

**Electronic Supplementary Information**

**Transition-metal solvated-electron precursors:  
Diffuse and 3d electrons in  $V(NH_3)_6^{0,\pm}$**

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### Detailed analysis on the excited states of V(NH<sub>3</sub>)<sub>6</sub>

CASSCF and CASPT2 excited-state energies at the optimal C<sub>2v</sub> structure for the ground <sup>4</sup>A<sub>2g</sub> state of Figure 1 are tabulated in Table 4. The 3d orbitals of vanadium split into two groups of nearly degenerate orbitals because of the pseudo-octahedral structure of V(NH<sub>3</sub>)<sub>6</sub>. The approximate t<sub>2g</sub> group consists of the three 3d orbitals which have vanishing amplitudes on the V-N axes, whereas its e<sub>g</sub> counterpart has two orbitals with high amplitudes aligned with the V-N axes that are destabilized by σ\* anti-bonding phase relationships. All five orbitals are illustrated in Figure 4 along with selected 1s, 1p and 1d outer orbitals.

The ground state has a t<sub>2g</sub><sup>3</sup>1s<sup>2</sup> electronic configuration with three t<sub>2g</sub> electrons coupled into a quartet (<sup>4</sup>A<sub>2g</sub>). The lowest states pertain to transitions between diffuse orbitals. Several states with dominant 1s<sup>1</sup>1p<sup>1</sup>, 1p<sup>2</sup> and 1s<sup>1</sup>1d<sup>1</sup> configurations retain their three, quartet-coupled electrons in t<sub>2g</sub> orbitals.

For <sup>6,4,2</sup>T<sub>2u</sub> states, the chief configurations result from coupling a <sup>4</sup>A<sub>2g</sub> multiplet arising from the inner t<sub>2g</sub><sup>3</sup> configuration to the nine states of the <sup>3</sup>P term generated by 1s<sup>1</sup>1p<sup>1</sup>. Because these states are closely spaced, with 0.541 ≤ T<sub>e</sub> ≤ 0.573, couplings between inner and outer orbitals must be weak. Averages of the sextet, quartet and doublet energies are 0.55-0.56 eV above the ground state.

When two diffuse electrons are in a 1p<sup>2</sup> configuration, <sup>3</sup>P, <sup>1</sup>D and <sup>1</sup>S terms result. In <sup>6,2</sup>T<sub>2g</sub> states, inner <sup>4</sup>A<sub>2g</sub> and outer <sup>3</sup>P terms from 1p<sup>2</sup> electrons are coupled to each other. Outer electrons in 1s<sup>1</sup>1d<sup>1</sup> configurations produce <sup>3</sup>D and <sup>1</sup>D terms. The former term couples with the inner <sup>4</sup>A<sub>2g</sub> multiplet to produce <sup>6,2</sup>T<sub>1g</sub> and <sup>6,2</sup>E<sub>g</sub> states. In the remaining quartets with outer-outer excitations, more complicated configuration mixing that descends from more than one of the three outer-electron terms results.

The first t<sub>2g</sub> → e<sub>g</sub> transitions to <sup>4</sup>T<sub>2g</sub> states occur at ~1.75 eV with CASPT2. No 3d ↔ diffuse transitions in the first forty-five states of V(NH<sub>3</sub>)<sub>6</sub> up to approximately 2.0 eV were found.

Table 4 lists both CASSCF and CASPT2 excitation energies. The latter are consistently larger by an averaged difference of δE = 0.236 eV. This value is close to the difference found for Li(NH<sub>3</sub>)<sub>4</sub> and Na(NH<sub>3</sub>)<sub>4</sub>, where excitations between only outer orbitals are present.<sup>1</sup> In cases where CASPT2 failed to converge, an estimated value is obtained by adding δE to the CASSCF result.

## Detailed analysis on the excited states of $V(NH_3)_6^+$

As an electron departs from the outer  $1s$  orbital, the ground state configuration of the cation is  $t_{2g}^3 ({}^4A_{2g}) 1s^1 ({}^2S)$ . Spin coupling between  $t_{2g}^3 ({}^4A_{2g})$  and  $1s^1 ({}^2S)$  generates  ${}^3A_{2g}$  and  ${}^5A_{2g}$  states which are practically degenerate (See Table 5; the optimized quintet's structure is used in calculations of vertical excitation energies). CASSCF and P3+ favor the quintet state by 0.016 and 0.012 eV, but CASPT2 favors the triplet by only 0.004 eV. Close agreement between wavefunction and electron-propagator results confirms the one-electron character of the electron detachment from the ground state of  $V(NH_3)_6$ .

As in the neutral system, the first excited states are created via  $1s \rightarrow 1p$  promotion. These  ${}^5T_{2u}$  and  ${}^3T_{2u}$  states are also nearly degenerate with their six spatial components lying 0.972–1.003 (CASPT2) or 0.994–1.012 (P3+) eV above the ground state. Such agreement between CASPT2 and P3+ results supports the  $1s \rightarrow 1p$  description of these excitations.

Next, transitions only within the 3d-shell take place. At first, a  $t_{2g}$  electron moves to an  $e_g$  orbital. The resulting  ${}^4T_{2g} (t_{2g}^2 e_g^1)$  state couples with the  $1s^1$  electron to produce the nearly degenerate  ${}^3T_{2g}$  and  ${}^5T_{2g}$  states. The next states involve an internal  $t_{2g}$  transition. The  $t_{2g}^3$  electrons are coupled to a doublet, making a five-fold degenerate state that resembles  ${}^2D (2s^2 2p^3)$  in the nitrogen atom. Under  $O_h$  symmetry, these five components split into  ${}^2T_{2g} + {}^2E_g$ , which combined with diffuse  ${}^2S (1s^1)$ , give the  ${}^1,{}^3T_{2g} + {}^1,{}^3E_g$  states in the 1.821 - 1.922 eV range.

The last manifold of states studied with CASPT2,  ${}^3,{}^5T_{1g} + {}^3,{}^5E_g$ , is related to the diffuse  $1s \rightarrow 1d$  transition from the ground state. Small splittings between twin triplet and quintet states for  $V(NH_3)_6^+$  are an additional indication of the weak spin coupling between inner and outer electrons. P3+ and CASPT2 results again are in close agreement and confirm the one-electron character of this set of transitions.

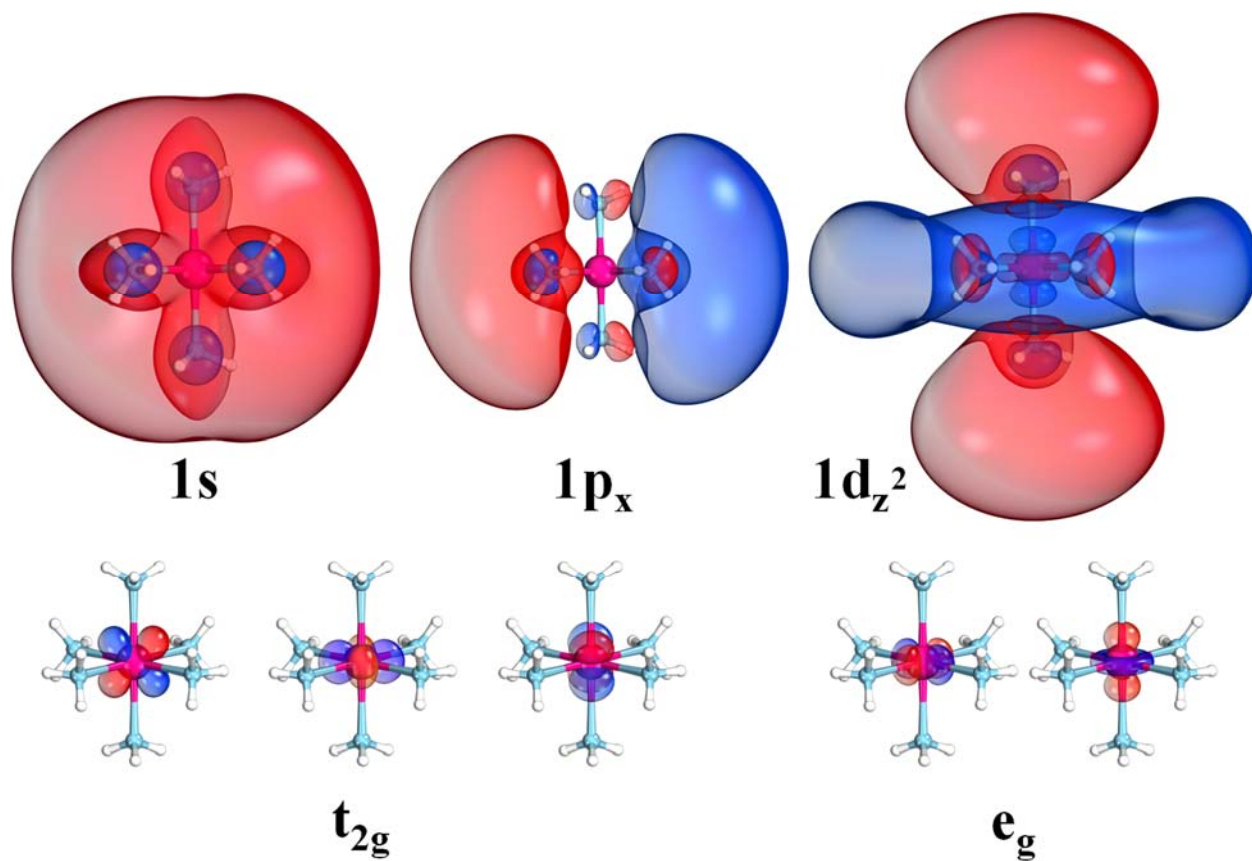
Excitations to higher diffuse orbitals were also calculated with the P3+ approach. Excitations to triplets and quintets with  $t_{2g}^3 2s^1 ({}^3,{}^5A_{2g})$ ,  $t_{2g}^3 1f^1 ({}^3,{}^5A_{1u}, {}^3,{}^5T_{1u}, {}^3,{}^5T_{2u})$ , and  $t_{2g}^3 2p^1 ({}^3,{}^5T_{2u})$  electronic configurations were obtained. These states lie between 2.387 and 3.260 eV with a  $2s^1 \approx 1f^1 < 2p^1$  energy order (see Table 5). Non-spherical symmetry allows two  $1f^1$  states,  ${}^3,{}^5A_{1u}$ , to lie below  $2s^1$  ones ( ${}^3,{}^5A_{2g}$ ). Similar interleaving was observed for  $Be(NH_3)_4$ .<sup>2</sup> As a result, the Aufbau principle reported here for  $V(NH_3)_6^+$  is identical to that of  $Be(NH_3)_4$ .<sup>2</sup> Representative Dyson orbitals for electron attachment to the dication are shown in Figure 7 for quintet states. For triplet states, the same shapes of Dyson orbitals were obtained and therefore

the labels numbering Dyson orbitals in the last column of Table 5 are identical for quintet and corresponding triplet states.

Dynamic correlation effects differ with respect to inner-electron configurations. CASPT2 predicts larger  $T_e$  values than CASSCF by an average of 0.278 eV for states with  $t_{2g}^3$  ( $^4A_{2g}$ ) configurations. The corresponding shift for the neutral complex is 0.236 eV (see Section IIIB). This trend is diminished in the six  $T_e$  values for  $^{3,5}T_{2g}$  states with  $t_{2g}^2 e_g^1$  ( $^4T_{2g}$ ) character, where the dynamic correlation shifts are  $0.050 \pm 0.011$  eV, with an average of 0.053 eV. In  $t_{2g}^3$  doublet ( $^2T_{2g}+^2E_g$ ) states, the opposite effect is obtained, for CASPT2 values are lower than CASSCF ones by  $0.206 \pm 0.017$  eV, with an average of 0.212 eV.

Because dynamic electron correlation effects are similar for the cationic and neutral systems with  $t_{2g}^3$  ( $^4A_{2g}$ ) states, the 0.053 eV correction may be added to the highest  $^4T_{2g}$  state components of Table 4 for  $V(NH_3)_6$ . This state has a  $t_{2g}^2 e_g^1$  ( $^4T_{2g}$ ) character and CASPT2 calculations were not possible for its components.

Excitation energies for states calculated with CASPT2 and P3+ are in very good agreement. The two sets of values differ on average by  $\sim 0.02$  eV or  $\sim 1.5\%$  (see Table 5). Consideration of V 3s and 3p electron correlation in geometry optimization and in P3+ calculations increases  $T_e$  values by only 0.015 eV or  $\sim 1\%$ , on average. These results suggest that the inclusion of computationally expensive outer-core correlation can be avoided in future calculations for similar systems when 1% accuracy is sufficient.



**Figure S1.** All five inner 3d orbitals ( $t_{2g}$  and  $e_g$ ) and selected outer diffuse molecular orbitals of  $V(NH_3)_6$ .

**Table S1.** Cartesian coordinates (Å) for the  $V(\text{NH}_3)_{n=1-6}^{0,\pm}$  species optimized at MP2/cc-pVTZ(V,N) aug-cc-pVTZ(H).

$V(\text{NH}_3)$				$V(\text{NH}_3)^+$				$V(\text{NH}_3)^-$			
V	-0.70406	0.00000	0.00002	V	-0.69081	0.00000	0.00001	V	-0.72295	0.00001	0.00001
N	1.50638	-0.00005	0.00009	N	1.46786	0.00000	0.00005	N	1.53975	0.00003	-0.00001
H	1.88207	0.31178	-0.89345	H	1.87075	-0.01494	-0.93532	H	1.94947	-0.80830	-0.47548
H	1.88335	0.61795	0.71609	H	1.87137	0.81736	0.45447	H	1.95005	0.81581	-0.46205
H	1.88332	-0.92931	0.17641	H	1.87138	-0.80244	0.48033	H	1.95007	-0.00788	0.93749
$V(\text{NH}_3)_2$				$V(\text{NH}_3)_2^+$				$V(\text{NH}_3)_2^-$			
V	0.00000	0.00000	0.00000	V	0.00000	0.00000	0.00000	V	0.00000	0.00000	0.00000
N	0.00000	2.17887	0.00000	N	0.00000	2.19372	0.00000	N	0.00000	2.25317	0.00000
H	-0.94884	2.54923	0.00000	H	-0.93349	2.59777	0.00000	H	-0.94764	2.63059	0.00000
H	0.47608	2.54535	0.82264	H	0.46810	2.59469	0.00000	H	0.47496	2.62782	0.82132
N	0.00000	-2.17887	0.00000	N	0.00000	-2.19372	0.00000	N	-0.00000	-2.25317	0.00000
H	-0.47608	-2.54535	-0.82264	H	-0.46810	-2.59469	-0.80924	H	-0.47496	-2.62782	-0.82132
H	0.94884	-2.54923	0.00000	H	0.93349	-2.59777	0.00000	H	0.94764	-2.63059	0.00000
H	0.47608	-2.54535	0.82264	H	-0.46810	-2.59469	0.80924	H	-0.47496	-2.62782	0.82132
H	0.47608	2.54535	-0.82264	H	0.46810	2.59469	-0.80924	H	0.47496	2.62782	-0.82132
$V(\text{NH}_3)_3$				$V(\text{NH}_3)_3^+$				$V(\text{NH}_3)_3^-$			
V	0.02614	-0.43044	-0.00038	V	0.01888	-0.32016	-0.00005	V	-0.00142	-0.47323	-0.00010
N	2.22110	-0.41638	0.00039	N	2.22878	-0.59185	0.00014	N	2.21033	-0.40769	-0.00011
H	2.58991	0.06106	-0.82254	H	2.67241	-0.17466	-0.81348	H	2.59041	0.10042	-0.80360
H	2.58947	0.06036	0.82393	H	2.67253	-0.17261	0.81263	H	2.59042	0.10095	0.80305
N	-0.10308	1.82027	-0.00002	N	-0.08580	1.92766	-0.00012	N	-0.00790	1.77612	0.00017
H	-0.61344	2.15298	-0.82298	H	-0.57818	2.29685	-0.80912	H	-0.50268	2.14693	-0.81213
H	-0.60851	2.15287	0.82602	H	-0.57129	2.29680	0.81308	H	-0.50016	2.14658	0.81417
N	-2.16620	-0.52672	0.00040	N	-2.17946	-0.68749	0.00005	N	-2.19812	-0.41400	0.00011
H	-2.51580	-1.48201	-0.00058	H	-2.43871	-1.67014	-0.00009	H	-2.62211	-1.34116	0.00021
H	-2.55922	-0.07027	0.82510	H	-2.64349	-0.29123	0.81273	H	-2.58032	0.07219	0.81873
H	-2.55985	-0.06850	-0.82303	H	-2.64364	-0.29098	-0.81242	H	-2.58057	0.07209	-0.81844
H	0.79511	2.30618	-0.00264	H	0.81701	2.39255	-0.00400	H	0.91532	2.21194	-0.00111
H	2.61833	-1.35276	0.00002	H	2.53451	-1.56112	0.00135	H	2.69209	-1.30651	0.00013

$V(NH_3)_4$				$V(NH_3)_4^+$				$V(NH_3)_4^-$			
V	0.00002	-0.00006	-0.00041	V	0.00005	-0.00001	-0.00004	V	-0.00003	0.00007	0.00954
N	-1.56146	-1.57792	0.00000	N	1.63960	-1.56677	-0.00020	N	1.46374	1.67842	-0.00743
N	1.57816	-1.56124	0.00026	N	1.56674	1.63963	0.00021	N	1.67856	-1.46349	-0.00269
N	1.56131	1.57803	0.00002	N	-1.63965	1.56671	-0.00020	N	-1.46352	-1.67857	-0.00721
H	1.48141	-2.15845	-0.82278	H	2.17644	1.58345	-0.81064	H	2.29203	-1.36367	0.80701
H	1.48158	-2.15709	0.82430	H	2.17553	1.58403	0.81179	H	2.28517	-1.35945	-0.81708
H	-2.16129	-1.47905	-0.82085	H	1.58251	-2.17717	-0.81046	H	1.41305	2.25059	0.83633
H	-2.15465	-1.48377	0.82628	H	1.58471	-2.17485	0.81196	H	1.31334	2.32489	-0.78300
H	2.16044	1.47995	-0.82147	H	-1.58271	2.17698	-0.81056	H	-1.36516	-2.29290	0.80205
H	2.15537	1.48317	0.82557	H	-1.58472	2.17491	0.81187	H	-1.35799	-2.28429	-0.82207
N	-1.57804	1.56128	0.00016	N	-1.56679	-1.63956	0.00020	N	-1.67873	1.46351	-0.00208
H	-2.54022	1.22606	-0.00460	H	-1.21330	-2.59098	-0.00102	H	-1.39424	2.44407	-0.00328
H	-1.47902	2.16212	-0.81993	H	-2.17697	-1.58285	-0.81025	H	-2.29201	1.36352	0.80780
H	2.54042	-1.22627	-0.00018	H	1.21308	2.59099	-0.00029	H	1.39395	-2.44401	-0.00424
H	-1.22620	-2.54007	-0.00425	H	2.59101	-1.21327	-0.00199	H	2.44183	1.39499	-0.08087
H	1.22616	2.54023	-0.00295	H	-2.59102	1.21311	-0.00182	H	-2.44407	-1.39398	-0.00993
H	-1.48413	2.15357	0.82713	H	-2.17508	-1.58426	0.81218	H	-2.28554	1.35955	-0.81629
$V(NH_3)_5$				$V(NH_3)_5^+$				$V(NH_3)_5^-$			
V	-0.00202	-0.01015	-0.31041	V	0.00000	0.00140	-0.26925	V	-0.00007	0.01219	-0.27852
N	0.01680	0.08472	1.94583	N	-1.60511	-1.59182	-0.36958	N	-1.58589	-1.56476	-0.39316
H	0.79521	-0.42435	2.37394	H	-1.74480	-1.65655	-1.37687	H	-1.86178	-1.71349	-1.36204
H	0.09635	1.04269	2.30011	H	-1.37565	-2.53355	-0.06249	H	-1.29308	-2.47234	-0.02923
N	1.75308	1.38957	-0.36339	H	-2.51954	-1.39069	0.02729	H	-2.43454	-1.32508	0.12111
H	2.58557	1.04784	0.11558	N	1.60546	-1.59147	-0.36961	N	1.59611	-1.55426	-0.39339
H	2.01167	1.52984	-1.33832	H	2.51987	-1.39010	0.02720	H	2.44323	-1.30900	0.12075
N	-1.41604	1.73370	-0.35848	H	1.37624	-2.53323	-0.06243	H	1.30929	-2.46372	-0.02938
H	-1.64851	1.91884	-1.33252	H	1.74509	-1.65622	-1.37690	H	1.87282	-1.70123	-1.36231
H	-2.29732	1.58220	0.13098	N	1.59560	1.60702	-0.34261	N	1.57046	1.60882	-0.30899
N	-1.74923	-1.42283	-0.29320	H	1.38902	2.52261	0.04884	H	1.31488	2.45439	0.20209
H	-1.95309	-1.65200	-1.26459	H	2.53420	1.37901	-0.02477	H	2.47365	1.31920	0.06730
H	-1.58782	-2.30567	0.18957	H	1.67105	1.74412	-1.34972	H	1.73076	1.88629	-1.27607
N	1.39907	-1.76653	-0.29959	N	0.00003	-0.03518	2.04295	N	0.00067	-0.11069	1.95489
H	1.54111	-2.03848	-1.27093	H	-0.80735	0.42342	2.45508	H	-0.81330	0.32492	2.40058
H	2.32245	-1.58156	0.08978	H	-0.00007	-0.97518	2.42819	H	0.00371	-1.07497	2.30478
H	-1.03865	2.60097	0.02159	H	0.80751	0.42324	2.45507	H	0.81210	0.32992	2.40029
H	1.57410	2.31391	0.02739	N	-1.59598	1.60665	-0.34260	N	-1.58121	1.59831	-0.30877
H	-0.82713	-0.29391	2.38470	H	-1.38960	2.52231	0.04881	H	-1.33127	2.44559	0.20229
H	1.05513	-2.59170	0.18970	H	-1.67147	1.74370	-1.34972	H	-1.74347	1.87470	-1.27584
H	-2.60827	-1.04548	0.10435	H	-2.53451	1.37843	-0.02473	H	-2.48241	1.30265	0.06760

$V(\text{NH}_3)_6$	$V(\text{NH}_3)_6^+$	$V(\text{NH}_3)_6^-$
V 0.00000 0.00001 0.00001	V 0.00000 0.00000 0.00000	V 0.00000 -0.00001 -0.00001
N 1.31502 1.21959 1.35760	N -1.31328 -1.17049 1.42025	N 1.33990 1.18933 1.36601
H 1.43389 0.78247 2.27439	H -1.48088 -0.67289 2.29569	H 1.49540 0.72556 2.26353
H 2.26115 1.34919 0.99215	H -2.24183 -1.37702 1.05091	H 2.27595 1.31982 0.97559
N -1.31377 1.76160 -0.48010	N 1.31041 -1.79665 -0.40833	N -1.33906 1.75974 -0.43131
H -1.43384 1.89006 -1.48747	H 1.47879 -1.93757 -1.40527	H -1.49570 1.89682 -1.43205
H -2.25948 1.67390 -0.10137	H 2.23864 -1.73634 0.01122	H -2.27473 1.64262 -0.03574
N -1.31606 -0.46461 1.76405	N 1.31525 0.54329 1.75694	N -1.34066 -0.50610 1.73848
H -2.26254 -0.74510 1.49756	H 2.24373 0.87398 1.49265	H -2.27710 -0.78666 1.43843
H -0.96485 -1.21715 2.36055	H 0.93499 1.27485 2.35851	H -1.01153 -1.26274 2.34022
N -1.31540 -1.29475 -1.28571	N 1.31367 1.24839 -1.35193	N -1.34031 -1.25208 -1.30831
H -0.96347 -1.43490 -2.23543	H 0.93186 1.40354 -2.28565	H -1.01095 -1.39472 -2.26440
H -1.43377 -2.23248 -0.89538	H 1.48285 2.18253 -0.97662	H -1.49495 -2.18845 -0.92871
N 1.31630 0.56420 -1.73457	N -1.31548 -0.64122 -1.72344	N 1.34092 0.58716 -1.71261
H 1.43385 1.57671 -1.81647	H -1.48418 -1.64799 -1.73133	H 1.49477 1.59647 -1.76179
H 2.26288 0.18443 -1.66193	H -2.24358 -0.21712 -1.71612	H 2.27753 0.18553 -1.62818
N 1.31390 -1.78604 0.37872	N -1.31056 1.81669 0.30652	N 1.33922 -1.77802 0.34777
H 2.25960 -1.53476 0.67538	H -2.23857 1.60109 0.67205	H 2.27493 -1.50541 0.65727
H 0.95997 -2.41975 1.09888	H -0.92714 2.51004 0.94988	H 1.00799 -2.44678 1.04489
H -2.26169 -0.92345 -1.39602	H 2.24156 0.85337 -1.50768	H -2.27666 -0.85176 -1.40145
H -0.95979 2.65452 -0.12956	H 0.92714 -2.68262 -0.07690	H -1.00757 2.65947 -0.07986
H -1.43390 0.34254 2.38076	H 1.48303 -0.24937 2.37794	H -1.49504 0.29103 2.35941
H 0.96247 2.16078 1.54565	H -0.93200 -2.07526 1.69899	H 1.00955 2.12791 1.59592
H 1.43400 -2.36105 -0.45833	H -1.47949 2.32623 -0.56177	H 1.49570 -2.32296 -0.50274
H 0.96546 0.25395 -2.64349	H -0.93493 -0.42947 -2.64648	H 1.01239 0.31432 -2.64027



**Table S2.** Cartesian coordinates (Å) for the  $V(\text{NH}_3)_6^{0,\pm}$  species optimized at B3LYP/cc-pVTZ(V,N) aug-cc-pVTZ(H).

$V(\text{NH}_3)_6$			$V(\text{NH}_3)_6^+$			$V(\text{NH}_3)_6^-$					
V	-0.000019	0.000314	-0.000384	V	0.000296	0.000438	0.000008	V	0.000145	-0.000121	0.000046
N	1.304009	1.766639	0.526425	N	-1.496275	0.696602	1.556484	N	-1.366655	-0.134879	-1.797256
H	1.163194	2.098485	1.484316	H	-1.846059	1.637050	1.364652	H	-1.310224	-1.031282	-2.287218
H	2.301946	1.545271	0.449715	H	-2.325844	0.103826	1.615523	H	-2.349781	-0.035884	-1.522117
N	-1.336839	1.296416	-1.277568	N	1.455956	-0.684081	1.599781	N	1.359456	1.506209	-0.999682
H	-1.183951	1.166778	-2.281249	H	1.838046	-1.611713	1.407238	H	1.307963	2.440066	-0.584884
H	-2.330222	1.101083	-1.117098	H	2.266591	-0.071730	1.704089	H	2.343081	1.226690	-0.920457
N	-1.364635	0.418839	1.748750	N	0.930554	2.068923	0.046054	N	1.359882	-1.616925	-0.808519
H	-2.353763	0.333388	1.494020	H	1.862646	2.105508	-0.369616	H	2.344196	-1.403192	-0.615024
H	-1.220902	-0.220595	2.534960	H	0.383867	2.777723	-0.446416	H	1.195776	-2.544922	-0.410195
N	-1.304831	-1.767409	-0.519389	N	1.480159	-0.624532	-1.602701	N	1.366725	0.110145	1.798686
H	-1.124654	-2.143484	-1.454070	H	1.248587	-1.512409	-2.051977	H	1.205688	0.919716	2.403223
H	-1.190831	-2.552561	0.127133	H	1.542548	0.056604	-2.361529	H	1.309204	-0.711291	2.406677
N	1.364440	-0.416164	-1.749965	N	-0.928185	-2.069030	0.040211	N	-1.359492	1.627736	0.786395
H	1.218236	0.222076	-2.536609	H	-1.120880	-2.389425	0.990850	H	-1.302319	2.499566	0.254045
H	2.353446	-0.327263	-1.495847	H	-1.819177	-2.131734	-0.454775	H	-2.343652	1.342956	0.738563
N	1.337807	-1.298713	1.272332	N	-1.442940	0.611405	-1.640056	N	-1.360220	-1.491965	1.020062
H	2.329360	-1.075189	1.140219	H	-2.407704	0.702386	-1.317774	H	-2.344572	-1.304945	0.800778
H	1.159638	-1.203867	2.275746	H	-1.214759	1.507028	-2.075425	H	-1.197698	-2.465282	0.749807
H	-2.301591	-1.529305	-0.499224	H	2.434513	-0.734990	-1.256366	H	2.350238	0.168897	1.513596
H	-1.215547	2.297300	-1.101007	H	1.040571	-0.748007	2.531062	H	1.187788	1.631845	-2.000420
H	-1.253369	1.362542	2.128939	H	1.042352	2.423396	0.997592	H	1.300491	-1.730776	-1.823535
H	1.149079	2.577619	-0.078483	H	-1.119429	0.734194	2.505324	H	-1.204943	0.584974	-2.506106
H	1.244625	-2.296111	1.062571	H	-1.473718	-0.063981	-2.405846	H	-1.299480	-1.468668	2.041105
H	1.256071	-1.360636	-2.129281	H	-0.333838	-2.788802	-0.375198	H	-1.192951	1.882062	1.763302

**Table S3.** Cartesian coordinates (Å) for the  $V(\text{NH}_3)_6^{0,\pm}$  species optimized at MP2/cc-pVTZ(V,N) aug-cc-pVTZ(H) under  $C_{2v}$  symmetry.

$V(\text{NH}_3)_6$				$V(\text{NH}_3)_6^+$				$V(\text{NH}_3)_6^-$			
V	-0.00000	0.00000	0.00004	V	0.00000	-0.00000	-0.00000	V	0.00000	-0.00000	0.00010
N	-2.25081	0.00000	0.00004	N	-2.26284	0.00000	-0.00000	N	-2.25361	0.00000	0.00010
N	-0.00000	1.59204	-1.59201	N	-0.00000	1.60017	-1.60017	N	-0.00000	1.59473	-1.59463
N	-0.00000	1.59204	1.59208	N	-0.00000	1.60017	1.60017	N	-0.00000	1.59473	1.59484
N	-0.00000	-1.59204	1.59208	N	0.00000	-1.60017	1.60017	N	-0.00000	-1.59473	1.59484
N	-0.00000	-1.59204	-1.59201	N	0.00000	-1.60017	-1.60017	N	-0.00000	-1.59473	-1.59463
N	2.25081	-0.00000	0.00004	N	2.26284	-0.00000	-0.00000	N	2.25361	-0.00000	0.00010
H	-2.65131	0.00000	-0.94080	H	-2.67258	0.00000	-0.93474	H	-2.64650	0.00000	-0.94159
H	2.65131	-0.00000	-0.94080	H	2.67258	-0.00000	-0.93474	H	2.64650	-0.00000	-0.94159
H	-2.65501	-0.81341	0.46966	H	-2.67242	-0.80957	0.46740	H	-2.65661	-0.81182	0.46881
H	-2.65501	0.81341	0.46966	H	-2.67242	0.80957	0.46740	H	-2.65661	0.81182	0.46881
H	2.65501	0.81341	0.46966	H	2.67242	0.80957	0.46740	H	2.65661	0.81182	0.46881
H	2.65501	-0.81341	0.46966	H	2.67242	-0.80957	0.46740	H	2.65661	-0.81182	0.46881
H	-0.00000	2.54390	-1.21904	H	-0.00000	2.55283	-1.23470	H	-0.00000	2.54901	-1.22891
H	-0.00000	-2.54390	-1.21904	H	0.00000	-2.55283	-1.23470	H	-0.00000	-2.54901	-1.22891
H	0.81512	1.54208	-2.20758	H	0.81058	1.55718	-2.21902	H	0.81332	1.54997	-2.21394
H	-0.81512	1.54208	-2.20758	H	-0.81058	1.55718	-2.21902	H	-0.81332	1.54997	-2.21394
H	-0.81512	-1.54208	-2.20758	H	-0.81058	-1.55718	-2.21902	H	-0.81332	-1.54997	-2.21394
H	0.81512	-1.54208	-2.20758	H	0.81058	-1.55718	-2.21902	H	0.81332	-1.54997	-2.21394
H	-0.00000	2.54390	1.21911	H	-0.00000	2.55283	1.23469	H	-0.00000	2.54901	1.22912
H	-0.00000	-2.54390	1.21911	H	0.00000	-2.55283	1.23469	H	-0.00000	-2.54901	1.22912
H	-0.81512	1.54208	2.20766	H	-0.81058	1.55718	2.21901	H	-0.81332	1.54997	2.21414
H	0.81512	-1.54208	2.20766	H	0.81058	-1.55718	2.21901	H	0.81332	-1.54997	2.21414
H	0.81512	1.54208	2.20766	H	0.81058	1.55718	2.21901	H	0.81332	1.54997	2.21414
H	-0.81512	-1.54208	2.20766	H	-0.81058	-1.55718	2.21901	H	-0.81332	-1.54997	2.21414

**Table S4.** Harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) for the  $\text{V}(\text{NH}_3)_{n=1-5}^{0,\pm}$  species at MP2/cc-pVTZ(V,N) aug-cc-pVTZ(H), and for  $\text{V}(\text{NH}_3)_6^{0,\pm}$  at DFT(B3LYP)/cc-pVTZ(V,N) aug-cc-pVTZ(H).

$\text{V}(\text{NH}_3)$	$\text{V}(\text{NH}_3)^+$	$\text{V}(\text{NH}_3)^-$
322.1	400.7	321.1
447.5	584.8	431.9
448.1	584.8	432.3
1206.8	1333.8	1188.4
1640.5	1661.6	1615.5
1640.8	1662.1	1615.6
3411.9	3448.8	3323.7
3562.5	3560.7	3452.2
3563.1	3560.9	3452.3
$\text{V}(\text{NH}_3)_2$	$\text{V}(\text{NH}_3)_2^+$	$\text{V}(\text{NH}_3)_2^-$
20.1 <i>i</i>	23.1	32.5 <i>i</i>
131.4	122.9	99.9
131.6	123.1	99.9
330.3	345.1	290.7
398.9	414.2	361.0
431.6	533.8	416.2
444.1	539.5	416.4
463.6	565.2	444.5
464.9	566.3	444.5
1167.8	1297.2	1106.9
1174.4	1299.7	1123.4
1627.8	1663.4	1620.2
1627.9	1664.8	1620.2
1630.8	1665.4	1621.7
1631.6	1666.1	1621.7
3391.7	3460.8	3349.9
3397.4	3461.2	3358.1
3550.9	3575.4	3516.8
3551.1	3576.5	3517.0
3551.2	3576.9	3517.4
3552.2	3576.9	3517.6

$V(NH_3)_3$	$V(NH_3)_3^+$	$V(NH_3)_3^-$
57.6	10.9	47.9
92.1	23.3	86.1
97.5	32.9	115.2
101.5	35.7	123.7
117.7	42.0	130.3
160.9	60.6	138.2
310.9	116.5	322.1
329.1	120.1	338.0
393.0	121.6	395.7
445.0	147.4	479.3
456.1	148.1	487.5
467.3	155.6	490.2
467.8	159.2	510.8
509.5	161.1	524.9
634.6	161.7	577.8
1181.5	272.7	1184.0
1190.8	272.8	1193.4
1195.3	314.6	1241.5
1608.5	328.6	1578.1
1614.4	329.0	1611.0
1626.7	329.1	1618.8
1631.4	456.0	1628.6
1641.0	456.7	1630.2
1669.6	460.8	1636.0
3308.1	517.6	3287.7
3358.6	517.9	3336.8
3376.1	519.0	3358.2
3455.0	533.5	3400.9
3484.8	534.1	3430.5
3501.6	534.3	3489.8
3517.4	562.8	3499.2
3552.8	563.2	3501.2
3556.3	564.4	3504.8

$V(\text{NH}_3)_4$	$V(\text{NH}_3)_4^+$	$V(\text{NH}_3)_4^-$
52.8	36.3	33.3 <i>i</i>
58.6	67.5	71.1
66.5	67.5	71.1
66.6	73.6	88.5
80.3	85.2	94.6
126.0	123.8	135.5
164.7	133.5	135.5
173.2	133.5	161.2
173.2	154.9	164.8
305.5	271.8	352.7
315.9	284.2	362.0
378.1	336.1	420.2
378.2	336.1	420.2
425.7	372.3	522.9
446.9	431.3	535.8
446.9	431.3	535.8
467.6	436.3	559.4
480.6	496.3	578.4
541.4	496.3	578.4
714.5	523.0	630.3
714.5	771.6	810.9
1185.2	1232.8	1266.7
1188.1	1238.8	1270.2
1546.1	1238.8	1326.6
1546.2	1248.1	1326.6
1615.3	1660.8	1594.8
1626.9	1665.7	1594.8
1631.5	1668.1	1605.0
1631.6	1668.1	1607.3
1634.8	1674.1	1608.1
1636.0	1674.1	1613.9
2802.7	1677.1	1668.8
2803.8	1683.1	1668.8
3336.8	3466.6	3305.9
3359.8	3471.7	3307.6
3490.1	3471.7	3307.6
3490.1	3472.8	3325.8
3496.5	3591.1	3414.9
3496.5	3591.1	3414.9
3498.4	3591.6	3428.5
3499.5	3593.4	3432.3
3518.1	3598.2	3433.8
3526.3	3598.9	3442.0
5497.1	3598.9	3442.0
5512.5	3599.0	3443.6

$V(\text{NH}_3)_5$	$V(\text{NH}_3)_5^+$	$V(\text{NH}_3)_5^-$
14.9 <i>i</i>	12.9 <i>i</i>	17.6 <i>i</i>
40.9	59.0	57.6
53.4	72.4	71.2
54.7	76.9	75.2
55.8	83.6	83.0
89.3	91.0	85.6
113.9	113.3	109.3
120.2	113.5	117.2
138.6	144.0	122.7
148.2	145.6	152.6
148.4	146.3	153.0
158.3	148.8	161.5
293.5	276.1	303.2
309.9	279.5	319.5
324.8	294.6	342.3
362.5	340.1	371.5
362.5	340.2	371.6
426.6	393.4	448.9
428.4	394.7	450.0
429.9	414.8	451.3
483.5	454.4	516.0
511.5	489.2	519.0
511.7	489.9	523.8
512.8	514.5	528.2
522.6	543.2	551.5
524.4	543.3	552.9
561.7	553.0	580.1
1206.1	1233.2	1207.6
1212.3	1238.3	1211.1
1215.2	1238.4	1213.2
1215.7	1243.6	1213.7
1233.0	1256.5	1233.5
1619.3	1641.7	1605.4
1620.3	1651.7	1609.2
1627.4	1651.7	1620.4
1634.8	1658.0	1622.8
1635.1	1659.4	1627.5
1639.8	1662.4	1629.1
1640.2	1662.5	1633.7
1644.0	1665.0	1635.0
1644.0	1670.6	1638.4
1646.6	1678.4	1638.5
3306.0	3422.8	3291.7
3378.0	3426.4	3363.4
3388.8	3427.1	3371.4
3389.2	3431.8	3371.6

3397.5	3469.1	3374.4
3432.1	3547.4	3416.6
3442.3	3551.0	3426.1
3520.4	3552.2	3490.9
3528.7	3553.8	3502.4
3531.5	3575.8	3504.4
3537.5	3576.7	3513.3
3537.5	3577.0	3520.3
3542.3	3577.9	3527.0
3543.3	3595.2	3530.7
3545.4	3595.2	3534.0
<b>V(NH<sub>3</sub>)<sub>6</sub></b>	<b>V(NH<sub>3</sub>)<sub>6</sub><sup>+</sup></b>	<b>V(NH<sub>3</sub>)<sub>6</sub><sup>-</sup></b>
13.6	25.4 <i>i</i>	35.9 <i>i</i>
22.7	14.0	31.9 <i>i</i>
30.7	23.8	36.3
41.1	32.6	38.1
48.3	38.0	47.4
55.4	55.3	61.1
124.0	116.2	119.7
125.2	119.1	129.3
127.2	119.5	130.1
151.0	146.7	141.5
151.8	147.8	141.9
153.2	154.6	156.2
164.5	158.3	161.4
166.0	159.1	162.4
166.8	160.4	180.0
283.2	272.4	280.2
283.6	272.7	280.3
320.2	314.6	318.1
337.8	328.1	334.2
338.7	328.9	334.4
340.4	329.4	338.6
463.8	455.3	462.1
466.4	455.3	476.9
466.5	460.6	477.2
524.4	516.3	527.0
525.0	516.4	532.0
529.7	519.1	532.1
547.6	532.7	554.5
547.9	533.6	555.1
549.4	533.9	556.5
567.6	562.2	557.0
567.7	562.7	571.8
570.7	563.3	585.0
1223.6	1256.1	1116.8
1223.9	1256.3	1117.0
1233.9	1266.1	1225.0

1237.9	1267.8	1225.1
1238.5	1268.2	1236.4
1248.0	1282.0	1251.7
1610.9	1630.2	1568.0
1611.5	1633.5	1568.8
1614.2	1633.5	1602.8
1614.4	1638.6	1603.1
1615.0	1639.1	1617.0
1615.6	1639.5	1620.0
1622.6	1639.7	1621.8
1622.9	1641.4	1622.1
1623.0	1641.5	1622.8
1623.2	1643.0	1624.5
1627.5	1644.5	1624.7
1630.9	1644.6	1634.6
3282.1	3331.9	3233.4
3282.3	3332.0	3234.2
3283.5	3334.5	3278.8
3283.8	3338.7	3279.9
3285.9	3338.8	3280.4
3303.5	3365.4	3292.5
3365.5	3432.9	3353.0
3371.9	3433.1	3361.1
3379.0	3436.5	3371.1
3379.3	3438.4	3371.9
3386.1	3438.4	3375.0
3386.3	3439.0	3375.8
3396.5	3442.1	3397.5
3396.9	3442.2	3398.8
3399.0	3445.5	3404.8
3399.2	3445.7	3405.9
3401.1	3447.0	3410.4
3413.5	3447.1	3417.4



**Table S5.** Cartesian coordinates (Å) and harmonic frequencies (cm<sup>-1</sup>) for the V(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> species optimized at MP2 and B3LYP/cc-pVTZ(V,N) aug-cc-pVTZ(H).

<i>MP2 optimal geometry</i>	<i>B3LYP optimal geometry</i>	<i>B3LYP frequencies</i>		
V -0.000002 -0.000009 -0.000015	V -0.000045 -0.000140 -0.000086	29.7	520.8	1690.8
N 1.323993 1.193007 1.431527	N -1.402829 -0.037514 1.813468	37.3	522.1	3438.9
H 1.523532 0.700501 2.299491	H -1.611146 0.891566 2.173952	42.7	583.7	3438.9
H 2.242473 1.433243 1.065246	H -2.314115 -0.453289 1.631665	47.1	584.0	3439.0
N -1.308901 1.826505 -0.419764	N 1.264155 -1.706903 0.863801	78.9	586.1	3439.4
H -1.510871 1.957668 -1.408573	H 1.488969 -2.422552 0.175455	92.5	595.4	3439.5
H -2.226002 1.806153 0.020682	H 2.165807 -1.415620 1.235972	116.3	599.0	3440.9
N -1.333695 -0.541979 1.775685	N 1.306362 1.523859 1.108263	118.5	599.2	3518.5
H -2.250876 -0.905654 1.526688	H 2.237533 1.644242 0.714868	119.1	1312.5	3518.6
H -0.952581 -1.243582 2.406357	H 0.921286 2.465377 1.147553	144.1	1312.7	3519.1
N -1.325053 -1.258945 -1.372944	N 1.404319 0.118855 -1.808772	144.4	1319.4	3519.4
H -0.934925 -1.455786 -2.291798	H 1.035013 -0.295044 -2.662312	149.4	1321.5	3519.4
H -1.536862 -2.179372 -0.993879	H 1.636008 1.075292 -2.069637	169.0	1321.8	3519.6
N 1.334349 0.625433 -1.747567	N -1.310240 -1.567766 -1.040616	170.4	1342.3	3519.9
H 1.544643 1.621141 -1.756583	H -1.554172 -2.347783 -0.433515	171.0	1658.7	3519.9
H 2.248123 0.178199 -1.769497	H -2.203803 -1.213520 -1.375890	260.3	1666.8	3520.0
N 1.309309 -1.844009 0.333084	N -1.261688 1.669709 -0.936001	260.5	1667.1	3520.2
H 2.224316 -1.652192 0.734892	H -2.188889 1.774603 -0.529000	304.4	1674.0	3520.6
H 0.913414 -2.552262 0.946994	H -0.849247 2.598430 -0.876395	310.9	1675.5	3520.7
H -2.237978 -0.856490 -1.573146	H 2.304831 -0.335879 -1.672377	311.2	1675.7	
H -0.915035 2.718548 -0.129295	H 0.824791 -2.217407 1.627065	312.4	1677.4	
H -1.536451 0.249406 2.382594	H 1.468544 1.274603 2.081948	453.4	1677.4	
H 0.939334 2.083821 1.737680	H -1.044444 -0.547736 2.618111	454.0	1679.7	
H 1.515894 -2.350651 -0.525040	H -1.431315 1.530011 -1.930107	460.4	1688.6	
H 0.949880 0.447428 -2.672627	H -0.885176 -2.003752 -1.856371	520.5	1688.6	

**Table S6.** Cartesian coordinates (Å) for the  $V(NH_3)_6^+$  species optimized at C-MP2/cc-pwCVTZ(V) cc-pVTZ(N) aug-cc-pVTZ(H) under  $C_{2v}$  symmetry.

$V(NH_3)_6^+$			
V	0.000000	0.000000	0.000010
N	-2.232504	0.000000	0.000010
N	0.000000	1.579245	-1.579235
N	0.000000	1.579245	1.579256
N	-0.000000	-1.579245	1.579256
N	-0.000000	-1.579245	-1.579235
N	2.232504	-0.000000	0.000010
H	-2.642175	0.000000	-0.935135
H	2.642175	-0.000000	-0.935135
H	-2.643161	-0.809485	0.467367
H	-2.643161	0.809485	0.467367
H	2.643161	0.809485	0.467367
H	2.643161	-0.809485	0.467367
H	0.000000	2.532685	-1.214920
H	-0.000000	-2.532685	-1.214920
H	0.810770	1.536419	-2.198399
H	-0.810770	1.536419	-2.198399
H	-0.810770	-1.536419	-2.198399
H	0.810770	-1.536419	-2.198399
H	0.000000	2.532685	1.214941
H	-0.000000	-2.532685	1.214941
H	-0.810770	1.536419	2.198420
H	0.810770	-1.536419	2.198420
H	0.810770	1.536419	2.198420
H	-0.810770	-1.536419	2.198420

**Table S7.** Vertical electron attachment energies (eV) to **alpha** spin-orbital and pole strengths (in parentheses) of  $V(NH_3)_6^{2+}$ , at cation geometry (optimized at MP2 level), from diagonal electron propagator methods<sup>a</sup> using the cc-pVTZ/<sub>V</sub> cc-pVTZ/<sub>N</sub> d-aug-cc-pVTZ/<sub>H</sub> basis sets. All valence electrons correlated.

No.	Orbital irrep	KT <sup>b</sup>	D2 <sup>c</sup>	OVGF <sup>d</sup>	P3 <sup>e</sup>	P3+ <sup>f</sup>
28	a1	-5.526	-6.287(0.976)	-6.228(0.975)	-6.276(0.973)	-6.277(0.974)
29	a1	-4.750	-5.301(0.982)	-5.268(0.981)	-5.301(0.979)	-5.301(0.979)
30	b2	-4.747	-5.296(0.982)	-5.264(0.981)	-5.297(0.979)	-5.297(0.979)
31	b1	-4.741	-5.290(0.982)	-5.257(0.981)	-5.291(0.979)	-5.290(0.979)
32	b2	-3.982	-4.361(0.987)	-4.342(0.986)	-4.365(0.984)	-4.365(0.984)
33	a1	-3.960	-4.354(0.986)	-4.336(0.985)	-4.359(0.984)	-4.359(0.984)
34	a2	-3.909	-4.234(0.989)	-4.223(0.988)	-4.242(0.987)	-4.241(0.987)
35	b1	-3.900	-4.343(0.986)	-4.325(0.984)	-4.349(0.983)	-4.349(0.983)
36	a1	-3.886	-4.289(0.987)	-4.275(0.986)	-4.297(0.985)	-4.296(0.985)
37	b2	-3.375	-3.886(0.984)	-3.857(0.983)	-3.888(0.981)	-3.888(0.982)
38	a1	-3.192	-3.481(0.991)	-3.454(0.990)	-3.475(0.989)	-3.476(0.990)
39	b1	-3.108	-3.407(0.990)	-3.395(0.989)	-3.413(0.988)	-3.413(0.988)
40	a2	-3.066	-3.324(0.991)	-3.317(0.990)	-3.333(0.989)	-3.332(0.989)
41	a1	-3.037	-3.273(0.992)	-3.269(0.991)	-3.283(0.990)	-3.282(0.990)
42	a1	-2.978	-3.175(0.993)	-3.174(0.992)	-3.185(0.992)	-3.184(0.992)
43	b1	-2.964	-3.165(0.993)	-3.164(0.992)	-3.175(0.991)	-3.174(0.992)
44	b2	-2.956	-3.161(0.993)	-3.160(0.992)	-3.171(0.991)	-3.170(0.991)
45	b1	-2.803	-3.073(0.991)	-3.050(0.991)	-3.068(0.990)	-3.068(0.990)

46	a1	-2.799	-3.065(0.991)	-3.043(0.991)	-3.061(0.990)	-3.061(0.990)
47	b2	-2.798	-3.066(0.991)	-3.044(0.991)	-3.062(0.990)	-3.062(0.990)
48	a1	-2.439	-2.719(0.991)	-2.699(0.990)	-2.717(0.990)	-2.717(0.990)
49	b1	-2.432	-2.707(0.991)	-2.689(0.991)	-2.706(0.990)	-2.706(0.990)
50	b2	-2.409	-2.597(0.993)	-2.583(0.993)	-2.595(0.992)	-2.595(0.993)
51	a1	-2.390	-2.573(0.994)	-2.562(0.993)	-2.573(0.993)	-2.573(0.993)
52	a2	-2.377	-2.543(0.994)	-2.534(0.994)	-2.545(0.993)	-2.545(0.994)
53	a2	-2.162	-2.279(0.996)	-2.278(0.995)	-2.285(0.995)	-2.285(0.995)
54	b1	-2.156	-2.259(0.996)	-2.259(0.996)	-2.265(0.995)	-2.265(0.996)
55	b2	-2.153	-2.271(0.996)	-2.269(0.996)	-2.276(0.995)	-2.276(0.995)
56	b1	-1.963	-2.137(0.994)	-2.126(0.994)	-2.137(0.993)	-2.137(0.993)
57	a1	-1.955	-2.240(0.991)	-2.231(0.990)	-2.248(0.989)	-2.247(0.989)
58	a2	-1.945	-2.137(0.993)	-2.127(0.993)	-2.139(0.992)	-2.139(0.992)
59	a1	-1.917	-2.071(0.995)	-2.066(0.994)	-2.075(0.994)	-2.074(0.994)

<sup>a</sup> Accuracy of the methods increases from left to right. For a brief introduction to and numerical comparison of propagator methods, see, for example, Dolgounitcheva, O.; Díaz-Tinoco, M.; Zakrzewski, V. G.; Richard, R. M.; Marom, N.; Sherill, C. D.; Ortiz J. V. *J. Chem. Theory Comput.* **2016**, *12*, 627-637.

<sup>b</sup> Koopmans's theorem

<sup>c</sup> Diagonal second-order approximation

<sup>d</sup> Outer valence Green function method

<sup>e</sup> Partial third-order quasiparticle method

<sup>f</sup> Renormalized partial third-order quasiparticle method

**Table S8.** Vertical electron attachment energies (eV) to **beta** spin-orbital and pole strengths (in parentheses) of  $V(NH_3)_6^{2+}$ , at cation geometry (optimized at MP2 level), from diagonal electron propagator methods using the cc-pVTZ/<sub>V</sub> cc-pVTZ/<sub>N</sub> d-aug-cc-pVTZ/<sub>H</sub> basis sets. All valence electrons correlated.

No.	Orbital irrep	KT	D2	OVGF	P3	P3+
25	a1	-5.516	-6.275(0.976)	-6.215(0.975)	-6.264(0.973)	-6.265(0.974)
26	a1	-4.746	-5.293(0.982)	-5.260(0.981)	-5.293(0.979)	-5.293(0.979)
27	b2	-4.742	-5.289(0.982)	-5.256(0.981)	-5.289(0.979)	-5.289(0.979)
28	b1	-4.736	-5.283(0.982)	-5.249(0.981)	-5.283(0.979)	-5.283(0.979)
29	b2	-3.993	-4.378(0.986)	-4.359(0.985)	-4.383(0.984)	-4.382(0.984)
30	a1	-3.968	-4.364(0.986)	-4.345(0.985)	-4.369(0.984)	-4.368(0.984)
31	a2	-3.911	-4.237(0.989)	-4.225(0.988)	-4.244(0.987)	-4.244(0.987)
32	b1	-3.888	-4.316(0.986)	-4.300(0.985)	-4.323(0.983)	-4.323(0.984)
33	a1	-3.877	-4.273(0.987)	-4.259(0.986)	-4.281(0.985)	-4.281(0.985)
34	b2	-3.369	-3.880(0.984)	-3.850(0.983)	-3.883(0.981)	-3.882(0.982)
35	a1	-3.192	-3.483(0.991)	-3.456(0.990)	-3.477(0.989)	-3.478(0.989)
36	b1	-3.108	-3.406(0.990)	-3.394(0.989)	-3.412(0.988)	-3.412(0.988)
37	a2	-3.069	-3.333(0.991)	-3.325(0.990)	-3.341(0.989)	-3.341(0.989)
38	a1	-3.036	-3.272(0.992)	-3.268(0.991)	-3.282(0.990)	-3.281(0.990)
39	a1	-2.977	-3.174(0.993)	-3.173(0.992)	-3.184(0.992)	-3.184(0.992)
40	b1	-2.962	-3.161(0.993)	-3.160(0.992)	-3.171(0.991)	-3.170(0.992)
41	b2	-2.956	-3.160(0.993)	-3.159(0.992)	-3.170(0.991)	-3.169(0.991)
42	b1	-2.797	-3.063(0.991)	-3.040(0.991)	-3.059(0.990)	-3.059(0.990)

43	b2	-2.792	-3.054(0.992)	-3.033(0.991)	-3.051(0.990)	-3.051(0.990)
44	a1	-2.792	-3.052(0.992)	-3.031(0.991)	-3.049(0.990)	-3.049(0.991)
45	a1	-2.457	-2.790(0.989)	-2.764(0.989)	-2.786(0.988)	-2.786(0.988)
46	b1	-2.428	-2.702(0.991)	-2.684(0.991)	-2.702(0.990)	-2.702(0.990)
47	b2	-2.410	-2.596(0.993)	-2.582(0.993)	-2.594(0.993)	-2.594(0.993)
48	a1	-2.392	-2.583(0.994)	-2.570(0.993)	-2.582(0.993)	-2.582(0.993)
49	a2	-2.383	-2.588(0.993)	-2.574(0.993)	-2.587(0.992)	-2.587(0.992)
50	a2	-2.178	-2.386(0.993)	-2.373(0.993)	-2.386(0.992)	-2.386(0.992)
51	b1	-2.155	-2.256(0.996)	-2.256(0.996)	-2.263(0.996)	-2.262(0.996)
52	b2	-2.152	-2.270(0.996)	-2.268(0.996)	-2.275(0.995)	-2.275(0.995)
53	a2	-2.035	-2.514(0.985)	-2.469(0.985)	-2.501(0.984)	-2.502(0.984)
54	a1	-2.009	-2.420(0.987)	-2.391(0.987)	-2.416(0.985)	-2.417(0.986)
55	b1	-1.963	-2.136(0.994)	-2.125(0.994)	-2.136(0.993)	-2.136(0.993)
56	a2	-1.924	-2.096(0.994)	-2.088(0.994)	-2.098(0.993)	-2.098(0.993)
57	a1	-1.916	-2.069(0.995)	-2.065(0.994)	-2.073(0.994)	-2.073(0.994)
58	a1	-1.893	-2.124(0.992)	-2.119(0.992)	-2.132(0.991)	-2.131(0.991)
59	b2	-1.887	-2.057(0.994)	-2.049(0.994)	-2.059(0.993)	-2.059(0.993)

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**Table S9.** Excitation energies (eV) for the quintet states of  $V(NH_3)_6^+$  inferred from electron affinities in Table S7.

No.	Orbital irrep	KT	D2	OVGF	P3	P3+
28	a1	0.000	0.000	0.000	0.000	0.000
29	a1	0.776	0.986	0.960	0.975	0.976
30	b2	0.779	0.991	0.964	0.979	0.980
31	b1	0.785	0.997	0.971	0.985	0.987
32	b2	1.544	1.926	1.886	1.911	1.912
33	a1	1.566	1.933	1.892	1.917	1.918
34	a2	1.617	2.053	2.005	2.034	2.036
35	b1	1.626	1.944	1.903	1.927	1.928
36	a1	1.640	1.998	1.953	1.979	1.981
37	b2	2.151	2.401	2.371	2.388	2.389
38	a1	2.334	2.806	2.774	2.801	2.801
39	b1	2.418	2.880	2.833	2.863	2.864
40	a2	2.460	2.963	2.911	2.943	2.945
41	a1	2.489	3.014	2.959	2.993	2.995
42	a1	2.548	3.112	3.054	3.091	3.093
43	b1	2.562	3.122	3.064	3.101	3.103
44	b2	2.570	3.126	3.068	3.105	3.107
45	b1	2.723	3.214	3.178	3.208	3.209
46	a1	2.727	3.222	3.185	3.215	3.216

47	b2	2.728	3.221	3.184	3.214	3.215
48	a1	3.087	3.568	3.529	3.559	3.560
49	b1	3.094	3.580	3.539	3.570	3.571
50	b2	3.117	3.690	3.645	3.681	3.682
51	a1	3.136	3.714	3.666	3.703	3.704
52	a2	3.149	3.744	3.694	3.731	3.732
53	a2	3.364	4.008	3.950	3.991	3.992
54	b1	3.370	4.028	3.969	4.011	4.012
55	b2	3.373	4.016	3.959	4.000	4.001
56	b1	3.563	4.150	4.102	4.139	4.140
57	a1	3.571	4.047	3.997	4.028	4.030
58	a2	3.581	4.150	4.101	4.137	4.138
59	a1	3.609	4.216	4.162	4.201	4.203

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**Table S10.** Excitation energies (eV) for the triplet states of  $V(NH_3)_6^+$  inferred from electron affinities in Table S8.

No.	Orbital irrep	KT	D2	OVGF	P3	P3+
25	a1	0.010	0.012	0.013	0.012	0.012
26	a1	0.780	0.994	0.968	0.983	0.984
27	b2	0.784	0.998	0.972	0.987	0.988
28	b1	0.790	1.004	0.979	0.993	0.994
29	b2	1.533	1.909	1.869	1.893	1.895
30	a1	1.558	1.923	1.883	1.907	1.909
31	a2	1.615	2.050	2.003	2.032	2.033
32	b1	1.638	1.971	1.928	1.953	1.954
33	a1	1.649	2.014	1.969	1.995	1.996
34	b2	2.157	2.407	2.378	2.393	2.395
35	a1	2.334	2.804	2.772	2.799	2.799
36	b1	2.418	2.881	2.834	2.864	2.865
37	a2	2.457	2.954	2.903	2.935	2.936
38	a1	2.490	3.015	2.960	2.994	2.996
39	a1	2.549	3.113	3.055	3.092	3.093
40	b1	2.564	3.126	3.068	3.105	3.107
41	b2	2.570	3.127	3.069	3.106	3.108
42	b1	2.729	3.224	3.188	3.217	3.218
43	b2	2.734	3.233	3.195	3.225	3.226

44	a1	2.734	3.235	3.197	3.227	3.228
45	a1	3.069	3.497	3.464	3.490	3.491
46	b1	3.098	3.585	3.544	3.574	3.575
47	b2	3.116	3.691	3.646	3.682	3.683
48	a1	3.134	3.704	3.658	3.694	3.695
49	a2	3.143	3.699	3.654	3.689	3.690
50	a2	3.348	3.901	3.855	3.890	3.891
51	b1	3.371	4.031	3.972	4.013	4.015
52	b2	3.374	4.017	3.960	4.001	4.002
53	a2	3.491	3.773	3.759	3.775	3.775
54	a1	3.517	3.867	3.837	3.860	3.860
55	b1	3.563	4.151	4.103	4.140	4.141
56	a2	3.602	4.191	4.140	4.178	4.179
57	a1	3.610	4.218	4.163	4.203	4.204
58	a1	3.633	4.163	4.109	4.144	4.146
59	b2	3.639	4.230	4.179	4.217	4.218

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**Table S11.** Vertical electron attachment energies (eV) to **alpha** spin-orbital and pole strengths (in parentheses) of  $V(NH_3)_6^{2+}$ , at cation geometry (optimized at MP2 / cc-pwCVTZ(V) cc-pVTZ(N) aug-cc-pVTZ(H) level with all valence electrons and outer core electrons on Vanadium correlated), from diagonal electron propagator methods using the cc-pwCVTZ/V cc-pVTZ/N d-aug-cc-pVTZ/H basis sets. All valence electrons and outer core (3s3p) electrons on Vanadium correlated.

No.	Orbital irrep	KT	D2	OvGF	P3	P3+
32	a1	-5.551	-6.330 (0.976)	-6.261 (0.975)	-6.312 (0.973)	-6.314 (0.973)
33	a1	-4.766	-5.324 (0.982)	-5.286 (0.981)	-5.320 (0.979)	-5.320 (0.979)
34	b2	-4.762	-5.320 (0.982)	-5.282 (0.981)	-5.316 (0.979)	-5.316 (0.979)
35	b1	-4.756	-5.313 (0.982)	-5.276 (0.981)	-5.309 (0.979)	-5.310 (0.979)
36	b2	-4.000	-4.389 (0.986)	-4.366 (0.985)	-4.390 (0.984)	-4.390 (0.984)
37	a1	-3.977	-4.381 (0.986)	-4.358 (0.985)	-4.382 (0.984)	-4.382 (0.984)
38	a2	-3.924	-4.257 (0.989)	-4.242 (0.988)	-4.263 (0.987)	-4.262 (0.987)
39	b1	-3.914	-4.370 (0.985)	-4.345 (0.984)	-4.370 (0.983)	-4.370 (0.983)
40	a1	-3.899	-4.315 (0.987)	-4.294 (0.986)	-4.317 (0.984)	-4.317 (0.985)
41	b2	-3.397	-3.930 (0.983)	-3.891 (0.983)	-3.926 (0.981)	-3.927 (0.981)
42	a1	-3.205	-3.505 (0.990)	-3.473 (0.990)	-3.495 (0.989)	-3.496 (0.989)
43	b1	-3.118	-3.424 (0.989)	-3.410 (0.988)	-3.428 (0.987)	-3.428 (0.988)
44	a2	-3.075	-3.338 (0.991)	-3.330 (0.990)	-3.345 (0.989)	-3.345 (0.989)
45	a1	-3.046	-3.288 (0.992)	-3.282 (0.991)	-3.296 (0.990)	-3.295 (0.990)
46	a1	-2.986	-3.188 (0.993)	-3.186 (0.992)	-3.197 (0.992)	-3.196 (0.992)
47	b1	-2.972	-3.177 (0.993)	-3.175 (0.992)	-3.186 (0.991)	-3.185 (0.992)
48	b2	-2.965	-3.174 (0.993)	-3.172 (0.992)	-3.183 (0.991)	-3.182 (0.991)

49	b1	-2.807	-3.080 (0.991)	-3.054 (0.991)	-3.073 (0.990)	-3.073 (0.990)
50	b2	-2.803	-3.073 (0.991)	-3.048 (0.991)	-3.066 (0.990)	-3.067 (0.990)
51	a1	-2.802	-3.071 (0.991)	-3.047 (0.991)	-3.064 (0.990)	-3.065 (0.990)
52	a1	-2.448	-2.734 (0.991)	-2.710 (0.990)	-2.729 (0.990)	-2.730 (0.990)
53	b1	-2.440	-2.722 (0.991)	-2.700 (0.991)	-2.719 (0.990)	-2.719 (0.990)
54	b2	-2.418	-2.609 (0.993)	-2.594 (0.993)	-2.606 (0.992)	-2.606 (0.992)
55	a1	-2.397	-2.584 (0.994)	-2.571 (0.993)	-2.583 (0.993)	-2.583 (0.993)
56	a2	-2.383	-2.552 (0.994)	-2.541 (0.994)	-2.552 (0.993)	-2.552 (0.994)
57	a2	-2.164	-2.283 (0.996)	-2.280 (0.995)	-2.288 (0.995)	-2.287 (0.995)
58	b1	-2.157	-2.263 (0.996)	-2.261 (0.996)	-2.268 (0.995)	-2.267 (0.996)
59	b2	-2.156	-2.278 (0.996)	-2.274 (0.996)	-2.282 (0.995)	-2.281 (0.995)
60	b1	-1.970	-2.147 (0.994)	-2.135 (0.993)	-2.146 (0.993)	-2.146 (0.993)
61	a1	-1.967	-2.249 (0.991)	-2.235 (0.990)	-2.252 (0.989)	-2.252 (0.989)
62	a2	-1.950	-2.141 (0.993)	-2.130 (0.993)	-2.142 (0.992)	-2.142 (0.993)

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**Table S12.** Vertical electron attachment energies (eV) to **beta** spin-orbital and pole strengths (in parentheses) of  $V(NH_3)_6^{2+}$ , at cation geometry (optimized at MP2 / cc-pwCVTZ(V) cc-pVTZ(N) aug-cc-pVTZ(H) level with all valence electrons and outer core electrons on Vanadium correlated), from diagonal electron propagator methods using the cc-pwCVTZ/V cc-pVTZ/N d-aug-cc-pVTZ/H basis sets. All valence electrons and outer core (3s3p) electrons on Vanadium correlated.

No.	Orbital irrep	KT	D2	OVGF	P3	P3+
29	a1	-5.541	-6.318 (0.976)	-6.248 (0.975)	-6.300 (0.973)	-6.302 (0.973)
30	a1	-4.761	-5.317 (0.982)	-5.279 (0.981)	-5.313 (0.979)	-5.313 (0.979)
31	b2	-4.758	-5.313 (0.982)	-5.275 (0.981)	-5.309 (0.979)	-5.309 (0.979)
32	b1	-4.751	-5.306 (0.982)	-5.268 (0.981)	-5.302 (0.979)	-5.302 (0.979)
33	b2	-4.014	-4.414 (0.986)	-4.389 (0.985)	-4.414 (0.984)	-4.414 (0.984)
34	a1	-3.987	-4.398 (0.986)	-4.372 (0.985)	-4.398 (0.984)	-4.398 (0.984)
35	a2	-3.928	-4.262 (0.989)	-4.246 (0.988)	-4.267 (0.987)	-4.267 (0.987)
36	b1	-3.902	-4.339 (0.986)	-4.319 (0.985)	-4.343 (0.983)	-4.342 (0.984)
37	a1	-3.890	-4.295 (0.987)	-4.277 (0.986)	-4.300 (0.985)	-4.299 (0.985)
38	b2	-3.391	-3.924 (0.983)	-3.884 (0.983)	-3.921 (0.981)	-3.921 (0.981)
39	a1	-3.206	-3.507 (0.990)	-3.474 (0.990)	-3.497 (0.989)	-3.498 (0.989)
40	b1	-3.117	-3.423 (0.989)	-3.408 (0.988)	-3.427 (0.987)	-3.427 (0.988)
41	a2	-3.078	-3.348 (0.991)	-3.338 (0.990)	-3.354 (0.989)	-3.354 (0.989)
42	a1	-3.045	-3.286 (0.992)	-3.280 (0.991)	-3.294 (0.990)	-3.294 (0.990)
43	a1	-2.985	-3.187 (0.993)	-3.185 (0.992)	-3.196 (0.992)	-3.195 (0.992)
44	b1	-2.970	-3.173 (0.993)	-3.171 (0.992)	-3.181 (0.991)	-3.181 (0.992)
45	b2	-2.964	-3.173 (0.993)	-3.170 (0.992)	-3.182 (0.991)	-3.181 (0.991)

46	b1	-2.802	-3.070 (0.991)	-3.045 (0.991)	-3.064 (0.990)	-3.064 (0.990)
47	b2	-2.797	-3.062 (0.991)	-3.038 (0.991)	-3.056 (0.990)	-3.057 (0.990)
48	a1	-2.796	-3.059 (0.992)	-3.035 (0.991)	-3.053 (0.990)	-3.054 (0.991)
49	a1	-2.467	-2.814 (0.989)	-2.779 (0.989)	-2.804 (0.988)	-2.805 (0.988)
50	b1	-2.436	-2.717 (0.991)	-2.696 (0.991)	-2.714 (0.990)	-2.715 (0.990)
51	b2	-2.420	-2.609 (0.993)	-2.593 (0.993)	-2.606 (0.992)	-2.606 (0.993)
52	a1	-2.398	-2.591 (0.994)	-2.576 (0.993)	-2.589 (0.993)	-2.589 (0.993)
53	a2	-2.387	-2.585 (0.993)	-2.569 (0.993)	-2.583 (0.993)	-2.583 (0.993)
54	a2	-2.181	-2.409 (0.993)	-2.387 (0.992)	-2.403 (0.992)	-2.404 (0.992)
55	b1	-2.156	-2.259 (0.996)	-2.259 (0.996)	-2.265 (0.996)	-2.264 (0.996)
56	b2	-2.155	-2.276 (0.996)	-2.272 (0.996)	-2.280 (0.995)	-2.280 (0.995)
57	a2	-2.038	-2.545 (0.985)	-2.474 (0.985)	-2.512 (0.984)	-2.515 (0.984)
58	a1	-2.017	-2.443 (0.987)	-2.397 (0.987)	-2.426 (0.986)	-2.428 (0.986)
59	b1	-1.969	-2.146 (0.994)	-2.133 (0.993)	-2.144 (0.993)	-2.144 (0.993)
60	a2	-1.929	-2.108 (0.994)	-2.096 (0.994)	-2.108 (0.993)	-2.108 (0.993)
61	a1	-1.928	-2.133 (0.993)	-2.123 (0.993)	-2.135 (0.992)	-2.135 (0.992)
62	a1	-1.910	-2.106 (0.994)	-2.097 (0.993)	-2.108 (0.992)	-2.108 (0.993)
63	b2	-1.895	-2.069 (0.994)	-2.059 (0.994)	-2.069 (0.993)	-2.069 (0.993)

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**Table S13.** Excitation energies (eV) for the quintet states of  $V(NH_3)_6^+$  inferred from electron affinities in Table S11.

No.	Orbital irrep	KT	D2	OVGF	P3	P3+
32	a1 (1s)	0.000	0.000	0.000	0.000	0.000
33	a1 (1p)	0.785	1.006	0.975	0.992	0.994
34	b2 (1p)	0.789	1.010	0.979	0.996	0.998
35	b1 (1p)	0.795	1.017	0.985	1.003	1.004
36	b2 (1d)	1.551	1.941	1.895	1.922	1.924
37	a1 (1d)	1.574	1.949	1.903	1.930	1.932
38	a2 (1d)	1.627	2.073	2.019	2.049	2.052
39	b1 (1d)	1.637	1.960	1.916	1.942	1.944
40	a1 (1d)	1.652	2.015	1.967	1.995	1.997
41	b2 (1f)	2.154	2.400	2.370	2.386	2.387
42	a1 (2s)	2.346	2.825	2.788	2.817	2.818
43	b1 (1f)	2.433	2.906	2.851	2.884	2.886
44	a2 (1f)	2.476	2.992	2.931	2.967	2.969
45	a1 (1f)	2.505	3.042	2.979	3.016	3.019
46	a1 (1f)	2.565	3.142	3.075	3.115	3.118
47	b1 (1f)	2.579	3.153	3.086	3.126	3.129
48	b2 (1f)	2.586	3.156	3.089	3.129	3.132
49	b1 (2p)	2.744	3.250	3.207	3.239	3.241
50	b2 (2p)	2.748	3.257	3.213	3.246	3.247

51	a1 (2p)	2.749	3.259	3.214	3.248	3.249
52	a1	3.103	3.596	3.551	3.583	3.584
53	b1	3.111	3.608	3.561	3.593	3.595
54	b2	3.133	3.721	3.667	3.706	3.708
55	a1	3.154	3.746	3.690	3.729	3.731
56	a2	3.168	3.778	3.720	3.760	3.762
57	a2	3.387	4.047	3.981	4.024	4.027
58	b1	3.394	4.067	4.000	4.044	4.047
59	b2	3.395	4.052	3.987	4.030	4.033
60	b1	3.581	4.183	4.126	4.166	4.168
61	a1	3.584	4.081	4.026	4.060	4.062
62	a2	3.601	4.189	4.131	4.170	4.172
63	a1	3.624	4.214	4.154	4.194	4.196

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**Table S14.** Excitation energies (eV) for the triplet states of  $V(NH_3)_6^+$  inferred from electron affinities in Table S12.

No.	Orbital irrep	KT	D2	OVGF	P3	P3+
29	a1 (1s)	0.010	0.012	0.013	0.012	0.012
30	a1 (1p)	0.790	1.013	0.982	0.999	1.001
31	b2 (1p)	0.793	1.017	0.986	1.003	1.005
32	b1 (1p)	0.800	1.024	0.993	1.010	1.012
33	b2 (1d)	1.537	1.916	1.872	1.898	1.900
34	a1 (1d)	1.564	1.932	1.889	1.914	1.916
35	a2 (1d)	1.623	2.068	2.015	2.045	2.047
36	b1 (1d)	1.649	1.991	1.942	1.969	1.972
37	a1 (1d)	1.661	2.035	1.984	2.012	2.015
38	b2 (1f)	2.160	2.406	2.377	2.391	2.393
39	a1 (2s)	2.345	2.823	2.787	2.815	2.816
40	b1 (1f)	2.434	2.907	2.853	2.885	2.887
41	a2 (1f)	2.473	2.982	2.923	2.958	2.960
42	a1 (1f)	2.506	3.044	2.981	3.018	3.020
43	a1 (1f)	2.566	3.143	3.076	3.116	3.119
44	b1 (1f)	2.581	3.157	3.090	3.131	3.133
45	b2 (1f)	2.587	3.157	3.091	3.130	3.133
46	b1 (2p)	2.749	3.260	3.216	3.248	3.250
47	b2 (2p)	2.754	3.268	3.223	3.256	3.257

48	a1 (2p)	2.755	3.271	3.226	3.259	3.260
49	a1	3.084	3.516	3.482	3.508	3.509
50	b1	3.115	3.613	3.565	3.598	3.599
51	b2	3.131	3.721	3.668	3.706	3.708
52	a1	3.153	3.739	3.685	3.723	3.725
53	a2	3.164	3.745	3.692	3.729	3.731
54	a2	3.370	3.921	3.874	3.909	3.910
55	b1	3.395	4.071	4.002	4.047	4.050
56	b2	3.396	4.054	3.989	4.032	4.034
57	a2	3.513	3.785	3.787	3.800	3.799
58	a1	3.534	3.887	3.864	3.886	3.886
59	b1	3.582	4.184	4.128	4.168	4.170
60	a2	3.622	4.222	4.165	4.204	4.206
61	a1	3.623	4.197	4.138	4.177	4.179
62	a1	3.641	4.224	4.164	4.204	4.206
63	b2	3.656	4.261	4.202	4.243	4.245

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**Table S15.** Calculation of the adiabatic electron binding energies (aEBE) for  $V(NH_3)_6^{2+,0}$  (species A): The P3+ vertical EBE (vEBE) values using  $C_{2v}$  geometries are corrected for the relaxation energies ( $E_{relax}$ ) from the  $C_{2v}$  to  $C_1$  structures and zero-point energies (ZPE) of species A and the produced species B,  $V(NH_3)_6^{+,0,-}$ . All values in eV.

Species A	$V(NH_3)_6^{2+}$	$V(NH_3)_6$	$V(NH_3)_6$
Species B	$V(NH_3)_6^+$	$V(NH_3)_6^+$	$V(NH_3)_6^-$
$C_{2v}$ geometry used <sup>a</sup>	$V(NH_3)_6^+$	$V(NH_3)_6$	$V(NH_3)_6^-$
vEBE <sup>b</sup>	6.26	3.44	0.46
$E_{relax}(A)$ <sup>c</sup>	0.075	0.018	0.020
$E_{relax}(B)$ <sup>c</sup>	0.009	0.034	0.013
ZPE(A) <sup>d</sup>	6.248	6.014	6.014
ZPE(B) <sup>d</sup>	6.085	6.085	5.984
aEBE	6.36 <sup>e</sup>	3.50 <sup>f</sup>	0.48 <sup>e</sup>

<sup>a</sup> MP2 optimized geometries using the cc-pVTZ (V,N) and aug-cc-pVTZ (H) basis sets (see Table S3).

<sup>b</sup> Calculated with P3+ using with the cc-pVTZ (V,N) and d-aug-cc-pVTZ (H) basis sets.

<sup>c</sup> The absolute energies are given in Table S16.

<sup>d</sup> Calculated as half of the sum of all B3LYP harmonic vibrational frequencies using the cc-pVTZ (V,N) and aug-cc-pVTZ (H) basis sets (see Table S4).

<sup>e</sup> Calculated as  $aEBE = vEBE + E_{relax}(B) - E_{relax}(A) + ZPE(A) - ZPE(B)$ .

<sup>f</sup> Calculated as  $aEBE = vEBE + E_{relax}(A) - E_{relax}(B) + ZPE(B) - ZPE(A)$ .

**Table S16.** Absolute energies for species A and B of Table S15: Energies for the optimal  $C_{2v}$  and  $C_1$  structures (in parenthesis) of Tables S1 and S3.

Species/Geom	$V(NH_3)_6^{2+}$	$V(NH_3)_6^+$	$V(NH_3)_6$	$V(NH_3)_6^-$
$V(NH_3)_6^{2+}$	-1281.495370 (-1281.496868)	-1281.494109		
$V(NH_3)_6^+$		-1281.726157 (-1281.726482)	-1281.725229	
$V(NH_3)_6$			-1281.850088 (-1281.850740)	-1281.849997
$V(NH_3)_6^-$				-1281.849578 (-1281.850051)