Supporting Information

Desorption of Oxygen from Cationic Niobium Oxide Clusters Revealed by Gas Phase Thermal Desorption Spectrometry and DFT Calculations

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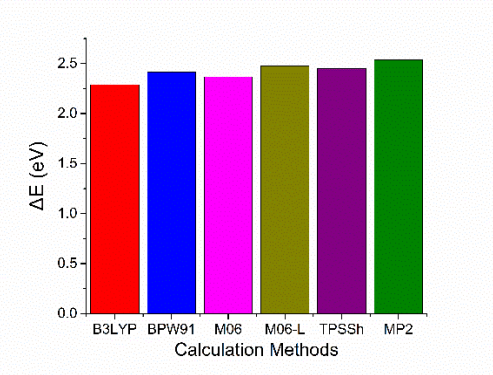

Figure S1. Binding energy of O_2 in $Nb_2O_6^+$, $\Delta E = E(Nb_2O_4^+) + E(O_2) - E(Nb_2O_6^+)$, calculated using different functionals, B3LYP, BPW91, M06, M06-L and TPSSh, and that calculated using MP2. There was no significant difference in the optimized stable structures of $Nb_2O_{4,6}^+$, except for $Nb_2O_4^+$ calculated using M06-L. However, the most stable structure given by M06-L is just 0.004 eV lower in energy than the second most stable structure that is given as the most stable structure by the other functionals. Moreover the difference of ΔE is at most 0.25 eV. Thus, B3LYP was adopted as a suitable functional in our calculations.

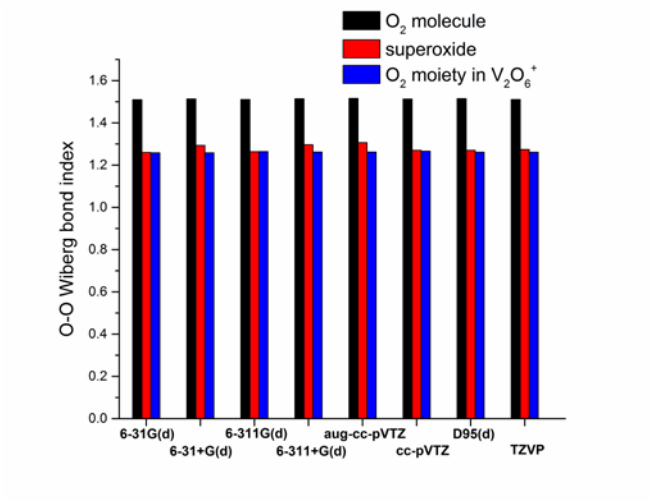

Figure S2. Wiberg bond index calculated using different basis sets (some basis sets with no diffuse functions were also used for comparison). In the present article, we assessed the O_2 moiety in terms of its bond length and by NBO analysis. Wiberg bond index was found to be independent of the basis sets, clearly supporting the experimental result that O_2 moieties of the most stable $M_2O_6^+$ and the metastable $M_2O_6^+$ have molecular O_2 and superoxide character, respectively.

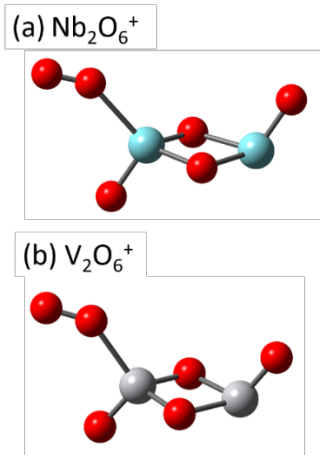

Figure S3. Metastable structures of $M_2O_6^+$ (M = V, Nb, (a) for Nb and (b) for V). All of their spin states are quartet. There are O_2 moieties in $M_2O_6^+$ having the bond nature of molecular O_2.

Table S1. Atomic coordinates (Å), natural charges, and Wiberg bond index matrix in the NAO basis of optimized $M_2O_x^+$ structures (M = V, Nb, x = 4, 6).
* O atoms of O_2 moiety in $M_2O_6^+$

$Nb_2O_4^+$
Atomic coordinates

Atom	X	Y	Z
Nb	1.423500	0.000000	−0.341388
Nb	−1.449179	−0.000000	0.324164
O	0.106446	−1.294932	0.022366
O	0.106446	1.294932	0.022364
O	−2.580513	−0.000001	−0.941894
O	2.499225	0.000001	0.985437

Natural charges

Atom	Natural charge
Nb	1.99597
Nb	1.81758
O	−0.84282
O	−0.84282
O	−0.57871
O	−0.54921

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6
1. Nb	0.0000	0.0998	1.1427	1.1427	0.0438	2.0393
2. Nb	0.0998	0.0000	0.6099	0.6099	2.0812	0.0422
3. O	1.1427	0.6099	0.0000	0.0252	0.0385	0.0786
4. O	1.1427	0.6099	0.0252	0.0000	0.0385	0.0786
5. O	0.0438	2.0812	0.0385	0.0385	0.0000	0.0055
6. O	2.0393	0.0422	0.0786	0.0786	0.0055	0.0000

$V_2O_4^+$
Atomic coordinates

Atom	X	Y	Z
V	1.296540	0.000067	−0.402348
V	−1.236521	−0.000300	0.405022
O	−0.098073	−1.212376	−0.013954
O	−0.098042	1.212146	−0.012794
O	−2.421216	0.000220	−0.596635
O	2.461764	−0.000218	0.608167

Natural charges

Atom	Natural charge
V	1.35620
V	1.26817
O	−0.56462
O	−0.56459
O	−0.21840
O	−0.27676

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6
1. V	0.0000	0.0820	0.6851	0.6851	0.0530	2.3384
2. V	0.0820	0.0000	1.3292	1.3292	2.2625	0.0513
3. O	0.6851	1.3292	0.0000	0.0423	0.1293	0.0590
4. O	0.6851	1.3292	0.0423	0.0000	0.1293	0.0590
5. O	0.0530	2.2625	0.1293	0.1293	0.0000	0.0070
6. O	2.3384	0.0513	0.0590	0.0590	0.0070	0.0000

$Nb_2O_6^+$

Atomic coordinates

Atom	X	Y	Z
Nb	1.008084	−0.190404	−0.159011
Nb	−1.975942	−0.121357	−0.002330
O	−0.628890	−0.146691	−1.332992
O	−0.545284	−0.163899	1.194955
O*	2.608250	1.156871	−0.165948
O	1.641245	−1.762888	−0.110878
O	−2.579238	1.471781	0.044601
O*	2.176455	1.104904	1.073530

Natural charges

Atom	Natural charge
Nb	1.81835
Nb	2.04009
O	−0.80733
O	−0.77185
O*	−0.15155
O	−0.49357
O	−0.53146
O*	−0.10269

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8
1. Nb	0.0000	0.0828	0.7586	0.6646	0.5999	2.1380	0.0445	0.5259
2. Nb	0.0828	0.0000	1.0534	1.1796	0.0077	0.0534	2.0599	0.0055
3. O	0.7586	1.0534	0.0000	0.0303	0.0116	0.0425	0.0722	0.0178
4. O	0.6646	1.1796	0.0303	0.0000	0.0173	0.0346	0.0822	0.0150
5. O*	0.5999	0.0077	0.0116	0.0173	0.0000	0.0250	0.0019	1.2423
6. O	2.1380	0.0534	0.0425	0.0346	0.0250	0.0000	0.0054	0.0282
7. O	0.0445	2.0599	0.0722	0.0822	0.0019	0.0054	0.0000	0.0016
8. O*	0.5259	0.0055	0.0178	0.0150	1.2423	0.0282	0.0016	0.0000

$V_2O_6^+$

Atomic coordinates

Atom	X	Y	Z
V	1.112573	−0.190438	−0.063309
V	−1.559025	−0.060989	0.057881
O	−0.353415	−0.454986	−1.128127
O	−0.310344	0.284461	1.147325
O*	2.527021	0.961470	−0.617576
O	1.728705	−1.518886	0.400355
O	−2.301341	1.247410	−0.311482
O*	2.183006	1.319999	0.057881

Natural charges

Atom	Natural charge
V	0.89298
V	1.30051
O	−0.47594
O	−0.43823
O*	−0.00296
O	−0.10084
O	−0.20032
O*	0.02479

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8
1. V	0.0000	0.0920	0.9456	0.7185	0.7294	2.4291	0.0538	0.6299
2. V	0.0920	0.0000	1.1719	1.4099	0.0084	0.0604	2.2777	0.0079
3. O	0.9456	1.1719	0.0000	0.0383	0.0201	0.0759	0.1149	0.0307
4. O	0.7185	1.4099	0.0383	0.0000	0.0252	0.0542	0.1395	0.0279
5. O*	0.7294	0.0084	0.0201	0.0252	0.0000	0.0443	0.0029	1.2641
6. O	2.4291	0.0604	0.0759	0.0542	0.0443	0.0000	0.0064	0.0458
7. O	0.0538	2.2777	0.1149	0.1395	0.0029	0.0064	0.0000	0.0030
8. O*	0.6299	0.0079	0.0307	0.0279	1.2641	0.0458	0.0030	0.0000

Table S2. Atomic coordinates (Å), natural charges, and Wiberg bond index matrix in the NAO basis of optimized $M_3O_x^+$ structures (M = V, Nb, x = 6, 8).

$Nb_3O_6^+$

Atomic coordinates

Atom	X	Y	Z
Nb	0.103644	−1.766595	−0.173170
Nb	−1.595189	0.805352	−0.151599
Nb	1.485005	0.992842	−0.134198
O	−1.642594	−1.065874	−0.654498
O	−2.013513	0.987806	1.490818
O	−0.119952	1.977194	−0.610459
O	0.123203	−2.248576	1.461643
O	1.759281	−0.862903	−0.632509
O	1.862199	1.224834	1.511499

Natural charges

Atom	Natural charge
Nb	1.72295
Nb	1.72231
Nb	1.72378
O	−0.86477
O	−0.52499
O	−0.86545
O	−0.52434
O	−0.86505
O	−0.52443

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8	9
1. Nb	0.0000	0.4411	0.4418	0.8504	0.0351	0.0313	2.0841	0.8529	0.0350
2. Nb	0.4411	0.0000	0.4398	0.8564	2.0826	0.8547	0.0350	0.0310	0.0349
3. Nb	0.4418	0.4398	0.0000	0.0311	0.0350	0.8509	0.0351	0.8539	2.0841
4. O	0.8504	0.8564	0.0311	0.0000	0.0595	0.0271	0.0592	0.0267	0.0045
5. O	0.0351	2.0826	0.0350	0.0595	0.0000	0.0595	0.0023	0.0045	0.0022
6. O	0.0313	0.8547	0.8509	0.0271	0.0595	0.0000	0.0045	0.0267	0.0593
7. O	2.0841	0.0350	0.0351	0.0592	0.0023	0.0045	0.0000	0.0592	0.0022
8. O	0.8529	0.0310	0.8539	0.0267	0.0045	0.0267	0.0592	0.0000	0.0593
9. O	0.0350	0.0349	2.0841	0.0045	0.0022	0.0593	0.0022	0.0593	0.0000

$V_3O_6^+$

Atomic coordinates

Atom	X	Y	Z
V	−0.955923	−1.171404	0.051726
V	1.566209	−0.184789	0.093436
V	−0.553998	1.611919	0.195550
O	0.541005	−1.599320	0.788647
O	0.015540	0.035216	−0.983495
O	2.970285	−0.350572	−0.548584
O	1.244670	1.315246	0.829480
O	−1.732069	0.059309	0.825522
O	−0.998860	2.857293	−0.598968

Natural charges

Atom	Natural charge
V	1.31822
V	1.03829
V	1.19318
O	−0.53938
O	−0.59691
O	−0.17740
O	−0.50476
O	−0.52879
O	−0.20246

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8	9
1. V	0.0000	0.1415	0.6929	1.2387	0.8314	0.0417	0.0400	1.5695	0.0334
2. V	0.1415	0.0000	0.1428	0.7917	0.7111	2.3068	1.3567	0.0356	0.0313
3. V	0.6929	0.1428	0.0000	0.0671	0.5694	0.0315	0.7023	0.5426	2.4046
4. O	1.2387	0.7917	0.0671	0.0000	0.0160	0.0726	0.0401	0.1021	0.0022
5. O	0.8314	0.7111	0.5694	0.0160	0.0000	0.0623	0.0141	0.0238	0.0346
6. O	0.0417	2.3068	0.0315	0.0726	0.0623	0.0000	0.1304	0.0042	0.0056
7. O	0.0400	1.3567	0.7023	0.0401	0.0141	0.1304	0.0000	0.0126	0.0699
8. O	1.5695	0.0356	0.5426	0.1021	0.0238	0.0042	0.0126	0.0000	0.0418
9. O	0.0334	0.0313	2.4046	0.0022	0.0346	0.0056	0.0699	0.0418	0.0000

$Nb_3O_8^+$

Atomic coordinates

Atom	X	Y	Z
Nb	1.609195	−0.064074	0.447721
Nb	−1.012473	1.607136	0.093815
Nb	−1.206306	−1.410831	0.217739
O	0.784579	1.603730	0.953124
O	−0.145649	−0.003489	−0.824197
O	−1.500116	2.777829	−1.049529
O	−2.247345	0.192330	0.672362
O	2.750960	−0.198498	−1.081925
O	0.581487	−1.567228	1.081862
O	−1.844233	−2.596393	−0.832534
O	3.497007	−0.195907	0.165753

Natural charges

Atom	Natural charge
Nb	1.93793
Nb	1.99497
Nb	1.99502
O	−0.82340
O	−0.83429
O	−0.52280
O	−0.82898
O	−0.27410
O	−0.82357
O	−0.52270
O	−0.29808

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8	9	10	11
1. Nb	0.0000	0.0682	0.0681	0.9796	0.4836	0.0305	0.0202	1.0471	0.9792	0.0305	1.0486
2. Nb	0.0682	0.0000	0.0819	0.7746	0.6600	2.0577	0.8762	0.0150	0.0233	0.0373	0.0148
3. Nb	0.0681	0.0819	0.0000	0.0233	0.6592	0.0373	0.8766	0.0149	0.7748	2.0577	0.0148
4. O	0.9796	0.7746	0.0233	0.0000	0.0140	0.0566	0.0220	0.0417	0.0312	0.0020	0.0372
5. O	0.4836	0.6600	0.6592	0.0140	0.0000	0.0403	0.0138	0.0103	0.0140	0.0402	0.0233
6. O	0.0305	2.0577	0.0373	0.0566	0.0403	0.0000	0.0641	0.0029	0.0020	0.0043	0.0027
7. O	0.0202	0.8762	0.8766	0.0220	0.0138	0.0641	0.0000	0.0007	0.0220	0.0641	0.0006
8. O	1.0471	0.0150	0.0149	0.0417	0.0103	0.0029	0.0007	0.0000	0.0417	0.0029	0.9889
9. O	0.9792	0.0233	0.7748	0.0312	0.0140	0.0020	0.0220	0.0417	0.0000	0.0566	0.0371
10. O	0.0305	0.0373	2.0577	0.0020	0.0402	0.0043	0.0641	0.0029	0.0566	0.0000	0.0026
11. O	1.0486	0.0148	0.0148	0.0372	0.0233	0.0027	0.0006	0.9889	0.0371	0.0026	0.0000

$V_3O_8^+$

Atomic coordinates

Atom	X	Y	Z
V	1.514419	−0.303911	0.353437
V	−0.965966	−1.213163	0.046647
V	−0.611663	1.436064	0.859679
O	0.608371	−1.819204	0.641499
O	0.039944	0.178982	−0.683275
O	2.904527	−0.361432	−0.318526
O	1.002065	1.063252	1.434215
O	−1.812891	−2.090728	−0.901922
O	−1.690859	0.076022	1.101497
O	−1.227611	3.047940	1.061012
O	−0.947145	2.733382	−0.275087

Natural charges

Atom	Natural charge
V	1.09879
V	1.09892
V	0.99962
O	−0.44993
O	−0.48858
O	−0.13256
O	−0.44625
O	−0.13258
O	−0.44629
O	−0.04493
O	−0.05620

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8	9	10	11
1. V	0.0000	0.1005	0.0829	1.0514	0.8265	2.3295	0.9088	0.0439	0.0307	0.0196	0.0193
2. V	0.1005	0.0000	0.0829	1.0519	0.8262	0.0439	0.0307	2.3295	0.9085	0.0196	0.0193
3. V	0.0829	0.0829	0.0000	0.0240	0.4833	0.0347	1.1837	0.0347	1.1840	1.2569	1.2005
4. O	1.0514	1.0519	0.0240	0.0000	0.0144	0.1027	0.0394	0.1028	0.0394	0.0011	0.0013
5. O	0.8265	0.8262	0.4833	0.0144	0.0000	0.0760	0.0165	0.0760	0.0165	0.0336	0.0180
6. O	2.3295	0.0439	0.0347	0.1027	0.0760	0.0000	0.0903	0.0075	0.0032	0.0046	0.0042
7. O	0.9088	0.0307	1.1837	0.0394	0.0165	0.0903	0.0000	0.0032	0.0557	0.0604	0.0674
8. O	0.0439	2.3295	0.0347	0.1028	0.0760	0.0075	0.0032	0.0000	0.0903	0.0046	0.0042
9. O	0.0307	0.9085	1.1840	0.0394	0.0165	0.0032	0.0557	0.0903	0.0000	0.0604	0.0674
10. O	0.0196	0.0196	1.2569	0.0011	0.0336	0.0046	0.0604	0.0046	0.0604	0.0000	1.0292
11. O	0.0193	0.0193	1.2005	0.0013	0.0180	0.0042	0.0674	0.0042	0.0674	1.0292	0.0000

Table S3. Atomic coordinates for optimized $M_4O_x^+$ structures (M = V, Nb, x = 9, 11) (unit Å), natural charges and Wiberg bond index matrix in the NAO basis.

$Nb_4O_9^+$

Atomic coordinates

Atom	X	Y	Z
Nb	0.013987	−0.000128	2.177599
Nb	1.984032	−0.129990	−0.583609
Nb	−0.884939	1.786294	−0.561855
Nb	−1.109381	−1.656713	−0.564095
O	−0.947921	−1.435268	1.446967
O	−1.997024	−2.980468	−1.184669
O	0.771867	−1.577414	−1.070962
O	1.730656	−0.113540	1.430262
O	3.567885	−0.233751	−1.220749
O	−0.755352	1.548710	1.449693
O	−1.593543	3.213726	−1.182776
O	0.971702	1.464772	−1.066905
O	−1.763705	0.114604	−1.050046

Natural charges

Atom	Natural charge
Nb	1.87064
Nb	1.94694
Nb	1.94656
Nb	1.94702
O	−0.85589
O	−0.53203
O	−0.84928
O	−0.85590
O	−0.53199
O	−0.85573
O	−0.53166
O	−0.84933
O	−0.84935

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8	9	10	11	12	13
1. Nb	0.0000	0.0590	0.0593	0.0590	1.0803	0.0249	0.0150	1.0807	0.0249	1.0793	0.0249	0.0151	0.0151
2. Nb	0.0590	0.0000	0.0600	0.0600	0.0146	0.0168	0.8630	0.6601	2.0670	0.0146	0.0167	0.8636	0.0143
3. Nb	0.0593	0.0600	0.0000	0.0600	0.0147	0.0168	0.0143	0.0147	0.0168	0.6616	2.0674	0.8622	0.8624
4. Nb	0.0590	0.0600	0.0600	0.0000	0.6604	2.0670	0.8629	0.0146	0.0168	0.0146	0.0167	0.0143	0.8633
5. O	1.0803	0.0146	0.0147	0.6604	0.0000	0.0381	0.0151	0.0359	0.0028	0.0358	0.0029	0.0013	0.0151
6. O	0.0249	0.0168	0.0168	2.0670	0.0381	0.0000	0.0596	0.0028	0.0048	0.0028	0.0048	0.0027	0.0597
7. O	0.0150	0.8630	0.0143	0.8629	0.0151	0.0596	0.0000	0.0151	0.0596	0.0013	0.0027	0.0215	0.0215
8. O	1.0807	0.6601	0.0147	0.0146	0.0359	0.0028	0.0151	0.0000	0.0381	0.0359	0.0029	0.0151	0.0013
9. O	0.0249	2.0670	0.0168	0.0168	0.0028	0.0048	0.0596	0.0381	0.0000	0.0028	0.0048	0.0597	0.0027
10. O	1.0793	0.0146	0.6616	0.0146	0.0358	0.0028	0.0013	0.0359	0.0028	0.0000	0.0382	0.0151	0.0151
11. O	0.0249	0.0167	2.0674	0.0167	0.0029	0.0048	0.0027	0.0029	0.0048	0.0382	0.0000	0.0596	0.0596
12. O	0.0151	0.8636	0.8622	0.0143	0.0013	0.0027	0.0215	0.0151	0.0597	0.0151	0.0596	0.0000	0.0214
13. O	0.0151	0.0143	0.8624	0.8633	0.0151	0.0597	0.0215	0.0013	0.0027	0.0151	0.0596	0.0214	0.0000

$V_4O_9^+$

Atomic coordinates

Atom	X	Y	Z
V	−0.001970	0.000718	2.045545
V	1.732329	−0.417634	−0.474570
V	−0.504352	1.708212	−0.479002
V	−1.228175	−1.291266	−0.477985
O	−1.088487	−1.143209	1.363704
O	−2.227726	−2.344749	−1.007508
O	0.466397	−1.578314	−0.951038
O	1.533030	−0.369870	1.365350
O	3.146424	−0.758791	−0.997315
O	−0.447988	1.513973	1.361581
O	−0.914141	3.102328	−1.005968
O	1.136407	1.193379	−0.949604
O	−1.601534	0.385476	−0.955542

Natural charges

Atom	Natural charge
V	1.38438
V	1.05115
V	1.05179
V	1.05204
O	−0.55277
O	−0.13156
O	−0.49560
O	−0.55229
O	−0.13178
O	−0.55271
O	−0.13152
O	−0.49540
O	−0.49573

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8	9	10	11	12	13
1. V	0.0000	0.0613	0.0612	0.0612	1.2281	0.0264	0.0172	1.2256	0.0265	1.2252	0.0264	0.0172	0.0171
2. V	0.0613	0.0000	0.0821	0.0821	0.0194	0.0193	1.0228	0.8087	2.3548	0.0194	0.0193	1.0238	0.0186
3. V	0.0612	0.0821	0.0000	0.0822	0.0194	0.0193	0.0186	0.0194	0.0194	0.8085	2.3553	1.0232	1.0224
4. V	0.0612	0.0821	0.0822	0.0000	0.8057	2.3553	1.0239	0.0193	0.0194	0.0194	0.0194	0.0186	1.0242
5. O	1.2281	0.0194	0.0194	0.8057	0.0000	0.0640	0.0268	0.0559	0.0043	0.0559	0.0043	0.0028	0.0269
6. O	0.0264	0.0193	0.0193	2.3553	0.0640	0.0000	0.0966	0.0043	0.0070	0.0043	0.0070	0.0041	0.0966
7. O	0.0172	1.0228	0.0186	1.0239	0.0268	0.0966	0.0000	0.0269	0.0967	0.0028	0.0041	0.0360	0.0361
8. O	1.2256	0.8087	0.0194	0.0193	0.0559	0.0043	0.0269	0.0000	0.0641	0.0557	0.0043	0.0270	0.0028
9. O	0.0265	2.3548	0.0194	0.0194	0.0043	0.0070	0.0967	0.0641	0.0000	0.0043	0.0070	0.0967	0.0041
10. O	1.2252	0.0194	0.8085	0.0194	0.0559	0.0043	0.0028	0.0557	0.0043	0.0000	0.0641	0.0269	0.0269
11. O	0.0264	0.0193	2.3553	0.0194	0.0043	0.0070	0.0041	0.0043	0.0070	0.0641	0.0000	0.0966	0.0965
12. O	0.0172	1.0238	1.0232	0.0186	0.0028	0.0041	0.0360	0.0270	0.0967	0.0269	0.0966	0.0000	0.0360
13. O	0.0171	0.0186	1.0224	1.0242	0.0269	0.0966	0.0361	0.0028	0.0041	0.0269	0.0965	0.0360	0.0000

$Nb_4O_{11}^+$

Atomic coordinates

Atom	X	Y	Z
Nb	−0.711393	2.022153	0.001008
Nb	2.007420	−0.198289	−0.002068
Nb	−0.937781	−0.931794	−1.731147
Nb	−0.935553	−0.935174	1.729272
O	1.089673	−0.906262	1.452221
O	3.988756	0.589454	−0.005809
O	1.225438	1.532284	0.003186
O	−1.303192	0.958218	1.536629
O	−1.122106	3.682315	0.003936
O	−1.473360	−1.653052	−0.001194
O	−1.627134	−1.682798	−3.103202
O	−1.306471	0.960928	−1.536606
O	1.088459	−0.902197	−1.457150
O	−1.623219	−1.688233	3.101082
O	4.036186	−0.735130	0.011949

Natural charges

Atom	Natural charge
Nb	1.96380
Nb	1.92145
Nb	1.96518
Nb	1.96545
O	−0.80526
O	−0.1080
O	−0.81863
O	−0.84569
O	−0.53336
O	−0.85172
O	−0.52852
O	−0.84581
O	−0.80553
O	−0.52867
O	−0.14462

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1. Nb	0.0000	0.0516	0.0589	0.0589	0.0128	0.0044	0.7055	0.8327	2.0673	0.0152	0.0166	0.8310	0.0128	0.0166	0.007
2. Nb	0.0516	0.0000	0.0492	0.0493	1.1974	0.5256	1.0545	0.0160	0.0184	0.0147	0.0227	0.0158	1.1983	0.0227	0.5875
3. Nb	0.0589	0.0492	0.0000	0.0585	0.0135	0.0050	0.0135	0.0146	0.0169	0.8612	2.0726	0.9022	0.6013	0.0166	0.0027
4. Nb	0.0589	0.0493	0.0585	0.0000	0.6024	0.0051	0.0135	0.9008	0.0169	0.8615	0.0166	0.0145	0.0136	2.0724	0.0027
5. O	0.0128	1.1974	0.0135	0.6024	0.0000	0.0265	0.0397	0.0130	0.0024	0.0148	0.0029	0.0024	0.0434	0.0355	0.0152
6. O	0.0044	0.5256	0.0050	0.0051	0.0265	0.0000	0.0151	0.0004	0.0012	0.0009	0.0012	0.0004	0.0261	0.0013	1.2266
7. O	0.7055	1.0545	0.0135	0.0135	0.0397	0.0151	0.0000	0.0150	0.0456	0.0021	0.0028	0.0150	0.0396	0.0028	0.0357
8. O	0.8327	0.0160	0.0146	0.9008	0.0130	0.0004	0.0150	0.0000	0.0577	0.0227	0.0030	0.0191	0.0024	0.0627	0.0003
9. O	2.0673	0.0184	0.0169	0.0169	0.0024	0.0012	0.0456	0.0577	0.0000	0.0028	0.0045	0.0576	0.0024	0.0045	0.0033
10. O	0.0152	0.0147	0.8612	0.8615	0.0148	0.0009	0.0021	0.0227	0.0028	0.0000	0.0597	0.0227	0.0148	0.0597	0.0008
11. O	0.0166	0.0227	2.0726	0.0166	0.0029	0.0012	0.0028	0.0030	0.0045	0.0597	0.0000	0.0628	0.0353	0.0047	0.0005
12. O	0.8310	0.0158	0.9022	0.0145	0.0024	0.0004	0.0150	0.0191	0.0576	0.0227	0.0628	0.0000	0.0131	0.0030	0.0003
13. O	0.0128	1.1983	0.6013	0.0136	0.0434	0.0261	0.0396	0.0024	0.0024	0.0148	0.0353	0.0131	0.0000	0.0029	0.0156
14. O	0.0166	0.0227	0.0166	2.0724	0.0355	0.0013	0.0028	0.0627	0.0045	0.0597	0.0047	0.0030	0.0029	0.0000	0.0005
15. O	0.0079	0.5875	0.0027	0.0027	0.0152	1.2266	0.0357	0.0003	0.0033	0.0008	0.0005	0.0003	0.0156	0.0005	0.0000

$V_4O_{11}^+$

Atomic coordinates

Atom	X	Y	Z
V	0.659080	1.818966	−0.017645
V	0.922678	−0.808186	1.554669
V	−1.748010	−0.208098	0.003642
V	0.919780	−0.836697	−1.540987
O	−0.957705	−0.848793	−1.340278
O	−3.574442	0.494499	0.001785
O	−1.096829	1.445641	−0.012889
O	1.239389	0.889451	−1.455899
O	0.981629	3.330176	−0.031786
O	1.449261	−1.530075	0.013094
O	1.529510	−1.470330	2.811569
O	1.242038	0.915903	1.436413
O	−0.956048	−0.824438	1.357232
O	1.523176	−1.522445	−2.786838
O	−3.561721	−0.807449	0.007224

Natural charges

Atom	Natural charge
V	1.05440
V	1.06396
V	0.93604
V	1.06382
O	−0.42056
O	0.03013
O	−0.45948
O	−0.48691
O	−0.13082
O	−0.49952
O	−0.12635
O	−0.48701
O	−0.42028
O	−0.12633
O	0.00891

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1. V	0.0000	0.0799	0.0690	0.0799	0.0183	0.0059	0.9681	0.9331	2.3553	0.0187	0.0201	0.9326	0.0183	0.0201	0.0102
2. V	0.0799	0.0000	0.0638	0.0808	0.0167	0.0059	0.0183	0.0185	0.0201	1.0208	2.3599	1.1226	0.6845	0.0194	0.0032
3. V	0.0690	0.0638	0.0000	0.0639	1.4580	0.6361	1.0891	0.0217	0.0185	0.0166	0.0244	0.0216	1.4604	0.0244	0.7276
4. V	0.0799	0.0808	0.0639	0.0000	0.6864	0.0060	0.0183	1.1222	0.0201	1.0194	0.0194	0.0185	0.0167	2.3599	0.0032
5. O	0.0183	0.0167	1.4580	0.6864	0.0000	0.0433	0.0604	0.0229	0.0038	0.0233	0.0045	0.0047	0.0848	0.0535	0.0296
6. O	0.0059	0.0059	0.6361	0.0060	0.0433	0.0000	0.0305	0.0008	0.0023	0.0018	0.0017	0.0008	0.0430	0.0017	1.2436
7. O	0.9681	0.0183	1.0891	0.0183	0.0604	0.0305	0.0000	0.0289	0.0863	0.0038	0.0044	0.0289	0.0605	0.0044	0.0511
8. O	0.9331	0.0185	0.0217	1.1222	0.0229	0.0008	0.0289	0.0000	0.0876	0.0406	0.0045	0.0282	0.0047	0.1057	0.0005
9. O	2.3553	0.0201	0.0185	0.0201	0.0038	0.0023	0.0863	0.0876	0.0000	0.0040	0.0066	0.0876	0.0038	0.0066	0.0049
10. O	0.0187	1.0208	0.0166	1.0194	0.0233	0.0018	0.0038	0.0406	0.0040	0.0000	0.0968	0.0407	0.0232	0.0967	0.0017
11. O	0.0201	2.3599	0.0244	0.0194	0.0045	0.0017	0.0044	0.0045	0.0066	0.0968	0.0000	0.1058	0.0533	0.0068	0.0006
12. O	0.9326	1.1226	0.0216	0.0185	0.0047	0.0008	0.0289	0.0282	0.0876	0.0407	0.1058	0.0000	0.0229	0.0045	0.0005
13. O	0.0183	0.6845	1.4604	0.0167	0.0848	0.0430	0.0605	0.0047	0.0038	0.0232	0.0533	0.0229	0.0000	0.0045	0.0298
14. O	0.0201	0.0194	0.0244	2.3599	0.0535	0.0017	0.0044	0.1057	0.0066	0.0967	0.0068	0.0045	0.0045	0.0000	0.0006
15. O	0.0102	0.0032	0.7276	0.0032	0.0296	1.2436	0.0511	0.0005	0.0049	0.0017	0.0006	0.0005	0.0298	0.0006	0.0000

Table S4. Atomic coordinates for metastable $M_2O_6^+$ structures (M = V, Nb) (unit Å), natural charges and Wiberg bond index matrix in the NAO basis.
* O atoms of O_2 moiety in $M_2O_6^+$

metastable $Nb_2O_6^+$

Atomic coordinates

Atom	X	Y	Z
Nb	0.973432	−0.301002	−0.000061
Nb	−1.955630	−0.015108	0.000047
O	−0.398731	−0.236486	−1.299530
O	−0.398640	−0.236551	1.299504
O*	2.790615	1.206599	−0.000066
O	1.634681	−1.879641	−0.000116
O	−2.622937	1.549459	0.000106
O*	3.991036	1.289660	0.000098

Natural charges

Atom	Natural charge
Nb	1.81549
Nb	1.80861
O	−0.82514
O	−0.82514
O*	−0.09891
O	−0.53677
O	−0.58866
O*	0.25051

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8
1. Nb	0.0000	0.1061	1.1477	1.1477	0.2502	2.0536	0.0442	0.0151
2. Nb	0.1061	0.0000	0.6228	0.6228	0.0023	0.0478	2.0653	0.0007
3. O	1.1477	0.6228	0.0000	0.0218	0.0056	0.0772	0.0401	0.0017
4. O	1.1477	0.6228	0.0218	0.0000	0.0056	0.0772	0.0401	0.0017
5. O*	0.2502	0.0023	0.0056	0.0056	0.0000	0.0075	0.0003	1.4915
6. O	2.0536	0.0478	0.0772	0.0772	0.0075	0.0000	0.0055	0.0024
7. O	0.0442	2.0653	0.0401	0.0401	0.0003	0.0055	0.0000	0.0003
8. O*	0.0151	0.0007	0.0017	0.0017	1.4915	0.0024	0.0003	0.0000

metastable $V_2O_6^+$

Atomic coordinates

Atom	X	Y	Z
V	1.927046	0.033683	0.000102
V	−0.700972	0.388232	−0.000146
O	0.512553	0.279347	−1.216045
O	0.512419	0.279963	1.215947
O*	−2.267536	−1.080999	0.000110
O	−1.377785	1.787536	−0.000542
O	2.569894	−1.371422	0.000489
O*	−3.469645	−1.119362	0.000175

Natural charges

Atom	Natural charge
V	1.34874
V	0.98546
O	−0.53240
O	−0.53241
O*	−0.05173
O	−0.19219
O	−0.29186
O*	0.26640

Wiberg bond index matrix in the NAO basis

Atom	1	2	3	4	5	6	7	8
1. V	0.0000	0.0906	0.6963	0.6963	0.0028	0.0576	2.3198	0.0011
2. V	0.0906	0.0000	1.3535	1.3535	0.3313	2.2966	0.0517	0.0159
3. O	0.6963	1.3535	0.0000	0.0360	0.0087	0.1260	0.0613	0.0014
4. O	0.6963	1.3535	0.0360	0.0000	0.0087	0.1260	0.0613	0.0014
5. O*	0.0028	0.3313	0.0087	0.0087	0.0000	0.0117	0.0003	1.4946
6. O	0.0576	2.2966	0.1260	0.1260	0.0117	0.0000	0.0067	0.0028
7. O	2.3198	0.0517	0.0613	0.0613	0.0003	0.0067	0.0000	0.0002
8. O*	0.0011	0.0159	0.0014	0.0014	1.4946	0.0028	0.0002	0.0000

Complete author list of Ref 23

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