field	
Apical	0.35		0.26	
Outer ring (V ₄)	0.93	2.73	0.13	0.93
	0.69		0.49	
	0.90		0.24	
	0.22		0.07	
Inner ring ring (V ₈)	0.46	4.31	0.54	4.25
	0.46		0.62	
	0.63		0.46	
	0.55		0.45	
	0.52		0.61	
	0.52		0.47	
	0.55		0.58	
	0.63		0.52	
Outer ring (V ₄)	0.93	2.71	0.97	3.86
	0.21		0.97	
	0.90		0.97	
	0.67		0.96	
Apical	0.36		0.98	

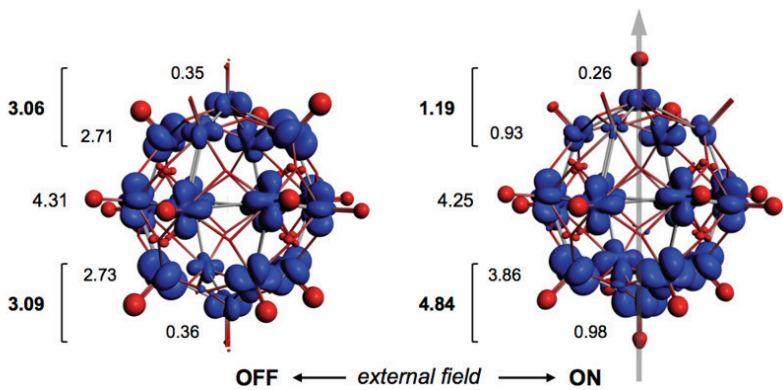


Figure 5.4 | Effect of an electric field on the spin density of the C₁ **(10:8)** species applied in the direction indicated by the thick arrow. Blue and red isosurfaces represent accumulation of α and β spin density, respectively. The computed region spin densities are indicated. In bold, the sum of apical and neighboring outer ring spin densities are indicated.

5.3.2 Electrochemistry

Calculation of the energy associated to addition/removal of electrons corresponding to V_{18} (10:8) are essential for further exploration of the physics of these systems and the differences among them. In water solvent, the (10:8) + 2e $\rightarrow$ (12:6) process is highly exothermic ($\Delta E = -10.41$ eV), directly related to the very negative energy of the LUMO of (10:8). The oxidation reaction (10:8) $\rightarrow$ (8:10) + 2e is endothermic ($\Delta E = 11.03$ eV), owing to the low-lying orbitals from which the electrons are removed. With CH_3CN as solvent, the (10:8) + 2e $\rightarrow$ (12:6) reduction gives $\Delta E = -10.00$ eV (0.4 eV less favorable than in water). Oxidation (10:8) $\rightarrow$ (8:10) + 2e gives $\Delta E = +10.24$ eV, that is 0.24 eV less positive than in water. This lower endothermicity responds to the lesser capacity of CH_3CN to stabilize highly charged species than water. Both aqueous and acetonitrile solutions of (10:8) make it the most stable form. Changes in this state of reduction are differently accessible in these solvents: reduction is easier in water (more exothermic process), whereas oxidation is easier in acetonitrile (less endothermic process). This trend is explained by the anionic nature of the V_{18} molecule and the different stabilization by the polar (water) and less-polar (MeCN) solvent.

Mapping the molecular electrostatic potential (MEP) for each ($\text{V}^{\text{V}}:\text{V}^{\text{V}}$) state on an electric density isosurface gives a graphical, intuitive tool to localize electro- and nucleophilic regions in molecules (see Figure 5.5 a). The MEP maps are 3D representations of the electrostatic potential (values depicted as colors) on a density isosurface, whose value is chosen such that it lies close to the surface, constructed by the superposition of the van der Waals atomic radii. The MEPs evolve from blue to red, indicating more negative electrostatic potentials (more cation-attractive and dipole-orienting) at the surface as the molecular charge gets more negative. Approximately, the average surface potential for (8:10), (10:8), (12:6), (16:2) and (18:0) is -0.21 , -0.38 , -0.56 , -0.93 and -1.10 a.u., respectively. This increment of the surface nucleophilicity upon reduction parallels the gradual energy increase of all the occupied molecular orbitals shown in Figure 5.5. Reducing the range of the colour code from $<-0.12, -1.21>$ to $<-0.98, -1.21>$ for the (18:0) system (shown in Figure 5.5 b), detailed information about the electro- and nucleophilicity of different regions of its surface can be traced. Common to most classical polyoxometalates, bridging oxygens are more nucleophilic than terminal ones. We expect that, for the most negatively charged

108 | 5.3 Study of its Stability, Geometric and Electronic Structure

POVs, the red regions strongly interact with water, leading to good solvation properties. On the other hand, anions with lower negative charge are likely to be less solvatable. This hypothesis of the solution behavior of V_{18} was investigated with MD calculations performed by Dr. Solé-Daura.

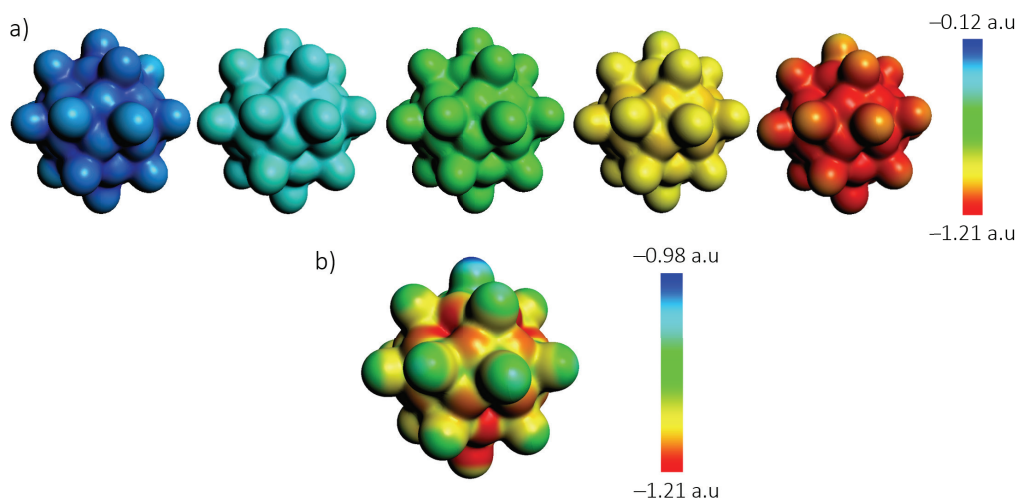


Figure 5.5 | a) MEP map projected on a density isosurface ($\rho = 0.003$) for each $(V^{IV}:V^V)$ state of V_{18} . The scale (shown on the right) is chosen to include the whole range of potentials. b) MEP for the (18:0) species, for which the electrostatic potential scale has been adjusted to a narrower range to discern regions of different nucleophilicities.

Solé-Daura demonstrated that our assumptions were correct, and that indeed the $V_{18} \cdots H_2O$ interactions become stronger as the POV increases its charge. In Figure 5.6 a), this fact is illustrated with the dependence of the individual $V_{18} \cdots$ water interaction energy as a function of the POV charge (figure taken from ref. 49). Moreover, for the less polar solvent MeCN the charge has also an important role in the agglomeration process. As this agglomeration is through tetraethylammonium (TEA) -mediated contacts in MeCN, POVs bearing low negative charges are not capable of removing the solvation shell from the MeCN cations (that are better solvated than in water), avoiding the agglomeration of the POVs. For the highly charged V_{18} there is a similar result: no agglomeration. In this case the agglomeration process is not possible because the dense shell of TEA counteranions around the POV shields any possible interactions with other POVs, avoiding agglomeration. Therefore, moderately charged V_{18} systems

present the most marked agglomeration. Figure 5.6 b) depicts these phenomena.

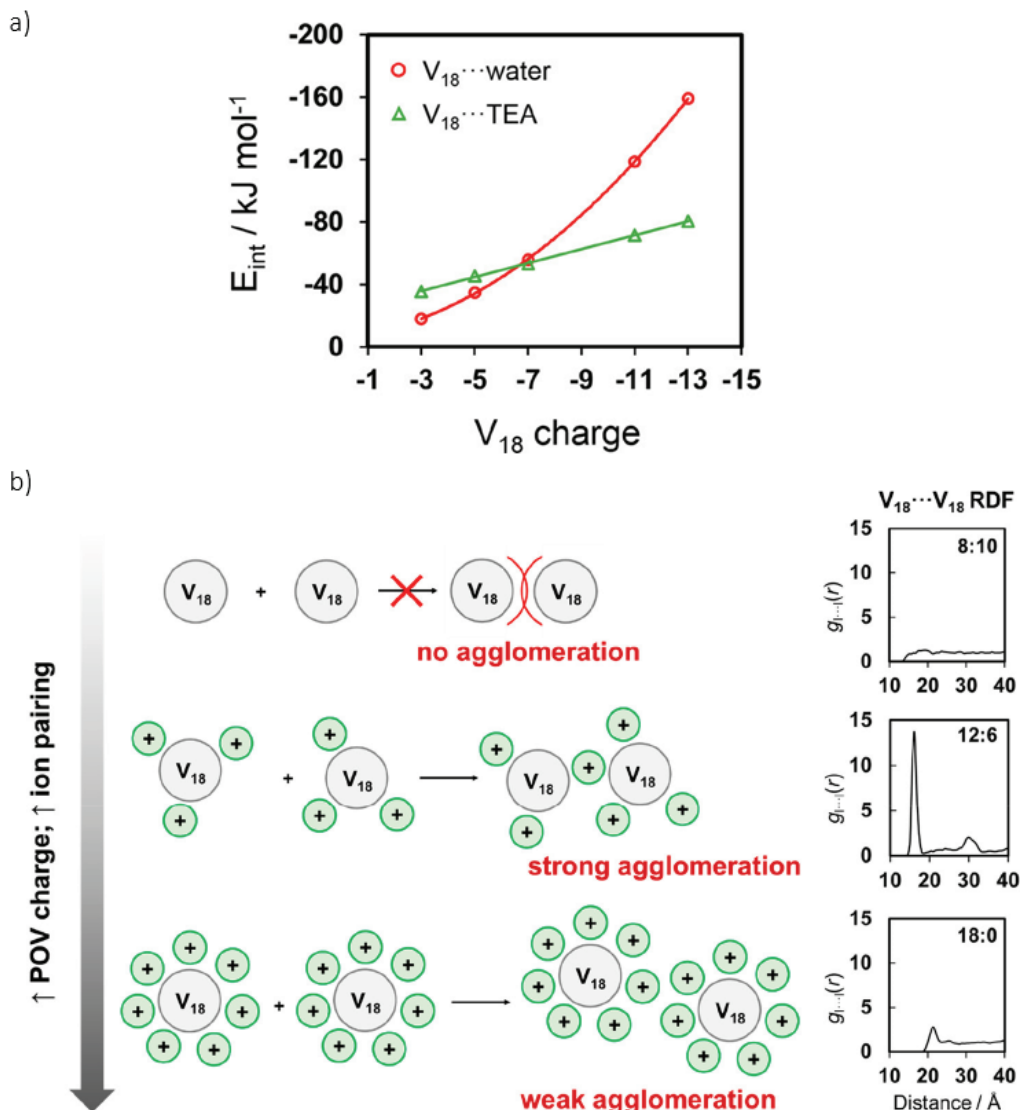
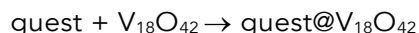


Figure 5.6 | a) Evolution of $\text{V}_{18}\cdots\text{TEA}$ (green) and 2.6% of $\text{V}_{18}\cdots\text{water}$ (red) nonbonding interaction energy per POV and TEA unit as a function of the anion charge. b) Relationship between increasing the molecular charge of the POV, from top to bottom, and ion pairing with TEA (green positive spheres) and agglomeration in pure MeCN. Figure taken from ref. 49)

5.3.3 Encapsulated guest

Returning to the electronic structure of the V_{18} complex, we have explored the preference of the $V_{18}O_{42}$ cage towards guests of different nature by estimating the energy of the hypothetical encapsulation process in solution:



for guest = I^- , K^+ and H_2O . The DFT results show that the encapsulation of iodide is highly favorable, with $\Delta E = -44.5 \text{ kcal mol}^{-1}$ at the present level of calculation. If a water molecule is taken as guest, ΔE reduces to $-12.1 \text{ kcal mol}^{-1}$,⁴⁹ and for a cation (K^+) the process is not favored ($\Delta E = +2.6 \text{ kcal mol}^{-1}$). There are basically two reasons for this preference for encapsulating not too hard negative ions. The first one is related to the stability of the guests in solution. K^+ is strongly solvated and a large amount of energy has to be inverted to strip off the solvation shell, which is intermediate for water and much smaller for I^- , a soft anion. The second one is intrinsic to the host. The local dipole moments (μ) located at each VO_5 block point towards the interior of the cage, a fact that might explain the larger stabilization of encapsulated anionic moieties. The values of μ have been estimated computationally to be close to $\mu = 82 \text{ D}$ for V^VO_5 and $\mu \approx 100 \text{ D}$ for $V^{IV}O_5$. There are no significant differences in μ for the three structural types of VO_5 units.

Next, we explored the energy cost for off-center displacements of the iodine guest induced by thermal motion or perturbations, such as external electric fields. Although the cage is not perfectly spherical, we assume that small displacements are nearly equivalent in any direction. Figure 5.7 a) shows the electrostatic potential in an arbitrary plane of the interior of the **(10:8)** cage. In the center of the cavity, the potential is fairly constant and takes intermediate values (green lines), moving further away from the center, the potential becomes less negative as one approaches the inner side of the cage (blue lines). If we analyze the energy increment vs. the iodine displacement from the equilibrium position (Figure 5.7 b), it arises that, up to $0.5 \text{ \AA}$, the energy requirement is moderate (ca. 6 kcal mol^{-1}), then it increases dramatically inline with the appearance of closer isopotential curves in Figure 5.7 b). Based on this flat potential energy surface, it is also expected that an external electric field is able to move the (negatively) charged guest away from the center of the complex. The same trend was observed for

(18:0) with a more gradual and faster energy increase because of the higher charge of the cage ($q = 13-$). These DFT calculations are in excellent agreement with CPMD ones where the maximum displacement of iodine inside the cage was 0.3 Å (approximately a cost of 10 kcal mol⁻¹ estimated by DFT), see Figure 5.8.

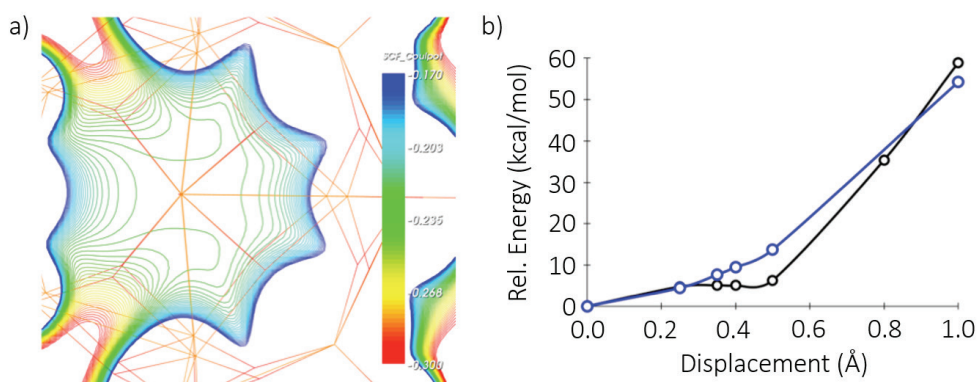


Figure 5.7 | a) 2D cut of the electrostatic potential plotted inside the cavity of V_{18} in oxidation state (10:8), on a plane containing the geometrical center. The potential gets more negative from blue to red. Note the large spacing between isopotential lines in the central region. b) Graphical representation of the energy variation (in kcal mol⁻¹) vs. displacement of the internal iodine for the (10:8) form (black line) and for the (18:0) form (blue line).

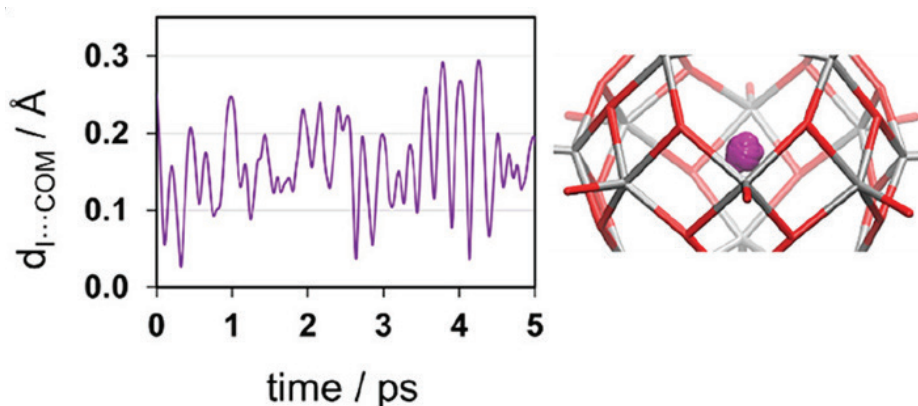


Figure 5.8 | Dynamic behavior of the $\{\text{I}@\text{V}_{18}\text{O}_{42}\}$ structure in aqueous solution. Evolution of the distance between the iodine atom and the center of mass (COM) along the simulation (left). Figure taken from ref. 49. (Indicar temperature de la simulació)

5.4 Adsorption of $\text{I@V}_{18}\text{O}_{54}$ on Au(111) Surface

After this exploration of the electronic structure of the solvated complex, we now turn our attention to the description of V_{18} absorbed on a gold surface. For this purpose, we switch from a discrete molecular model to a periodic approach. First, we explore the stability of V_{18} (10:8) on gold surface. V_{18} presents two adsorption modes: both with three Au- O_{POV} contacts (in blue in Figure 5.9 a) and b). All contacts arise from apical oxygens bonded to vanadiums of the outer V_4 ring and the third is either bonded to a vanadium of the inner V_8 ring (adsorption mode 1) or an apical vanadium (adsorption mode 2). The most striking difference between the two modes is that in adsorption mode 2 a μ_3 oxygen (in yellow) is found at the center of the triangle formed by the oxygens in contact with the surface, while the center is empty in adsorption mode 1.

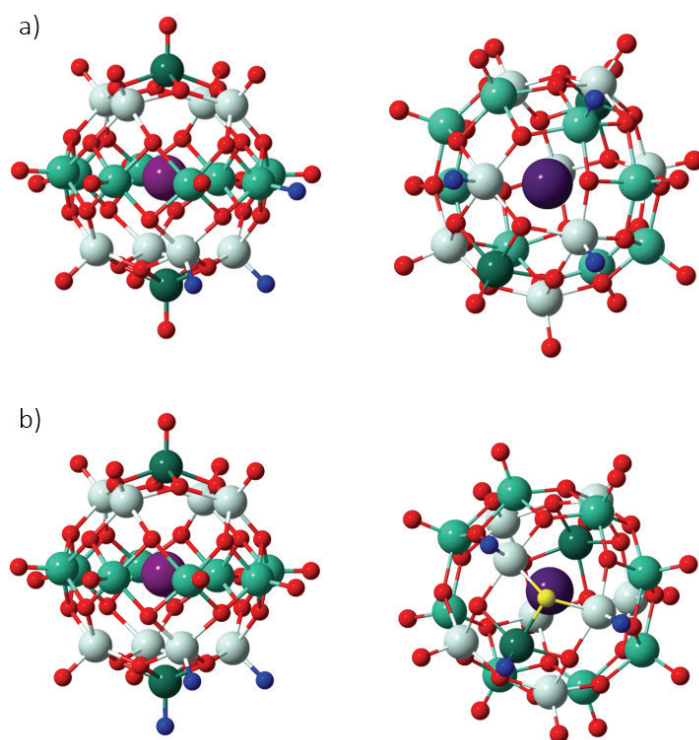


Figure 5.9 | Ball and stick representation of V_{18} . a) two different views for the isolated V_{18} with adsorption mode 1 and b) 2. Oxygen atoms that will be in contact with the gold surface are depicted in blue and the μ_3 oxygen for 2 in yellow. The rest of atoms follow the colour code of Figure 5.2.

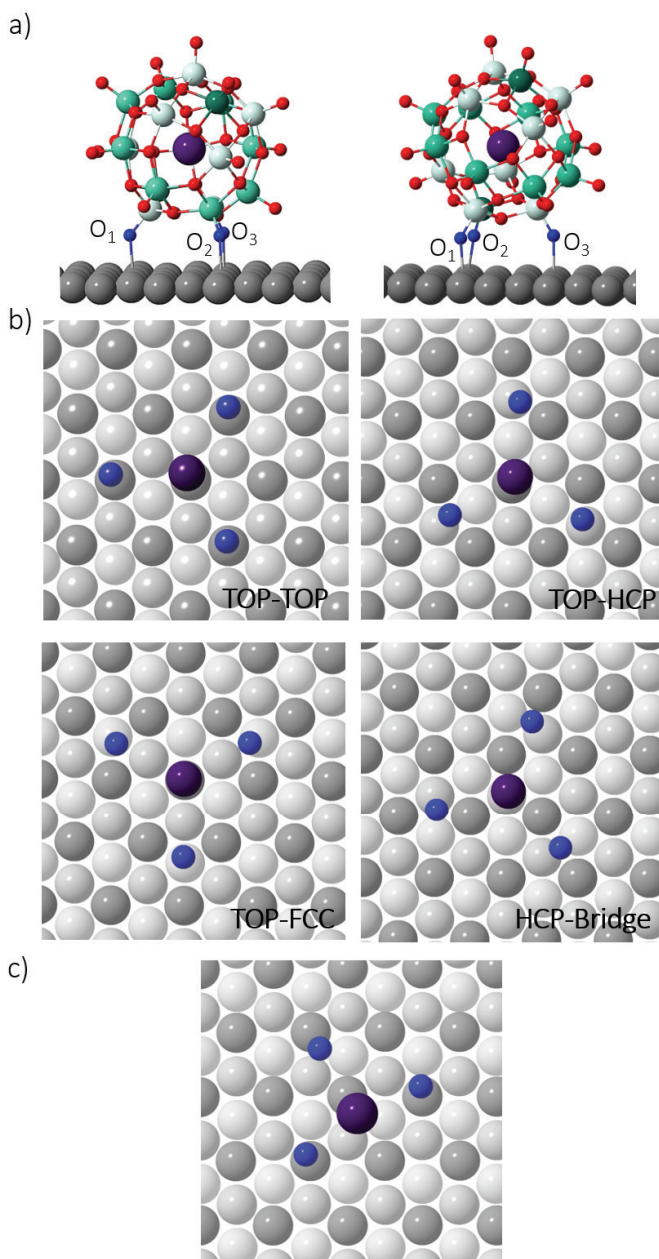


Figure 5.10 | a) Ball and stick representation of V_{18} adsorbed on gold in side view. for adsorption mode 1 (left) and 2 (right). b) Top view of the different adsorption positions for V_{18} in adsorption mode 1. c) Top view of the tested adsorption mode 2. Only oxygens (in blue) and iodide (purple) in contact with the surface are shown. Colour code for the remaining atoms: red for oxygen; green, turquoise, pale turquoise and big blue balls for vanadium atoms; deep grey, medium grey and light grey balls for gold of the 1st, 2nd and, 3rd layer, respectively.

For a first impression of the most stable position on the surface, we have tested four different positions for adsorption mode 1: TOP-TOP, TOP-HCP, TOP-FCC, and HCP-Bridge. This nomenclature reflects the position of the iodide and the three terminal oxygen atoms on gold, see Figure 5.10 b). The optimizations were performed as follows: initially, the geometry of V_{18} and the first two layers of the gold surface were optimized (with a charged unit cell); then, freezing the POV and the surface, the counteranions were added and their position optimized. As for V_6 -type POM⁵⁰, very similar energies have been obtained for the different adsorption positions (Table 5.3), which indicates that the POV can be adsorbed in any of these positions and no ordering is expected to occur when more POVs are adsorbed on the surface. Limiting the study to the most stable position (TOP-TOP for adsorption mode 1), we have compared the two adsorption modes by a complete geometry optimization of surface, POV and cations. Adsorption mode 2 is slightly more favourable than 1 (by 0.09 eV), however this energy difference is definitely not large enough to exclude one adsorption over another.

Table 5.3 | Relative energy of different positions for adsorption mode 1.

	Relative energy (eV)
TOP-TOP	0
TOP-FCC	0.35
TOP-HCP	0.10
HCP-Bridge	0.12

Table 5.4 shows that the O-Au distances are slightly smaller for adsorption mode 2. However, these distances are significantly larger in both cases than the corresponding optimized distances for the completely oxidized V_6 -type⁵⁰ (2.32-2.40 Å for orientations with three O-Au contacts). The longer contacts likely originate in a higher negative charge of V_{18} (−5) compared to V_6 (−2), which causes a stronger POM-surface repulsion. Despite this larger distance between surface and POV, the adsorption energy of V_{18} is slightly larger than for V_6 ; −1.09 eV for mode 1 and −1.18 for mode 2 versus −0.66/−0.41 eV (depending on the adsorption mode and functionalization) for V_6 . This apparent contradiction can be possibly attributed to the larger polarizability of V_{18} . In a simple energy versus

external electric field calculation we have estimated the polarizability along the surface normal to V_{18} to be more than twice that of V_6 : 943 au versus 410 au.

Table 5.4 | O-Au distances for adsorbed V_{18} (**10:8**) on Au(111) surface in the most stable orientations. All the distances are shown in Å. Oxygen types are specified in Figure 5.10 a).

Distance	Adsorption mode 1	Adsorption mode 2
$\text{O}_1\text{-Au}$	2.47	2.41
$\text{O}_2\text{-Au}$	2.49	2.52
$\text{O}_3\text{-Au}$	2.50	2.47

5.5 Electronic Structure of the Adsorbed Species

5.5.1 Analysing the isolated POV with band structure calculations

To investigate the effect on the electronic structure of the adsorption of V_{18} on Au(111) we apply the same computational setup to the isolated molecule and to the combined Au-POV system. Figure 5.11 shows the density of states (DOS) calculated for a single V_{18} (**10:8**) (and two Mg^{2+} and one Na^+ to compensate the -5 charge) in the $<-10,+2>$ eV interval. In addition to the total DOS (in black), the figure also depicts the projected DOS (PDOS) of oxygen (red) and vanadium (blue) levels. The low-lying levels show very little spin polarization; densities above and below the energy axis are very similar. Integrating β band for the complete system (in black in Figure 5.11), from -10 to 0 eV, adds up to 129 electrons, the expected number of electrons in this range of energies. Nevertheless, the same procedure only gives 0.57 extra for the α band, instead of the expected 10 for V_{18} (**10:8**). The states at lower energy are clearly dominated by contributions from the oxygens atoms (as are the highest occupied orbitals in the molecular calculations), but significant contributions are observed from V-d levels. This is a direct indication of the relatively large covalent character of the V-O bonds, especially the one with the apical oxygens. The V-PDOS below 0 eV integrates to 27 electrons, meaning that each of the 18 vanadiums shares on average about 1.5 electrons with the five oxygens around it. The β levels that contribute to the density of states with positive energy are strictly unoccupied,

but this is not the case for the α levels. In order to be consistent with the calculations where also the Au surface is taken into account, we have applied a 'smearing' of the occupied levels. This means that occupation numbers are not either one or zero, but smoothly interpolate between these values for the levels near the Fermi level. There are 18 partially occupied bands, which sum exactly 10 electrons. As these bands are strongly dominated by V-3d levels, we can indeed confirm that the periodic approach gives results that are essentially in line with the molecular calculation. One word of warning, the integration of the DOS in the interval spanned by the partially occupied bands (approximately from 0 to 1 eV) does not lead to the expected 10 α electrons in excess because the DOS does not take into account the partial occupation of these levels. Because of the partial occupation of the α levels, the Fermi level, normally represented as the zero of energy, cannot be easily defined.

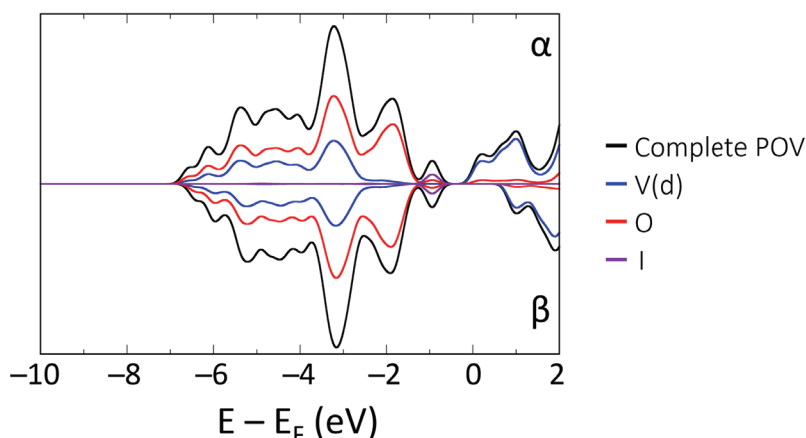


Figure 5.11 | Density of states and projected density of states for isolated V_{18} (10:8). All energies refer to the Fermi level (E_F). Accordingly, the bands located at negative energies are occupied.

5.5.2 Electronic structure for (8:10), (10:8), and (12:6)

The projected density of states of V_{18} (10:8) in the isolated and the most stable adsorbed forms are compared in Figure 5.12. For both adsorption modes the same behaviour can be perceived, which shows that: the orientation of the POM on the surface does not affect its electronic structure, as was also observed for the V_6 type. Upon adsorption the gap between the oxo-band and the vanadium levels is practically unchanged, although we do observe an overall stabilization

of the levels for the adsorbed species. The onset of the oxo-band at approximately -1.3 eV for the isolated complex is shifted below -2 eV when the molecule is placed on a Au surface. Again, there are many partially occupied levels crossing the Fermi level, actually many more due to the presence of a metallic surface. This severely hinders a more detailed analysis of the electronic structure. We observe a significant spin polarization in the V-3d bands, but it is practically impossible to determine how many d-electrons occupy the alpha and beta levels.

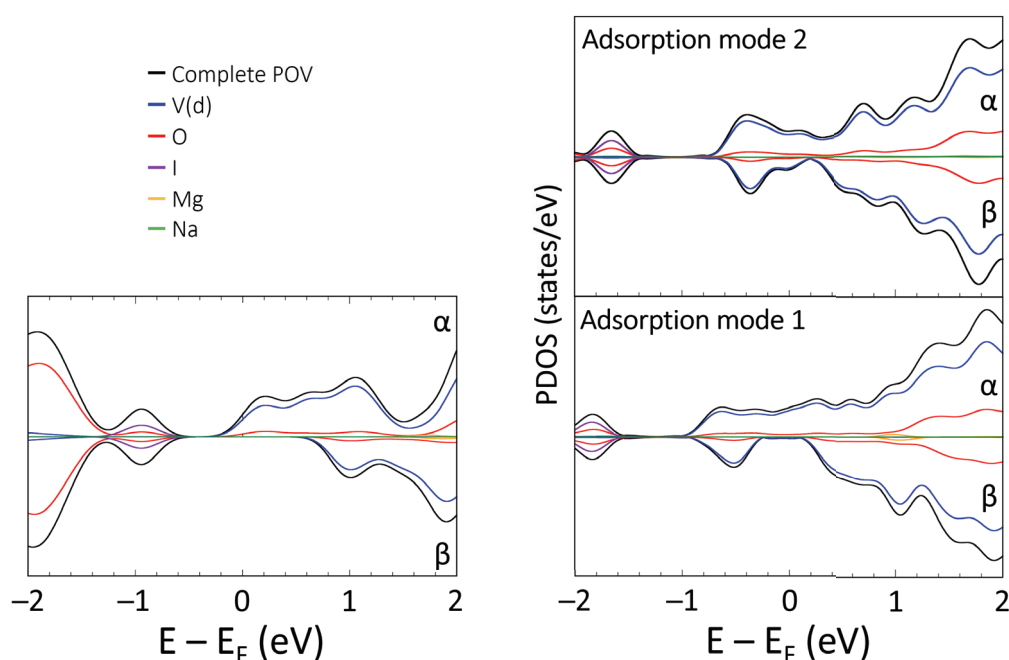


Figure 5.12 | Density of States and Projected Density of States for V_{18} (**10:8**) for a) when it is isolated and b) adsorbed on Au(111) with two different adsorption modes: 1 (below) and 2 (above). All energies refer to the Fermi level (E_F). Accordingly, the bands located at negative energies are occupied.

Additional support to the claim that the electronic structure of the POV is not drastically changed by the adsorption process and keeps its initial redox state (**10:8**). It is provided by the Bader atomic charge analysis which shows (Table 5.5), that the molecular charges for both adsorption types of -5.03 and -5.26 , are essentially equal to the isolated form (-5). Looking at the charge density

difference, shown in Figure 5.13, we can observed a region of electron density depletion ($\Delta\rho < 0$, blue colour). As for V_6 in the previous chapter, V_{18} -Au interaction is weakly, and not many changes are expected regarding the electronic structure of the two fragments separately (gold and V_{18}).

Table 5.5 | Calculated and theoretical Bader charges per fragment for the two tested adsorption modes for V_{18} (**10:8**) on Au(111).

	Σ POV atoms		Σ counteranions		Surface	
	Calc.	Theor.	Calc.	Theor.	Calc.	Theor.
Adsorption mode 1	-5.03	-5	4.32	5	0.71	0
Adsorption mode 2	-5.26		4.34		0.92	

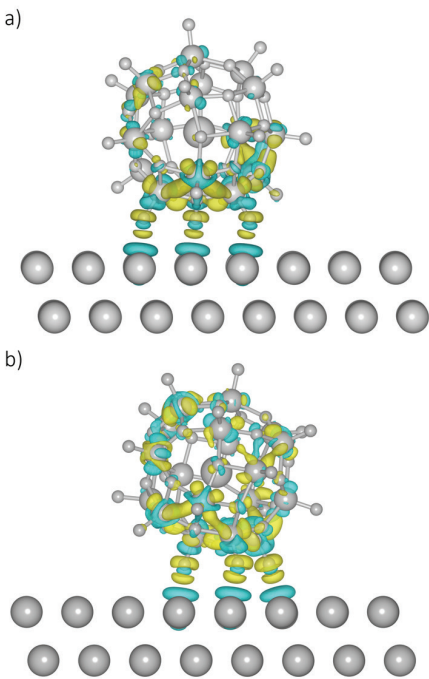


Figure 5.13 | Charge density difference computed for V_{18} (**10:8**) in adsorption mode a) 1 and b) 2. The yellow regions represent electron density accumulation and blue regions indicate electron density depletion. The surface isosurface is set to 0.002 e/Bohr³.

Oxidizing and reducing the system, the electrons are introduced and removed from vanadium atoms, as in the isolated form, see Figure 5.14 for the PDOS for (**8:10**) and (**12:6**) forms. By changing the total charge on the counteranions, we

can control the number of electrons shared by the Au and POV system. Due to the complications in determining the number of electrons based on integration of the DOS (partially occupied levels crossing the Fermi level), it is not possible to certify that the POV is oxidized or reduced or that the electrons are taken from or added to the Au surface. Indirect evidence for changes in the oxidation state of the POV is provided by the change in the on-set of the oxo-band which is shifted to lower energy with respect to the resting state in the oxidized form and to higher energy in the reduced form. Additional arguments for oxidation/reduction of the POV is given by the Bader charges, which suffer much larger changes for the POV than for the surface (Table Table 5.5).

In comparison with V_6 -type where the system was reduced up to 3 electrons, V_{18} system can be completely reduced until 18 electrons. Nevertheless, we restrict our study to the **(8:10)**, **(10:8)** and **(12:6)** oxidation states. For V_6 the maximum electron population per vanadium is 1/2 (with the 3e-reduced system), but this number increases for V_{18} in the **(12:6)** oxidation state until 2/3. For this reason, we have tested the necessity of including the effective on-site repulsion parameter in the description of the electronic structure. This parameter is considered to mimic to some extent the effect of the Fock exchange if the hybrid functionals. We have tested three different values for U: 3.25 eV, 4 eV and 5 eV.^{51,52} However, the inclusion of U seems to destroy some of the essential features of the electronic structure of the POV, like the gap between the top of the oxo-band and the bottom of the V-3d levels. Moreover, it introduces heavy spin polarization in the lower-lying occupied levels, which has never been observed in molecular calculations. Therefore, we disregard these results and continue with the GGA results.

Table 5.5 | Calculated (black) and theoretical (grey) Bader charges per fragment for the two tested adsorption modes for V_{18} **(10:8)** on Au(111).

	POV		Contractions		Surface	
	Calc.	Theor.	Calc.	Theor.	Calc.	Theor.
8e	-3.68	-3	2.63	3	1.05	0
10e	-5.03	-5	4.32	5	0.71	0
12e	-6.28	-7	5.73	7	0.55	0

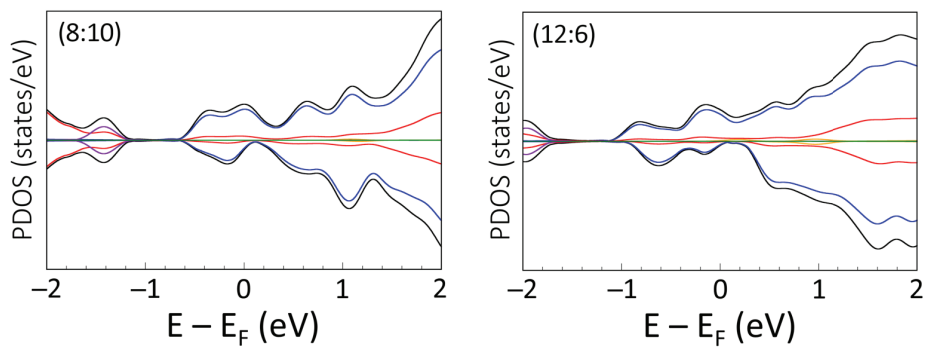


Figure 5.14 | Projected density of states for V_{18} (8:10) and (12:6). All energies refer to the Fermi level (E_F). Accordingly, the bands located at negative energies are occupied. Colour code as in Figure 5.13.

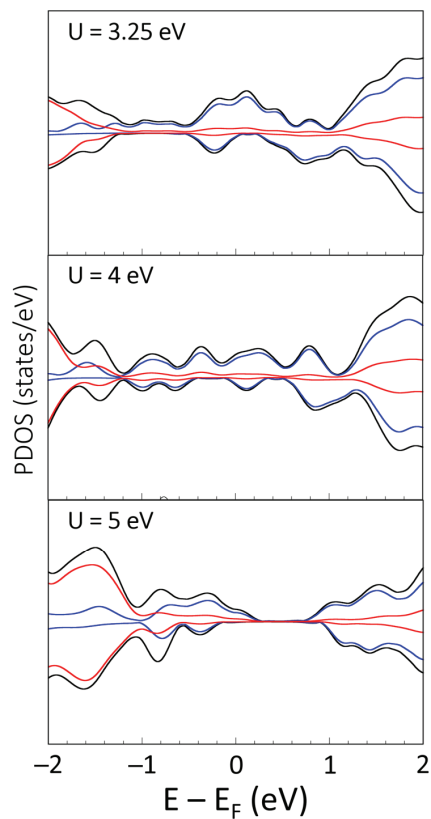


Figure 5.15 | Projected density of states for V_{18} (10:8) at GGA+U level. All energies refer to the Fermi level (E_F). Accordingly, the bands located at negative energies are occupied. Colour code as in Figure 5.11. Only oxygen and vanadium PDOS are represented for clarity.

5.6 First Insight into Molecular Conductivity

As explained before, depending on the solvent, concentration, pH and other factors, V_{18} can be isolated or form aggregates, protonated or non-protonated, forming a monolayer or multilayer on gold, etc. Hence, many factors should be taken into account for a complete description of its conduction properties. To begin with, this section studies its conductivity as isolated V_{18} (without forming aggregates) on gold with different number of unpaired electrons as for V_6 in the previous chapter. In this case, the redox compounds that are studied are the most stable, **(10:8)**, the bi-oxidized, **(8:10)**, and the bi-reduced, **(12:6)** ones.

5.6.1 Device model

Gold has been used for both electrodes of the device. The optimized structure of **(10:8)** adsorbed on gold in the previous section (section 5.3) has been used for the calculations. Then, one of the electrodes is a 8-layer gold surface where the POV is adsorbed, and the other electrode is made of an optimized 8-layer gold surface with the smallest tip possible, formed by 4 atoms. The chosen O-Au

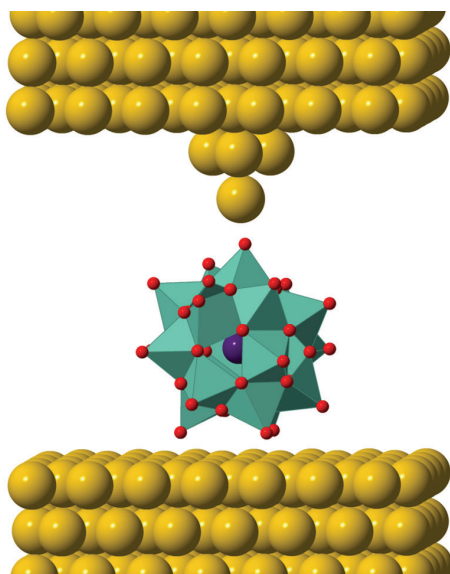


Figure 5.16 | V_{18} device. Turquoise polyhedra: V, red: O, purple: I, and gold: Au. Counterions are omitted for clarity.

distance between the tip and the model was fixed to 2.32 Å, as for V_6 device. For **(8:10)** and **(12:6)** the same methodology to build the model was used, however, only the positions of the counteranions were optimized, keeping the POV-Au(111) structure as for **(10:8)**. In this case, the tip was put on top of a terminal oxygen, see Figure 5.16.

5.6.2 Transmission at $V = 0$ for 8-, 10- and 12-electron reduced system

The main motivation for studying the conductivity of V_{18} arises from the peculiar behaviour of V_6 . The reduction of this complex upon increasing bias potential is coupled to a step-wise increase of the conductivity. Similar behavior could be expected but with more differentiated states, since the V_{18} can be reduced many times, to finally accommodate eighteen extra electrons. Unfortunately, the calculated transmission spectra do not support this hypothesis. Transmission spectra for **(8:10)**, **(10:8)**, and **(12:6)** are rather similar, showing quite a few peaks near the Fermi level, see Figure 5.17. For comparison, V_6 presented only one, two and three peaks for the completely oxidized, one- and two-electron reduced systems, respectively. Therefore, these pronounced differences between the different redox states for V_6 produced a stepwise conductivity, since more states were accessible to conduct electrons upon reduction. However, the absence of such differences in the V_{18} compound can be ascribed to the fact that its resting state has already eight unpaired electrons giving rise to many peaks near the Fermi level, making it much more complicated to introduce a qualitatively different behaviour when the system changes its oxidation state. Furthermore, the large number of V atoms open many different, but equally plausible conduction channels. Figure 5.18 shows some of the eigenchannel scattering states, all involving mostly V-3d orbitals.

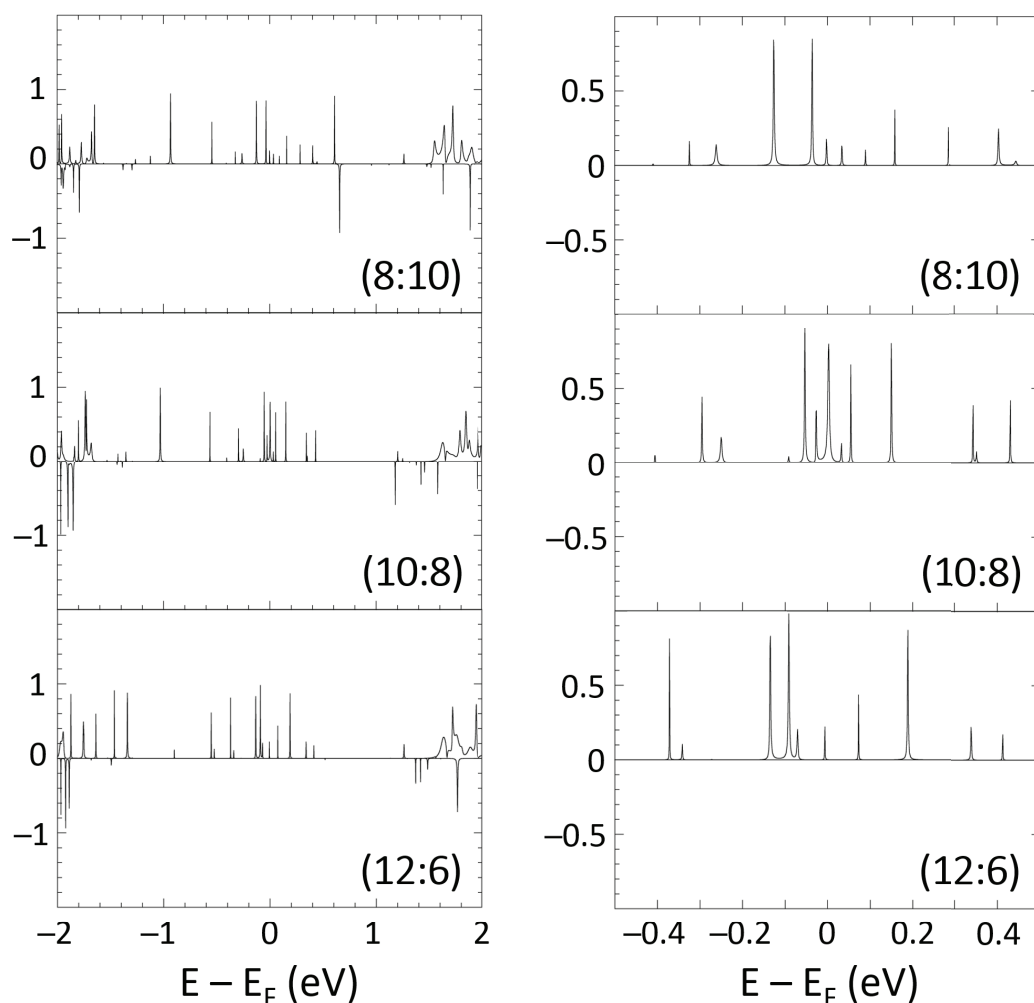


Figure 5.17 | Zero bias ($V = 0$) transmission spectra for (8:10), (10:8), and (12:6) with two different scales (left: from -2 to 2, and right: from -0.5 to 0.5). Positive and negative transmission values correspond to α and β spin-orbital contributions.

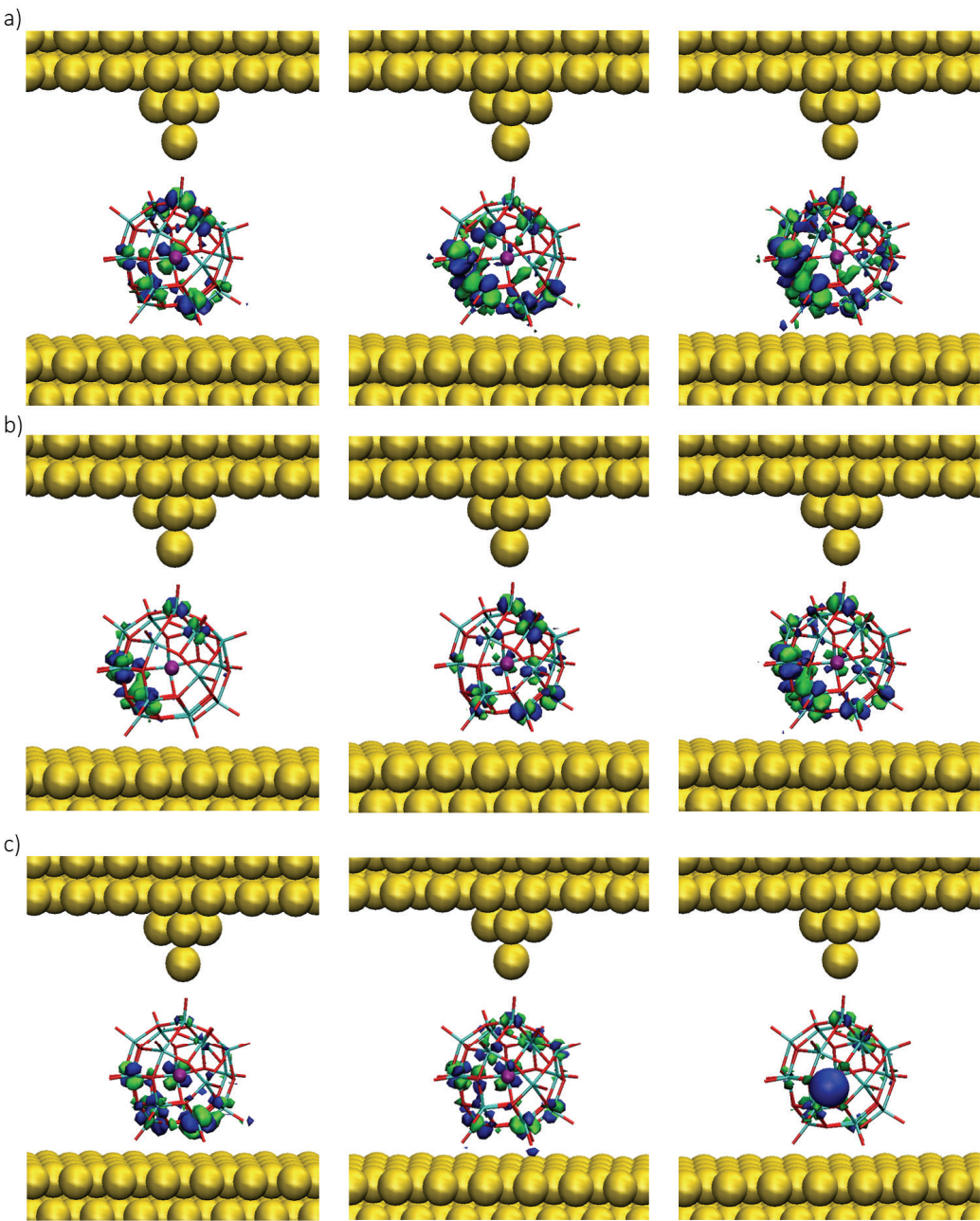


Figure 5.18 | Isosurface plots of the real part of the most transmitting eigenchannel scattering states of a) (8:10), b) (10:8) and, c) (12:6) structures.

5.7 Concluding Remarks

This chapter describes the results obtained from DFT calculations on $[\text{I}@\text{V}_{18}\text{O}_{42}]^{9-}$. We have analyzed their electronic structure when it is adsorbed and isolated. Moreover, we carried out a first insight into its molecular conductivity expecting a step-like behaviour as the Lindqvist-type hexavanadates studied in the previous chapter.

DFT calculations show that, in the absence of crystal packing effects, electrons tend to be distributed evenly over virtually all the vanadium atoms. Moreover, DFT calculations of the isolated molecule, in combination with CPMD data done by Dr. Solé-Daura, suggest certain mobility (at least 0.2 Å away from the center of mass) of the encapsulated iodine at room temperature.

The adsorption study of $[\text{I}@\text{V}_{18}\text{O}_{42}]^{5-}$ on Au(111) surface shows it is a favourable process with energies of approximately 1 eV. This adsorption does not affect the integrity of the POV, keeping unchangeable its electronic structure. Moreover, the mode of the POV on the surface in gas phase does not follow a certain pattern, since the adsorption energies are practically the same.

The conductivity calculations of $[\text{I}@\text{V}_{18}\text{O}_{42}]^{2-}$, $[\text{I}@\text{V}_{18}\text{O}_{42}]^{5-}$, and $[\text{I}@\text{V}_{18}\text{O}_{42}]^{7-}$ show that they will present very similar conductivity behaviour and we do not expect to be step-like as for $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CCHR'SMe}\}_2]^{2-}$ and $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CCHR'SPh}\}_2]^{2-}$.

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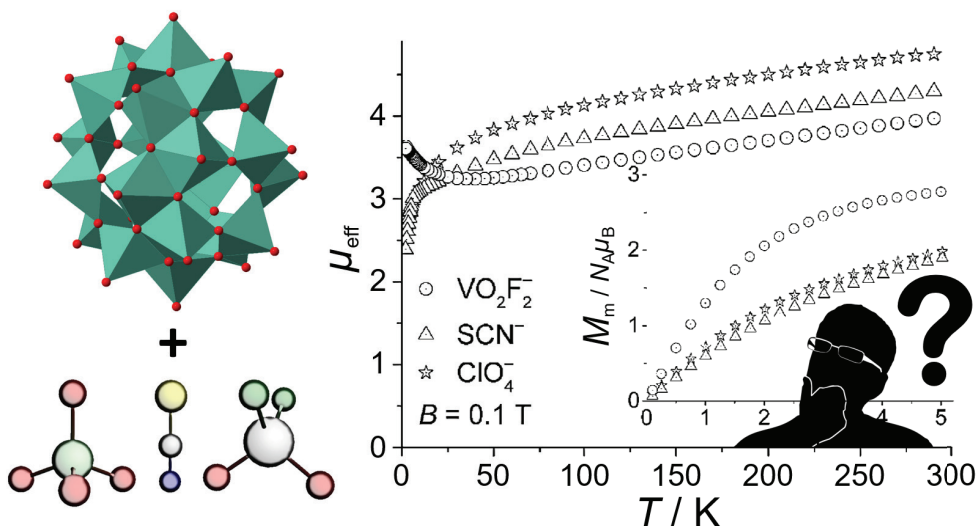
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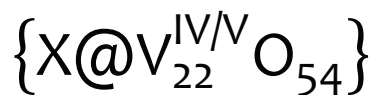
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CHAPTER 6

Connection between Valence State
and Magnetism in Mixed-Valent



Related Publications:

Kozłowski, P.; Notario-Estévez, A.; de Graaf, C.; López, X.; Monakhov, K. Y. Reconciling the Valence State with Magnetism in Mixed-Valent Polyoxometalates: The Case of a $\{\text{VO}_2\text{F}_2@\text{V}_{22}\text{O}_{54}\}$ Cluster. *Phys. Chem. Chem. Phys.* **2017**, 19, 29767.

Notario-Estévez, A.; Kozłowski, P.; Linnenberg, O.; de Graaf, C.; López, X.; Monakhov, K. Y. Decoding the Role of Encapsulated Ions in the Electronic and Magnetic Properties of Mixed-Valence Polyoxovanadate Capsules $\{\text{X}@\text{V}_{22}\text{O}_{54}\}$ ($\text{X} = \text{ClO}_4^-$, SCN^- , VO_2F_2^-): A Combined Theoretical Approach. *Phys. Chem. Chem. Phys.* **2018**, 20, 17847.

CHAPTER 6

Connection between Valence State and Magnetism in Mixed-Valent $\{X@V_{22}^{IV/V}O_{54}\}$

Electronic structure and magnetism of mixed-valent, host-guest polyoxovanadates $\{X@V_{22}^{IV/V}O_{54}\}$ with diamagnetic ($X =$) ClO_4^- (T_d , **1**), SCN^- (C_∞ , **2**), and $VO_2F_2^-$ (C_{2v} , **3**) template anions are analyzed using density functional theory (DFT) and model Hamiltonian calculations. Herein we describe the results of model Hamiltonian calculations of the aforementioned large, mixed-valent POVs taking into account the dynamics of the delocalized electrons. The particular form of the effective Hamiltonian was inspired by the results of DFT calculations that were introduced to shed light on the geometric and electronic peculiarities of this polyoxoanion. The self-consistent use of these two complementary theoretical techniques allows us to determine the valence state and microscopic parameters.

This work was carried out in collaboration with the experimental group of Dr. Kirill Yu Monakhov from RWTH Aachen University in Aachen (Germany), and Dr. Piotr Kozłowski from Adam Mickiewicz University in Poznań (Poland), who performed the model Hamiltonian calculations.

6.1 Background

POVs have a strong tendency toward the formation of supramolecular host-guest compounds.^{1–6} One of this POVs is the $\{X@V_{22}^{IV/V}O_{54}\}$ cluster—or V_{22} -cluster for short—, where X is the guest moiety. Some examples of guests for this host are ClO_4^- and SCN^- , studied in the early 1990s by Müller and coworkers.^{7,8} In 2015, Monakhov's group synthesized a new supramolecular host-guest system of this family: $[VO_2F_2@H_nV_{7+n}^{IV}V_{15-n}^{V}O_{54}]^{6-}$.⁹ The effective magnetic moment and the molar magnetization for the three compounds are shown in Figure 6.1. The newest compound presents different behavior compared to the other two

complexes. While the compounds with $X = \text{ClO}_4^-$ and SCN^- present an antiferromagnetic behaviour below 40 K, the magnetic properties of the POV with VO_2F_2^- are dominated by ferromagnetic interactions.

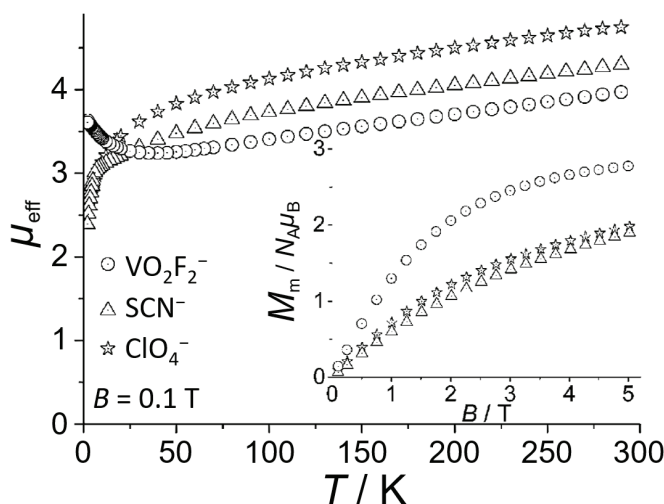


Figure 6.1 | Temperature dependence of the magnetic susceptibility in terms of the effective magnetic moment for $\{X@V^{IV/V}_{22}O_{54}\}$ with $X = \text{VO}_2\text{F}_2^-$, SCN^- or ClO_4^- in an external magnetic field of $B = 0.1$ Tesla. Inset: Molar magnetization at 2K. Figure taken from Ref. 9.

To explain the different behaviour of this new compound, Monakhov and co-workers decided to study its electronic and magnetic properties with DFT and simple model Hamiltonian calculations.⁹ They compared the electrochemical behaviour of the three compounds and, as a result of the presented similarities, assumed the V^{IV}/V^V ratio for $X = \text{VO}_2\text{F}_2^-$ to be 8:14, the same as for ClO_4^- and SCN^- as Müller and coworkers established before. The model Hamiltonian applied was:

$$H_n = \sum_{n=1}^7 J_{i,j} S_i \cdot S_{i+1} \delta_i^n \delta_{i+1}^n + J_{81} S_8 \cdot S_1 \delta_8^n \delta_1^n + g \mu_B B \sum_{i=1}^{10} S_i^z \delta_i^n \quad (6.1)$$

The parameters $\delta_i^n \in \{0,1\}$ are occupation numbers of the eight belt atoms and the two apical sites that are potential V^{IV} sites in the n -th electron distribution, (see ref. 9 for more information). The electron distribution, shown in Figure 6.2, was obtained with Bond-Valence-Sum (BVS) calculations and used in this first

magnetochemical modelling. Two electrons are located in apical positions and the remaining electrons are distributed over the 8 vanadium atoms in the central ring. The model only takes into account exchange interactions J_{ij} between nearest neighbors, therefore only couplings between vanadium atoms in the inner ring are considered. With this assumptions, two models were explored. Model A follows the structural symmetry of the system and only introduces two different exchange interactions ($J_1 = J_{12} = J_{34} = J_{56} = J_{78}$ and $J_2 = J_{23} = J_{45} = J_{67} = J_{81}$). Model B removes all the restrictions on the exchange parameters. However, none of both models gives a unique set of parameters that correctly fits the molar magnetization and magnetic susceptibility. It became clear at this point that the model Hamiltonian had to be improved. But doubts also arouse about the validity of the V^{IV}/V^V ratio for $X = VO_2F_2^-$ of 8:14. The large number of unpaired electrons and the intrinsic complexity of the electronic structure observed in related POMs make that other V^{IV}/V^V ratios should also be explored in more detail.

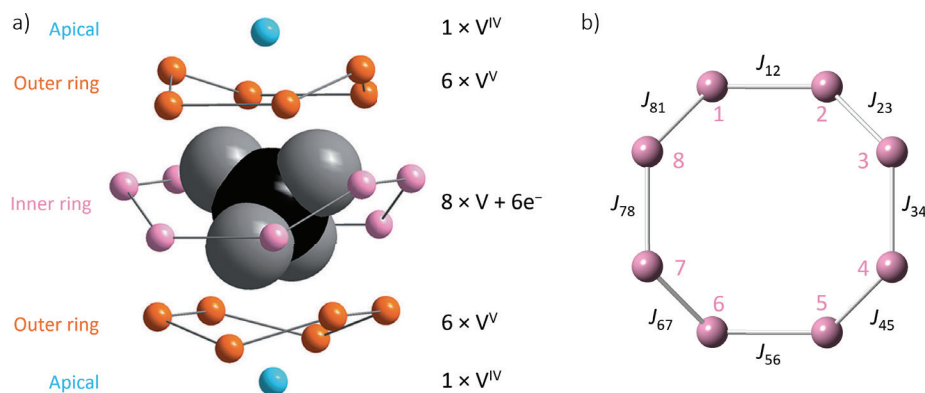


Figure 6.2 | a) Charge distribution in the V_{22} -cluster of $[VO_2F_2@HV^IV_8V^V_{14}O_{54}]^{6-}$, qualitatively determined from BVS theory. $V^VO_2F_2^-$ is shown in space filling model (V = black, O/F = dark gray). Figure taken from Ref. 9. b) Top view of the inner ring showing the different J_{ij} .

This chapter adds a detailed DFT analysis of the electronic structure of the three POVs to the study performed so far. We carefully analyse the V^{IV}/V^V ratio and the distribution of the unpaired electrons over the POV. The results are used to define a refined model Hamiltonian capable to describe their magnetic properties of the three compounds. This combination of DFT and model

Hamiltonian analysis can shed light on the differences observed for the POV with internal VO_2F_2^- .

6.2 Computational Details

DFT calculations were carried out using the ADF2016 package.^{10–12} Structural minima were obtained with the BP86 functional¹³ and a Slater-type basis set of triple- ζ + polarization (TZP)¹⁴ quality with internal electron shells treated by the frozen (medium) core approximation.¹⁵ With the BP86-optimized geometries, molecular properties were obtained from B3LYP single point energy calculations with all-electron TZ2P basis sets and the conductor-like screening model (COSMO)^{16,17} to mimic aqueous solutions ($\epsilon = 78.4$).

Scalar relativistic effects at the Zeroth Order Regular Approximation (ZORA)¹⁸ level were taken into account throughout this study. The spin-unrestricted formalism for open-shell electronic configurations, taking all unpaired spins parallel in each case, and Grimme's dispersion corrections were employed in all the calculations.^{19–25} The number of unpaired electrons associated to the different atoms in the structure were calculated by integrating the spin density in the atomic basins defined by Bader's partition of the electron density. We will refer to these values as atomic spin densities (ASDs).²⁶

6.3 Detailed DFT study of $\text{X@V}_{22}\text{O}_{54}$

We analyse the possible differences induced on the electron distribution of the mixed-valence $\text{X@V}^{\text{IV/V}}_{22}\text{O}_{54}$ host-guest structure by three anionic guest species, $\text{X} = \text{ClO}_4^-$ (**1n**), SCN^- (**2n**), or VO_2F_2^- (**3n**), represented in Figure 6.3. We focus on the hydrogen-free $[\text{X@V}^{\text{IV}}_7\text{V}^{\text{V}}_{15}\text{O}_{54}]^{6-}$ (**Xb**), $[\text{X@V}^{\text{IV}}_8\text{V}^{\text{V}}_{14}\text{O}_{54}]^{7-}$ (**Xa**), and $[\text{X@V}^{\text{IV}}_9\text{V}^{\text{V}}_{13}\text{O}_{54}]^{8-}$ (**Xc**) forms where the label **n** = **a**, **b**, **c** stands for the structures with 8, 7 and 9 electrons, respectively. Even if the structure is protonated, we assume that it behaves as an itinerant proton that does not break the molecular symmetry. Because of that, it does not change any local property appreciably either as it is not strongly attached to any site.

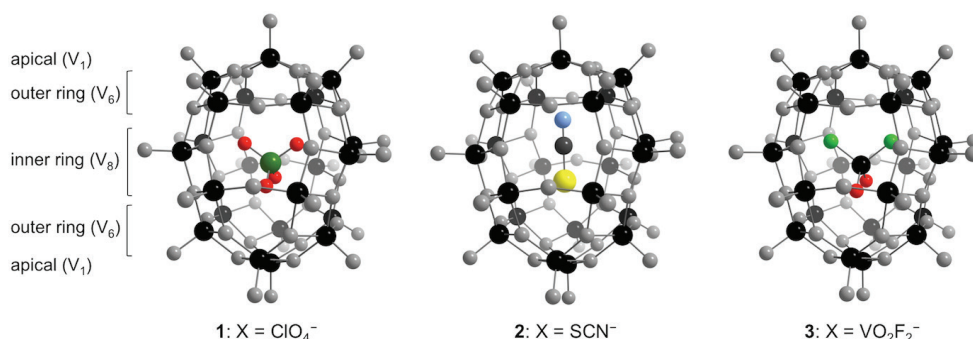


Figure 6.3 | Representation of POV structures **1**, **2** and **3**. Different regions of the V_{22} cage (apical, outer rings and the inner ring) are indicated on the left-hand side of the figure. Black and grey spheres represent V and O atoms, respectively. Guest moieties (X) are shown in colour: Cl = dark green, O = red, N = blue, C = grey, S = yellow and F = light green.

Our first concern has been to establish the correct V^{IV}/V^V ratio for **3**. For that purpose we have compared DFT results on **3a**, **b** and **c**. This exercise was repeated for **1** and **2** to give additional support to our findings for **3**. To complete the picture we have also checked the oxidation state of the empty cage.

6.3.1 Electronic structure

Geometry optimizations imposing the constraints of highest symmetry (D_{2d} for **1** and C_{2v} for **2** and **3**) lead to structures that have several vibrational normal modes with negative eigenvalues, the so-called imaginary frequencies. This indicates that the high symmetry structures do not correspond to the minimal-energy geometries. We therefore applied atomic displacements following the imaginary vibrational normal modes and re-optimized the molecular geometries removing some of the symmetry constraints. The real minima found for structures **1n** have C_2 symmetry due to a pseudo Jahn-Teller (PJT) effect.²⁷ The associated energy stabilizations caused by the symmetry descent are 0.13 eV (**1a**) and 0.09 eV (**1b** and **1c**) with concomitant increments of SOMO-LUMO gaps, as shown in Figure 6.4. For the **2n** structures we observed a similar trend, that is, a symmetry decrease from C_{2v} to C_1 with somewhat smaller energy stabilizations of 0.08 eV (**2a**) and 0.06 eV (**2b** and **2c**). For the **3n** structures the symmetry decrease is the same as in **2n**, with energy stabilizations of 0.14 eV (**3a**), 0.12 eV (**3b**) and 0.11 eV (**3c**). The evolution of the molecular orbitals from

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the high to the low symmetry situation depending on the total electron count is shown in Figures 6.4, 6.5, and 6.6 for **1**, **2**, and **3**, respectively. Low-symmetry compounds feature a steady HOMO destabilization as electrons are added to the system (**1b** $\rightarrow$ **1a** $\rightarrow$ **1c**) due to the molecular negative charge increase. This process pushes the HOMO to higher energy by 0.22 eV and 0.16 eV for the first and second reductions. For **2b** $\rightarrow$ **2a** $\rightarrow$ **2c** reductions, the destabilization of the HOMO is larger (0.26 eV and 0.25 eV respectively). However, **3b** $\rightarrow$ **3a** $\rightarrow$ **3c** reductions present the smallest destabilization of the doubly occupied MOs, being ca. 0.15 eV per molecular unit charge increase.

The number of valence metal electrons in the POVs studied is smaller than the number of V centres, hence the systems feature a mixture of $V^{IV/V}$ centres. For the understanding of magnetic properties it is critical to know how these valence electrons are distributed among the metal atoms. So the ground-state electronic structures of POVs have been estimated by DFT calculations. Not entering into the details of how electrons couple or which is the ground-state total S value, the location of metal electrons is reasonably well described by the high-spin DFT solution of the system, which is straightforwardly computed and formally correct. Under the assumption that low spin coupling does not lead to localization of two unpaired electrons in the same region of space (which would result in a certain degree of bond formation), the distribution of the unpaired electrons in low-spin, intermediate-spin and high-spin coupled states can be considered to be similar in all cases.²⁸ In the case of POMs, several studies showed that valence metal electrons, if present, tend to spread out over as many metal sites as possible by virtue of intersite hopping and Coulomb repulsion, with a concomitant tendency to multi-site delocalisation.²⁹ This evidence explains why only slight differences in the distribution of metal electrons (and in the electronic structure in general) are obtained when the real low-spin configuration is estimated from a high-spin DFT calculation. Following the above reasoning, we base the discussion of the distribution of unpaired electrons on the hypothetical empty cage and in structures **1–3** on the atomic spin densities (ASDs) of the electronic state with maximum spin multiplicity.

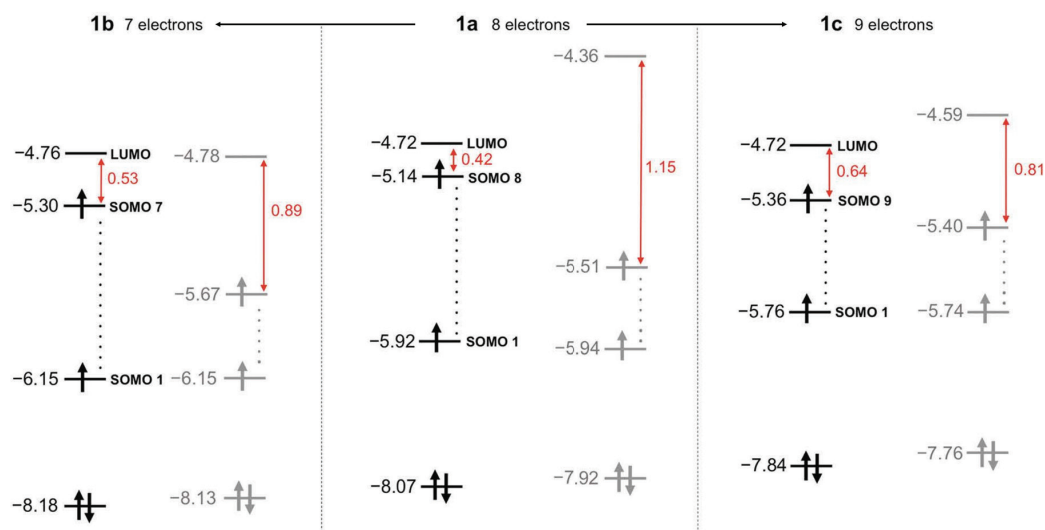


Figure 6.4 | Electronic structure of 1, highlighting orbital energies for 1a–1c in the D_{2d} (black) and C_2 (grey) forms, and SOMO-LUMO energy gaps (red). Energies are given in eV.

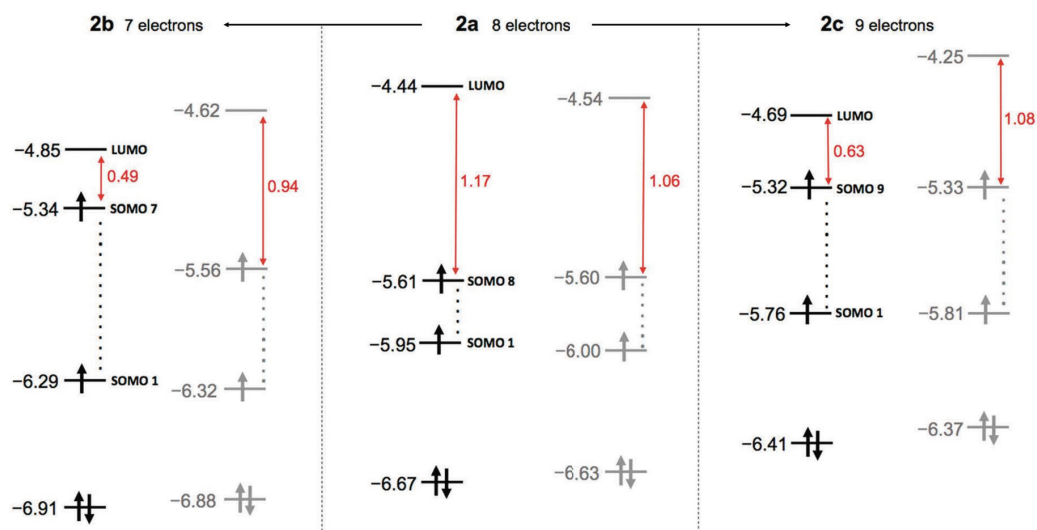


Figure 6.5 | Electronic structure of 2, highlighting orbital energies for 2a–2c in the C_{2v} (black) and C_1 (grey) forms, and SOMO-LUMO energy gaps (red). Energies are given in eV.

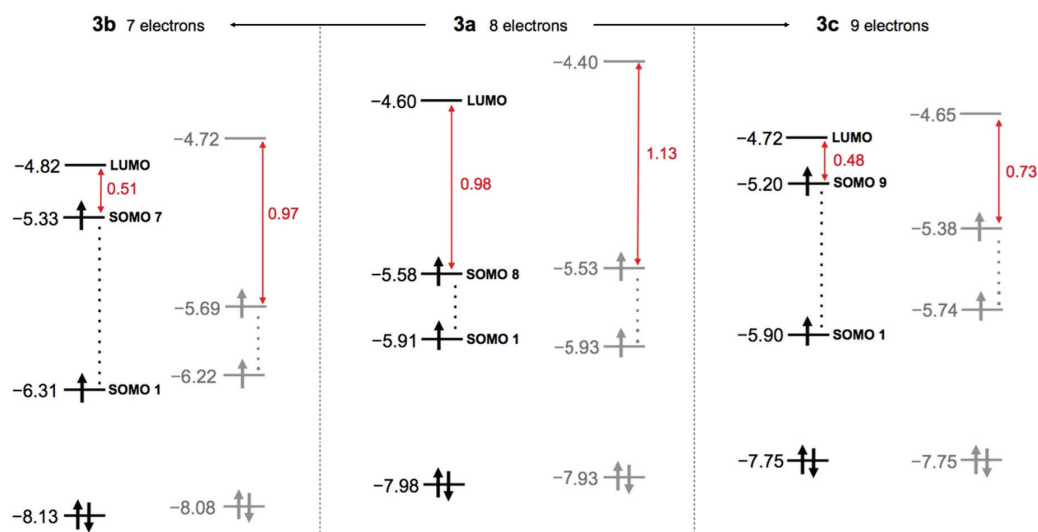
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Figure 6.6 | Electronic structure of **3**, highlighting orbital energies for **3a–3c** in the C_{2v} (black) and C₁ (grey) forms, and SOMO-LUMO energy gaps (red). Energies are given in eV.

As shown in Figure 6.7, two equivalent low-symmetry minima of each compound exist, resulting from distortions of the high-symmetry structure in two different directions of the potential energy surface. The distribution of the unpaired electrons is of course equivalent in the two minima, but this does not necessarily apply for the transition state that connects them and that defines the interconversion energy barrier. For **2** and **3**, the transition state has lower symmetry (C_s) than the highest symmetry structure (C_{2v}). From the relatively large energy barriers connecting the low symmetry minima for **1a–c** (0.10 eV = 1160 K) it can be inferred that the interconversion between both minima can be of some importance only close to room temperature. However, since the two low-symmetry isomers are magnetically equivalent, the interconversion does not influence the magnetic modelling as long as the system spends short times in the high-symmetry state. The population ratio of both states is obtained applying the Boltzmann factor:

$$\frac{p_i}{p_j} = e^{\frac{\epsilon_j - \epsilon_i}{kT}} \quad (6.2)$$

For **1**, the probability of being in the high symmetry state, $p(D_{2d})$ (assuming the canonical ensemble), is about 109 times smaller (at $T = 290$ K) than for the low symmetry state $p(C_2)$. Therefore, in the range of temperatures of interest, it can be safely assumed that each of these systems is trapped in one of the low symmetry minima. For **2a–c**, the barrier is much smaller (0.02 eV = 230 K) and interconversion can be important at much lower temperatures. The ratio $p(C_1)/p(C_s)$ is 4.5 at $T = 290$ K and 20 at $T = 100$ K. For **3** this probability is in between **1** and **2** with a ratio of 14 at $T = 290$ K.

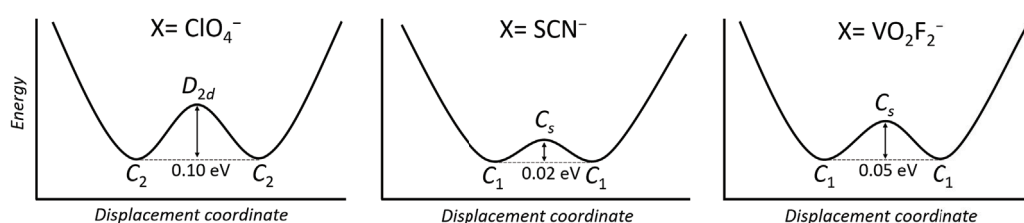


Figure 6.7 | Schematic view of the energy stabilization upon structural distortion for **1–3** compounds. The computed barriers of interconversion between equivalent low-symmetry minima are indicated.

In Table 6.3 we list the values of region spin densities (RSDs), defined as the sum of ASDs of the vanadium atoms located in the different regions of the complex. The following discussion is based on ASDs and RSDs listed in Tables 6.1 to 6.3. The fact that the sum of ASDs does not add up to the formal number of unpaired electrons originates in the spin polarization of oxygen atoms (which have small negative ASDs) coordinating vanadium centers. ASDs and RSDs listed in the tables are referred to as unnormalized spin densities.

Empty cage. The low-symmetry empty cage has C_2 symmetry and is similar to the one obtained for **1**. ASDs of this hypothetical structure show delocalized unpaired electrons over almost all the vanadium centers of the cage in the 7- and 9-electron-containing structures (**b** and **c**). Only two centers feature an unambiguous V^V character and, in the structure with nine valence metal electrons, one could consider the apical centers as V^{IV} to some extent. The situation is quite different in the 8-electron structure (**a**). There, the inner ring vanadium atoms show a clear alternating pattern of V^V and V^{IV} centers, while the electron

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distribution in the outer rings and in the apex centers is more in line with what was found for **b** and **c** structures, that is, one V^V center and the rest of electrons equally shared by the other centers. By imposing D_{2d} symmetry restrictions on the empty cage structure, the ASDs follow the same tendency in **a**, **b** and **c** forms. There are two V^V centers in the outer rings, V^{IV} centers on apex positions and the remaining electrons are delocalized over the other centers. Oxidation or reduction of the 8-electron structure does not affect the electron count on the inner ring. Instead, the total spin density on the outer rings decreases or increases significantly. At variance with the above, changes in the RSDs for the low-symmetry structure are more complex. Both oxidation and reduction lead to an increase of the spin density in the inner ring and in the apical position, while the outer ring of vanadium centers loses spin density in both cases.

$X = ClO_4^-$. This structure is equivalent to the hypothetical empty cage in many aspects, one of them being that both hemispheres are equivalent in the low- and high-symmetry forms. Starting with low symmetry and the least electron populated form (**1b**), ASDs suggest that apical sites have nearly one electron each (V^{IV} character), outer ring regions have roughly one electron each (RSD = 1.43) with two V^V sites, and the inner V_8 ring has between three and four electrons (RSD = 3.77). Recall that the unexpectedly large RSDs indicate, in general, that some spin polarisation is present, oxygen ligands carrying some negative ASDs that compensate the total value. This electron distribution concentrates more electrons in the apical and inner ring regions than the empty cage (**b**). As for the empty cage, **1a** shows a clear electron depletion in the apical positions and in the central ring, whereas outer rings increase their RSDs from 1.4 to 3.0. The 9-electron form (**1c**) has V^{IV} apical sites and the inner rings recover a large fraction of the electron density like for the empty cage. Remarkably, no V^{IV} sites appear in **1a**, which again has the most regular electron distribution. For high-symmetry structures, we observed the same behaviour as for the empty cage, with two formal V^{IV} in the apical positions, four V^V , two in each outer ring (V_6), and the rest of the electrons distributed over 16 vanadium centers.

$X = SCN^-$. Because of the dipolar nature of the guest, the ASDs of compound **2** present a less regular electron distribution than compound **1**, mostly because the two hemispheres are non-equivalent. Despite that, for the least electron populated form, **2b**, the unpaired electrons in the inner ring are as evenly

distributed as in the other compounds but, interestingly, this is the most highly populated region of all the series ($RSD = 4.42$). The electronically depleted outer ring in the N-hemisphere ($RSD = 0.59$) is nearly electron-free and may be seen as a set of six V^{IV} sites, whereas the S-hemisphere has $RSD = 1.60$. Apical sites show notable V^{IV} character. The 8-electron form **2a** presents important changes. First, the two outer rings are electron-rich ($RSDs = 2.55$ and 2.96) and the inner ring has between 1 and 2 electrons less than in **2b**. It is worth mentioning that the inner ring of **2a** has unevenly distributed ASDs following an alternating $(V_21e)(V_2)(V_21e)(V_2)$ arrangement. This is present in no other form or compound so clearly. Figure 6.8 depicts schematically this electron distribution. Such a pattern is obviously a consequence of the internal SCN^- dipole moment orientation, which polarizes the unpaired electrons towards the less electron populated N-hemisphere. Finally, form **2c** has one electron more in the inner ring than **2a**. Minor changes occur in the other regions. In high symmetry structures, the differences between hemispheres due to the guest are maintained, but the apical position is V^{IV} in all the oxidation states.

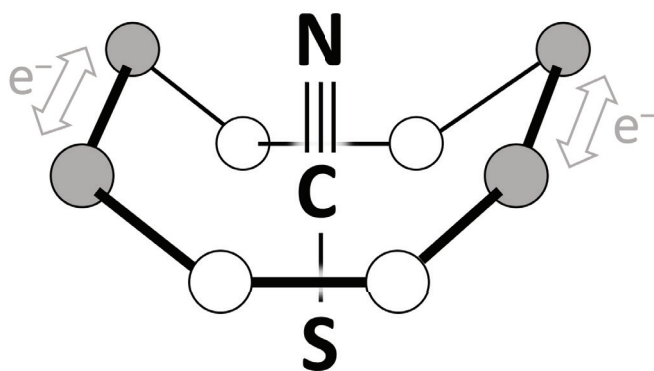


Figure 6.8 | Schematic view of the inner V_8 ring and the orientation of the SCN^- guest in compound **2a**. Each couple of neighbouring grey V atoms share one unpaired electron, whereas the white V atoms possess only a residual fraction of an electron.

Table 6.1 | Vanadium unnormalized ASD computed for low-symmetry minima (C₂ or C₁, see text) in different oxidations states (**a** (8e⁻), **b** (7e⁻), and **c** (9e⁻)). In the case of structure **2** and **3**, we denote the N or F- or the S or O-hemisphere, respectively. Shaded cells correspond to formally V^{IV} centres (ASD < 0.20)

Empty cage									X = ClO ₄ ⁻ (1)			X = SCN ⁻ (2)			X = VO ₂ F ₂ ⁻ (3)		
Apical	b	a	c	b	a	c	b	a	c	b	a	c	b	a	c	N or F	
	0.64	0.40	0.79	0.81	0.45	0.86	0.80	0.77	0.54	0.45	0.50	0.89	0.45	0.50	0.89		
Outer ring	0.51	0.61	0.61	0.52	0.55	0.55	0.08	0.52	0.55	0.46	0.51	0.56	0.08	0.52	0.55	0.56	
	0.03	0.04	0.04	0.03	0.04	0.04	0.20	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	
	0.53	0.57	0.51	0.55	0.62	0.56	0.08	0.57	0.63	0.62	0.63	0.62	0.62	0.63	0.63	0.62	
	0.40	0.67	0.26	0.21	0.64	0.19	0.03	0.29	0.57	0.64	0.60	0.15	0.64	0.60	0.63	0.62	
	0.29	0.58	0.64	0.06	0.52	0.59	0.10	0.52	0.55	0.53	0.53	0.53	0.53	0.53	0.53	0.53	
Inner ring	0.34	0.60	0.54	0.06	0.62	0.59	0.10	0.62	0.62	0.62	0.63	0.59	0.62	0.63	0.62	0.59	
	0.45	0.51	0.46	0.47	0.51	0.46	0.56	0.57	0.58	0.57	0.63	0.42	0.57	0.63	0.58	0.42	
	0.33	0.07	0.63	0.56	0.08	0.63	0.53	0.66	0.07	0.06	0.06	0.55	0.53	0.66	0.07	0.55	
	0.34	0.65	0.32	0.30	0.65	0.33	0.55	0.57	0.60	0.56	0.55	0.53	0.56	0.55	0.60	0.53	
	0.34	0.05	0.54	0.55	0.06	0.54	0.60	0.39	0.08	0.07	0.08	0.64	0.60	0.39	0.08	0.64	
Outer ring	0.34	0.65	0.32	0.30	0.65	0.33	0.54	0.21	0.66	0.07	0.06	0.54	0.54	0.21	0.66	0.54	
	0.34	0.05	0.54	0.55	0.06	0.54	0.53	0.06	0.67	0.54	0.64	0.34	0.53	0.06	0.67	0.34	
	0.45	0.51	0.46	0.47	0.51	0.46	0.56	0.15	0.53	0.08	0.07	0.64	0.56	0.15	0.53	0.64	
	0.33	0.07	0.63	0.56	0.08	0.63	0.56	0.08	0.49	0.62	0.53	0.48	0.62	0.53	0.49	0.48	
	0.29	0.58	0.64	0.06	0.52	0.59	0.61	0.59	0.61	0.62	0.63	0.62	0.62	0.63	0.62	0.62	
Outer ring	0.03	0.04	0.04	0.03	0.04	0.04	0.26	0.03	0.22	0.60	0.69	0.17	0.26	0.03	0.22	0.17	
	0.34	0.60	0.54	0.06	0.62	0.59	0.57	0.58	0.57	0.45	0.50	0.55	0.57	0.58	0.57	0.55	
	0.40	0.67	0.26	0.21	0.64	0.19	0.03	0.58	0.04	0.03	0.04	0.04	0.03	0.04	0.04	0.04	
	0.51	0.61	0.61	0.52	0.55	0.55	0.07	0.59	0.61	0.07	0.63	0.49	0.07	0.63	0.63	0.49	
	0.53	0.57	0.51	0.55	0.62	0.56	0.06	0.58	0.59	0.07	0.52	0.45	0.06	0.58	0.59	0.45	
Apical	0.64	0.40	0.79	0.81	0.45	0.86	0.77	0.50	0.83	0.48	0.40	0.87	0.77	0.50	0.83	0.87	

Table 6.2 | Vanadium unnormalized ASD computed for high-symmetry minima (D_{2d} or C_{2v} , see text) in different oxidations states (**a** ($8e^-$), **b** ($7e^-$), and **c** ($9e^-$)). In the case of structure **2** and **3**, we denote the N or F- or the S or O-hemisphere, respectively. Shaded cells correspond to formally V^{IV} centres ($ASD < 0.20$)

Empty cage									
X = ClO_4^- (1)			X = SCN^- (2)			X = $VO_2F_2^-$ (3)			
Apical	b	a	c	b	a	c	b	a	c
Outer ring	0.27	0.38	0.57	0.94	0.94	0.95	0.91	0.92	0.92
	0.06	0.06	0.06	0.25	0.47	0.56	0.10	0.55	0.57
	0.27	0.38	0.57	0.05	0.05	0.05	0.06	0.07	0.07
	0.06	0.06	0.06	0.25	0.47	0.56	0.10	0.55	0.57
	0.27	0.38	0.57	0.05	0.05	0.05	0.06	0.07	0.07
Inner ring	0.27	0.38	0.57	0.25	0.47	0.56	0.10	0.55	0.57
	0.27	0.38	0.57	0.25	0.47	0.56	0.10	0.55	0.57
	0.51	0.54	0.50	0.53	0.46	0.51	0.55	0.58	0.47
	0.51	0.54	0.50	0.53	0.46	0.51	0.55	0.58	0.47
	0.51	0.54	0.50	0.53	0.46	0.51	0.55	0.58	0.47
Outer ring	0.27	0.38	0.57	0.25	0.47	0.56	0.35	0.60	0.57
	0.06	0.06	0.06	0.05	0.05	0.05	0.06	0.06	0.06
	0.27	0.38	0.57	0.25	0.47	0.56	0.35	0.60	0.57
	0.06	0.06	0.06	0.05	0.05	0.05	0.06	0.06	0.06
	0.27	0.38	0.57	0.25	0.47	0.56	0.35	0.60	0.57
Apical	0.92	0.92	0.93	0.94	0.94	0.95	0.93	0.90	0.93

Table 6.3 | Vanadium RSD computed for high and low symmetry structures. In the case of structure **2** and **3**, we indicate the N or F- or the S or O-hemisphere, respectively.

Low symmetry												
Empty cage			X = ClO ₄ ⁻ (1)			X = SCN ⁻ (2)			X = VO ₂ F ₂ ⁻ (3)			
	b		a	c	b	a	c	b	a	b	a	c
V ₁	0.64	0.40	0.79	0.81	0.45	0.86	0.80	0.77	0.54	0.45	0.50	0.89
V ₆	2.10	3.06	2.59	1.43	2.98	2.52	0.59	2.55	2.96	2.91	2.94	2.49
V ₈	2.91	2.57	3.88	3.77	2.64	3.94	4.42	2.68	3.67	2.57	2.62	4.14
V ₆	2.10	3.06	2.59	1.43	2.98	2.52	1.60	2.96	2.63	1.84	3.01	2.32
V ₁	0.64	0.40	0.79	0.81	0.45	0.86	0.77	0.50	0.83	0.48	0.40	0.87
High symmetry												
Empty cage			X = ClO ₄ ⁻ (1)			X = SCN ⁻ (2)			X = VO ₂ F ₂ ⁻ (3)			
	b		a	c	b	a	c	b	a	b	a	c
V ₁	0.92	0.92	0.93	0.94	0.94	0.95	0.91	0.92	0.92	0.96	0.95	0.97
V ₆	1.18	1.65	2.40	1.11	1.99	2.36	0.52	2.33	2.42	1.42	2.46	2.50
V ₈	4.09	4.32	3.99	4.22	3.68	4.08	4.37	2.70	3.95	4.56	3.44	4.76
V ₆	1.18	1.65	2.40	1.11	1.99	2.36	1.50	2.52	2.42	0.32	1.64	1.46
V ₁	0.92	0.92	0.93	0.94	0.94	0.95	0.93	0.90	0.93	0.94	0.96	0.97

Table 6.4 | Number of V^{IV} , V^V and $V^{IV/V}$ centres in structures **1–3** at different reduction states with high and low symmetry, estimated from DFT calculations.

		Low symmetry			High symmetry		
		b (7e ⁻)	a (8e ⁻)	c (9e ⁻)	b (7e ⁻)	a (8e ⁻)	c (9e ⁻)
Empty Cage	V^{IV}	0	0	0	2	2	2
	V^V	2	6	2	4	4	4
	$V^{IV/V}$	20	16	20	16	16	16
X = ClO ₄ ⁻ (1)	V^{IV}	2	0	2	2	2	2
	V^V	6	6	4	4	4	4
	$V^{IV/V}$	14	16	16	16	16	16
X = SCN ⁻ (2)	V^{IV}	2	1	1	2	2	2
	V^V	7	5	4	8	8	4
	$V^{IV/V}$	13	16	17	12	16	16
X = VO ₂ F ₂ ⁻ (3)	V^{IV}	0	0	2	2	2	2
	V^V	8	6	4	8	4	4
	$V^{IV/V}$	14	16	16	12	16	16

X = VO₂F₂⁻. The atomic spin densities (ASDs) of **3c** are nearly identical for the C_{2v} and C₁ minima, with apical V centers having ASDs close to 1.0 (i.e. V^{IV}) and, neighboring to each apical site, two fully oxidized V^V sites (ASDs 0.04-0.17). The rest of the metal centers are partially populated by the remaining seven unpaired electrons (ASDs 0.34-0.64) in the C_{2v} and C₁ minima, thus most unpaired electrons are delocalized over the major part of the V₂₂ framework (16 mixed-valent vanadium atoms, see Table 6.5). Removal of one electron from the high-symmetry structure (**3c** → **3a**) leads to electron density loss from the central V₈ ring, but if the C₁ structure is considered, in addition to electron loss from the central ring, the electrons initially localized in apical positions partially delocalize over the outer V₆ rings and, then, the apical V centers are better described as mixed valent V^{IV/V}. The MOs show that pure apical-like orbitals in **3c** (Figure 6.9, right) delocalize over a neighboring site in **3a**, thus reducing the spin on apical sites to half (Figure 6.9, left), partially explaining that both V₆ rings gain electron density. Remarkably, the central V₈ ring has four V^V centers. The electronic distribution of the less stable C_{2v} form of **3a** has two V^{IV} on the apical positions

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and two V^V sites in each V_6 ring. No V^V atoms are found in the central ring. Another electron removal (from **3a** to **3b**) in the C_{2v} structure results in a net loss of one electron in both outer V_6 rings combined with a one-electron increase in the central V_8 ring, the apical centers remaining as V^{IV} . The electron distribution of its C_1 form is identical to that of **3a** except for one electron removed from the V_6 ring situated in proximity of the internal oxygens. The internal fragment orientation has some effect on the electron distribution. In the C_{2v} form, **3a-3c** invariably feature one electron more in the hemisphere closer to F and the C_1 form of **3b** also concentrate more unpaired electrons in the F-hemisphere likely due to the electrostatic effect of the $VO_2F_2^-$ unit. However, in the more electron-rich species **3a** and **3c**, both hemispheres carry the same spin density.

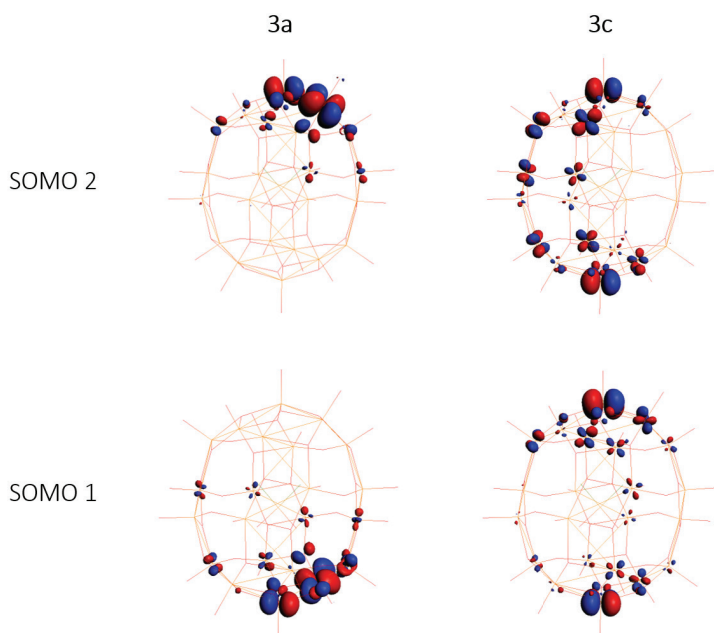


Figure 6.9 | SOMO 1 and SOMO 2 for species **3a** and **3c**.

When compared with the structures discussed above, compound **2** presents, in general, less evenly distributed ASDs due to the presence of the SCN^- guest. Nevertheless, for the most electron populated compound **2c** we observe almost the same ASDs as for other 9-electron systems, suggesting that the guest anion has little effect in the distribution of the unpaired electrons in this case. The two apical metal centres are V^{IV} and the inner ring electrons are evenly shared among

the centres, whereas outer rings feature again two V^V centres each. D_{2d} and C_{2v} structures (i.e. not absolute minima) have ASDs that follow the high structural symmetry (see Table 6.2), with a marked $(V^{IV})_{\text{apical}}$ character at variance with the mixed $(V^{V/IV})_{\text{apical}}$ character in low symmetry minima. Also, the inner region concentrates more unpaired electrons, and the most electron depopulated regions are the outer rings. Structural distortion causes more even electron distributions. So, apparently, structural distortion distributes the electron density in a more equitable way.

6.3.2 Redox properties

Species **a-c** of the same formula can be electrochemically interconverted. **1a** can be oxidized to **1b**, reduced to **1c**. The same happens with species **2** and **3**. The computed energies associated to these processes are:

Oxidation:	1a $\rightarrow$ 1b + e^-	$E_1 = 5.21 \text{ eV}$
	2a $\rightarrow$ 2b + e^-	$E_2 = 5.18 \text{ eV}$
	2a $\rightarrow$ 2b + e^-	$E_3 = 5.13 \text{ eV}$
Reduction:	1a + $e^- \rightarrow$ 1c	$E_4 = -4.86 \text{ eV}$
	2a + $e^- \rightarrow$ 2c	$E_5 = -4.88 \text{ eV}$
	3a + $e^- \rightarrow$ 3c	$E_6 = -4.85 \text{ eV}$

These energies correspond to 0.73 (E_1), 0.70 (E_2), 0.65 (E_3), 0.38 (E_4), 0.40 (E_5) and, 0.37 (E_6) V vs. Ag/AgCl (−4.48 eV). Another oxidation of **2b** has been theoretically calculated with an associated value of 0.83 V. The analogous value for the oxidation of **1b** has also been calculated (0.72 V) but for a species with residual imaginary frequencies of −33.78 and −25.93 cm^{-1} . If we consider the hypothetical empty cage $[V_{22}O_{54}]^{6-}$, oxidation and reduction energies are 5.57 and −5.04 eV, respectively (1.09 V and 0.56 V vs. Ag/AgCl), showing that it is more difficult to take electrons from and easier to give electrons to than for host-guest species, in line with the lower negative charge of the empty structure. In general, the trends obtained from calculations reproduce well the experimental evidence (see Figure 6.10). Considering that the reported resting potential for species **3a** is close to 0.3 V vs. Ag/AgCl, reduction and oxidation can be considered to be highly accessible in terms of energy, and the three species, **3a**–

3c, could coexist in some ratio in the same medium. From the perspective of DFT calculations, **3c** can be considered stable: (i) This is because of its very negative reduction energy. Taking as the reference the well-known oxidised POM structure $[P_2W_{17}MoO_{62}]^{6-}$,³⁰ the presently computed reduction of **3a** to produce **3c** is 0.25 eV more exothermic. This fact suggests that, in comparison, species **3c** can be obtained at even lower potentials. (ii) The stability of **3c** is also due to the very low energy of the highest SOMO, -5.38 eV. Although this absolute value is not self-explanatory, it can be compared to that of another member of the POV family as an indicator of the relative stability of the system. For comparison, a species of the same family of compounds previously reported, $[I@V_{18}O_{42}]^{5-}$ presents $E(\text{HOMO}) = -4.79$ eV. Hence, these computed electronic structures point out considerable electrochemical stability for **3c**. Moreover, observing the cyclic voltammogram (Figure 6.10) a third oxidation peak is only present in compound **3**. However, with these results alone we cannot affirm the reduction state of **3**.

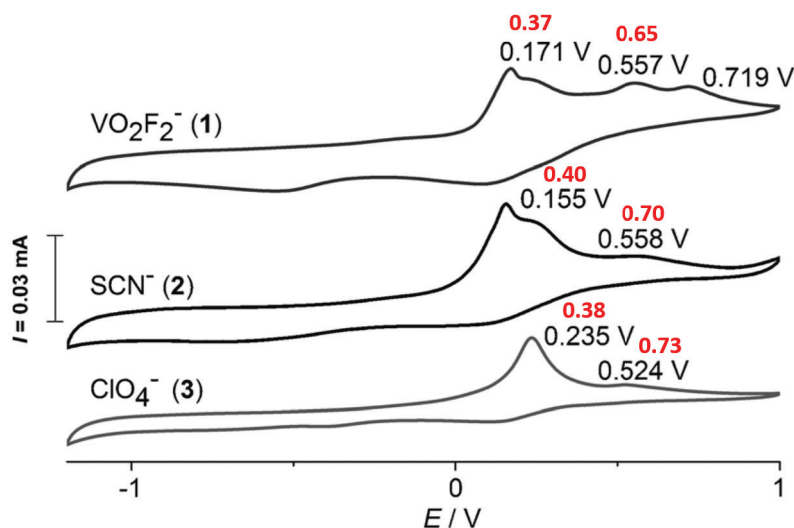
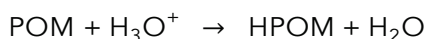


Figure 6.10 | Cyclic voltammogram of compounds **1–3** with a scan rate of 25 mV s^{-1} versus a Ag/AgCl reference electrode. The theoretical values are indicated in red.

6.3.3 Study of basicity

Studying the basicity of the **1-3** we will have other data about our systems. Protonation of the POV produces stabilization of the vanadium d-orbitals allowing, then, to be more accessible to accommodate an electron. Knowing the protonation energies of **1-3** we can have an idea about how likely they are to be protonated. This protonation could change their magnetism because of a different electron distribution than when they are not protonated. So, it is important to perform this study. The Molecular Electrostatic Potential (MEP) can provide information about the electrostatic affinity that molecules have for other charged species, for instance H^+ . In our graphical representation of the MEP, red colour corresponds to more negative potentials, so a priori it identifies nucleophilic regions of higher basicity. Figure 6.11 depicts the MEPs for the hydrogen-free species **1a**, **2a**, **3a**, and **3c** identifying the selected bridging oxygen sites A to C (or D) in each case as the most nucleophilic ones by their electrostatic potential value. After this qualitative view of basicity, a more quantitative description of protonation was obtained. Considering the reaction:



Thus, theoretical protonation energies can be calculated with the following formula:

$$E_{\text{prot}} = (E_{\text{POM-H}} + E_{\text{H}_2\text{O}}) - (E_{\text{POM}} + E_{\text{H}_3\text{O}^+}) \quad (6.3)$$

where, $E_{\text{POM-H}}$ is the energy of the protonated POM, $E_{\text{H}_2\text{O}}$ the energy of water, E_{POM} the energy of the POM and, $E_{\text{H}_3\text{O}^+}$ the energy of the hydronium ion. All the energies have been obtained using the COSMO to mimic the effects of water as solvent. For compound **1a** (charge -7), the calculated protonation energies are: A: $-0.73/-0.81$ eV, B: -0.82 eV, C: -0.73 eV, showing that the most basic oxygen is B (triple bridging, OV_3), in clear competition with an A-type site (the closest to the guest). For species **2a**, protonation energies are: A: -0.79 eV, B: -0.84 eV, C: -0.97 eV, D: -1.00 eV. The most basic sites are C and D, latter being an OV_3 site with the most acute V-O-V angles, which is typically linked to a higher reactivity. All these basic oxygens are located in the N-hemisphere, the most electron-rich regions, as discussed above (see Tables 6.1 and 6.2). For **3b**, the protonation

energies all lie between -0.86 and -1.07 eV. As for $X = SCN^-$, the MEP plot and the protonation energies indicate that the upper hemisphere of the $V_{22}O_{54}$ cage has an increased basicity with respect to the rest of the structure which is directly related to the electron density concentration/depletion in the cage produced by the polar guest, making one hemisphere more nucleophilic than the other. As the number of unpaired electrons of compound **3** is subject to uncertainty, we have also calculated the protonation energies of **3c**. The higher negative charge makes that the protonation energies take more negative values, from -1.07 to -1.34 eV. The most basic oxygen is B-type (OV_3), as expected.³¹ The small energy range associated with the most nucleophilic positions, A and B (8 in total), suggests that attached protons might be itinerant within this set of oxygen atoms. This aspect will be discussed in more detail in the next section.

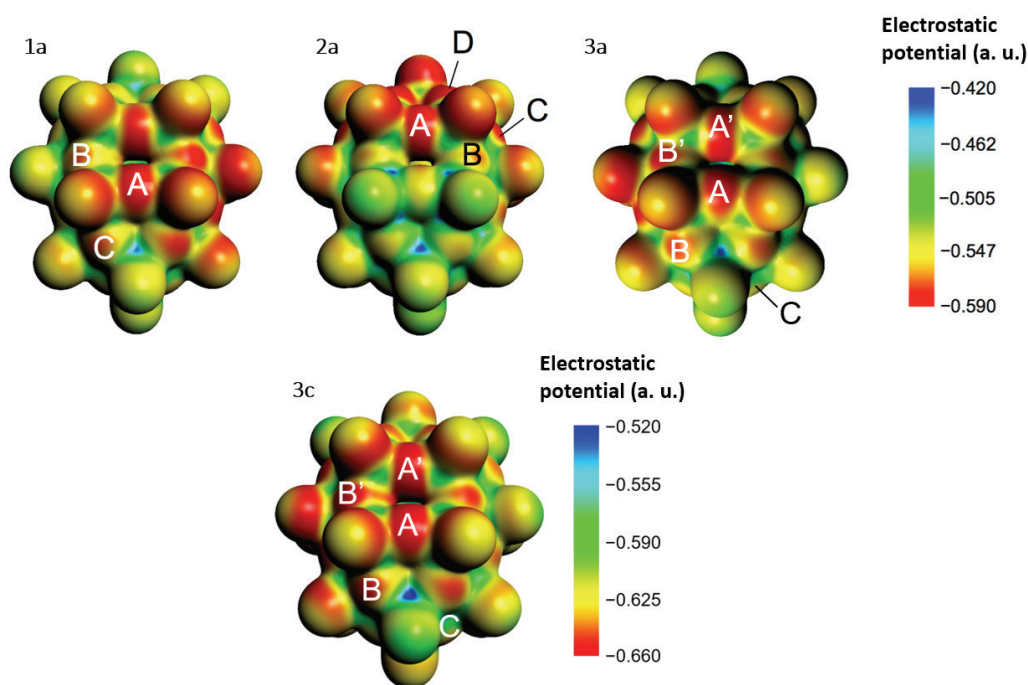


Figure 6.11 | Nucleophilicity of **1a**, **2a**, **3a**, and **3c**. The molecular electrostatic potential (MEP), coloured as indicated in the scale, is plotted on an isodensity surface. The most nucleophilic oxygen sites in each case are labelled A-D.

To further explore protonation in the $\{VO_2F_2@V_{22}O_{54}\}$ structure, we have studied the local geometry of the protonation site in the monoprotinated

structure. It was found that single-bridge oxygens (A type), when protonated, allow for two different H orientations that may be close in energy. Namely, the H atom can be positioned (i) towards the solvent bulk or, (ii) towards another bridging oxygen in proximity forming a weak O...H interaction, as indicated in Figure 6.12. In order to have conclusive data on this topic, we explored computationally the energetics of the mentioned options. Depending on the model adopted for these calculations, results may seem contradictory. We clarify these aspects below.

Model 1: In the model shown in Figure 6.12 a), with no explicit water molecules included, orientation (ii) is 5 kcal mol⁻¹ more stable than (i) thanks to the intramolecular hydrogen bond formed between two A-type oxygens. The process that interconverts situations (i) and (ii) was studied doing a relaxed scan (keeping constant the dihedral angle and optimizing the rest of the molecule) by changing the dihedral angle shown in Figure 6.12 a) (right). A marginal energy barrier of approximately 0.02 eV (0.46 kcal mol⁻¹) was found connecting both orientations.

Model 2: Using a second, more realistic model with one explicit water molecule Figure 6.12 a) (down), orientations (i) and (ii) were re-evaluated performing geometry optimization calculations. It turns out that, at variance with **model 1**, orientation (i) (in this case, the H forms a hydrogen bridge with the explicit water molecule) is 0.1 eV (2.36 kcal mol⁻¹) more stable than orientation (ii). Moreover, when a water molecule is situated at sufficient proximity of the H in orientation (iii), as in Figure 6.12 a) (down, (iii)), this H atom leaves its original position and freely adopts orientation (i). These results show, therefore, that (i) is probably the preferred and only orientation in this POV.

Another aspect tackled in this analysis is the protonation-deprotonation process. We computed an equilibrium structure in which a monoprotinated POV molecule is hydrogen bonded to an explicit water molecule. From this initial conformation, an energy scan was performed along the O-H distance d_1 (see Figure 6.12 b) optimizing the geometry of the whole system and fixing d_1 at each step. The scan tracks the deprotonation of the POV, during which we found an energy barrier of approximately 0.15 eV (~3.5 kcal mol⁻¹) while it leads at the same time to protonation at a nearby oxygen site, indicated with the blue arrow.

In this process, distance d_2 decreases freely and concertedly with increasing d_1 . The relatively low energy barrier for this concerted protonation/deprotonation process suggests that the protonation site changes rapidly. Thus, an itinerant proton moving across the molecule in aqueous solution is possibly the most realistic situation when we refer to the protonated POV system.

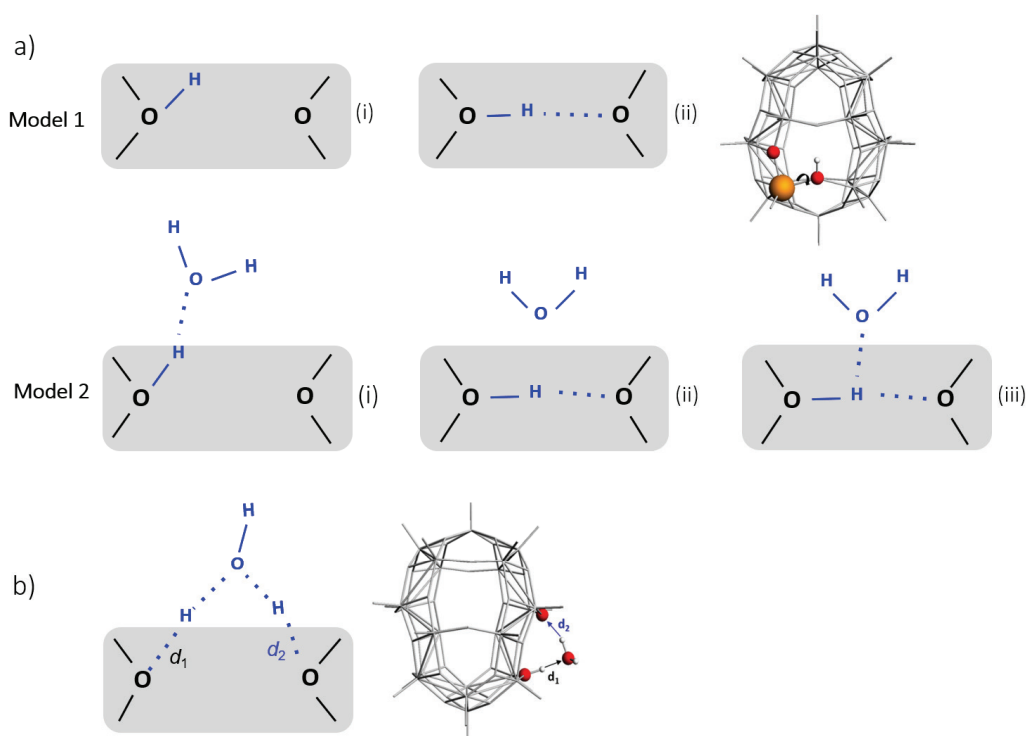


Figure 6.12 | a) **Model 1** and **model 2** for monoprotated $VO_2F_2@V_{22}O_{54}$. Differences between the models are explained in the text. The picture on the right shows the dihedral angle that is varied in the relaxed scan study. b) Conformation of highest energy along a restricted geometry scan of a water-assisted proton hopping from one oxygen to a neighbouring one. The structure on the right shows the starting point of the scan, with d_1 and the black arrow showing the distance and the direction that are tracked. The concerted deprotonation-protonation process is completed as indicated by d_2 and the blue arrow. In the final step, a new covalent O-H bond is formed (d_2). Red colour is used for oxygen atoms, white for hydrogen and orange for vanadium atoms.

In summary, calculations suggest that these species can be protonated. Upon protonation, occupied molecular orbitals of the system are stabilized and the

POV can be further reduced. In addition, comparing both structures it is easy to observe that the SCN-POV and VO_2F_2 -POV are slightly more basic than the

ClO_4 -POV by virtue of their more negative protonation energies. Moreover, the deeper study of the protonation of $\{\text{VO}_2\text{F}_2@V_{22}\text{O}_{54}\}$ suggests that the proton is itinerant across the molecule in aqueous solution.

At this point we cannot assign the oxidation state of structure **3** with absolute certainty. Neither the comparison between different electronic structures, stability, redox properties or protonation of **1n–3n** compounds give a clear definite answer to the question of how many unpaired electrons the structure **3** carries. Consequently, other techniques must be explored to overcome this problem.

6.4 Magnetochemical Modeling

Since we are not able to resolve the oxidation state of the $\text{VO}_2\text{F}_2@V_{22}\text{O}_{54}$ complex from purely theoretical arguments alone, we need to find a way to connect our findings with experimental results. For this purpose, the model Hamiltonian studies published in ref. 9 will not suffice as the physics that it contains is not capable of distinguishing between the different oxidation states. Therefore, a more sophisticated model was developed by P. Kozłowski, which will be briefly described in the next section. However, it should be noted that the complexity of the newly proposed model Hamiltonian is such that it cannot be resolved in a brute force manner, that is, some initial electron distribution has to be provided for the model to be computationally manageable.

6.4.1 Model Hamiltonian and coupling schemes

An extension accounting for the electronic kinetic energy (the second term in equation 6.4) was introduced to the original model Hamiltonian. It allows electrons to be delocalized by hopping from occupied to unoccupied vanadium centres. Thus, any V centre can have oxidation states IV or V. In the following expressions:

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$$H = \sum_{\langle i,j \rangle} J_{i,j} \delta_i \delta_j S_i \cdot S_j + \sum_{i,j=1}^N t_{i,j} \delta_i (1 - \delta_j) - g\mu_B B \sum_{i=1}^N \delta_i S_i^z \quad (6.4)$$

$$\sum_{i=1}^N \delta_i = n \quad (6.5)$$

$$\delta_i = 0, 1 \quad (6.6)$$

δ_i are occupation numbers of vanadium centers, n is the number of unpaired electrons of the system (equal to 8 for **a**, 7 for **b** and 9 for **c**) and N is the number of vanadium sites that can host a valence electron. The value of N depends on the species and its symmetry, and counts all vanadium atoms which are not formally V^V . This new t - J model Hamiltonian depends not only on spin states (S_i), but also on the spin distribution (δ_i). The first term of equation 6.4 describes the superexchange interaction between unpaired electrons/spins ($S = 1/2$). The second term accounts for electron hopping 'classically', and the last term describes the Zeeman energy in a magnetic field B with gyromagnetic ratio $g = 1.965$ and the Bohr magneton μ_B . Inter-site electron repulsion was shown to be important for POMs,³² however, in the present formulation, it is not explicitly considered. Tests were done introducing the inter-site electron repulsion but no improvement in the results was obtained. The values for J were practically the same and only the t values varied. Hence, it was assumed that the present 'classical' treatment of the kinetic electronic energy accounts for the inter-site electron repulsion in an implicit form. Note that the t parameter in the model Hamiltonian does not have exactly the same physical meaning as the t parameter in the model Hamiltonians used by Suaud and co-workers.³³ In the latter, t accounts solely for the hopping probability between two sites, while in the present work it is meant to describe the classical electronic kinetic energy. Hence, it is not impossible that the present t is an effective parameter taking into account the balance between two sites and the electron-electron repulsion.

The final ingredient to complete the definition of the model Hamiltonian is the choice of a basis to span the model space, the simplest choice including all the possible electron distributions resulting from having 7, 8 or 9 electrons over 22

sites, but this obviously leads to a model of unmanageable size. Therefore, restrictions must be imposed.

As for the model used in Ref. 9, the summations over i and j in the Hamiltonian are limited to nearest neighbors. Superexchange interactions

between 3d electrons at vanadium sites are mediated by three different oxo bridges: single (μ_2 -O), single-shared (μ_3 -O) and double ($(\mu_2$ -O) $_2$), see Figure 6.13. This distinction defines the basic coupling scheme (scheme I), leading to three different J 's and t 's. Nevertheless, a closer look at the V—V distances and V—O—V distances reveals two clearly distinguishable groups for the single and single-shared bridges (blue and green dots in Figure 6.13 a). This gives rise to a parametrization labeled as scheme II. Introducing the differences in the environment of the double- and single-shared oxygen bridges we can further fine-tune the Hamiltonian to include 15 different parameters (scheme III). This distinction intends to treat the couplings of the double and single-shared oxygen bridges in a different way depending on the oxidation state of the third vanadium atom bonded to the bridging oxygen.

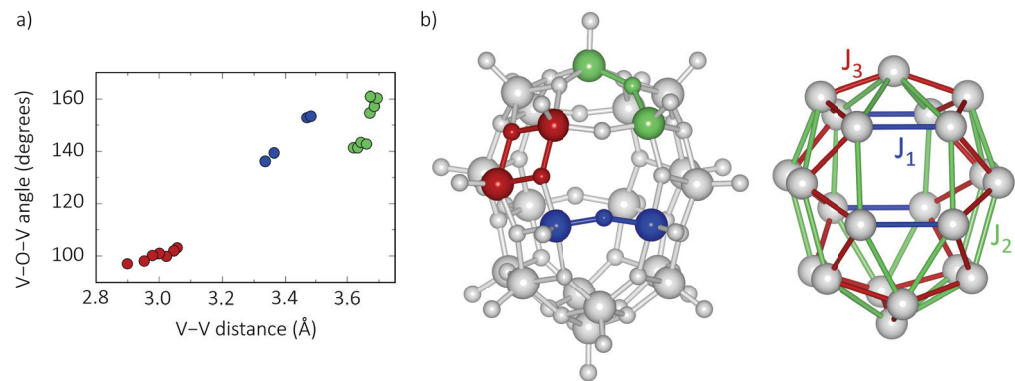


Figure 6.13 | a) V—O—V angles vs. V-V distances for different bridging oxygen types. For double bridges (red dots) the average of the two V—O—V angles is shown. b) Left: vanadium atoms of the empty cage connected by three types of oxygen bridges: single (blue), single-shared (green) and double (red). Small and large spheres are oxygen and vanadium atoms, respectively. Right: all possible exchange paths: J_1 (blue), J_2 (green), J_3 (red). Grey spheres stand for V atoms. Oxygen atoms are omitted.

Table 6.5 | Geometrical parameters and coupling schemes I–III. For scheme III, the oxidation state of the third connecting V atom is given in parentheses.

Bond	d(V—O) [Å]	a(V—O—V) [°]	I	II	III
Single	3.47 - 3.48	153	J ₁ t ₁	J ₁ t ₁	J ₁ t ₁
	3.33 - 3.36	136 - 139	J ₁ t ₁	J ₂ t ₂	J ₂ t ₂
Single-shared	3.62 - 3.67	141 - 143	J ₂	J ₃	J ₃ (V ^V)
	3.67 - 3.69	155 - 160	J ₂ t ₂	J ₄ t ₄	J ₄ t ₄ (V ^V) J ₅ t ₅ (V ^{IV})
Double	2.9-3.05	97 - 105	J ₃ t ₃	J ₅ t ₅	J ₆ t ₆ (V ^V)
					J ₇ t ₇ (V ^V /V ^{IV})
					J ₈ t ₈ (V ^{IV})
Total number of parameters			6	9	15

6.5 Self-consistent Approach and Final Results

After defining the model Hamiltonian and three different coupling schemes, we searched for the best fit of the different oxidation states studied with DFT (a-c) to find the correct oxidation state for compound **3**. This study is also done for **1** and **2** to determine the microscopic parameters of all the members of this POV family. For this goal, different sets of t and J were determined by fitting the experimental temperature dependence of susceptibility and the field dependence of magnetization at T = 2K. The determination of the optimal microscopic parameters for each oxidation state was done by varying them in the ranges [–600 K, 1000 K] and [–8000 K, 8000 K] for J and t, respectively. For each set of J and t, the model Hamiltonian was diagonalized and, from the resulting energy eigenvalues, the magnetic susceptibility and the magnetization curves were calculated with Boltzmann population formulas for the energy levels based on classical Statistical Mechanics. The resulting theoretical curves are compared to the experimental ones, varying J and t to minimize the deviation using equation 6.7.

$$\Delta = \sqrt{\frac{1}{N_e} \sum_{i=1}^{N_e} \left(\frac{x_i^e - x_i^t}{x_i^e} \right)^2}$$

(6.7)

$X = VO_2F_2^-$. The smallest model Hamiltonian is defined by imposing the symmetry constraints of the empty cage (D_{2d}) on the electron distributions that are compatible with the DFT ASDs listed in Table 6.2 and the bottom of Table 6.3. These conditions impose that all the electron distributions have V^{IV} atoms at the apical positions, and two V^V atoms in each outer ring, occupying opposite sites. The rest of the electrons are distributed in all possible ways over the remaining 16 sites respecting the D_{2d} symmetry (Figure 6.14).

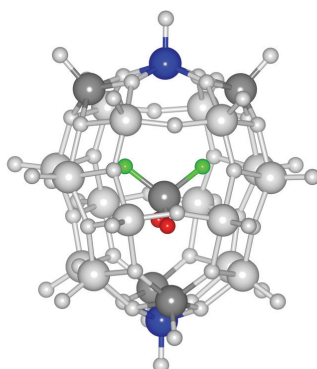


Figure 6.14 | Ball-and-stick representation of the distribution of formally V^V (dark grey), V^{IV} (blue) and V^{IVV} (light grey big spheres) of **3a**. Oxygen atoms of the cluster are represented by small light grey spheres, oxygen atoms belonging to the guest in red, and fluorine atoms in green.

Starting with **3a** (8 electrons), we obtained very poor fits for the three different schemes, see Figure 6.15 a) and Table 6.6, especially poor results were obtained for the magnetization curve. An even number of unpaired electrons in compound **3a** can be at the origin of this since the ground state, which largely determines the magnetism at low temperatures, will have an integer total spin moment (S_{tot}) and the experimental curve suggests saturation at a value corresponding to $S_{tot} = 3/2$. For the same reason, we expect evenly poor-quality fits when lifting the symmetry constraints or changing the parametrization scheme for I to II or III. Carrying on with **3b**, reducing the electron count by one ($n = 7$), we set up the Hamiltonian following the DFT prediction of four V^{IV} centers. This reduces N from 18 to 14 and fixes the occupation of the apex sites to 1 electron. However, poor fits are also obtained, see Figure 6.15 b) and Table 6.6. Although the fit to magnetization improves compared to **3a**, it is difficult to model properly the susceptibility at low temperatures. We have obtained the best fit for **3c** ($n = 9$, N

= 18, and both $\delta_{\text{apical}} = 1$). The distribution of formal V^{IV} , V^V and, $V^{IV/V}$ in structure **3c** follows the D_{2d} symmetry. Nevertheless, the electron distribution of the lowest energy solution of the model Hamiltonian does not coincide with the one found with DFT. To solve this problem, the model Hamiltonian was refined by introducing asymmetry in the parameter set. J_1 and t_1 (the blue interactions in Figure 6.13 b) were assigned different values in the F– and O–hemispheres (see Figure 6.14). With this adjustment, two different sets of parameters reproduce the experimental curves accurately. Nevertheless, just one of these sets has a ground state that matches the valence electron distribution obtained with rescaled ASDs for **3a** at DFT level, see Figure 6.16 and Table 6.7. The rescaled ASDs consider that the system has 9 unpaired electrons instead of 10.66, as the sum of the individual ASDs show due to spin polarization, so the individual ASDs are recalculated with the total sum equal to 9.

Table 6.6 | Relative average difference Δ (in %) between experimental data and theoretical predictions **3a-c** in different coupling schemes and symmetries.

	3a			3b		3c
	I, C_{2v}	II, C_{2v}	III, C_{2v}	I, C_{2v}	I, C_1	I, C_{2v} asym. J_1
Δ [%]	11.21	10.41	8.83	9.37	3.11	2.07
Δ for χ [%]	2.51	3.38	4.35	9.45	1.63	0.80
Δ for M [%]	21.86	19.87	15.90	9.13	5.51	3.87

Table 6.7 | Probability of finding an electron (in the ground state) at $V^{IV/V}$ sites from DFT and t-J model Hamiltonian calculation for **3c** in C_{2v} symmetry.

Position in the cage	Rescaled ASD	t-J model Hamiltonian
Upper outer ring (F–hemisphere)	0.51	0.5
Inner ring	0.50-0.51	0.5
Lower outer ring (O–hemisphere)	0.29	0.25

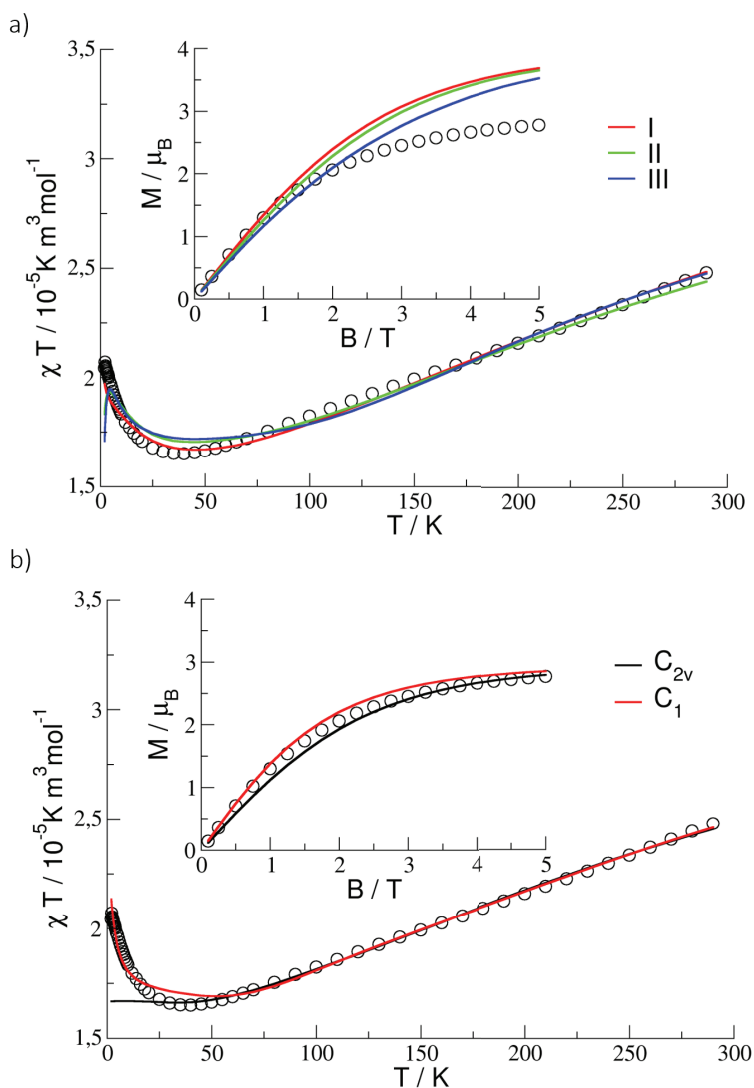


Figure 6.15 | Best fits to molar susceptibility ($B = 0.1 \text{ T}$) and magnetization ($T = 2 \text{ K}$) for a) **3a** (C_{2v}) using coupling schemes I–III, and **3b**. Experimental results are shown in circles.

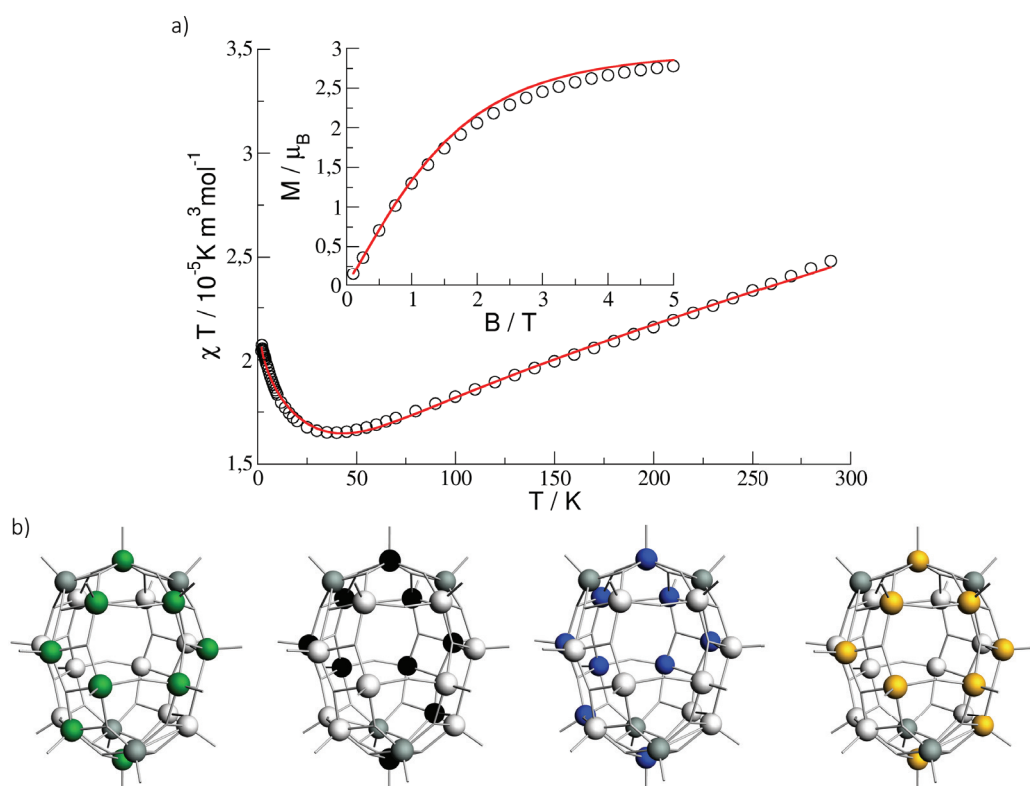


Figure 6.16 | a) best fits to molar susceptibility ($B = 0.1 \text{ T}$) and magnetization ($T = 2 \text{ K}$) for **3c** (C_{2v}). Experimental results are shown in circles. b) Four ground state electron distributions for **3c**. In each case, the coloured vanadium atoms (green, black, blue or orange, respectively) carry one unpaired electron and grey atoms are always electron depopulated (V^V ions). White spheres stand for electron depopulated sites in that specific electron distribution but do have non-zero occupation in other, equivalent electron distributions. Oxygen atoms and the guest anion have been removed for clarity.

In summary, the self-consistent approach combines two theoretical methods (model Hamiltonian and DFT calculations) and can be used to study the electronic structure of mixed-valent POMs or other nanosized systems with multiple unpaired (delocalized) electrons. The steps to be followed are:

- 1) The DFT calculations are carried out for a range of potentially relevant oxidation states of the system.
- 2) The information on the distribution of valence electrons obtained is used to narrow down the dimension of the t - J model Hamiltonian.

- 3) The experimental magnetic data (susceptibility vs. temperature and magnetization vs. magnetic field) are compared to those derived from the model Hamiltonian.
- 4) The parameter set giving the best fit is checked for its electron distribution. If it coincides with the outcomes of the DFT calculation, the predicted oxidation state likely coincides with the experimental one.
- 5) If there is no ground state concordant with the DFT results, the coupling scheme must be refined, for example by introducing the effect of the guest on the cluster and differentiating J_1 depending on the molecule region.

Using the same methodology, we have performed an equivalent study for **1** and **2**. All model Hamiltonian calculations were done with scheme I, because this parametrization already gives accurate fits in both cases.

$X = ClO_4^-$. As expected, the best fit for structure **1** is obtained for **1a** with 8 electrons in the V-3d orbitals (see Figure 6.17 and Table 6.8). For **1b** and **1c**, with an odd number of unpaired electrons, the fit is especially poor for the magnetization profile, like was observed for **3**, where an even number of electrons did not seem to be compatible with the magnetization measurements. So, **1a** (8 electrons) is indeed the valence state of **1**, as Müller proposed.^{7,8} However, two different sets of t and J can fit the experimental data rather accurately: $\Delta = 6.24\%$ for set (i) and 5.36% for set (ii). While (i) presents only antiferromagnetic exchange interactions, (ii) presents also ferromagnetic interactions, see Table 6.9. Parameter set (i) reproduces the experimental magnetic susceptibility at low temperatures and the low-temperature ($T = 2$ K) magnetization data slightly better. Since we are using DFT results to find the most suitable description of the electronic structure and temperature is not defined in this approach, it appears especially relevant to reproduce correctly the low-temperature data. Therefore, we conclude that set (i) is the most adequate to describe compound **1a**. Nevertheless, we cannot discard that, as the temperature increases, the magnetism of **1** changes because of structural distortions suffered by **1**. The ground state (at $B = 0$)—which is consistent with the DFT results—is 8-fold degenerate. The C_2 geometry causes 2-fold spatial symmetry and the limitation of the exchange parameters to nearest neighbours causes a singlet-triplet degeneracy of four different wave functions arising from

two non-interacting doublets, see Figures 6.18 and 6.19. Figure 6.18 shows two different colours to differentiate these non-interacting clusters (light and dark, green or blue, depending on the electron distribution), one of them with three V^{IV} and the other one with five. These results agree with the DFT calculations. After rescaling the number of valence electron to 8 (as we did for **3**), the inner ring presents 2.2 electrons and each hemisphere (not counting the inner ring) 2.9 electrons. Moreover, the probability of finding an electron with rescaled DFT values is 0.38 for both apical positions and between 0.43 and 0.55 in the other positions, which when compared to 0.5 (predicted by the model Hamiltonian) shows how consistent the two theoretical approaches are.

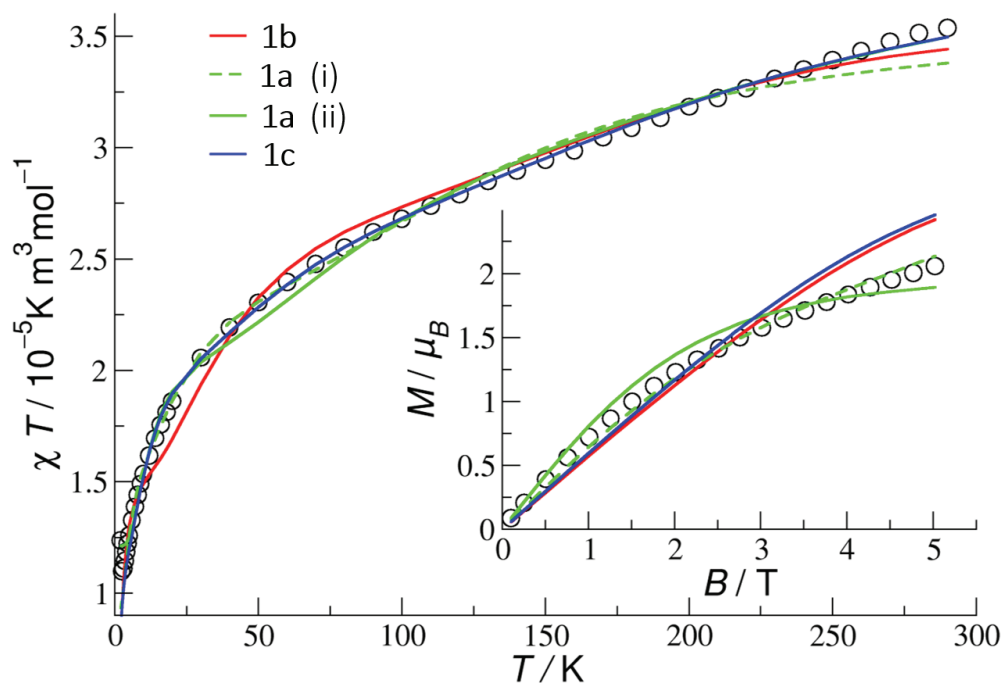


Figure 6.17 | Fits to molar susceptibility ($B = 0.1 \text{ T}$) and magnetization ($T = 2 \text{ K}$) for **1** with C_2 symmetry with different number of valence electrons. Experimental results are shown with circles.

Table 6.8 | Relative average difference Δ (in %) between experimental data points and theoretical predictions for various compounds in different coupling schemes and symmetries. The best fits used for analysis are in bold.

	1a		1b	1c	2a	2b	2c	2abc
	(i) C ₂	(ii) C ₂	C ₂	C ₂	C _{2v}	C _{2v}	C _{2v}	C _{2v}
Δ [%]	6.24	5.36	10.89	10.34	4.81	6.33	6.42	2.19
Δ for χ [%]	4.58	2.90	6.45	5.72	2.67	3.82	3.87	1.32
Δ for M [%]	8.74	8.45	16.73	16.20	7.52	9.68	9.81	3.34

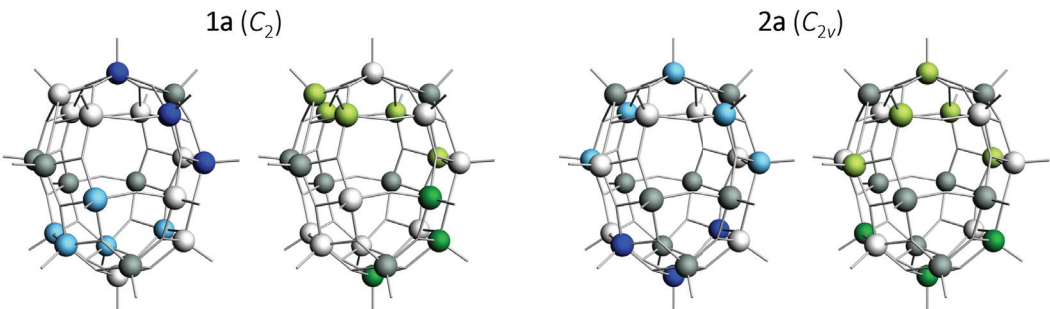


Figure 6.18 | Ground state electron distributions for the $8e^-$ -containing compounds **1a** (left) and **2a** (right). For each, two electron distributions (green and blue) are shown, which, in turn, can be represented as two non-interacting clusters with 5 and 3 electrons (light- and dark-coloured vanadium atoms, respectively). Grey atoms are electron-free sites (V^V ions). White spheres stand for electron depopulated vanadium sites in that specific electron distribution but do have non-zero occupation in other, equivalent electron distributions. Oxygen atoms and the guest anion have been removed for clarity.

X = SCN⁻. For structure **2**, the best fit is found for oxidation state **2a**, with 8 unpaired electrons (see Figure 6.20 and Table 6.8). However, the lowest energy electron distribution of the model Hamiltonian arising from the t-J parameters that best fit the experimental data is not compatible with the ASDs of the DFT calculation unless symmetry constraints are imposed. Obviously, a spatially non-degenerate electron distribution leads to 0 or 1 occupation numbers for vanadium sites, instead of the fractional occupation numbers (mixed-valent sites) found with DFT. Therefore, the only way to obtain fractional occupations with this model Hamiltonian is to enforce spatial degeneracy to the electronic ground state. To introduce this possibility, we increase the symmetry to C_{2v} .

Consequently, the fits shown hereinafter are obtained with this symmetry. The

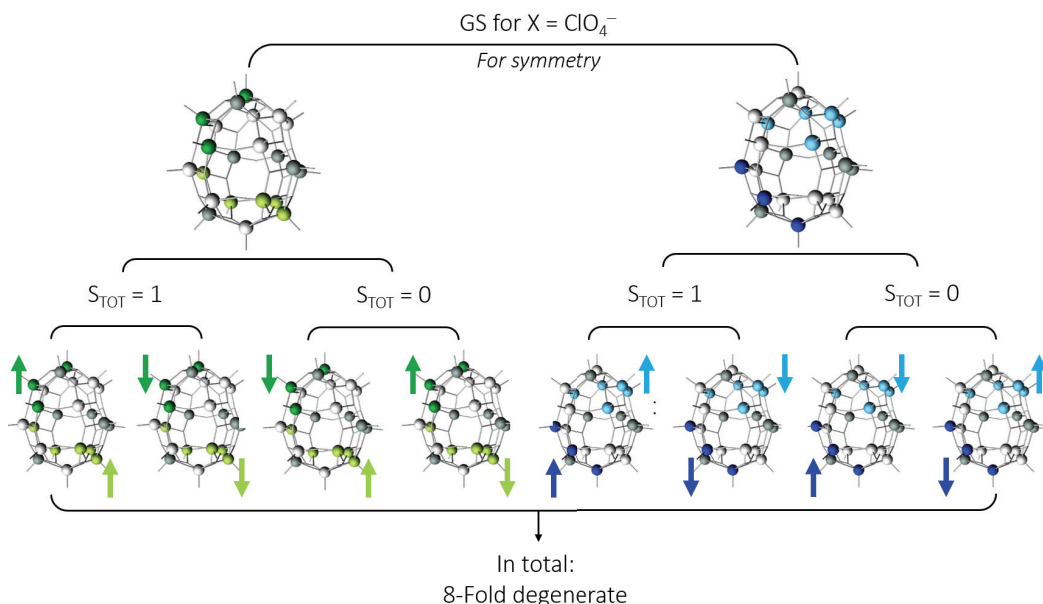


Figure 6.19 | Ground-state electron distribution for **1a**, showing 8-fold degeneracy. Colour code as in Figure 6.18.

best fit ($\Delta = 4.81\%$) is obtained for **2a** (C_{2v}) presenting only antiferromagnetic exchange couplings (Table 6.9). The ground state has 2-fold spatial degeneracy and, as already described for **1**, the ground state is also 4-fold spin degenerate. This solution gives us a number of electrons in the inner ring equal to 2 and has 3 electrons in each hemisphere, in good agreement with rescaled DFT results where there are 2.29 electrons in the inner ring and 2.79/2.92 in the N-/S-hemispheres. The net probability of finding an electron at a given $\text{V}^{\text{IV/V}}$ site is also quite similar with both approaches, namely between 0.47 and 0.51 from DFT calculations and 0.50 with the model Hamiltonian.

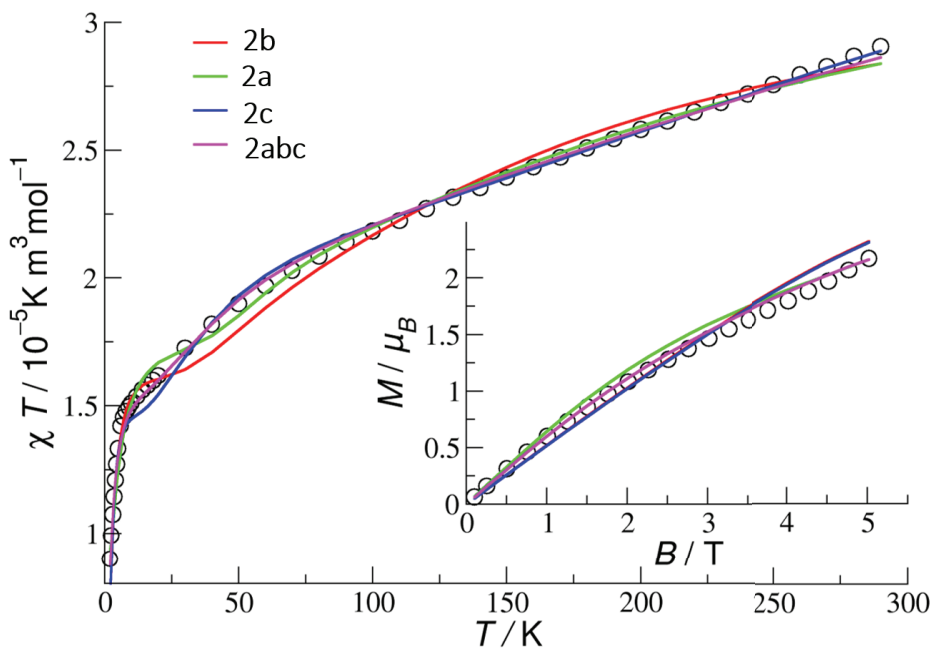


Figure 6.20 | Fits for **2** with C_{2v} symmetry with different number of valence electrons, to molar susceptibility ($B = 0.1 \text{ T}$) and magnetization ($T = 2 \text{ K}$). Experimental results are shown in circles.

Table 6.9 | Optimal Hamiltonian parameters (in K) for **1a** with C_2 symmetry (for two different solutions (i) and (ii)), **2a** and **3a** with C_{2v} symmetry. Two values of J_1 and t_1 for **3a** correspond to F- and O-hemispheres, respectively.

	1a (i)	1a (ii)	2a	3c (F, O)
J_1	297	247	431	581, 385
J_2	54	-413	6	-185
J_3	9	343	541	609
t_1	-3201	221	-173	1456, 2421
t_2	-3502	871	-70	3205
t_3	224	86	-78	1162

As expected, the exchange interactions in the here-studied POVs are mainly of antiferromagnetic character. Only for **3c** we obtained ferromagnetic interactions. The effect of guest anions on the magnetism of $\{X@V_{22}^{IV/V}O_{54}\}$ works basically through modification of the electronic structure, especially by stabilizing

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different oxidation states of the $V_{22}O_{54}$ cage. For **1** and **2**, with 8 V-3d valence electrons, a similar magnetic behavior can be observed. However, the magnetism of **3** differs substantially from the other, coinciding in the presence of 9 electrons in the V-3d orbitals. The magnetic properties of the complexes are due to the combination of localized and delocalized unpaired electrons, albeit in **1** only delocalized electrons were found.

This model Hamiltonian has flaws: the parameters obtained by fitting to experimental data should be considered with caution, since we can fall into overparameterization. However, in the present study, this negative influence has been minimised by eliminating solutions which are not concordant with the DFT results.

To finish the discussion on the model Hamiltonian, we would like to say a few words on the dangers of overparameterization. The fact that more than one set of substantially different parameters can fit to the experimental data implies that their numerical values should be looked critically. Even though, the search region of exchange couplings has been limited (ranges of $[-600\text{ K}, 1000\text{ K}]$ for J and $[-8000\text{ K}, 8000\text{ K}]$ for t), to ensure realistic t - and J -values in line with those reported in the literature.^{34,35} We cannot consider the Hamiltonian parameters reported in Table 6.9 as unique (as other sets of parameters have been found with only slightly higher associated Delta values). Another matter of concern is the easiness of redox processes in these compounds, which very well may lead to the existence of mixtures of **a**, **b** and **c**. We have studied this scenario for **2** and **3**. The fits for **3** do not improve much, so, the slight improvement observed is most probably due to overparameterization. For **2** there is a somewhat more substantial improvement of the fits (see Table 6.8 and Figure 6.20) and, consequently, we cannot exclude that some mixtures of structures **a**, **b** and **c** exist. However, the improvement is not large enough to clearly prefer a mixture of **a**, **b** and **c** above the sole presence of **a** in experiment, and overparameterization may also play a role here if we also consider that the magnetic behaviour of V_{16} -type POVs can only be reproduced with a mixture of components with different valence states.³⁶ It is most likely that the magnetism is basically due to the individual components **1a**, **2a** and **3c**.

6.6 Concluding Remarks

Herein we have solved the the electron distribution and the magnetic properties of $\{X@V^{IV/V}_{22}O_{54}\}$ with $X = ClO_4^-$, SCN^- , and $VO_2F_2^-$. Using the self-consistent approach outlined in this chapter we have elucidated the valence state of $\{VO_2F_2^-@V^{IV/V}_{22}O_{54}\}$, and analyzed the electronic and magnetic properties of the three compounds.

It has been demonstrated that magnetic properties strongly depend on the valence state of vanadium atoms which are in turn dependent on the guest anions. $\{X@V^{IV/V}_{22}O_{54}\}$ with $X = ClO_4^-$ and SCN^- features 8 valence electrons and $S_{tot} = 0$ and 1 ground states, whereas with the one with $X = VO_2F_2^-$ it carries 9 electrons and an $S_{tot} = 3/2$ ground state.

The results obtained for mixtures of POVs with different valence states leads to the conclusion that in general better fits for the mixtures do not explain better various physical features, which allows us to assume that the improvement of the fits' quality is due only to an overparameterization of the model Hamiltonian, and, thus, pure components should be preferred.

Our approach suffers from the typical deficiencies of model Hamiltonians. Nevertheless, we improve and minimize these shortcomings in two different ways: (1) some details of the model Hamiltonian are fixed by using the position of the formal V^{IV} and V^V obtained at DFT level, and (2) the optimal fit is chosen by rejecting the fits that lead to electron distributions incompatible with the DFT solution.

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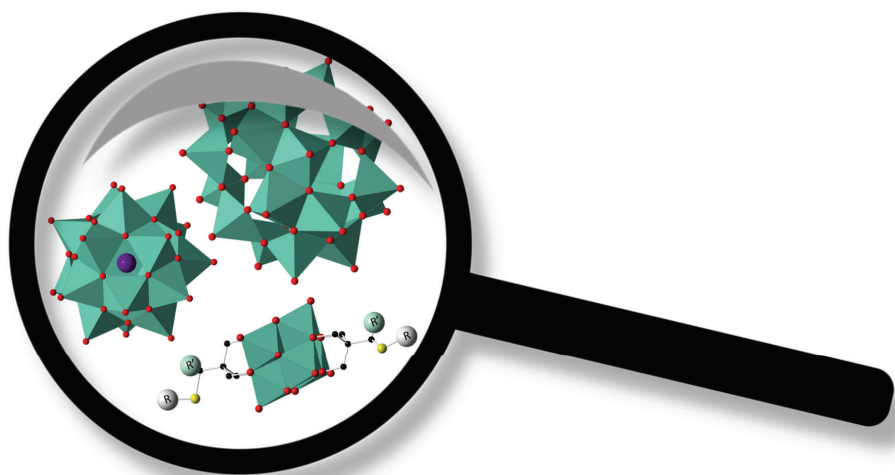
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CHAPTER 7

General Conclusions

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CHAPTER 7

General Conclusions

This last chapter summarizes the most important achievements and conclusions of this doctoral thesis. Despite the problems encountered due to the size of the studied systems and the difficulties to converge their geometric and electronic structures, we have managed to solve all the proposed objectives. Even though, obviously, more detailed answer to some of the research objectives would have required more time. A brief chapter-by-chapter summary of the concluding remarks for each project is contained in the following pages.

Chapter 4: Conductivity of a Functionalized V_6O_{19} structure and its link with Molecular Redox States

Combining the experimental data of both functionalized POMs ($[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$), provided by the groups of Dr. Monakhov and Dr. Waser, with the outcomes of the present computational study, the main conclusions of this project are:

- The adsorption of $[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$ on Au(111) surface is equally favourable in all the positions and adsorption modes. The POMs are most probably disordered on the surface and with no packing preference.
- Both V_6 derivatives are neither oxidized nor reduced when adsorbed on Au(111) surface, keeping their chemical integrity.

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- The adsorbed POM gains electron density when an external electric field perpendicular to the Au surface is applied to it.
- Reduction of the POMs increases the electron count on vanadium atoms, converting them from V^V to mixed-valent $V^{IV/V}$.
- Molecular conductivity does not depend on the position of the POM on the surface, but the position of the tip is important: being in contact with a terminal POM oxygen gives larger transmission near the Fermi level than in the case of the bridging oxygen.
- The POM presents stepped conductivity associated to reduction processes.
- Vanadium atoms in the POM are responsible for conductivity, as the most transmitting eigenchannels are mainly composed of vanadium d-orbitals.

Chapter 5: Multi-electron Redox Activity of $I@V_{18}O_{42}$

From the study of $I@V_{18}O_{42}$, the following conclusions are drawn:

- The DFT study of the isolated compound with different number of unpaired electrons shows that this compound presents a lower real symmetry than the idealized one. As a result, electrons tend to be distributed over all vanadium atoms. Furthermore, DFT calculations, in combination with CPMD data provided by Dr. Solé-Daura, suggest certain mobility of the encapsulated iodine.
- The adsorption of $[I@V_{18}O_{54}]^{5-}$ on Au(111) surface is favorable, with adsorption energies around 1 eV. There is no preference for any particular adsorption position.

- The $[I@V_{18}O_{54}]^{5-}$ keeps its electronic nature when adsorbed on gold. Bader charges show that the molecule is not reduced or oxidized by simply being in contact with the surface.
- The calculated transmission spectra show that a stepped conductivity, as in the case of $[V_6O_{13}\{(OCH_2)_3CCHR'SMe\}_2]^{2-}$ and $[V_6O_{13}\{(OCH_2)_3CCHR'SPh\}_2]^{2-}$, is highly unlikely.

Chapter 6: Connection between Valence State and Magnetism in Mixed-Valent $\{X@V^{IV/V}_{22}O_{54}\}$

Following our objective of determining the number of valence electrons in this family of POVs, we have arrived at the following conclusions during the research:

- The real symmetry of $\{X@V^{IV/V}_{22}O_{54}\}$ is C_2 for $X = ClO_4^-$ and C_1 for $X = SCN^-$ and $VO_2F_2^-$. This distortion produces a better delocalization of d electrons over the majority of the vanadium atoms. For $X = SCN^-$ and $VO_2F_2^-$ two hemispheres can be differentiated depending on the orientation of the guest and this produces changes in the distribution of the electrons compared to the ideal isolated cage and with $X = ClO_4^-$.
- All compounds holding 8 d electrons present negative protonation energies, meaning that the protonation is favorable. The small energy range associated with the most nucleophilic positions (8 in total) suggests that attached protons have no prevalence for a particular oxygen and might be itinerant over this set of oxygen atoms.
- $\{X@V^{IV/V}_{22}O_{54}\}$ with $X = ClO_4^-$ and SCN^- features 8 valence electrons, whereas the one with $X = VO_2F_2^-$ carries 9 electrons.

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- The magnetic properties of this family of POVs strongly vary with the valence state of the vanadium atoms, which in turn depend on the guest anion. $\{X@V^{IV/V}_{22}O_{54}\}$ with $X = ClO_4^-$ and SCN^- features 8 valence electrons and a monoconfigurational singlet spin ground state, whereas the one with $X = VO_2F_2^-$ has a quartet ground state with at least two degenerate electron distributions. To arrive at this conclusion, we combined DFT with model Hamiltonian calculations in a self-consistent manner.

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Collaborations

The projects in this thesis have been carried out in collaboration with other research groups. Hereunder, they are listed grouped by institutions:

- **Aachen University (Germany)**

- Dr. Kirill Yu. Monakhov



- **Adam Mickiewicz University in Poznań (Poland)**

- Dr. Piotr Kozłowski



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