Computational study of the staircase molecular conductivity of polyoxovanadates adsorbed on Au(111)

Almudena Notario-Estévez,[†] Xavier López*[,†] and Coen de Graaf*[,†,‡]

[†] *Universitat Rovira i Virgili, Departament de Química Física i Inorgànica, c/Marcel·lí Domingo 1, 43007 Tarragona, Spain*

[‡]*ICREA, Passeig Lluís Companys 23, 08010, Barcelona, Spain*

Supporting Information

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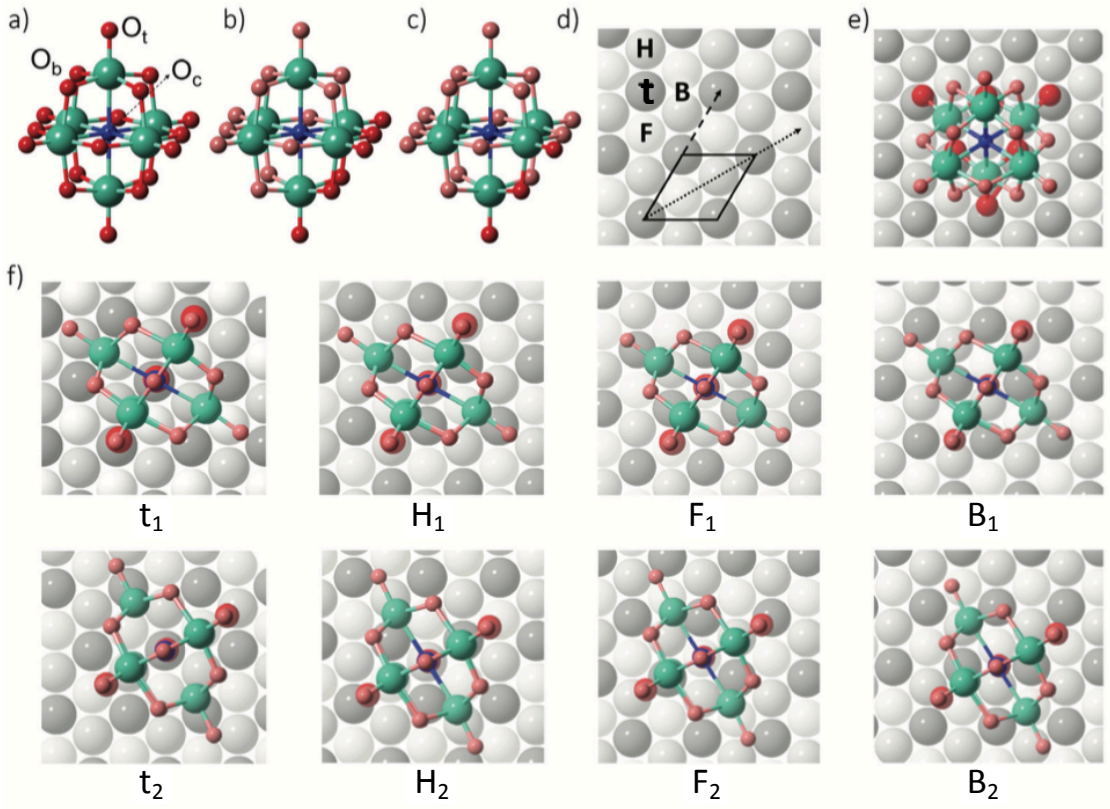

Figure S1. a) Ball and stick representation with oxygen labelling for Lindqvist $[V_6O_{19}]^{8-}$. The central oxygen (O_c, in blue) is the reference for the nomenclature of adsorptions.[27] Adsorption of the POM on Au(111): b) Representation with red balls representing oxygen atoms in contact with 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 S1. A) Relative energy (in eV) of different adsorption modes for V_6-S-Ph with fixed counterions. B) O-Au distances for adsorbed compounds V_6-S-CH_3 and V_6-S-Ph compounds on Au(111) surface in the most stable orientations (distances in Å). Oxygen types are specified in Figure 2 in the main text.

A)

Orientation	Adsorption mode	Relative energy
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

B)

	V_6-S-CH_3		V_6-S-Ph	
Type of contact	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

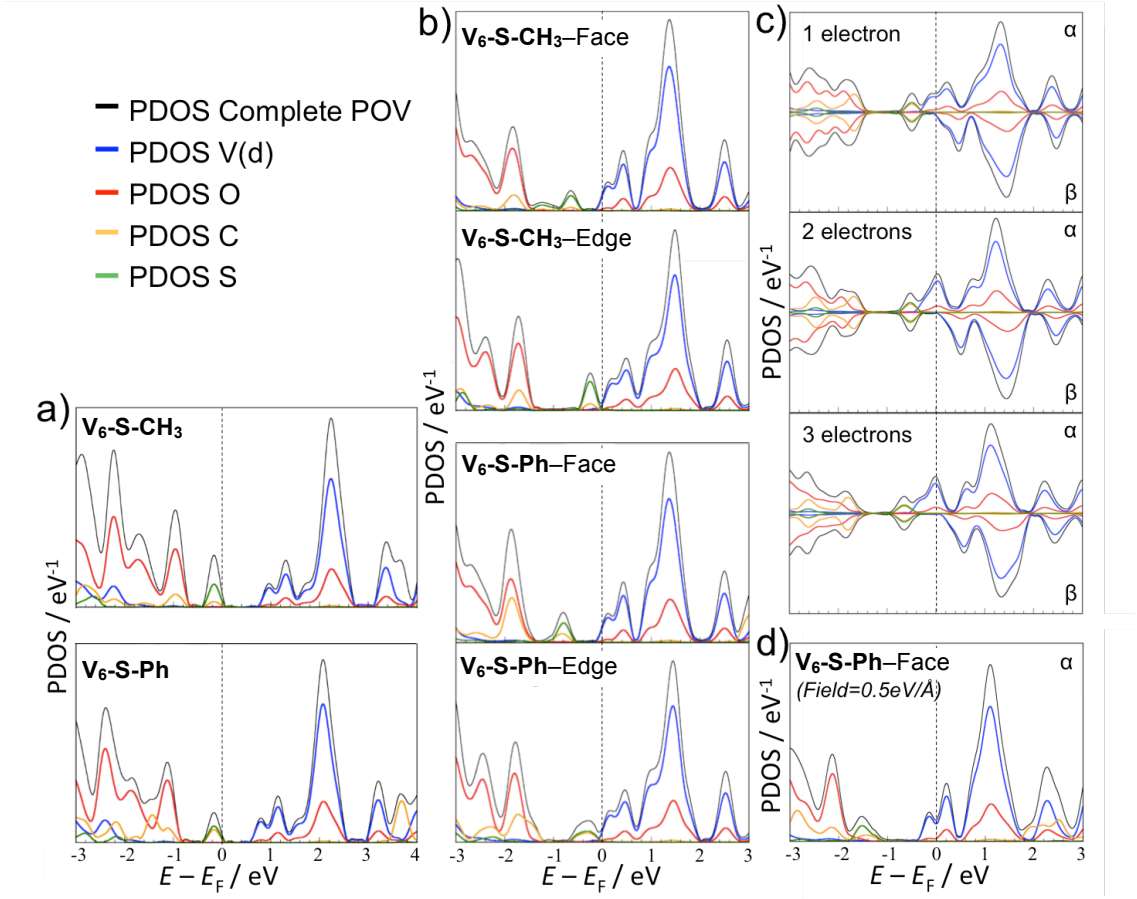

Figure S2. Projected density of states (PDOS). a) PDOS of isolated molecules V_6-S-CH_3 and V_6-S-Ph. b) PDOS of and V_6-S-Ph adsorbed on Au(111) in the face- and edge-orientation. c) One-, two-, and three-electron reduced V_6-S-Ph adsorbed in the edge-orientation. d) Adsorbed V_6-S-Ph with an applied field of $E_{ext} = 0.5$ eV Å^{-1}. All energies refer to the Fermi level. The highest occupied band, located between −1.0 and 0.0 eV below the Fermi level (E_F), corresponds to S and C atoms of the ligands, whereas the polyoxovanadate (POV) oxo band (red line) lies lower in energy, $E < -1.0$ eV. Empty d-vanadium bands (blue line), essential for the molecular conductivity, appear slightly above E_F.

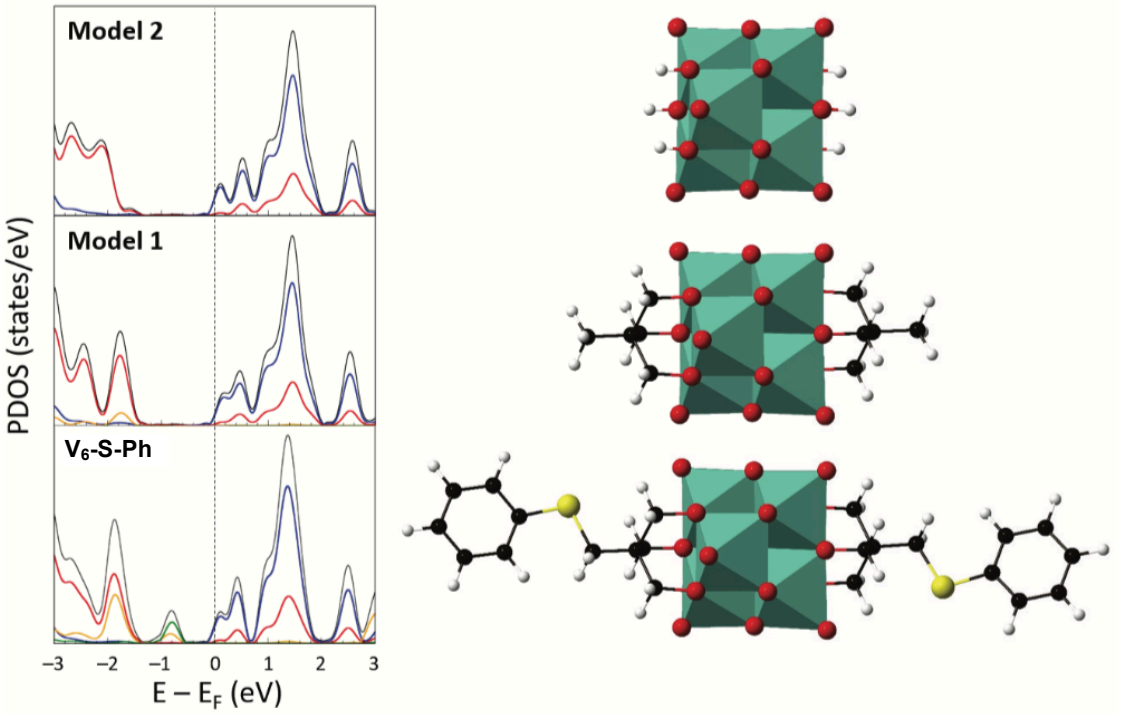

Figure S3. Projected density of states (PDOS) of V_6-S-Ph (bottom) and two different models (top: Model 2 and middle: Model 1) adsorbed on Au(111). Colour code for PDOS as in Figure S2.

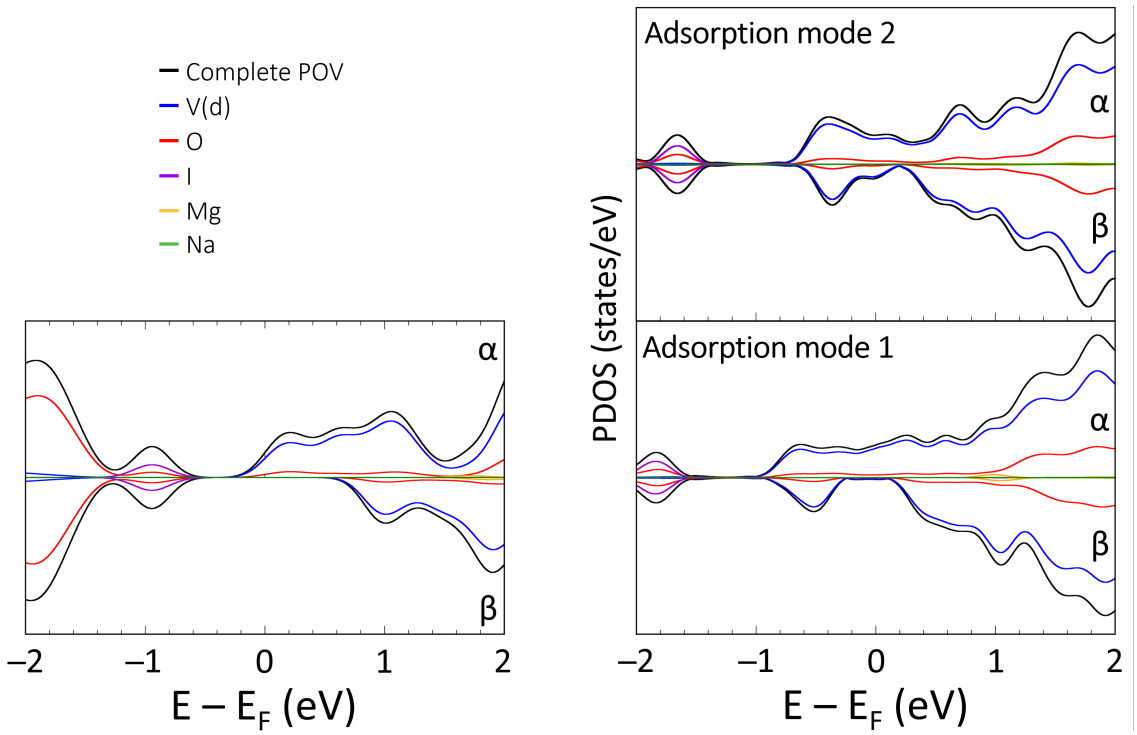

Figure S4. DOS and PDOS of V_{18} (10:8) in isolated form (left panel) and adsorbed on Au(111) with two different adsorption modes (right panel). All energies refer to the Fermi level (E_F). Accordingly, the bands located at negative energies are occupied.

Table S2. Calculated and theoretical Bader charges per fragment for the two tested adsorption modes for V_{18} (8:10, 10:8 and 12:6 states) on Au(111).

	POV		Countercations		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

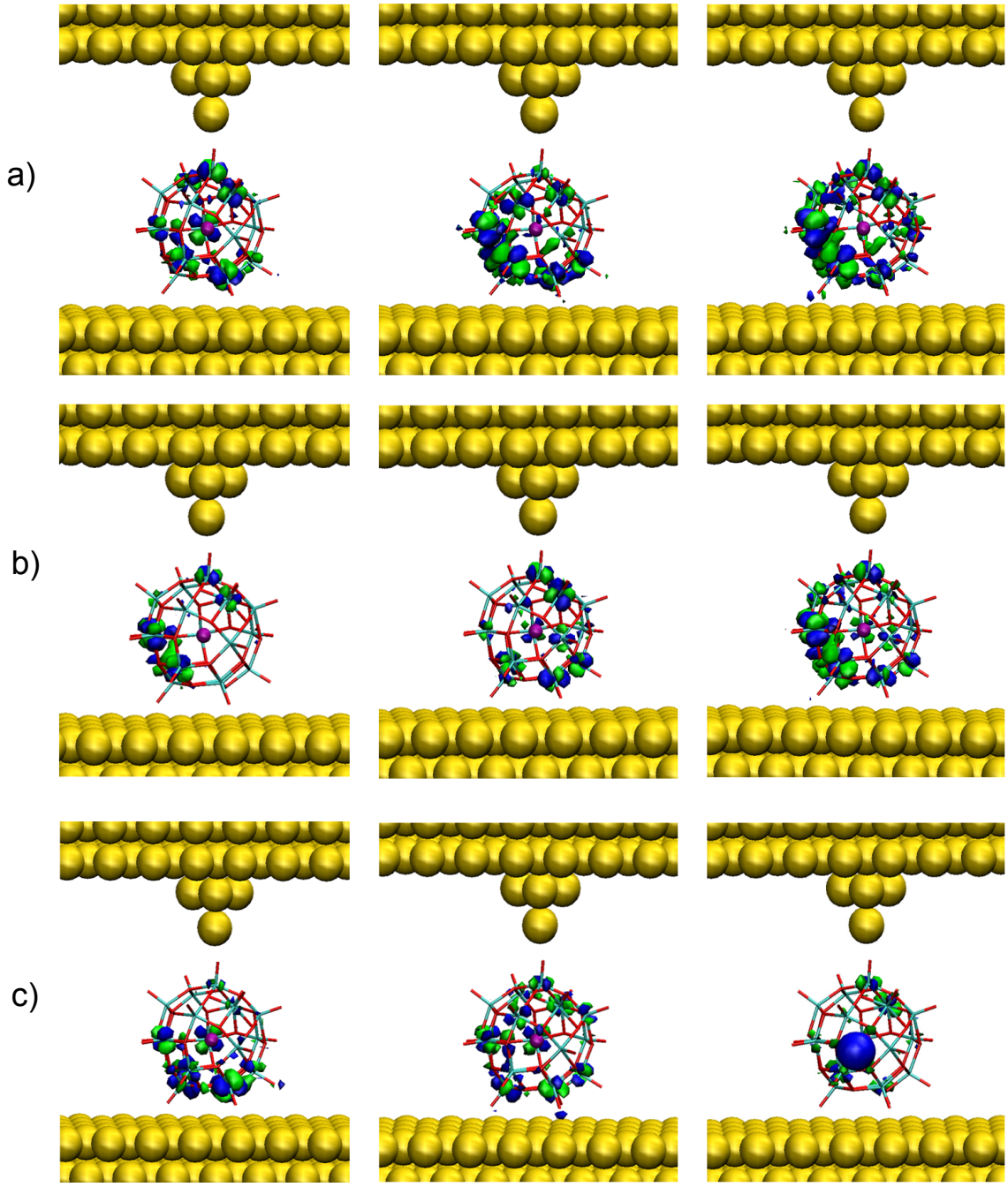

Figure S5. Isosurface plots of the real part for the most transmitting eigenchannel scattering states of V_{18} in a) (8:10), b) (10:8) and c) (12:6) redox forms.