Structure of V(H2) Clusters for N = 1−6

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Structure of V(H₂)ₙ⁺ Clusters for *n* = 1—6

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Geometries, vibrational frequencies, spin states, H₂ binding energies, and ΔS values have been determined for V(H₂)ₙ⁺, for *n* = 1—6, using the B3LYP hybrid functional. The binding energies and ΔS values are in good agreement with experiment, thus showing that the B3LYP functional offers a reliable approach for optimizing the geometry and determining the H₂ binding energies for this system. The calculations show that the increase in the binding energy and entropy associated with the addition of the sixth H₂ to V⁺ is due to a change in spin state from quintet for the smaller clusters to triplet for V(H₂)₆⁺. The results for V(H₂)ₙ⁺ are compared with those for Co(H₂)ₙ⁺.

I. Introduction

Bowers and co-workers[1,2] have measured the successive binding energies of up to six H₂ molecules to V⁺ and Co⁺. The trends in the binding energies are quite different; for Co⁺ the values[2] are 18.2 ± 1.0, 17.0 ± 0.7, 9.6 ± 0.5, 9.6 ± 0.6, 4.3 ± 0.7, and 4.0 ± 0.7 kcal/mol, while for V⁺ the values[1] are 10.2 ± 0.5, 10.7 ± 0.5, 8.8 ± 0.4, 9.0 ± 0.4, 4.2 ± 0.5, and 9.6 ± 0.5 kcal/mol. The first two H₂ binding energies are significantly larger for Co⁺ than for V⁺, while the binding energies for V⁺ and Co⁺ are very similar for the third through fifth H₂ molecules. Somewhat surprisingly, the sixth H₂ binding energy is larger for V⁺ than Co⁺.

In previous work[3,4] we computed the first two H₂ binding energies for V⁺ and Co⁺. The larger binding energies for Co⁺ were attributed to the larger electrostatic interaction due to the smaller size of Co⁺ than V⁺ and to a greater metal 3d to H₂ σ* donation for Co⁺ than V⁺. The greater donation for Co⁺ arises because the doubly occupied 3d orbitals can donate more electrons than the singly occupied ones on V⁺. Part of this difference arises because donation from a singly occupied 3d orbital reduces the metal 3d—3d exchange energy, while donation from a doubly occupied 3d orbital increases the 3d—3d exchange energy.

More recently, we studied[5] the Co(H₂)ₙ⁺ (*n* = 1—6) series of clusters. We showed that the decrease in the third H₂ binding energy for Co⁺ was due to a change in the bonding mechanism. Namely, the binding of the first two H₂ molecules is enhanced by sdσ hybridization, and this results in a buildup of electron density on Co⁺ in the plane perpendicular to the H₂—Co—H₂ axis. The third and fourth H₂ molecules bond to the same side of the H₂—Co—H₂ system. The singly occupied s—dσ hybrid orbital mixes in some p character to polarize away from the third and fourth H₂ molecules and the lobes of the second singly occupied 3d orbital point at these H₂ molecules. This bonding mechanism retains the favorable sdσ hybridization for the first two H₂ molecules, but results in the third and fourth H₂ molecules being less strongly bound than the first two. With the addition of the fifth and sixth H₂ molecules, the importance of polarization and hybridization of the Co atom as a mechanism of reducing the Co—H₂ repulsion is greatly diminished, and hence the fifth and sixth binding energies are even smaller. Thus for Co(H₂)ₙ⁺ the ground state of all systems is a triplet with a

Co atom having an essentially 3d⁸ occupation. The trends in binding energies are therefore determined by geometry and hybridization.

In the case of V⁺, with a ⁵D(3d⁴) ground state, the situation is quite different because there is an empty 3d orbital. For VH₂⁺ and V(H₂)₂⁺ both ligands interact with the empty 3dσ orbital. Because the population of the 3dσ orbital arises from H₂ to V donation, sdσ hybridization is less important than for Co(H₂)ₙ⁺, where the 3dσ orbital is occupied, and hence for V⁺ there is only a small increase of the metal electron density in the plane perpendicular to the H₂—V—H₂ axis. Thus, the third and fourth H₂ molecules can be added to the sides of V(H₂)₂⁺ and not suffer the increased repulsion found for Co(H₂)ₙ⁺ for *n* = 3 and 4. For V(H₂)₃⁺ and V(H₂)₄⁺ the H₂ molecules are all pointing at the empty 3d orbital; for example, if the H₂ molecules are along the *x* and *y* axes, the 3d$_{x^2-y^2}$ orbital is empty. This is very similar to the bonding in VH₂⁺ and V(H₂)₂⁺, and, therefore, it is not surprising that the first four H₂ binding energies are very similar. Clearly five H₂ molecules cannot point at a lobe of the empty 3d orbital, and hence there is a drop in the fifth H₂ binding energy. If the bonding of the sixth H₂ was similar to the fifth, it would be expected to have about the same binding energy. This is not what is observed experimentally.

One suggestion[6] is for the V⁺ to switch from a quintet with one empty 3d orbital to a triplet with two empty 3d orbitals and one doubly occupied 3d orbital. This is consistent with ligand field theory for octahedral coordination. The d orbitals split into an e orbital, which is destabilized, because it points at the ligands, and a t orbital, which is relatively unshifted. Thus if the splitting between the e and t orbitals is sufficiently large, the occupation changes from quintet t³e¹ to the triplet t⁴. This change in occupation allows all the H₂ molecules to interact with an empty 3d orbital, which minimizes the metal—ligand repulsion, and the doubly occupied 3d orbital will allow an enhancement in the metal to H₂ σ* donation, which will also increase the binding energy. Such a spin flip is common for metal ligand systems as the number of ligands increases. For example, Fe(CO)ₙ⁺ changes from a quartet to doublet when the fifth CO is added.[7] In this case the change from two doubly and three singly occupied 3d orbitals to three doubly occupied, one singly occupied, and one empty 3d orbital reduces the Fe—CO σ repulsion and enhances the 3d to CO 2π* donation. Considering that the binding energy is almost 30 kcal/mol per CO molecule, such a promotion is not unexpected. However, for V(H₂)ₙ⁺ the binding energy per ligand is much smaller, the metal—ligand repulsion smaller, and the metal to ligand donation

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is less important than in $Fe(CO)_n^+$. Therefore, it is not obvious that the enhancement in bonding can compensate for the more than 32 kcal/mol promotion energy[8] to reach the lowest triplet state with a $3d^4$ occupation. (Note the lowest V^+ triplet state is ^3F, but has a $3d^3 4s^1$ occupation and it not suitable for clustering because of the occupied 4s orbital.)

In this manuscript we report on our study of $V(H_2)_n^+$ to determine the origin of the increase in the sixth H_2 binding energy. We fully optimize the structures and consider both quintet and triplet states. We also compare the results with those obtained previously for $Co(H_2)_n^+$, with special attention to the differences in structure for $M(H_2)_4^+$.

II. Methods

We fully optimize the geometries and compute the harmonic frequencies and the binding energies using the density functional theory (DFT) approach. We use a hybrid functional[9] of the form

$$(1 - A)E_x^{Slater} + AE_x^{HF} + BE_x^{Becke} + CE_c^{LYP} + (1 - C)E_c^{VWN}$$

where E_x^{Slater} is the Slater exchange, E_x^{HF} is the Hartree—Fock exchange, E_x^{Becke} is the gradient part of the exchange functional of Becke,[10] E_c^{LYP} is the correlation functional of Lee, Yang, and Parr,[11] E_c^{VWN} is the correlation functional of Vosko, Wilk, and Nusair,[12] and A, B, and C are the coefficients determined by Becke[9] using his three-parameter fit to the experimental heats of formation for a different choice of correlation functional. This modification of the original Becke hybrid functional[9] is described in ref 13. This method is commonly denoted B3LYP. We should note that we have recently[7] found that the B3LYP performs much better than the older BLYP[10,11] approach for the calculation of binding energies for systems involving transition metal atoms, and therefore we do not investigate the BLYP approach in this work.

The V basis set used in the DFT calculations is an [8s 4p 3d] contraction of the (14s 9p 5d) primitive set developed by Wachters.[14] The s and p spaces are contracted using contraction number 3, while the d space is contracted (311). To this basis set two diffuse p functions are added; these are the functions optimized by Wachters multiplied by 1.5. A diffuse d function[15] and an f polarization function ($\alpha = 0.4134$) are added. The final V basis set is of the form (14s 11p 6d 1f)/[8s 6p 4d 1f]. The hydrogen basis set is the scaled (4s)/[2s] set of Dunning,[16] supplemented with a diffuse s (0.071) and three p (1.2, 0.40, and 0.13) functions. The diffuse s and p functions are added to describe the polarizability of H_2.

The binding energies are also computed using the modified coupled pair functional (MCPF) method[17] and the coupled cluster singles and doubles approach[18] that includes a perturbational estimate of the connected triple excitations[19] [CCSD-(T)] at the DFT minima. The V 1s—3p electrons are not correlated in the MCPF and CCSD(T) calculations. In the MCPF calculations the V basis set is the (20s 15p 10d 6f)/[(6 + 1)s (5 + 1)p 4d 1f] averaged atomic natural orbital[20,21] set described in ref 22 and the hydrogen basis set is the s and p part of the augmented correlation-consistent polarized valence triple ζ set.[23] In the CCSD(T) calculations the V basis set is the (20s 15p 10d 6f 4g)/[(6 + 1)s (5 + 1)p 4d 3f 2g] averaged atomic natural orbital set described in ref 22, and the hydrogen basis set is the augmented correlation-consistent polarized valence quadruple ζ set.[23] Only the pure spherical harmonic component of the basis functions are used.

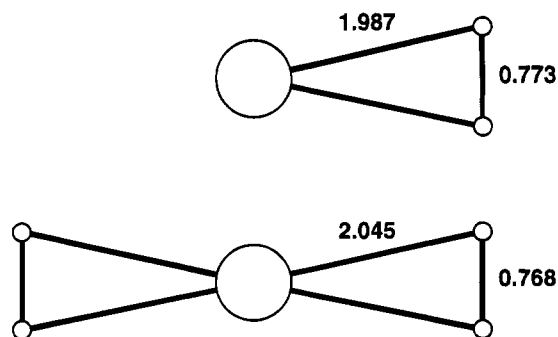We should note that we started this project fully optimizing the geometries using spin-unrestricted second-order Møller—

Figure 1. The optimal DFT structures for the quintet states of VH_2^+ and $V(H_2)_2^+$. The H—H distance in free H_2 is 0.745 Å at the same level of theory.

Plesset perturbation theory[24] (MP2), which we found to be in good agreement with higher levels of theory for several systems.[3,25] We used the effective core potentials (ECPs) and valence basis sets developed by Hay and Wadt.[26] In these ECPs only the 3d, 4s, and 4p orbitals are included in the valence space. The 3d basis set is contracted to three functions instead of the default two (the two outermost Gaussians are left uncontracted). The H basis set is the same as used in the DFT calculations. While the MP2 approach worked well for the quintet states, it appeared that it did not perform as well for the triplet states, which are not as well described by a single configuration. This is similar to $Fe(CO)_n^+$, where the MCPF, MP2, and DFT results agreed for the quartet states, while only the MCPF and DFT results agree for the doublet.[7] Therefore, in this work we focus on the DFT results; however, we note some interesting differences between the MP2 and DFT results for the quintet states. Of particular interest is the difference in the MCPF binding energies using the MP2 geometries compared with those obtained using the DFT geometries.

The ΔS values are computed using the rigid rotor/harmonic oscillator approximation. While it is probably better to treat the H_2 rotations as hindered rotors, this approximation is sufficiently accurate to allow a comparison with experiment, where the ΔS value for the sixth H_2 is qualitatively different from the first five.

The DFT and MP2 calculations were performed using Gaussian 92/DFT,[27] while the MCPF calculations were performed using the SEWARD/SWEDEN program system.[28,29] The CCSD(T) calculations were performed using MOLPRO 94.[30] The open-shell systems were treated using a restricted open-shell CCSD(T) approach.[31] The calculations were performed on the NASA Ames Central Computer Facility CRAY C90 and Computational Chemistry IBM RISC System/6000 computers.

III. Results and Discussion

The optimized structures are shown in Figures 1—7, the computed binding energies are summarized in Table 1, and, the computed harmonic frequencies and IR intensities are summarized in Table 2. The computed ΔS values for the H_2 association reactions are summarized in Table 3. For the $V(H_2)_n^+$ clusters, the n highest frequency modes correspond to the H—H stretches, the next n to the antisymmetric V—H₂ stretches, and the next n to the symmetric V—H₂ stretches.

We first consider the structures of these systems. VH_2^+ has C_{2v} symmetry where the V^+ sits at the H—H bond midpoint (see Figure 1). As discussed previously,[3,4] this structure is favored by both the electrostatic charge—quadruple interaction and the dative interactions, namely, H_2 σ donation to V^+ and V^+ donation to the H_2 σ^* orbital. The H—H distance (0.773 Å) is longer and the H—H vibrational frequency (3936 cm⁻¹)
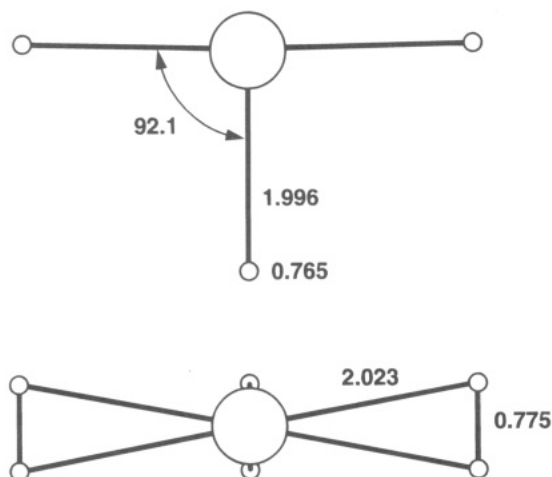
Figure 2. The optimal DFT structure for quintet state $V(H_2)_3{}^+$.
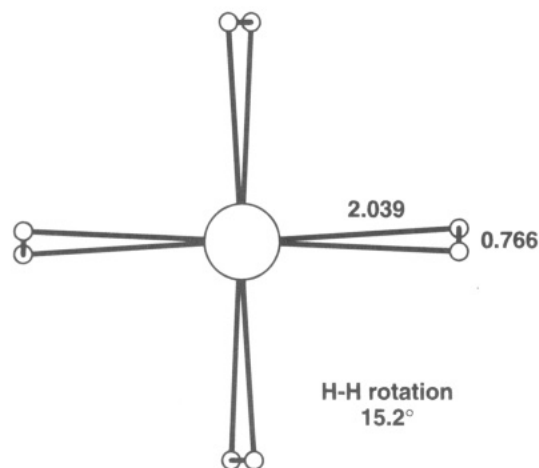

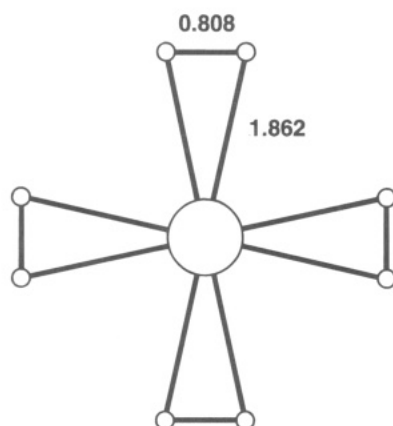**Figure 3.** The optimal DFT structure for the quintet state of $V(H_2)_4{}^+$.

Figure 4. The optimal DFT structure for the triplet state of $V(H_2)_4{}^+$.

Figure 5. The optimal MP2 structure for the quintet state of $V(H_2)_5{}^+$.
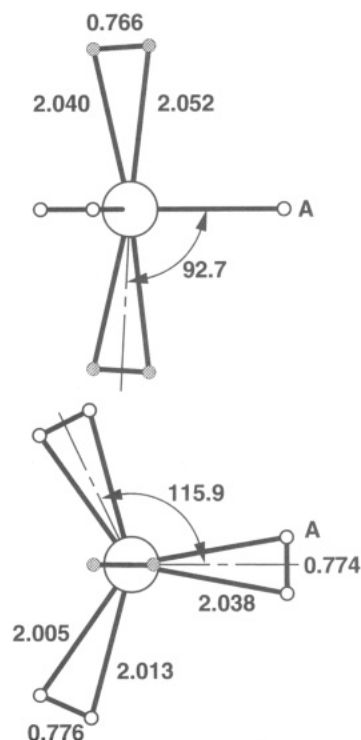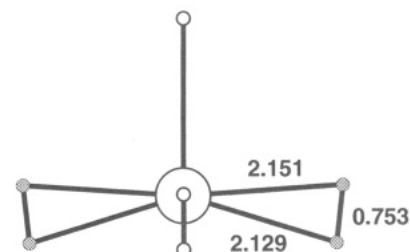
Figure 6. The optimal DFT structure for the quintet state of $V(H_2)_5{}^+$.

is lower than those (0.745 Å and 4420 cm^{-1}) in free H_2 due to the V to σ^* donation. These changes in H_2 are smaller than those in $CoH_2{}^+$ because of the smaller metal to H_2 donation associated with the singly occupied 3d orbital in V. The second H_2 is on the opposite side of the first H_2. This minimizes the ligand–ligand repulsion and allow both H_2 molecules to interact with a lobe of the empty 3d orbital to minimize the H_2–V repulsion. The slightly shorter H–H bond, longer V–H bond, and higher H–H frequencies than in $VH_2{}^+$ (see Figure 1 and Table 2) are consistent with a smaller V donation per H_2 molecule.

Adding a third H_2 results in the structure shown in Figure 2. This T shape is not the one that minimizes the ligand–ligand
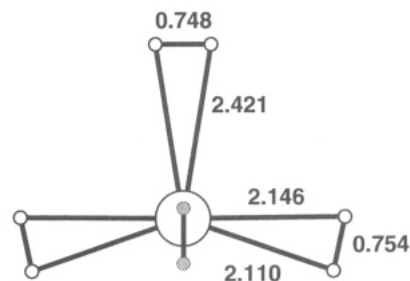
repulsion. As noted in the Introduction, each H_2 molecule is located so that the lobes of the empty 3d orbital point at the H_2 molecules to minimize the V–H_2 repulsion. Therefore, it is no surprise that $V(H_2)_4{}^+$ has the structure shown in Figure 3. We find a small rotation of the H–H molecules about the axis connecting the H_2 bond midpoint to the V atom. The potential for this rotation is quite flat. Thus while $V(H_2)_n{}^+$ and $Co(H_2)_n{}^+$ have relatively similar structures for $n = 1-3$, they greatly differ for $n = 4$. This is a result of the structure of $V(H_2)_4{}^+$ being determined by the interaction of the four H_2 molecules with one empty 3d orbital, while that in $Co(H_2)_4{}^+$ being determined by one pair of H_2 molecules interacting with the singly occupied sdσ hybrid orbital, while the second pair interacts with the singly occupied $3d_{x^2-y^2}$ orbital.

The triplet state of $V(H_2)_4{}^+$ is shown in Figure 4. Unlike the quintet state, it is planar. If the bond midpoints of the H_2 molecules are along the x and y axes, the $3d_{x^2-y^2}$ orbital is empty
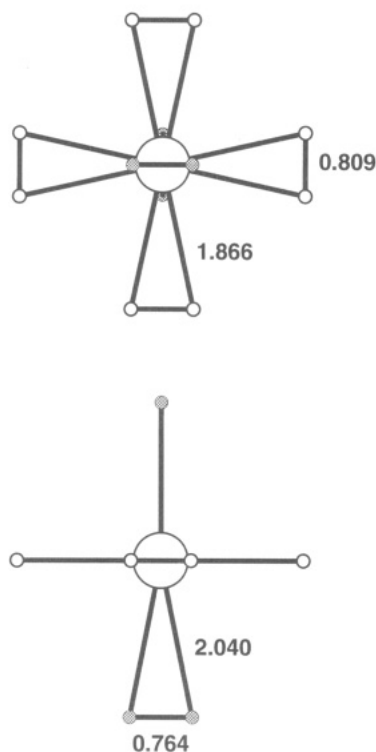
Figure 7. The optimal DFT structure for triplet state of $V(H_2)_6^+$.

to minimize the metal–H_2 repulsion and the $3d_{xy}$ orbital is doubly occupied to allow for donation into the four H_2 σ^* orbitals. This effect decreases the V–H distance, increases the H–H distance, and decreases the H–H frequency relative to the quintet state. In fact, the triplet results are more similar to those obtained[5] for $Co(H_2)_n^+$, for $n = 1-4$, than to the quintet states of $V(H_2)_n^+$. This is not unexpected because the doubly occupied 3d orbital dramatically increases the metal to H_2 donation, which strengthens the metal–H_2 bond and weakens the H–H bond. It is interesting to note that the average H_2 binding energy, calculated with respect to V⁺ with the same triplet electronic configuration, is 21.0 kcal/mol. This is slightly larger than the first two H_2 binding energies to Co⁺ and is not unexpected because the empty 3d orbital in $V(H_2)_4^+$ yields less metal–H_2 repulsion than the singly occupied $3d\sigma$ orbital in Co-$(H_2)_n^+$ for $n = 1$ or 2. However, in spite of the stronger bonding, the triplet state of $V(H_2)_4^+$ is about 3 kcal/mol (7 kcal/mol with zero-point effects) above the quintet. That is, the stronger bonding does not compensate for the promotion energy.

Given the structure for the quintet state of $V(H_2)_4^+$, the quintet state of $V(H_2)_5^+$ is expected to be formed by adding an H_2 molecule to the "top" of $V(H_2)_4^+$. This is what is found at the MP2 level (see Figure 5). The added H_2 interacts with a singly occupied 3d orbital and hence has a longer V–H and shorter H–H distance than those in the "plane", which have bond lengths similar to the quintet states of the smaller clusters. The optimal DFT structure for the quintet state of $V(H_2)_5^+$ is quite different, however (see Figure 6). It has an approximately trigonal bipyramid structure, where, relative to the MP2 structure, two of the H_2 molecules in the base bend away from the apex H_2 molecule. Let the H_2 molecule labeled A in Figure 6 be along the z axis and the other H_2 molecules along the x and y axes. For this orientation, the $3d_{x^2-y^2}$ and $3d\sigma$ orbitals mix. That is, rather than retain the $3d_{x^2-y^2}$ orbitals as empty and have inequivalent H_2 molecules as found at the MP2 level, the 3d orbitals mix at the DFT level so that all five H_2 molecules are nearly equivalent. We note that while the MCPF binding

energies computed using the DFT and MP2 geometries are similar for $V(H_2)_n^+$ for $n = 1-4$, the DFT geometry produces an MCPF binding energy that is 1.76 kcal/mol larger than the MP2 geometry for $V(H_2)_5^+$ (see Table 1). Thus the MCPF result supports the DFT geometry over that obtained using the MP2 level of theory.

The triplet state of $V(H_2)_5^+$ is a square pyramid, where the fifth H_2 is added to the top of the planar triplet $V(H_2)_4^+$. With the fifth H_2 molecule along the z axis and the others along the x and y axes, the $3d_{x^2-y^2}$ and $3d\sigma$ orbitals are empty and the $3d_{xy}$ orbital is doubly occupied. Thus in this structure the extra H_2 interacts with an empty 3d orbital without impacting the favorable bonding in the $V(H_2)_4^+$ fragment. The calculations show that the triplet is more stable than the quintet without accounting for zero-point effects, but above it when the zero-point energy is added (see Table 1). The energy difference is sufficiently small that we cannot definitively determine the ground state based on the energy alone. However, the large change in the vibrational frequencies for the triplet state relative to the quintet state (see Table 2) leads to a very different ΔS value (see Table 3). The value for the quintet state is in good agreement with experiment, while the value for the triplet is inconsistent with experiment. Thus we assign the ground state of $V(H_2)_5^+$ as a quintet based on the ΔS value.

The difference between the MP2 and DFT results for the quintet state of $V(H_2)_5^+$ carries over to $V(H_2)_6^+$. For the DFT approach, we find the sixth H_2 very weakly bound to $V(H_2)_5^+$ (see Table 1); that is, the DFT approach yields a first coordination number of 5 for the quintet states of $V(H_2)_n^+$. The MP2 approach yields an octahedral complex, which adds one H_2 to the bottom of the $V(H_2)_5^+$ system. The MP2 binding energy is slightly smaller than that of $V(H_2)_5^+$. The MCPF approach at the MP2 geometry finds the $V(H_2)_6^+$ to be above $V(H_2)_5^+ + H_2$; therefore, as in the case of the $V(H_2)_5^+$, the MCPF results appear to support the DFT results over those obtained at the MP2 level of theory. Regardless of the differences in the MP2 and DFT structures for the quintet state of $V(H_2)_6^+$, the binding energies obtained with these methods and that obtained with the MCPF approach show that the large binding energy is $V(H_2)_6^+$ cannot arise from a quintet state.

At the DFT level the ground state of $V(H_2)_6^+$ is a triplet. The structure is shown in Figure 7 and is best viewed as adding one H_2 molecule to the bottom of the triplet state of $V(H_2)_5^+$. The 3d occupation is the same as that in $V(H_2)_5^+$. Thus it is not surprising that the H_2 molecules above and below the plane have longer V–H bond lengths and shorter H–H bond lengths than those in the plane, because those in the plane have the extra V to H_2 donation from the doubly occupied 3d orbital. Since those above and below the plane only interact with an empty 3d orbital, the bond lengths are similar to those found for the quintet states of the smaller systems. As expected, we find the triplet state becoming more stable relative to the quintet states as the number of H_2 ligands increases. For four, the quintet is clearly the ground state, while at five they are very close in energy and for six the triplet is clearly lower. The very different frequencies for the triplet state than those for the quintet states leads to the large change in ΔS (see Table 3) as is observed experimentally[1] for the sixth H_2.

The binding energies are in reasonable agreement with experiment[1] (see Table 1), where the second H_2 binding energy is larger than the first. While the second MP2 D_e value is larger than the first, once zero-point energy is accounted for, either at the DFT or MP2 levels of theory, the first is more strongly bound. However, we do not attribute any significance to this difference with experiment, as these two binding energies are

TABLE 1: Summary of the $V(H_2)_n^+$ Binding Energies (in kcal/mol)[a]

	quintet			triplet				expt[1]
	MP2	MCPF[b]	CCSD(T)	DFT				
	D_e	D_e	D_e	D_e	D_0	D_e	D_0	D_0
V^+-H_2	7.12	9.78 (9.55)	10.56	13.96	12.14			10.2 ± 0.5
$VH_2^+-H_2$	7.56	9.53 (9.34)	10.60	12.20	9.58			10.7 ± 0.5
$V(H_2)_2^+ - H_2$	7.60	10.34 (10.31)		11.28	8.30			8.8 ± 0.4
$V(H_2)_3^+ - H_2$	7.80	9.17 (9.21)		10.48	7.62	7.72	0.36	9.0 ± 0.4
$V(H_2)_4^+ - H_2$	2.00	4.87 (3.11)		5.77	2.60	8.26	0.84	4.2 ± 0.5
$V(H_2)_5^+ - H_2$	1.39	(−0.81)		0.37		12.85c	5.52c	9.6 ± 0.5

[a] The MP2 calculations are performed at the MP2 equilibrium geometries, while the DFT calculations are performed at the DFT equilibrium geometries. The MCPF calculations are performed at both sets of geometries. [b] The values in parentheses use the MP2 geometries, while the others use the DFT geometries. [c] Computed with respect to the quintet state of $V(H_2)_5^+$, the D_e and D_0 values, with respect to the triplet state of $V(H_2)_5^+$, are 10.36 and 7.28 kcal/mol, respectively.

TABLE 2: Summary of the Computed Harmonic Frequencies (in cm⁻¹)[a]

H_2

4420

VH_2^+

731 (32.0)	1030 (13.0)	3936 (22.7)

$V(H_2)_2^+$

160 (0.1)	173 (0.0)	248 (3.8)	638 (66.3)	711 (0.0)
968 (0.0)	996 (0.0)	4022 (37.7)	4038 (0.0)	

$V(H_2)_3^+$

106 (0.0)	174 (0.3)	250 (0.0)	261 (0.0)	271 (4.1)
290 (0.2)	623 (62.5)	684 (22.9)	696 (10.3)	977 (0.0)
1013 (38.6)	1037 (19.5)	3988 (33.8)	4035 (26.4)	4055 (0.2)

$V(H_2)_4^+$

147 (0.0)	173 (0.0)	177 (0.0)	198 (0.2)	198 (0.2)
199 (0.6)	318 (5.4)	318 (5.4)	320 (0.0)	622 (54.5)
622 (54.5)	679 (0.0)	682 (0.0)	984 (3.3)	984 (3.3)
1013 (0.0)	1019 (79.0)	4049 (28.7)	4049 (28.7)	4058 (0.0)
4071 (0.0)				

$V(H_2)_4^+$ (triplet)

350 (0.0)	386 (5.1)	594 (34.8)	595 (34.8)	604 (0.1)
639 (0.0)	658 (0.0)	660 (0.0)	772 (0.1)	806 (187.4)
806 (187.4)	934 (0.0)	954 (0.0)	1379 (0.0)	1397 (0.0)
1451 (48.1)	1451 (48.1)	3366 (353.3)	3368 (353.0)	3409 (0.2)
3450 (0.0)				

$V(H_2)_5^+$ (quintet)

63 (0.1)	114 (2.0)	152 (4.5)	205 (8.5)	284 (16.0)
288 (3.7)	312 (10.9)	327 (5.7)	329 (0.0)	370 (0.0)
418 (0.0)	420 (0.0)	646 (14.4)	652 (12.5)	670 (5.1)
673 (35.5)	689 (9.9)	977 (16.8)	1006 (0.1)	1023 (4.5)
1031 (4.1)	1034 (72.3)	3881 (77.5)	3891 (27.3)	3919 (20.5)
4071 (2.2)	4076 (1.1)			

$V(H_2)_5^+$ (triplet)

118 (0.0)	199 (0.3)	296 (1.2)	380 (0.0)	407 (7.2)
592 (36.0)	595 (34.4)	607 (0.0)	642 (0.1)	649 (0.1)
655 (0.0)	674 (3.6)	765 (0.6)	810 (179.6)	815 (183.0)
934 (0.2)	958 (0.0)	1035 (15.8)	1387 (0.0)	1407 (0.0)
1455 (45.5)	1465 (45.7)	3345 (340.6)	3371 (340.3)	3397 (4.5)
3448 (0.4)	4088 (2.9)			

$V(H_2)_6^+$

88 (0.0)	157 (0.0)	234 (0.3)	234 (0.3)	313 (3.8)
313 (3.8)	423 (0.0)	435 (11.0)	593 (38.4)	593 (38.4)
627 (0.1)	627 (0.1)	629 (0.0)	653 (5.9)	660 (0.0)
668 (0.0)	752 (0.0)	818 (178.6)	818 (178.6)	935 (0.0)
963 (0.0)	1019 (21.2)	1019 (21.2)	1396 (0.0)	1414 (0.0)
1468 (44.2)	1468 (44.2)	3350 (344.3)	3350 (344.3)	3392 (0.0)
3441 (0.0)	4107 (0.0)	4109 (6.3)		

[a] The intensities, in km/mol, are given in parentheses.

TABLE 3: The $-\Delta S_{300}$ Values for the H_2 Association Reaction, $V(H_2)_{n-1}^+ + H_2 \rightarrow V(H_2)_n^+$ (in cal/mol K)

n	present work[a]	expt[1]
1	19.0	19.1 ± 1.1
2	23.0	22.2 ± 1.3
3	23.4	21.7 ± 1.4
4	25.2	26.1 ± 1.5
5	27.1 (39.4)	26.1 ± 1.5
6	37.8 (25.6)	40.9 ± 2.8

[a] The values in parentheses are based on the assumption that $V(H_2)_5^+$ has a triplet ground state.

sensitive to the level of theory. The first MCPF D_e value is larger than the second and this difference is increased (9.97 and 9.50 kcal/mol) by optimizing the geometry at the MCPF level. This is different from that found previously[3] at the MCPF level using a larger basis set. The CCSD(T) results using the very large basis set yield the second H_2 to be slightly more strongly bound than the first; however, if the DFT or MP2 zero-point energy is added, the first is more strongly bound. Thus we conclude that we cannot comment on the small differences between theory and experiment. However, all levels of theory agree with experiment that the first four H_2 binding energies are very similar and that the fifth is much smaller. We should note that recent work[32] on $Ti(H_2)_n^+$ finds the first six H_2 binding energies to be very similar. This is consistent with our description of the bonding in $V(H_2)_n^+$. In the case of Ti^+, with two empty 3d orbitals, six H_2 molecules can all interact with the lobes of empty 3d orbitals. This is clearly not the case for $V(H_2)_n^+$ and there is a reduction in the fifth binding energy. The distortion from a square pyramid to a trigonal bipyramid for $V(H_2)_5^+$, which allows all five ligands to see a 3d orbital with less than one electron, spreads out the repulsion, but cannot alter the fact that only four H_2 molecules can interact with one empty 3d orbital. The sixth binding energy for triplet $V(H_2)_n^+$ at the DFT level is larger than the fifth, but smaller than the experiment. For the fourth and fifth H_2 binding energies, the DFT D_0 values are about 1.5 kcal/mol too small, while the error in $V(H_2)_6^+$ is about 4 kcal/mol. This is probably a result of the calculations being slightly biased against the lower spin state. In spite of this bias, the calculations clearly show that $V(H_2)_6^+$ has a triplet ground state. The computed ΔS values support the assignment of the spin flip occurring for $n = 6$. Thus in spite of the relatively weak binding of H_2 to V^+ and sizable promotion energy, the lower-spin state becomes favored for the sixth ligand.

The spin flip is easily explained by the results of our calculations. The average H_2 binding energy for the triplet state of $V(H_2)_4^+$ is about 21 kcal/mol compared with about 10 kcal/mol for the quintet state. The stronger bonding in the triplet state arises from the extra donation associated with a doubly occupied 3d orbital, and is consistent with the binding energy found for CoH_2^+. However, this stronger bonding is not sufficient to overcome the large promotion energy to the triplet

Structure of V(H$_2$)$_n^+$ Clusters

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state, leaving the triplet state about 7 kcal/mol above the quintet state. With only one doubly occupied orbital, additional H$_2$ molecules cannot bond in the same manner. However, the promotion to the triplet state creates a second empty 3d orbital, allowing the next two H$_2$ moelcules to bond in the same manner as the first four H$_2$ molecules in the quintet state. Thus two H$_2$ can be added to the triplet state of V(H$_2$)$_4^+$ with a binding energy of about 10 kcal/mol. This is in contrast to the quintet state of V(H$_2$)$_4^+$ where additional H$_2$ molecules will be weakly bound because of the larger repulsion arising from having a singly occupied 3d orbital pointing at the H$_2$ σ orbital. This difference in the bonding mechanism results in the triplet and quintet states of V(H$_2$)$_5^+$ being very close in energy, and the triplet being lower for V(H$_2$)$_6^+$.

Very recent work[33] on Nb$^+$ shows that a spin flip occurs for fewer H$_2$ molecules because of the smaller d$-$d exchange energy for the second transition row. The Co(H$_2$)$_n^+$ and V(H$_2$)$_n^+$ show very interesting changes in the bonding with the number of ligands and changes between the metals due to differing 3d occupations. These systems are sufficiently small that accurate calculations can be performed, which, in conjunction with experiment, can yield important information about how the bonding changes with number of ligands. Clearly these M(H$_2$)$_n^+$ systems deserve more study, both theoretical and experimental.

After this work was completed, a study of the V(H$_2$)$_n^+$ clusters by Niu et al.[34] was published. On the basis of their results, they concluded that all V(H$_2$)$_n^+$ clusters, for $n = 1-6$, have quintet ground states. They found the sixth H$_2$ binding energy to be larger than the fifth, but offered no explanation for the origin of this effect. We suggest that they observe this trend because they do not optimize geometry of V(H$_2$)$_5^+$ at the same level of theory as the other clusters. They concluded that this approximation introduces an error of only 0.04 eV per H$_2$ molecule. We note that this corresponds to an estimated error of 4.6 kcal/mol for the binding energy of V(H$_2$)$_5^+$ and that a correction of this magnitude would lead to their fifth H$_2$ being more strongly bound than their sixth, in agreement with our results for the quintet states. We feel that the level of theory used by Niu et al. is insufficient for this problem. The fact that our calculations show correct trend in both the binding energies and ΔS values gives us confidence in our conclusion that there is a spin flip with the addition of the sixth H$_2$. In addition we should note that we are comparing D$_0$ values with experiment while Niu et al. compared their D$_e$ values with experiment. Thus some of their apparent good agreement comes from the neglect of zero$-$point energy.

IV. Conclusions

The computed binding energies are in good agreement with experiment, as was found in our recent study of Co(H$_2$)$_n^+$. Thus these results support the use of the B3LYP hybrid functional for the study of these metal ion$-$H$_2$ clusters. While the ground states of V(H$_2$)$_n^+$, for $n = 1-5$, are quintets, calculations clearly show that V(H$_2$)$_6^+$ has a triplet ground state. For V(H$_2$)$_5^+$ the assignment of the ground state is based on both the relative energies and on comparing the computed ΔS values with experiment. The spin flip for the larger clusters explains why the sixth H$_2$ binding energy is larger than the fifth. The stronger bonding in the triplet states is clearly visible in the computed geometries and vibrational frequencies, showing more similarity with Co(H$_2$)$_n^+$ than the quintet states of V(H$_2$)$_n^+$; this is a direct result of doubly versus singly occupied 3d orbitals. The change in the vibrational frequencies between the quintet and triplet states is consistent with the change in the entropy for the addition of the sixth H$_2$ molecule. The structures are consistent with

orienting the empty 3d orbitals to minimize the V$-$H$_2$ repulsion and orienting the doubly occupied 3d orbital to maximize V to H$_2$ donation. The only unexpected structure is V(H$_2$)$_5^+$ where the trigonal bipyramid is more stable than the expected square pyramid. Analysis of the wave function shows that this is a result of mixing the 3d orbitals to allow all five H$_2$ molecules to interact with an orbital with less than one electron.

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