

Supplementary material:

Gas Phase Vibrational Spectroscopy of Mass-Selected Vanadium Oxide Anions

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Table S1: Total B3LYP/TZVP energies (in Hartree).

	<u>reference species</u>		
O ₂		-150.32213	
O		-75.06560	
VO ₂		-1094.37901	
VO ₂ ⁻		-1094.41670	
VO ₃	² A''	-1169.58586	
VO ₃ ⁻	¹ A'	-1169.73552	
V ₂ O ₄ ⁻	C _{2v} ⁴ A ₂	-2189.01801	
V ₂ O ₅		-2264.15692	
V ₂ O ₅ ⁻	C _s ² A'	-2264.304568	
V ₃ O ₇ ⁻	C _{2v} ³ A ₂	-3358.85683	
V ₃ O ₈	C _{2v} ² B ₂	-3433.91990	
V ₄ O ₉ ⁻ tetra	C _s ⁴ A''	-4453.42836	
V ₄ O ₁₀		-4528.553928	
	<u>optimized anions</u>		<u>neutral//anion</u>
V ₂ O ₆ ⁻	C _{2v} ² B ₂	-2339.51460	-2339.30530
V ₂ O ₇ ⁻ Superoxo	C _s ² A''	-2414.69233	-2414.48824
V ₃ O ₈ ⁻ RING	C _{2v} ¹ A ₁	-3434.12579	-3433.90236
V ₄ O ₁₀ ⁻ Tetra	D _{2d} ² B ₁	-4528.71582	-4528.55090
V ₄ O ₁₁ ⁻ dioxo-bridge	C _s	-4603.85693	-4603.61234
V ₅ O ₁₃ ⁻ pyramidal	C _{4v} ¹ A ₁	-5698.48186	
V ₆ O ₁₅ ⁻ cage	C _s ² A'	-6793.05053	-6792.85637
V ₇ O ₁₈ ⁻ pyramidal	C _{2v} ¹ A ₁	-7962.81976	
V ₈ O ₂₀ ⁻ cage	C _s a''	-9057.38660	-9057.18532

Table S2: Scaled harmonic vibrational frequencies (in cm^{-1}) above 550 cm^{-1} (and V-O• mode), relative intensities (in parentheses) and mode assignment for additional isomers of vanadium oxide anions from B3LYP/TZVP calculations. Scaling factors of 0.9167 (V=O modes) and 0.9832 (V-O-V modes) were taken from K. R. Asmis, G. Meijer, M. Brümmer, C. Kaposta, G. Santambrogio, L. Wöste and J. Sauer, J. Chem. Phys., 2004, 120, 6461.

Anion	Symmetry	Type	Scaled Harmonic Frequency (cm^{-1})
$\text{V}_4\text{O}_{11}^-$ $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$	${}^2\text{A}' (C_s)$	V=O	1002 (a', 0.07), 984 (a', 0.88), 972 (a', 0.78) , 966 (a'', 1.00)
		O-O V-O-V	853 ^a (a', 0.06) 811 (a'', 0.43), 806 (a', 0.66), 739 (a', 0.60), 701 (a'', 0.38), 635 (a', 0.08), 616 (a'', 0.07) , 594 (a', 0.06)
$\text{V}_4\text{O}_{11}^-$ $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxoanion}$	${}^2\text{B}_2 (C_{2v})$	V=O	1009 (a ₁ , 0.07), 990 (b ₁ , 0.84), 979 (a ₁ , 0.78), 971 (b ₂ , 1.00)
		O...O O-V-O	640 ^a (a ₁ , 0.07) 822 (a ₁ , 0.91), 807 (b ₂ , 0.59), 756 (b ₁ , 0.63), 658 (a ₂ , 0.00), 639 (a ₁ , 0.02), 614 (b ₂ , 0.13), 585 (b ₁ , 0.01)
$\text{V}_4\text{O}_{11}^-$ dioxo-open	${}^2\text{A}' (C_s)$	V=O	989 (a', 0.11), 975 (a'', 0.34), 950 (a', 0.20), 947 (a', 0.11), 849 (a', 0.17)
		V-O• O-V-O	424 (a', 0.00) 885 (a', 0.38), 867 (a'', 0.27), 837 (a', 1.00), 722 (a'', 0.16), 627 (a', 0.04), 619 (a'', 0.00)
$\text{V}_5\text{O}_{13}^-$ bridged	${}^1\text{A}_1 (C_{2v})$	V=O	1002 (a ₁ , 0.09), 982 (b ₁ , 0.46), 980 (a ₁ , 0.09), 980 (b, 0.57), 950 (a ₁ , 0.03), 949 (b ₁ , 0.24)
		O-V-O	932 (a ₁ , 0.77), 915 (b ₂ , 0.74), 871 (a ₁ , 1.00), 850 (b ₁ , 0.42), 718 (b ₂ , 0.29), 644 (a ₂ , 0.00), 635 (a ₁ , 0.03), 587(b ₁ , 0.11) , 585 (b ₂ , 0.00)
$\text{V}_7\text{O}_{18}^-$ bridged	${}^1\text{A}' (C_s)$	V=O	1008 (a', 0.03), 991 (a', 0.17), 988 (a'', 0.21), 988 (a', 0.14), 982 (a', 0.00), 981 (a'', 0.03) , 955 (a', 0.01) , 951 (a', 0.10)
		V-O-V	960 (a', 0.04), 955 (a'', 0.30), 938 (a', 0.29), 913 (a', 1.00), 909 (a'', 0.32), 890 (a', 0.51), 746 (a'', 0.12), 650 (a'', 0.00), 620 (a', 0.01), 605 (a'', 0.01), 592 (a', 0.01), 567 (a', 0.01)

^a Scaling factor for V=O modes applied.

Table S3: DFT energy V_{pot} (in mHartree) as a function of the difference of the two V-O distances in the V-O-V bridge, $q = R(\text{O-V}_1) - R(\text{O-V}_2)$ (in Bohr), which corresponds to the normal coordinate of the saddle point and minimum structures.

q	V_{pot}
0.0	3.7397
0.04811	3.3458
0.08051	2.9457
0.18355	0.3887
0.23464	0.0930
0.25444	0.0307
0.28124	0.0000
0.30802	0.0312
0.32785	0.0960
0.35513	0.2446
0.37766	0.4204
0.38885	0.5260
0.44262	1.2140
0.46248	1.5450
0.51977	2.7604
0.55307	3.6466
0.598110	5.0819
0.631100	6.3075
0.668440	7.8547
0.695790	9.1140
0.722610	10.4570

Parameters for the Quartic and Manning Potentials Derived from DFT results

Table S4 shows the DFT results of the harmonic frequency, $\omega(q_0)$, at the energy minimum C_s structures, $q_0 = R_0(\text{O}-V_1) - R_0(\text{O}-V_2)$ for this structure, and the barrier V_b , the energy difference between the C_{2v} and C_s structures.

The harmonic and quartic force constants F and Q we get from the barrier height V_b and the position of the minima q_0 ,

$$F = 4 \frac{V_b}{q_0^2} \quad Q = 24 \frac{V_b}{q_0^4}.$$

We get the parameters for the Manning potential,

$$a \equiv \frac{A}{2Mr^2}, \quad d \equiv \frac{D}{2Mr^2}$$

from V_b and an assumed $U_d = 12,000 \text{ cm}^{-1}$,

$$a + d = -2U_d + 2\sqrt{-U_d V_b}; \quad d = -(U_d - V_b) + 2\sqrt{-U_d V_b}$$

and we get $2r$ from a and d with q_0

$$\frac{q_0}{2r} = \ln \left(\sqrt{\frac{2d}{a+d}} - 1 + \sqrt{\frac{2d}{a+d}} \right)$$

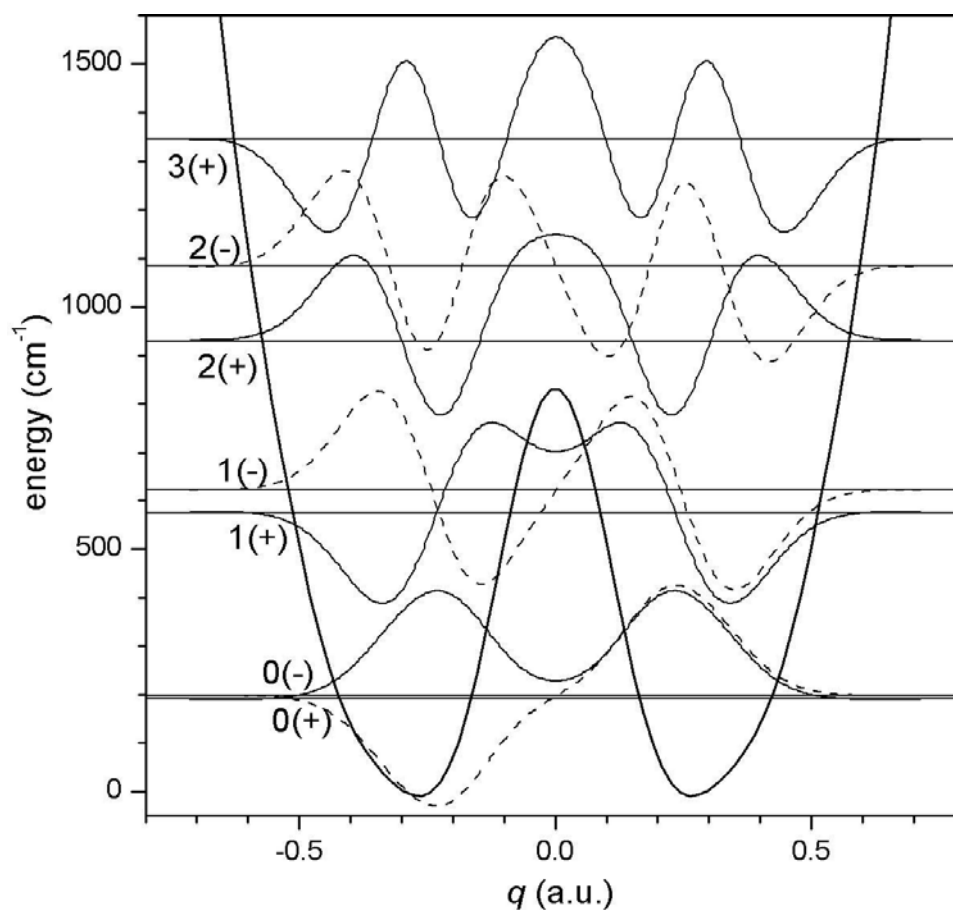
Table S4: DFT results for the minimum and saddle point structures as well as potential parameters of the quartic and Manning-type potentials for $V_6O_{15}^-$ and $V_8O_{20}^-$.

DFT results	$V_8O_{20}^-$		$V_6O_{15}^-$	
$\omega(q_0) / \text{cm}^{-1}$	878 (864) ^a		931 (915) ^a	
$V_b / \text{mHartree} (\text{cm}^{-1})$	3.32036 (729)		3.73966 (821)	
q_0 / Bohr	0.339023		0.281240	
Parameters	Quartic	Manning ^b	Quartic	Manning ^b
$-F/2 / \text{mHartree}$	-57.77725		-94.56005	
$Q/24 / \text{mHartree}$	251.34404		597.75543	
$a+d / \text{mHartree}$		136.29970		137.95062
$d / \text{mHartree}$		84.94404		87.01426
$2r / \text{Bohr}$		0.70924538		0.57234389

^a Scaled harmonic frequency.

^b $U_d = 54.676 \text{ mHartree} (=12000 \text{ cm}^{-1})$

Figure S1: Eigenvalues (horizontal lines) and eigenfunctions χ_i (ungerade wavefunctions are represented by dashed lines for better visibility) of the double-well potential connecting two equivalent C_s minima via a C_{2v} saddle point in $V_6O_{15}^-$. The potential energy was approximated by a 16th-degree polynomial function, which was fit to 21 points (see Table 3 of the supplementary material) calculated along the normal coordinate q of the relaxed DFT potential energy curve.



Relative transitions intensities I_{ik} in Table S4 of the manuscript were approximated within the linear dipole approximation by calculating the square of the transition matrix elements \mathbf{M}_{ik} :

$$I_{ik} \propto \mathbf{M}_{ik}^2 = \langle \chi_i | q | \chi_k \rangle^2 .$$