

Supporting Information

Detailed Voltammetric and EPR Study of Protonation Reactions Accompanying the One-Electron Reduction of Keggin-type Polyoxometalates, $[XV^V M_{11} O_{40}]^{4-}$ (X=P, As; M=Mo, W) in Acetonitrile

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Further description of EPR results

For $PV^{IV}Mo_{11}$, addition of 0.4 mM CF_3SO_3H resulted in the appearance of two new species, labeled as B and C, where these contributed about 10 % for B and 20% for C while the original species, labeled as A, contributed approximately 70% to the total resonance intensity. Addition of 5 mM CF_3SO_3H resulted in the almost complete disappearance of the resonances due to A and B.

In the case of $AsV^{IV}Mo_{11}$, addition of acid to 0.4 mM, resulted in the observation of two additional species, labelled as B and C. The relative concentrations were estimated as 40, 25, and 35 % for species A, B and C respectively. After addition of 5.0 mM acid, species A and B comprised only about 5 % of the paramagnetic species present, leaving species C as the major component. Species C also showed indications of orthorhombic symmetry.

For $PV^{IV}W_{11}$, the addition of 0.4 mM CF_3SO_3H resulted in the observation of two species, namely the original species A, and a distinctly different species, labelled as B. Resonances due to species A comprised about 55% and B 45% of the spectral intensity. The spectrum after addition of 5 mM acid was very similar to that of the 0.4 mM acid solution, with both species A and B being present but with their relative concentrations reversed. Spectrum simulations gave the values for the spin Hamiltonian parameters listed in Table 4.

For $AsV^{IV}W_{11}$ in CH_3CN , the addition of 0.4 mM CF_3SO_3H resulted in two clearly distinguishable species, namely the species present before addition of acid (species A in Table 5) and species B. After addition of 5.0 mM CF_3SO_3H , species A had disappeared completely. Resonances due to species B comprised about 70 % of the total spectral intensity, with resonances due to another new species, species C, accounting for the remaining 30 % of the total EPR intensity.

Figure S1. Cyclic voltammograms for reduction of 0.5 mM $\text{As}^{\text{V}}\text{W}_{11}$ in CH_3CN (0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$) as a function of acid concentration. $[\text{CF}_3\text{SO}_3\text{H}] =$ (a) 0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 1.0; (f) 5.0 mM. Scan rate: 100 mV s^{-1} . Arrows indicate new peaks that appear and then shift on addition of more acid.

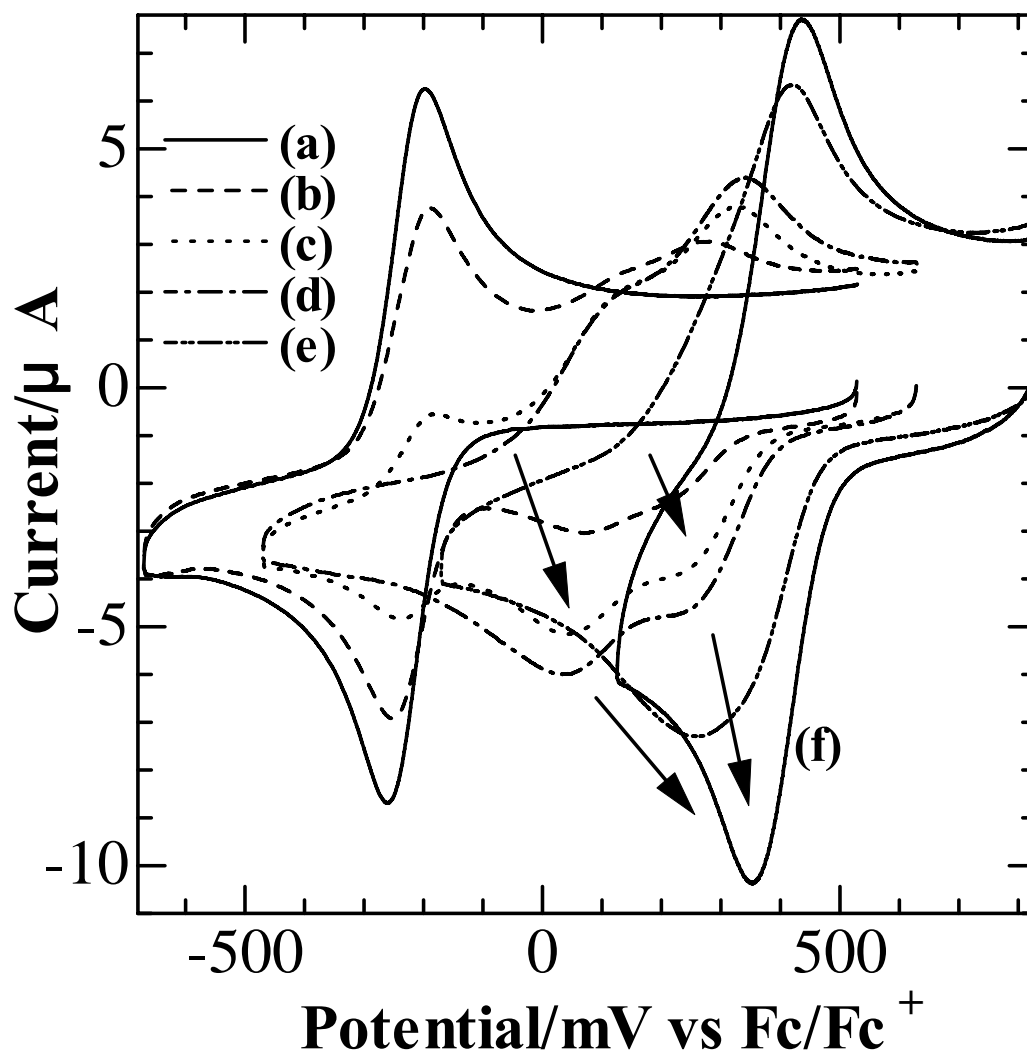


Figure S2. Cyclic voltammograms for reduction of 0.5 mM $\text{AsV}^{\text{V}}\text{Mo}_{11}$ in CH_3CN (0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$) as a function of acid concentration. $[\text{CF}_3\text{SO}_3\text{H}] =$ (a) 0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.7; (f) 1.0; (g) 5.0 mM. Scan rate: 100 mV s^{-1} .

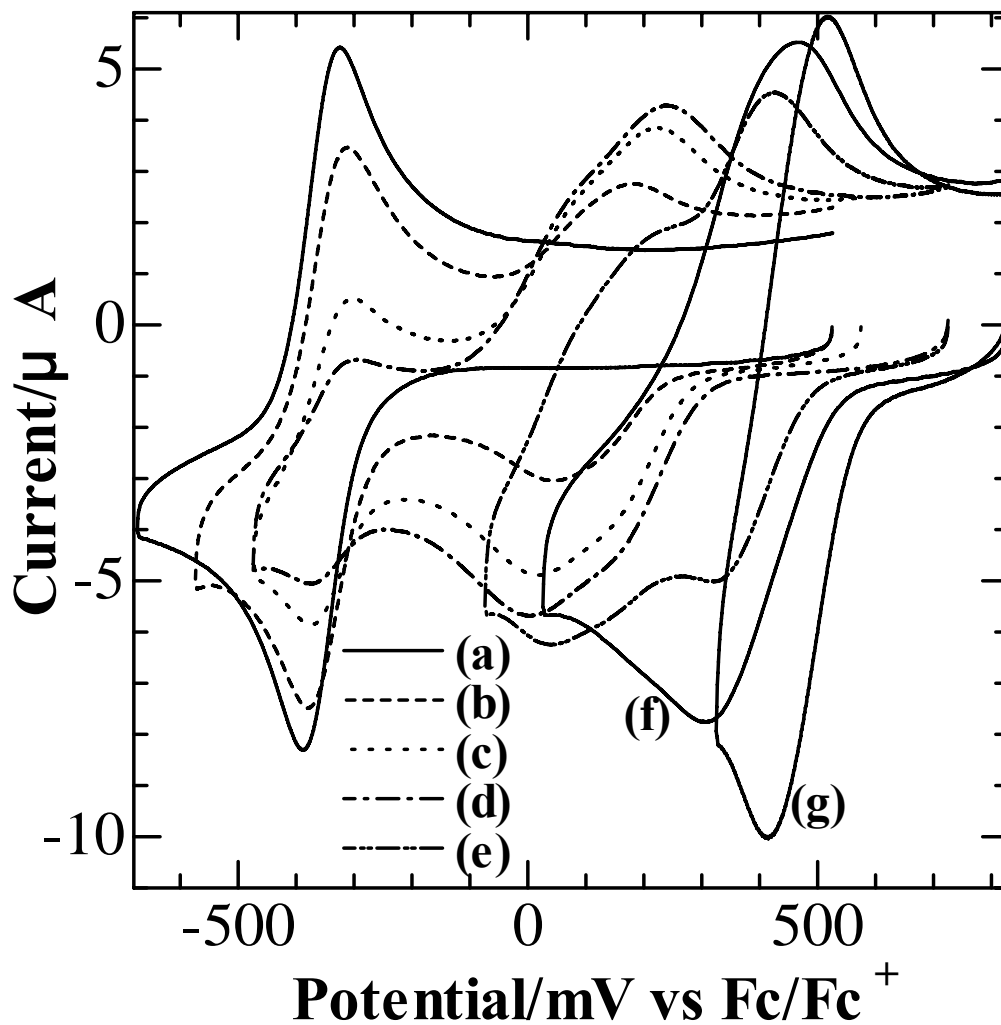


Table S1. Parameters used in the digital simulation of cyclic voltammograms for reduction of $\text{AsV}^{\text{V}}\text{W}_{11}$ to $\text{AsV}^{\text{IV}}\text{W}_{11}$ in acidified acetonitrile solution

Heterogeneous reactions				
Process	$\text{A} + \text{e}^- = \text{B}$	$\text{HA} + \text{e}^- = \text{HB}$	$\text{H}_2\text{A} + \text{e}^- = \text{H}_2\text{B}$	
E_{mid}/mV	-230	170	400	
Homogeneous reactions				
Process	$\text{HA} \rightleftharpoons \text{A} + \text{H}^+$	$\text{H}_2\text{A} \rightleftharpoons \text{HA} + \text{H}^+$	$\text{HB} \rightleftharpoons \text{B} + \text{H}^+$	$\text{H}_2\text{B} \rightleftharpoons \text{HB} + \text{H}^+$
Acid dissociation const. $K(\text{M})$	2.00×10^{-6}	1.21×10^{-3}	3.47×10^{-13}	1.57×10^{-7}
Forward rate const. $k_f(\text{s}^{-1})$	2.00×10^4	1.21×10^7	3.47×10^{-3}	1.57×10^3
Back rate const. $k_b(\text{M}^{-1}\text{s}^{-1})$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}
Disproportionation reaction				
Process	$2\text{HA} \rightleftharpoons \text{A} + \text{H}_2\text{A}$		$2\text{HB} \rightleftharpoons \text{B} + \text{H}_2\text{B}$	
Equilibrium const. $K_{\text{eq}}(\text{M})$	1.66×10^{-3}		2.22×10^{-6}	

A: $[\text{AsV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{4-}$; B: $[\text{AsV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$

Table S2. Parameters used in the digital simulation of cyclic voltammograms for reduction of $\text{AsV}^{\text{V}}\text{Mo}_{11}$ to $\text{AsV}^{\text{IV}}\text{Mo}_{11}$ in acidified acetonitrile solution

Heterogeneous reactions				
Process	$\text{A} + \text{e}^- = \text{B}$	$\text{HA} + \text{e}^- = \text{HB}$	$\text{H}_2\text{A} + \text{e}^- = \text{H}_2\text{B}$	$\text{H}_3\text{A} + \text{e}^- = \text{H}_3\text{B}$
E_{mid}/mV	-355	105	425	775
Homogeneous reactions				
Process	$\text{HA} \rightleftharpoons \text{A} + \text{H}^+$	$\text{H}_2\text{A} \rightleftharpoons \text{HA} + \text{H}^+$	$\text{H}_3\text{A} \rightleftharpoons \text{H}_2\text{A} + \text{H}^+$	
Acid dissociation const. $K(\text{M})$	7.02×10^{-7}	1.83×10^{-2}	6.53	
Forward rate const. $k_f(\text{s}^{-1})$	7.02×10^3	1.83×10^8	6.53×10^{10}	
Back rate const. $k_b(\text{M}^{-1}\text{s}^{-1})$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}	
Process	$\text{HB} \rightleftharpoons \text{B} + \text{H}^+$	$\text{H}_2\text{B} \rightleftharpoons \text{HB} + \text{H}^+$	$\text{H}_3\text{B} \rightleftharpoons \text{H}_2\text{B} + \text{H}^+$	
Acid dissociation const. $K(\text{M})$	1.18×10^{-14}	7.14×10^{-8}	1.17×10^{-5}	
Forward rate const. $k_f(\text{s}^{-1})$	1.18×10^{-4}	7.14×10^2	1.17×10^5	
Back rate const. $k_b(\text{M}^{-1}\text{s}^{-1})$	1.00×10^{10}	1.00×10^{10}	1.00×10^{10}	
Disproportionation reactions				
Process	$2\text{HA} \rightleftharpoons \text{A} + \text{H}_2\text{A}$	$2\text{HB} \rightleftharpoons \text{B} + \text{H}_2\text{B}$	$2\text{H}_2\text{A} \rightleftharpoons \text{HA} + \text{H}_3\text{A}$	$2\text{H}_2\text{B} \rightleftharpoons \text{HB} + \text{H}_3\text{B}$
Equilibrium const. $K_{\text{eq}}(\text{M})$	3.84×10^{-5}	1.65×10^{-7}	2.80×10^{-3}	6.09×10^{-3}

A: $[\text{AsV}^{\text{V}}\text{Mo}_{11}\text{O}_{40}]^{4-}$; B: $[\text{AsV}^{\text{IV}}\text{Mo}_{11}\text{O}_{40}]^{5-}$