Supplementary material:

Gas Phase Vibrational Spectroscopy of Mass-Selected Vanadium Oxide Anions


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

<table>
<thead>
<tr>
<th>reference species</th>
<th>B3LYP/TZVP energies (in Hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>-150.32213</td>
</tr>
<tr>
<td>O</td>
<td>-75.06560</td>
</tr>
<tr>
<td>VO2</td>
<td>-1094.37901</td>
</tr>
<tr>
<td>VO2^-</td>
<td>-1094.41670</td>
</tr>
<tr>
<td>VO3 2A''</td>
<td>-1169.58586</td>
</tr>
<tr>
<td>VO3^- 1A'</td>
<td>-1169.73552</td>
</tr>
<tr>
<td>V2O4^- C2v 4A2</td>
<td>-2189.01801</td>
</tr>
<tr>
<td>V2O5</td>
<td>-2264.15692</td>
</tr>
<tr>
<td>V2O5^- C2v 2A1</td>
<td>-2264.304568</td>
</tr>
<tr>
<td>V3O7^- C2v 3A2</td>
<td>-3358.85683</td>
</tr>
<tr>
<td>V3O8</td>
<td>-3433.91990</td>
</tr>
<tr>
<td>V3O8^- RING</td>
<td>-3433.90236</td>
</tr>
<tr>
<td>V4O10^- Tetra</td>
<td>-4528.71582</td>
</tr>
<tr>
<td>V4O10^- dioxo-bridge</td>
<td>-4603.58593</td>
</tr>
<tr>
<td>V5O13^- pyramidal</td>
<td>-5698.48186</td>
</tr>
<tr>
<td>V6O15^- cage</td>
<td>-6793.05053</td>
</tr>
<tr>
<td>V7O18^- cage</td>
<td>-7962.81976</td>
</tr>
<tr>
<td>V8O20^- cage</td>
<td>-9057.18532</td>
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</table>

<table>
<thead>
<tr>
<th>optimized anions</th>
<th>neutral/anion</th>
</tr>
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<tbody>
<tr>
<td>V2O6^- C2v 2B2</td>
<td>-2339.51460</td>
</tr>
<tr>
<td>V2O7^- Superoxo C2v 2A1</td>
<td>-2414.69233</td>
</tr>
<tr>
<td>V3O8^- RING D2d 2B1</td>
<td>-4528.71582</td>
</tr>
<tr>
<td>V4O10^- dioxo-bridge C5</td>
<td>-4603.85693</td>
</tr>
<tr>
<td>V5O13^- pyramidal C5v 1A</td>
<td>-5698.48186</td>
</tr>
<tr>
<td>V6O15^- cage C5 2A1</td>
<td>-6793.05053</td>
</tr>
<tr>
<td>V7O18^- pyramidal C5v 1A</td>
<td>-7962.81976</td>
</tr>
<tr>
<td>V8O20^- cage C5 1a''</td>
<td>-9057.38660</td>
</tr>
</tbody>
</table>
**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.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Symmetry</th>
<th>Type</th>
<th>Scaled Harmonic Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>V₄O₁₁⁻</strong>&lt;br&gt;μ-η² : η²-peroxo</td>
<td>²A' (C₃)</td>
<td>V=O</td>
<td>1002 (a’, 0.07), 984 (a’, 0.88), 972 (a’, 0.78), 966 (a’’, 1.00)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-O</td>
<td>853⁵ (a’, 0.06)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V-O-V</td>
<td>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)</td>
</tr>
<tr>
<td><strong>V₄O₁₁⁻</strong>&lt;br&gt;μ-η² : η²-peroxoanion</td>
<td>²B₂ (C₂ᵥ)</td>
<td>V=O</td>
<td>1009 (a₁, 0.07), 990 (b₁, 0.84), 979 (a₁, 0.78), 971 (b₂, 1.00)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-O</td>
<td>640⁵ (a₁, 0.07)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-V-O</td>
<td>822 (a₁, 0.91), 807 (b₂, 0.59), 756 (b₁, 0.63), 658 (a₂, 0.00), 639 (a₁, 0.02), 614 (b₂, 0.13), 585 (b₁, 0.01)</td>
</tr>
<tr>
<td><strong>V₄O₁₁⁻</strong>&lt;br&gt;dioxo-open</td>
<td>²A' (C₃)</td>
<td>V=O</td>
<td>989 (a’, 0.11), 975 (a’’, 0.34), 950 (a’, 0.20), 947 (a’, 0.11), 849 (a’, 0.17)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V-O-V</td>
<td>424 (a’, 0.00)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-V-O</td>
<td>885 (a’, 0.38), 867 (a’’, 0.27), 837 (a’, 1.00), 722 (a’’, 0.16), 627 (a’, 0.04), 619 (a’’, 0.00)</td>
</tr>
<tr>
<td><strong>V₅O₁₃⁻</strong>&lt;br&gt;bridged</td>
<td>¹A₁ (C₂ᵥ)</td>
<td>V=O</td>
<td>1002 (a₁, 0.09), 982 (b₁, 0.46), 980 (a₁, 0.09), 980 (b, 0.57), 950 (a₁, 0.03), 949 (b₁, 0.24)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-V-O</td>
<td>932 (a₁, 0.77), 915 (b₂, 0.74), 871 (a₁, 1.00), 850 (b₁, 0.42), 718 (b₂, 0.29), 644 (a₂, 0.00), 635 (a₁, 0.03), 587(b₁, 0.11), 585 (b₂, 0.00)</td>
</tr>
<tr>
<td><strong>V₇O₁₈⁻</strong>&lt;br&gt;bridged</td>
<td>¹A’ (C₃)</td>
<td>V=O</td>
<td>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)</td>
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<tr>
<td></td>
<td></td>
<td>V-O-V</td>
<td>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)</td>
</tr>
</tbody>
</table>

⁵ 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, $q = R(O-V_1) - R(O-V_2)$ (in Bohr), which corresponds to the normal coordinate of the saddle point and minimum structures.

<table>
<thead>
<tr>
<th>$q$</th>
<th>$V_{pot}$</th>
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<tbody>
<tr>
<td>0.0</td>
<td>3.7397</td>
</tr>
<tr>
<td>0.04811</td>
<td>3.3458</td>
</tr>
<tr>
<td>0.08051</td>
<td>2.9457</td>
</tr>
<tr>
<td>0.18355</td>
<td>0.3887</td>
</tr>
<tr>
<td>0.23464</td>
<td>0.0930</td>
</tr>
<tr>
<td>0.25444</td>
<td>0.0307</td>
</tr>
<tr>
<td>0.28124</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.30802</td>
<td>0.0312</td>
</tr>
<tr>
<td>0.32785</td>
<td>0.0960</td>
</tr>
<tr>
<td>0.35513</td>
<td>0.2446</td>
</tr>
<tr>
<td>0.37766</td>
<td>0.4204</td>
</tr>
<tr>
<td>0.38885</td>
<td>0.5260</td>
</tr>
<tr>
<td>0.44262</td>
<td>1.2140</td>
</tr>
<tr>
<td>0.46248</td>
<td>1.5450</td>
</tr>
<tr>
<td>0.51977</td>
<td>2.7604</td>
</tr>
<tr>
<td>0.55307</td>
<td>3.6466</td>
</tr>
<tr>
<td>0.598110</td>
<td>5.0819</td>
</tr>
<tr>
<td>0.631100</td>
<td>6.3075</td>
</tr>
<tr>
<td>0.668440</td>
<td>7.8547</td>
</tr>
<tr>
<td>0.695790</td>
<td>9.1140</td>
</tr>
<tr>
<td>0.722610</td>
<td>10.4570</td>
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</table>
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, $q_0 = R_0(O-V_1) - R_0(O-V_2)$ 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 $q_0$, $F = 4 \frac{V_b}{q_0^2}$, $Q = 24 \frac{V_b}{q_0^4}$.

We get the parameters for the Manning potential, $a \equiv \frac{A}{2Mr^2}$, $d \equiv \frac{D}{2Mr^2}$ from $V_b$ and an assumed $U_d=12,000$ cm$^{-1}$, $a + d = -2U_d + 2\sqrt{-U_dV_b}$; $d = -(U_d - V_b) + 2\sqrt{-U_dV_b}$ and we get $2r$ from $a$ and $d$ with $q_0$ $q_0 \frac{2r}{2r} = \ln \left( \frac{2d}{\sqrt{a+d} - 1 + \sqrt{2d}} \right)$

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 $V_8O_{20}^-$. 

<table>
<thead>
<tr>
<th>DFT results</th>
<th>$V_8O_{20}^-$</th>
<th>$V_6O_{15}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega(q_0)$ /cm$^{-1}$</td>
<td>878 (864)$^a$</td>
<td>931 (915)$^a$</td>
</tr>
<tr>
<td>$V_b$/mHartree (cm$^{-1}$)</td>
<td>3.32036 (729)</td>
<td>3.73966 (821)</td>
</tr>
<tr>
<td>$q_0$/Bohr</td>
<td>0.339023</td>
<td>0.281240</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Quartic</th>
<th>Manning$^b$</th>
<th>Quartic</th>
<th>Manning$^b$</th>
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<tbody>
<tr>
<td>$-F/2$ /mHartree</td>
<td>-57.77725</td>
<td>-94.56005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q/24$ /mHartree</td>
<td>251.34404</td>
<td>597.75543</td>
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<tr>
<td>$a+d$ /mHartree</td>
<td>136.29970</td>
<td>137.95062</td>
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<tr>
<td>$d$ /mHartree</td>
<td>84.94404</td>
<td>87.01426</td>
<td></td>
<td></td>
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<tr>
<td>$2r$ /Bohr</td>
<td>0.70924538</td>
<td>0.57234389</td>
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</tbody>
</table>

$a$ Scaled harmonic frequency.

$b$ $U_d=54.676$ mHartree (=12000 cm$^{-1}$)
**Figure S1:** Eigenvalues (horizontal lines) and eigenfunctions $\chi_i$ (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 $M_{ik}$:

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