Supporting Information for

Hydrogen Release from a Single H₂O Molecule on Vₙ⁺ (3 ≤ n ≤ 30)

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S1 Experimental Details of “$V_n^+ + H_2^{18}O$”

**Supplementary Figure 1** Mass spectra of (a) cationic vanadium clusters and (b-d) $V_n^+$ reacting with different amount of $H_2^{18}O$. The pure vanadium clusters are labelled by numbers, vanadium monohydrates are labelled by blue arrows, vanadium monoxides are labelled by red circles, vanadium dioxides are labelled by green circles, vanadium trioxides are labelled by purple circles, and hydrated vanadium monoxides are labelled by yellow triangles.
**Supplementary Figure 2** Mass abundance analysis for the reactions of $V_n^+ + H_2^{18}O$ with different $H_2^{18}O$ doses, based on the equations: (A) $-\ln \left( \frac{V_n^+ + V_n^{18}O^+ + V_nH_2^{18}O^+ + V_n^{18}OH_2^{18}O^+ + V_n^{18}O_2^+ + V_n(H_2^{18}O)_2^+ + V_n^{18}O_3^+}{V_n^{18}O^+} \right)$, (B) $\frac{V_nH_2^{18}O^+}{V_n^{18}O^+}$, and (C) $\frac{V_n^+ + V_n^{18}O^+ + V_nH_2^{18}O^+ + V_n^{18}OH_2^{18}O^+ + V_n^{18}O_2^+ + V_n(H_2^{18}O)_2^+ + V_n^{18}O_3^+}{V_n^{18}O^+}$. 
**Supplementary Table 1** The estimated rate constants of $V_n^+$ clusters in reacting with $\text{H}_2^{18}\text{O}$.

| $V_n^+$ clusters | Rate coefficients (cm$^3$·molecule$^{-1}$·s$^{-1}$) |
|------------------|-----------------------------------------------|
| 1                | $\sim 1.1 \times 10^{-11}$ (Bohme’s work$^1$) |
|                  | $< 10^{-11}$                                   |
| 2                | $< 10^{-11}$                                   |
| 3                | $4.50 \times 10^{-10}$                         |
| 4                | $1.15 \times 10^{-9}$                         |
| 5                | $1.49 \times 10^{-9}$                         |
| 6                | $1.20 \times 10^{-9}$                         |
| 7                | $1.54 \times 10^{-9}$                         |
| 8                | $1.49 \times 10^{-9}$                         |
| 9                | $1.54 \times 10^{-9}$                         |
| 10               | $1.65 \times 10^{-9}$                         |
| 11               | $1.66 \times 10^{-9}$                         |
| 12               | $1.69 \times 10^{-9}$                         |
| 13               | $1.84 \times 10^{-9}$                         |
| 14               | $1.89 \times 10^{-9}$                         |
| 15               | $1.80 \times 10^{-9}$                         |
| 16               | $1.59 \times 10^{-9}$                         |
| 17               | $1.73 \times 10^{-9}$                         |
| 18               | $1.69 \times 10^{-9}$                         |
| 19               | $1.75 \times 10^{-9}$                         |
| 20               | $1.83 \times 10^{-9}$                         |

**Note:** These rate constants are estimated based on the following parameters: The partial pressure of water in the reaction tube is 57 mPa, the reaction gas ($\text{H}_2^{18}\text{O}$) molecule density in the reaction tube is $1.39 \times 10^{19}$ molecule·m$^{-3}$, the effective residence time in the reactor is 60 μs. The reaction temperature is 298 K.
S2 Reactions of “$V_n^+ + D_2O$”

**Supplementary Figure 3** Mass spectra of (a) cationic vanadium clusters and (b-d) $V_n^+$ reacting with different amount of $D_2O$, with the expanded areas shown in (e-h) respectively. The pure vanadium clusters are labelled by numbers.
S3 Collision Experiments of “V\textsubscript{n}^+ + He”

**Supplementary Figure 4** Mass spectra of (a) the cationic vanadium clusters produced with helium as buffer gas, (b-c) and after suffering from the downstream collision experiments by introducing pure helium gas as reactant in place of H\textsubscript{2}O/He mixture. The V\textsubscript{n}^+ clusters are labelled by numbers.
### S4 Structure Optimization

**Supplementary Table 2** Relative energies of $V_n^+$ (n=1-13) isomers, calculated at BP86-D3/def2-TZVP level of theory. Energies are given in in eV. Values of $M$ refer to spin multiplicity.

| $V_n^+$ | **Energies** | $V_n^+$ | **Energies** |
|---------|--------------|---------|--------------|
|         | M=1 | M=3 | M=5 | M=7 |           | M=2 | M=4 | M=6 | M=8 |
| n=1     |     |     |     |     |     | 2.73 | 1.08 | **0.00** | 33.87 |
| n=2     |     |     |     |     |     | 0.07 | **0.00** | 1.61 | 1.60 |
| n=3     | 0.57 | **0.00** | 0.29 | 2.13 | n=4   |     |     |     |     |
| n=4     | a    | **0.00** | 0.34 | 0.97 | 2.16 |
|         | b    | 0.70 | 0.59 | 0.88 | 1.23 |
| n=5     | a    | 0.22 | **0.00** | 0.20 | 0.57 |
|         | b    | 0.47 | 0.52 | 1.31 | n=6   | a    | 0.67 | **0.00** | 0.65 |
|         |     |     |     |     |     |     |     |     |     |
| n=7     | a    | **0.00** | 0.13 | 0.43 | 0.95 |
|         | b    | 0.26 | 0.11 | 0.37 | 0.83 |
|         | c    | 0.71 | 0.71 | 0.78 |     |
|         | d    | 0.78 | 0.73 | 0.78 | 1.09 |
| n=8     | a    | **0.00** |     | 0.47 | 2.02 |
|         | b    | 0.18 | 0.60 | 1.18 |     |
|         | c    | 0.50 | 0.49 | 0.88 |     |
|         | d    | 0.59 | 0.91 | 2.42 |     |
|         | e    | 1.42 | 1.64 | 1.75 |     |
| n=9     | a    | **0.00** | 0.04 | 0.28 |     |
|         | b    | 0.30 | 0.36 | 0.63 |     |
| n=10    | a    | **0.00** | 0.03 | 0.69 |     |
|         | b    | 1.23 | 0.75 | 1.18 |     |
| n=11    | a    | **0.00** |     | 0.69 |     |
|         | b    | 1.27 | 1.27 | 1.28 |     |
|         | c    | 0.82 | 0.78 | 1.08 |     |
| n=12    | a    | **0.00** |     | 0.29 |     |
|         | b    | 1.27 | 1.27 | 1.28 |     |
|         | c    | 0.82 | 0.78 | 1.08 |     |
| n=13    | a    | **0.00** |     | 0.29 |     |
|         | b    | 1.27 | 1.27 | 1.28 |     |
|         | c    | 0.82 | 0.78 | 1.08 |     |
|         | d    | 0.47 | 1.39 | 1.39 |     |
Supplementary Figure 5 Structures of the $V_n^+$ (n=1-13) isomers in Supplementary Table 2 and their relative energy difference (in eV), calculated at BP86-D3/def-2TZVP level. M indicates spin multiplicity.
**Supplementary Table 3** A comparison of the relative energies of vanadium cluster isomers (taking $V_5^+$ and $V_9^+$ as example) at different convergence thresholds. The calculations are conducted using Gaussian 09 program at BP86-D3/def2-TZVP level. The energies are corrected with zero-point vibration energies and given eV. Values of $M$ refer to spin multiplicity.

| $V_n^+$ Cluster | Relative Energies (eV) | $V_{n'}^+$ Cluster | Relative Energies (eV) |
|-----------------|------------------------|---------------------|------------------------|
| M=1             | M=3                    | M=5                 | M=7                    |
| $V_5^+$ isomer A | 0.215                  | **0.000**           | 0.196                  | 0.568                  |
| isomer B        | 0.466                  | 0.524               | 1.307 \              |
| $V_9^+$ isomer A | **0.000**              | 0.041               | 0.281                  | \                      |
| isomer B        | 0.298                  | 0.355               | 0.634                  | \                      |

Default Convergence Threshold

| Force Maximum   | 0.000450 |
| Force RMS       | 0.000300 |
| Displacement Maximum | 0.001800 |
| Displacement RMS | 0.001200 |

Tight Convergence Threshold

| Force Maximum   | 0.000015 |
| Force RMS       | 0.000010 |
| Displacement Maximum | 0.000060 |
| Displacement RMS | 0.000040 |
Supplementary Table 4 Relative energies of $V_nH_2O^+$ (n=1-13) isomers calculated at BP86-D3/def2-TZVP level of theory. Energies are given in eV. Values of $M$ refer to spin multiplicity.

| $V_nH_2O^+$ | Energies | $V_nH_2O^+$ | Energies |
|-------------|----------|-------------|----------|
|             | $M=1$    | $M=3$    | $M=5$    | $M=7$    |
| $n=1$       | 3.29     | 1.00     | **0.00** | 5.42     |
| $n=3$       | a 0.52   | **0.00** | 0.31     |          |
|             | b 0.52   | 0.11     | 0.40     |          |
|             | c 0.53   | 0.32     | 0.40     |          |
| $n=5$       | a 0.24   | **0.00** | 0.15     | 0.69     |
|             | b 0.35   | 0.15     | 0.21     | 0.71     |
| $n=7$       | a **0.00** | 0.18 | 0.43     |          |
|             | b 0.15   | 0.28     | 0.53     |          |
| $n=9$       | a **0.00** | 0.11 | 0.43     |          |
|             | b 0.07   | 0.15     | 0.36     |          |
|             | c 0.18   | 0.27     | 0.47     |          |
|             | d 0.20   | 0.32     | 0.46     |          |
| $n=11$      | a **0.00** | 0.04 |          |          |
|             | b 0.03   | 0.002   |          |          |
|             | c 0.11   | 0.14    |          |          |
|             | d 0.14   | 0.16    |          |          |
|             | e 0.15   | 0.18    |          |          |
|             | f 0.20   | 0.24    |          |          |
|             | g 0.34   | 0.42    |          |          |
| $n=13$      | a **0.00** | 0.11 |          |          |
|             | b 0.07   | 0.09    |          |          |
|             | c 0.13   | 0.21    |          |          |
Supplementary Figure 6 Isomer structures and the relative energies (in eV) of \( V_nH_2O^+ \) (n=1-13) clusters calculated at BP86-D3/def-2TZVP level. M indicates spin multiplicity.
**Supplementary Table 5** Relative energies of $V_nO^+$ isomers calculated at BP86-D3/def2-TZVP level of theory. Energies are given in eV. The values of M refer to spin multiplicity.

| $V_nO^+$ | Energies | $V_nO^+$ | Energies |
|----------|----------|----------|----------|
|          | M=1     | M=3     | M=5     | M=2     | M=4     | M=6     |
| $n=1$    | 1.09    | **0.00**| 3.57    |          |          |          |
| $n=3$    | a 0.00  | 0.42    | 0.86    |          |          |          |
|          | b 0.73  | 0.79    | 0.86    |          |          |          |
| $n=5$    | a **0.00**| 0.14    | 0.64    |          |          |          |
|          | b 0.07  | 0.49    | 0.62    |          |          |          |
| $n=7$    | a **0.00**| 0.25    | 0.63    |          |          |          |
|          | b 0.55  | 0.17    | 0.93    |          |          |          |
| $n=9$    | a **0.00**| 0.05    | 0.22    |          |          |          |
|          | b 0.15  | 0.17    | 0.47    |          |          |          |
|          | c 0.31  | 0.63    | 0.76    |          |          |          |
|          | d 0.39  | 0.32    | 0.56    |          |          |          |
|          | e 0.37  | 0.33    | 0.57    |          |          |          |
|          | f 0.47  | 0.62    | 0.65    |          |          |          |
| $n=11$   | a **0.00**| 0.26    |          |          |          |          |
|          | b 0.13  | 0.20    |          |          |          |          |
|          | c 0.16  | 0.27    |          |          |          |          |
|          | d 0.23  | 0.17    |          |          |          |          |
|          | e 0.21  | 0.33    |          |          |          |          |
|          | f 0.22  | 0.31    |          |          |          |          |
|          | g 0.33  | 0.36    |          |          |          |          |
|          | h 0.47  | 0.33    |          |          |          |          |
|          | i 0.47  | 0.45    |          |          |          |          |
|          | j 0.48  | 0.47    |          |          |          |          |
| $n=13$   | a **0.00**| 0.01    |          |          |          |          |
|          | b 0.11  | 0.05    |          |          |          |          |
|          | c 0.09  | 0.21    |          |          |          |          |
| $n=2$    | a **0.00**| 0.40    | 0.39    | b 0.26  | 0.40    | 0.39    |
| $n=4$    | a **0.00**| 1.04    | 1.27    | b 0.35  | 0.79    | 0.65    |
|          | c 0.62  | 1.10    | 0.65    |          |          |          |
| $n=6$    | a **0.00**| 0.44    | 0.68    | b 0.54  | 0.57    | 0.70    |
|          | c 0.61  | 0.83    | 1.17    | d 1.01  | 1.12    | 1.35    |
|          | e 1.07  | 1.15    | 1.58    | f 1.34  | 1.25    | 1.60    |
| $n=8$    | a **0.00**| 0.28    | 0.74    | b 0.38  | 0.50    | 0.71    |
|          | c 0.39  | 1.18    | 0.94    | d 0.75  | 1.11    | 1.69    |
|          | e 0.94  | 0.86    | 1.23    | f 0.95  | 1.23    | 1.30    |
|          | g 2.10  | 1.01    | 1.96    |          |          |          |
| $n=10$   | a **0.00**| 0.31    |          | b 0.02  | 0.43    |          |
|          | c 0.21  | 0.64    |          | d 0.34  | 0.67    |          |
| $n=12$   | a **0.00**| 0.18    |          | b 0.06  |          |          |
|          | c 0.13  |          |          | d 0.18  | 0.36    |          |
|          | e 0.32  | 0.46    |          | f 0.38  |          |          |
Supplementary Figure 7 The isomer structures and the relative energy difference (in eV) of $V_nO^+$ ($n=1$-$13$) clusters calculated at BP86-D3/def-2TZVP level. M indicates spin multiplicity.
**Supplementary Table 6** Electronic states of the low-lying energy isomers of Vₙ⁺, VₙH₂O⁺, VₙO⁺ clusters (n=1-13) calculated at BP86-D3/def-2TZVP level.

| Number of V Atoms | Vₙ⁺ (symmetry) | VₙH₂O⁺ | VₙO⁺ |
|-------------------|----------------|--------|------|
| n=1               | ⁵D             | ⁵B₁    | ³Σ   |
| n=2               | ⁴∑₉ (Dₓᵧh)     | ²A     | ²A'  |
| n=3               | ³B₁ (C₂ᵥ)      | ³B₁    | ¹A'  |
| n=4               | ²A' (C₃)       | ²A     | ²A   |
| n=5               | ³A             | ³A     | ¹A   |
| n=6               | ⁴A (C₂)        | ⁴A     | ²A   |
| n=7               | ¹A             | ¹A     | ³A   |
| n=8               | ²A             | ²A     | ²A   |
| n=9               | ¹A' (C₈)       | ¹A     | ¹A   |
| n=10              | ²B₃ (D₂)       | ²A     | ²A   |
| n=11              | ¹A             | ¹A     | ¹A   |
| n=12              | ²A             | ²A     | ²A   |
| n=13              | ¹A             | ¹A     | ¹A   |
**S5 DFT-Calculated Vibration Modes**

**Supplementary Figure 8** The IR activities of the VₙH₂O⁺ (n = 1, 2, 3, 5, 9) clusters at ground states calculated at BP86-D3/def2-TZVP level of theory. The frequency values are not corrected by any scale factor.

The calculated IR activities of the VₙH₂O⁺ clusters show that there are O-H bending vibrations for V₁⁺H₂O⁺ at ~550 cm⁻¹ which benefit the following formation of O-H-V transition state (Figure 4 of the main text). However, this O-H bending mode is almost negligible for V₃H₂O⁺ and V₉H₂O⁺ (which begin to display more and more weak low-frequency vibrations); instead, the out-of-plane wagging and H-O-H scissoring allow the subsequent steering of -OH₂ towards the formation of an O-VV-V transition state (Figure 5 of the main text).
S6 Energetics

**Supplementary Table 7** The DFT-calculated V-atom removal energy, \( V_{n}^{+} \rightarrow V_{n-1}^{+} + V \) (eV), with a comparison with the previous calculation results and experimental study.

| \( V_{n}^{+} \) | BP86-D3 /def2TZVP (ZPVE) | BP86-D3 /def2TZVP (Gibbs free energy at 1 atm, 298 K) | Literature work \( ^2 \) BPW91-D2 /6-311++G(2d,2p) | Experimental dissociation thresholds \( ^3 \) | Other literature work |
|---------------|--------------------------|---------------------------------|---------------------------------|-------------------------------|---------------------|
| 1             | ---                      | ---                             | ---                             | ---                          |                     |
| 2             | 4.69                     | 4.41                            | 3.54                            | 3.143 (0.003)                |                     |
| 3             | 3.49                     | 3.23                            | 2.4                             | 2.27 (0.09)                  |                     |
| 4             | 4.65                     | 4.23                            | 3.32                            | 3.53 (0.08)                  |                     |
| 5             | 4.07                     | 3.72                            | 2.83                            | 3.24 (0.17)                  |                     |
| 6             | 4.99                     | 4.56                            | 3.69                            | 4.13 (0.16)                  |                     |
| 7             | 4.95                     | 4.52                            | 3.58                            | 3.86 (0.17)                  |                     |
| 8             | 5.00                     | 4.60                            | 3.75                            | 3.99 (0.17)                  |                     |
| 9             | 4.74                     | 4.32                            | 3.22                            | 3.67 (0.23)                  |                     |
| 10            | 5.14                     | 4.73                            | 3.85                            | 3.96 (0.21)                  |                     |
| 11            | 4.75                     | 4.35                            | 3.16                            | 3.96 (0.24)                  |                     |
| 12            | 5.06                     | 4.70                            | 3.46                            | 4.13 (0.29)                  |                     |
| 13            | 5.26                     | 4.86                            | 3.73                            | 4.65 (0.32)                  |                     |

**Supplementary Figure 9** DFT-calculated V-atom removal energy (given by Gibbs free energy at 298K), \( V_{n}^{+} \rightarrow V_{n-1}^{+} + V \), with a comparison with the previous calculation results, \( ^2 \) and experimental study, \( ^3, ^4, ^5, ^6 \).
In actual experiments, there is coexistence of cations and anions and electrons generated in the LaVa source. Thus, the subsequent cluster reaction products may undergo dissociation and neutralization processes in the collision cell. In view of this, we examined the adiabatic ionization energies (I.E.) of the neutral $\text{V}_n\text{H}_2\text{O}$ clusters, as shown in Supplementary Figure 10, where the clusters $\text{V}_{1,2}\text{H}_2\text{O}^+$ show larger electron affinities than other sizes indicating likely neutralization under multiple collisions.

**Supplementary Table 8** Relative energies of neutral $\text{V}_n\text{H}_2\text{O}$ ($n=1$-$13$) isomers, calculated at BP86-D3/def2-TZVP level of theory. Energies are given in eV. Values of $M$ refer to spin multiplicity.

| $\text{V}_n\text{H}_2\text{O}$ | Energy | $\text{V}_n\text{H}_2\text{O}$ | Energy |
|-----------------------------|--------|-----------------------------|--------|
| $n=1$                       | 0.311  | $n=2$                       | 0.344  |
| $n=3$                       | 0.000  | $n=4$                       | 0.060  |
| $n=5$                       | 0.000  | $n=6$                       | 0.081  |
| $n=7$                       | 0.000  | $n=8$                       | 0.000  |
| $n=9$                       | 0.000  | $n=10$                      | 0.000  |
| $n=11$                      | 0.003  | $n=12$                      | 0.000  |
| $n=13$                      | 0.000  |                             | 0.156  |
|                             |        |                             |        |

**Supplementary Figure 10** Adiabatic ionization energies (I.E.) of neutral $\text{V}_n\text{H}_2\text{O}$ clusters, indicating the varying electron affinities of the cationic $\text{V}_n\text{H}_2\text{O}^+$ clusters. The red dot line at IE = 5.3 eV is just drawn to guide the eye.
Supplementary Table 9 The DFT-calculated H$_2$O-binding energy, with a comparison with the previous calculation results and experimental study. Energies are given in eV.

| $V_n^*$ | BP86-D3 /def2TZVP (ZPVE) | BP86-D3 /def2TZVP (Gibbs free energy at 1 atm, 298 K) | BPW91-D2 /6-311++G(2d,2p) | Experiment |
|--------|--------------------------|---------------------------------------------------|---------------------------|------------|
| 1      | 1.860                    | 1.612                                             | 1.643344                  | 1.52 (0.05)$^4$; 1.57 (0.13)$^8$; 1.52 (0.17)$^9$ |
| 2      | 1.349                    | 1.023                                             | 1.166384                  |            |
| 3      | 1.279                    | 0.923                                             | 1.005952                  |            |
| 4      | 1.140                    | 0.796                                             | 0.971264                  |            |
| 5      | 1.282                    | 0.921                                             | 0.93224                   |            |
| 6      | 1.213                    | 0.835                                             | 1.023296                  |            |
| 7      | 1.321                    | 0.949                                             | 1.092672                  |            |
| 8      | 1.224                    | 0.856                                             | 0.992944                  |            |
| 9      | 1.324                    | 0.961                                             | 1.092672                  |            |
| 10     | 1.173                    | 0.805                                             | 0.923568                  |            |
| 11     | 1.190                    | 0.817                                             | 1.005952                  |            |
| 12     | 1.151                    | 0.778                                             | 0.884544                  |            |
| 13     | 1.197                    | 0.795                                             | 0.927904                  |            |

Supplementary Figure 11 A comparison of DFT-calculated H$_2$O-binding energy, with the previous calculation results and experimental study. The detailed values correspond to the above table.
Supplementary Table 10 The DFT-calculated O-bonding energy $E_{O\text{-binding}} = E(V_n^+O) - E(V_n^+) - E(O)$ on optimized ground-state $V_n^+O$ structures, and a comparison with the previous experimental dissociation threshold analysis. Energies are given in eV.

| $V_n^+$ | DFT calculations at BP86-D3/def2TZVP (ZPVE) | BP86-D3/def2TZVP (Gibbs free energy at 1 atm, 298 K) | Experimental (ref.10) threshold analysis |
|--------|---------------------------------|-------------------------------------------------|---------------------------------------|
| 1      | 6.76 (ZPVE)                     | 6.50 (BP86-D3/def2TZVP)                         | 5.99 (0.10)                           |
| 2      | 6.40                            | 6.11                                            | 5.1 (0.3)                             |
| 3      | 7.95                            | 7.51                                            | 7.3 (0.3)                             |
| 4      | 7.48                            | 7.10                                            | 7.5 (0.3)                             |
| 5      | 8.18                            | 7.72                                            | 7.3 (0.4)                             |
| 6      | 7.86                            | 7.47                                            | 7.4 (0.7)                             |
| 7      | 7.85                            | 7.22                                            | 7.0 (0.7)                             |
| 8      | 7.52                            | 7.12                                            | 5.6 (0.4)                             |
| 9      | 7.45                            | 7.05                                            | 6.0 (0.8)                             |
| 10     | 7.18                            | 6.78                                            | 6.7 (0.4)                             |
| 11     | 7.52                            | 7.11                                            | 5.3 (0.4)                             |
| 12     | 7.64                            | 7.20                                            | 4.5 (0.6)                             |
| 13     | 7.85                            | 7.42                                            | 5.1 (0.5)                             |

Note: ZPVE, total energy corrected by zero-point vibrations; the Gibbs free energies correspond to 298K.

Supplementary Figure 12 A comparison of DFT-calculated O-binding energy, with a comparison with the previous experimental study.10 The detailed values correspond to the above table.
By comparing the DFT-calculated O-binding energy with the previous experimental study on the bond energies of $V_n^+$-O by dissociation threshold analysis, there is a general consistence except a few clusters such as $V_8^+$ and $V_{11-13}^+$. The occasional inconsistence may be due to the following factors.

1) Vanadium clusters could radiate with a high recurrent fluorescence rate as established a long time ago,\(^5\) while this radiative cooling effect was not considered by the mentioned literature in their data of the dissociation threshold analysis.\(^4,\)\(^11\) One simple estimate suggests a 20% change in the value of the fitted dissociation energy,\(^4\) and so display the error bars of the mentioned literature.\(^10\)

2) Another effect that was not attracted sufficient attention is the thermal properties of metal clusters at high excitation energies. These are most likely not possible to describe by simple harmonic oscillator models. That is, the difference of the experimentally determined threshold values are likely associated with a variation of radiation-induced residual energy which could cause electronic excitation states or unthermalized geometric deformation/aggravated vibrations, as well as melting effect at reduced sizes.\(^12,\)\(^13,\)\(^14,\)\(^15,\)\(^16\) Melting alone is enough to disprove the simplified harmonic oscillator hypothesis, such as that by the group of Haberland and von Issendorff on sodium clusters.\(^17\) For vanadium clusters the consequences of this effect will most likely have an impact on numbers extracted from experiments but the magnitude is difficult to quantify before thermal properties of these clusters have been measured.

3) From the point of view of DFT calculations, a universally correct exchange and correlation functional is not yet available to the scientific community. Apart from that, the theoretical calculation method and basis set could also bring forth overall energy differences, although the size-dependent tendency is almost parallel.
Supplementary Figure 13 Natural population analysis (NPA) charge on H$_2$O in V$_n$H$_2$O$^+$ clusters calculated at BP86-D3/def2-TZVP level using NBO6.0 method. The red dot line at 0.11 is just drawn to guide the eye.
**Supplementary Table 1** NPA charge distributions on the atoms of VₙH₂O⁺ (n = 1-13) calculated at BP86-D3/def2-TZVP level using NBO6.0 method. The vanadium atom adsorbing the water molecule is defined as V-1 and the other vanadium atoms connecting with V-1 are identified as V-2, V-3, V-4 and V-5, etc. Among them, the V-2 corresponds to the one with the largest positive partial charge, while V-3 aims at the minima.

![Vanadium complex with water molecules](image)

|       | H  | O   | V-1 | V-2 | V-3 | V-4 | V-5 |
|-------|----|-----|-----|-----|-----|-----|-----|
| V₁H₂O⁺| 0.53 | -0.96 | 0.89 | \   | \   | \   | \   |
| V₂H₂O⁺| 0.52 | -0.94 | 0.39 | 0.51   | \   | \   | \   |
| V₃H₂O⁺| 0.52 | -0.97 | 0.47 | 0.23 | 0.23 | \   | \   |
| V₄H₂O⁺| 0.52 | -0.95 | 0.44 | 0.08 | 0.04 | 0.08 | \   |
| V₅H₂O⁺| 0.53 | -0.94 | 0.34 | 0.20 | 0.07 | 0.20 | 0.07 |
| V₆H₂O⁺| 0.52 | -0.92 | 0.09 | 0.14 | 0.10 | 0.14 | 0.19 |
| V₇H₂O⁺| 0.52 | -0.90 | 0.15 | 0.12 | 0.06 | 0.07 | 0.07 |
| V₈H₂O⁺| 0.52 | -0.89 | -0.01 | 0.16 | 0.03 | 0.14 | 0.03 |
| V₉H₂O⁺| 0.52 | -0.87 | -0.03 | 0.14 | 0.04 | 0.14 | 0.10 |
| V₁₀H₂O⁺| 0.52 | -0.88 | -0.03 | 0.11 | 0.07 | 0.11 | 0.10 |
| V₁₁H₂O⁺| 0.52 | -0.88 | -0.07 | 0.13 | 0.07 | 0.14 | 0.11 |
| V₁₂H₂O⁺| 0.52 | -0.88 | -0.02 | 0.24 | 0.05 | 0.24 | 0.10 |
| V₁₃H₂O⁺| 0.52 | -0.88 | 0.01 | 0.19 | 0.06 | 0.21 | 0.13 |
Supplementary Figure 14 The HOMO and LUMO energy levels of the chosen clusters $V_{1}^{+}$, $V_{5}^{+}$, $V_{9}^{+}$, $V_{10}^{+}$, with a comparison to that of H$_2$O. The dotted line at -7.1 eV corresponds to the HOMO energy level of H$_2$O.

The HOMO-LUMO gaps are often associated with the cluster stability and reaction inertness. Displayed here, are the HOMO and LUMO patterns of $V_{1,5,9,10}^{+}$ and H$_2$O, as well as their relative orbital energy levels. Considering that $V_{n}^{+}$ react with water by transfer of electron, the proximity of the HOMO of H$_2$O relative to the LUMO of $V_{5,9}$ facilitates electron transfer from oxygen lone pair of water to the vanadium cluster.
**Supplementary Figure 15** HOMO-LUMO gaps of \( V_n^+ \) and \( V_nH_2O^+ \) clusters. Energies are given in eV.

**S9 Energy Decomposition Analysis**

Energy decomposition analysis (EDA) based on natural orbitals for chemical valence (NOCV) \(^\text{19,20,21}\) was conducted using ADF software package. By taking \( V_n^+ \) and \( H_2O \) as interacting fragments, EDA-NOCV results for \( V_nH_2O^+ \) are calculated at the BP86-D3/TZ2P level using BP86-D3/ def2-TZVP optimized geometries. According to the general principle of EDA, \(^\text{21,22}\) the interaction energy (\( \Delta E_{\text{int}} \)) between \( V_n^+ \) and \( H_2O \) in \( V_nH_2O^+ \) can be divided into three parts: 

\[
\Delta E_{\text{int}} = \Delta E_{\text{pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orb}},
\]

where \( \Delta E_{\text{pauli}} \) is the repulsion energy caused by the Pauli exclusion principle, and \( \Delta E_{\text{elstat}} \) and \( \Delta E_{\text{orb}} \) are the attraction energies due to electrostatic and orbital interactions, respectively. As seen in Supplementary Figure 16 and Table 12 below, the contribution of \( \Delta E_{\text{elstat}} \) to \( \Delta E_{\text{int}} \) is larger than that of \( \Delta E_{\text{orb}} \); also, the plots of \( \Delta E_{\text{ind}} \) values show the same tendency of odd-even oscillations as that of the \( E_{\text{ad}} \) value plots (Figure 3a). From the ADF-calculated EDA results, the electrostatic interaction contributes about 2/3 to the attractive \( V_n^+-H_2O \) interaction, while the orbital interaction does \( \sim 1/3 \) contribution.
Supplementary Figure 16 Energy decomposition analysis for \( \text{V}_n\text{H}_2\text{O}^+ \) showing the contributions of electrostatic interactions and orbital interactions to the total bonding energies. Detailed energy values are given in Supplementary Table 12 below.
**Supplementary Table 12** EDA-NOCV results for $V_2\text{H}_2\text{O}^+$ at the BP86-D3/TZ2P level using BP86-D3/def2-TZVP optimized geometries, taking $V_n^+$ and $\text{H}_2\text{O}$ as interacting fragments. Energy values are given in kcal/mol.

| Complex (charge, $\alpha$-$\beta$) | Metal Cluster (charge, $\alpha$-$\beta$) | Total Energy $\Delta E_{tot}$ | Electrostatic Interaction $\Delta E_{elstat}$ | Pauli Repulsion $\Delta E_{pauli}$ | Orbital Interactions $\Delta E_{orb}$ | Converged? |
|-----------------------------------|----------------------------------------|-------------------------------|---------------------------------------------|-------------------------------|----------------------------------------|------------|
| $V_1\text{H}_2\text{O}$ (1, 4)   | (1, 4)                                 | -45.48                        | -57.57                                      | 66.13                         | -52.37                                 | yes        |
| $V_2\text{H}_2\text{O}$ (1, 1)   | (1, 1)                                 | -32.11                        | -39.28                                      | 26.44                         | -18.06                                 | yes        |
| $V_3\text{H}_2\text{O}$ (1, 2)   | (1, 2)                                 | -26.94                        | -44.71                                      | 40.65                         | -21.23                                 | yes        |
| $V_4\text{H}_2\text{O}$ (1, 1)   | (1, 1)                                 | -23.97                        | -42.08                                      | 38.36                         | -19.09                                 | yes        |
| $V_5\text{H}_2\text{O}$ (1, 2)   | (1, 2)                                 | -27.11                        | -45.22                                      | 42.88                         | -22.12                                 | yes        |
| $V_6\text{H}_2\text{O}$ (1, 3)   | (1, 3)                                 | -26.31                        | -43.54                                      | 40.94                         | -20.71                                 | yes        |
| $V_7\text{H}_2\text{O}$ (1, 0)   | (1, 0)                                 | -28.58                        | -44.42                                      | 41.77                         | -22.19                                 | yes        |
| $V_8\text{H}_2\text{O}$ (1, 1)   | (1, 1)                                 | -26.71                        | -41.58                                      | 39.86                         | -20.92                                 | yes        |
| $V_9\text{H}_2\text{O}$ (1, 0)   | (1, 0)                                 | -28.84                        | -44.40                                      | 42.77                         | -22.44                                 | yes        |
| $V_{10}\text{H}_2\text{O}$ (1, 1) | (1, 1)                               | -25.04                        | -44.06                                      | 44.99                         | -21.86                                 | yes        |
| $V_{11}\text{H}_2\text{O}$ (1, 0) | (1, 0)                               | -12001.32                     | -115.41                                     | 50.26                         | -11931.98                              | no         |
| $V_{12}\text{H}_2\text{O}$ (1, 1) | (1, 1)                               | -7949.85                      | -115.61                                     | 173.81                        | -8003.99                               | moderately |
| $V_{13}\text{H}_2\text{O}$ (1, 0) | (1, 0)                               | 7332.57                       | -48.34                                      | 49.85                         | 7335.27                                | no         |

(Charge, $\alpha$-$\beta$): (number net charge, number of spin-$\alpha$-spin-$\beta$ electrons)

$\Delta E_{tot} = \Delta E_{pauli} + \Delta E_{elstat} + \Delta E_{orb}$
S10 Reaction Coordinate of “$V_3^+ + 2\text{H}_2\text{O}$”

Supplementary Figure 17 Reaction coordinate of “$V_3^+ + 2\text{H}_2\text{O} \rightarrow V_3\text{O}_2\text{H}_2^+ + \text{H}_2$”. The energy values are relative to the entrance channel, calculated at BP86 /def2-TZVP level of theory.

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