

Structure of  $V(H_2)_n^+$  Clusters for  $n = 1-6$ Philippe Maitre<sup>†</sup> and Charles W. Bauschlicher, Jr.\*

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Geometries, vibrational frequencies, spin states,  $H_2$  binding energies, and  $\Delta S$  values have been determined for  $V(H_2)_n^+$ , for  $n = 1-6$ , using the B3LYP hybrid functional. The binding energies and  $\Delta S$  values are in good agreement with experiment, thus showing that the B3LYP functional offers a reliable approach for optimizing the geometry and determining the  $H_2$  binding energies for this system. The calculations show that the increase in the binding energy and entropy associated with the addition of the sixth  $H_2$  to  $V^+$  is due to a change in spin state from quintet for the smaller clusters to triplet for  $V(H_2)_6^+$ . The results for  $V(H_2)_n^+$  are compared with those for  $Co(H_2)_n^+$ .

## I. Introduction

Bowers and co-workers<sup>1,2</sup> have measured the successive binding energies of up to six  $H_2$  molecules to  $V^+$  and  $Co^+$ . The trends in the binding energies are quite different; for  $Co^+$  the values<sup>2</sup> are  $18.2 \pm 1.0$ ,  $17.0 \pm 0.7$ ,  $9.6 \pm 0.5$ ,  $9.6 \pm 0.6$ ,  $4.3 \pm 0.7$ , and  $4.0 \pm 0.7$  kcal/mol, while for  $V^+$  the values<sup>1</sup> are  $10.2 \pm 0.5$ ,  $10.7 \pm 0.5$ ,  $8.8 \pm 0.4$ ,  $9.0 \pm 0.4$ ,  $4.2 \pm 0.5$ , and  $9.6 \pm 0.5$  kcal/mol. The first two  $H_2$  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  $H_2$  molecules. Somewhat surprisingly, the sixth  $H_2$  binding energy is larger for  $V^+$  than  $Co^+$ .

In previous work<sup>3,4</sup> we computed the first two  $H_2$  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  $H_2$   $\sigma^*$  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<sup>5</sup> the  $Co(H_2)_n^+$  ( $n = 1-6$ ) series of clusters. We showed that the decrease in the third  $H_2$  binding energy for  $Co^+$  was due to a change in the bonding mechanism. Namely, the binding of the first two  $H_2$  molecules is enhanced by  $sd\sigma$  hybridization, and this results in a buildup of electron density on  $Co^+$  in the plane perpendicular to the  $H_2-Co-H_2$  axis. The third and fourth  $H_2$  molecules bond to the same side of the  $H_2-Co-H_2$  system. The singly occupied  $s-d\sigma$  hybrid orbital mixes in some p character to polarize away from the third and fourth  $H_2$  molecules and the lobes of the second singly occupied 3d orbital point at these  $H_2$  molecules. This bonding mechanism retains the favorable  $sd\sigma$  hybridization for the first two  $H_2$  molecules, but results in the third and fourth  $H_2$  molecules being less strongly bound than the first two. With the addition of the fifth and sixth  $H_2$  molecules, the importance of polarization and hybridization of the Co atom as a mechanism of reducing the  $Co-H_2$  repulsion is greatly diminished, and hence the fifth and sixth binding energies are even smaller. Thus for  $Co(H_2)_n^+$  the ground state of all systems is a triplet with a

Co atom having an essentially  $3d^8$  occupation. The trends in binding energies are therefore determined by geometry and hybridization.

In the case of  $V^+$ , with a  $^5D(3d^4)$  ground state, the situation is quite different because there is an empty 3d orbital. For  $VH_2^+$  and  $V(H_2)_2^+$  both ligands interact with the empty 3d orbital. Because the population of the 3d orbital arises from  $H_2$  to V donation,  $sd\sigma$  hybridization is less important than for  $Co(H_2)_n^+$ , where the 3d orbital is occupied, and hence for  $V^+$  there is only a small increase of the metal electron density in the plane perpendicular to the  $H_2-V-H_2$  axis. Thus, the third and fourth  $H_2$  molecules can be added to the sides of  $V(H_2)_2^+$  and not suffer the increased repulsion found for  $Co(H_2)_n^+$  for  $n = 3$  and 4. For  $V(H_2)_3^+$  and  $V(H_2)_4^+$  the  $H_2$  molecules are all pointing at the empty 3d orbital; for example, if the  $H_2$  molecules are along the x and y axes, the  $3d_{y^2-x^2}$  orbital is empty. This is very similar to the bonding in  $VH_2^+$  and  $V(H_2)_2^+$ , and, therefore, it is not surprising that the first four  $H_2$  binding energies are very similar. Clearly five  $H_2$  molecules cannot point at a lobe of the empty 3d orbital, and hence there is a drop in the fifth  $H_2$  binding energy. If the bonding of the sixth  $H_2$  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<sup>6</sup> 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  $t^3e^1$  to the triplet  $t^4$ . This change in occupation allows all the  $H_2$  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  $H_2$   $\sigma^*$  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.<sup>7</sup> 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  $\sigma$  repulsion and enhances the 3d to CO  $2\pi^*$  donation. Considering that the binding energy is almost 30 kcal/mol per CO molecule, such a promotion is not unexpected. However, for  $V(H_2)_n^+$  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<sup>8</sup> to reach the lowest triplet state with a  $3d^4$  occupation. (Note the lowest  $V^+$  triplet state is  $^3F$ , but has a  $3d^34s^1$  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<sup>9</sup> of the form

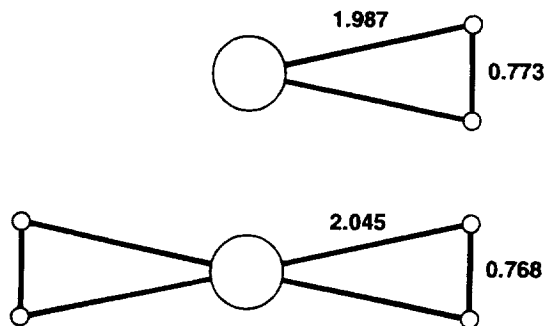
$$(1 - A)E_x^{\text{Slater}} + AE_x^{\text{HF}} + BE_x^{\text{Becke}} + CE_c^{\text{LYP}} + (1 - C)E_c^{\text{VWN}}$$

where  $E_x^{\text{Slater}}$  is the Slater exchange,  $E_x^{\text{HF}}$  is the Hartree-Fock exchange,  $E_x^{\text{Becke}}$  is the gradient part of the exchange functional of Becke,<sup>10</sup>  $E_c^{\text{LYP}}$  is the correlation functional of Lee, Yang, and Parr,<sup>11</sup>  $E_c^{\text{VWN}}$  is the correlation functional of Vosko, Wilk, and Nusair,<sup>12</sup> and  $A$ ,  $B$ , and  $C$  are the coefficients determined by Becke<sup>9</sup> 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<sup>9</sup> is described in ref 13. This method is commonly denoted B3LYP. We should note that we have recently<sup>7</sup> found that the B3LYP performs much better than the older BLYP<sup>10,11</sup> 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.<sup>14</sup> 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<sup>15</sup> 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,<sup>16</sup> 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<sup>17</sup> and the coupled cluster singles and doubles approach<sup>18</sup> that includes a perturbational estimate of the connected triple excitations<sup>19</sup> [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<sup>20,21</sup> set described in ref 22 and the hydrogen basis set is the  $s$  and  $p$  part of the augmented correlation-consistent polarized valence triple  $\zeta$  set.<sup>23</sup> 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  $\zeta$  set.<sup>23</sup> 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<sup>24</sup> (MP2), which we found to be in good agreement with higher levels of theory for several systems.<sup>3,25</sup> We used the effective core potentials (ECPs) and valence basis sets developed by Hay and Wadt.<sup>26</sup> 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.<sup>7</sup> 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.

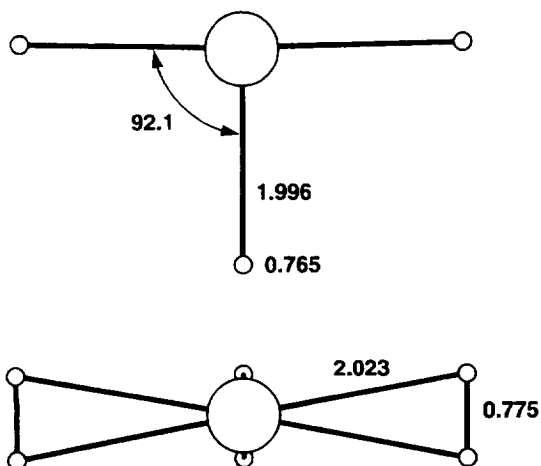
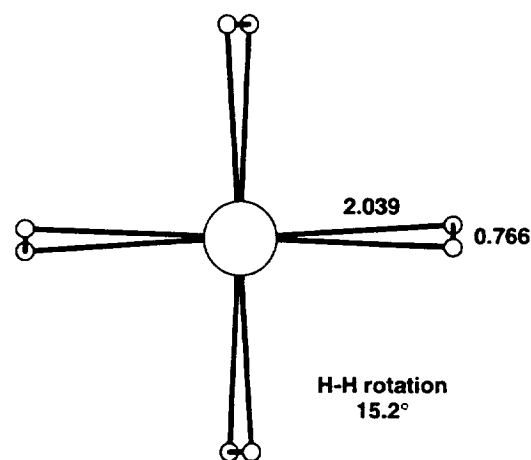
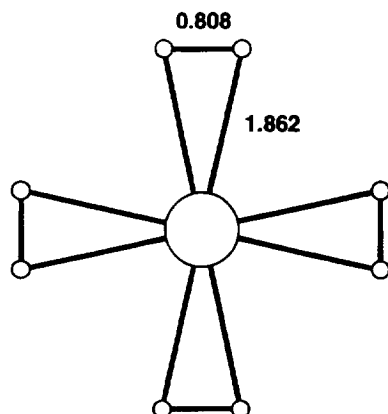
The  $\Delta S$  values are computed using the rigid rotor/harmonic oscillator approximation. While it is probably better to treat the  $H_2$  rotations as hindered rotors, this approximation is sufficiently accurate to allow a comparison with experiment, where the  $\Delta S$  value for the sixth  $H_2$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

The DFT and MP2 calculations were performed using Gaussian 92/DFT,<sup>27</sup> while the MCPF calculations were performed using the SEWARD/SWEDEN program system.<sup>28,29</sup> The CCSD(T) calculations were performed using MOLPRO 94.<sup>30</sup> The open-shell systems were treated using a restricted open-shell CCSD(T) approach.<sup>31</sup> 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

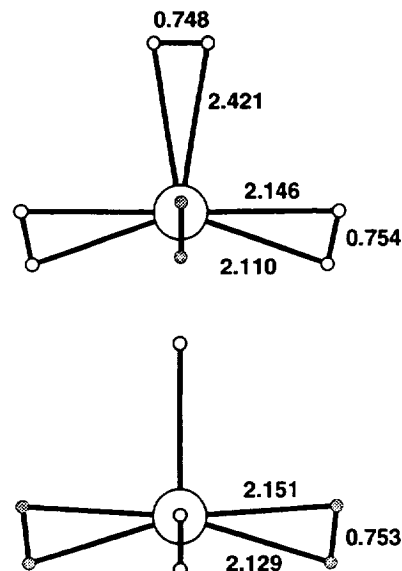
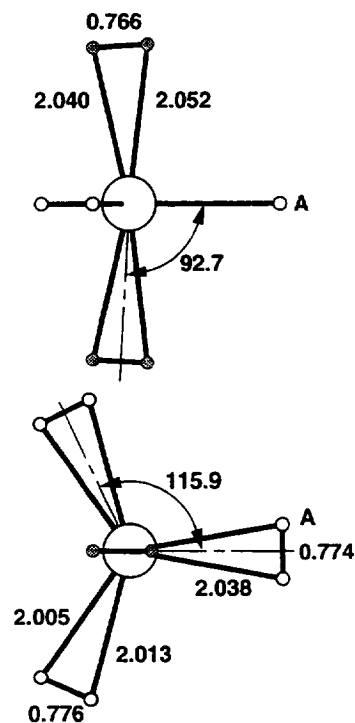
The optimized structures are shown in Figures 1-7, the computed binding energies are summarized in Table 1, and the computed harmonic frequencies and IR intensities are summarized in Table 2. The computed  $\Delta S$  values for the  $H_2$  association reactions are summarized in Table 3. For the  $V(H_2)_n^+$  clusters, the  $n$  highest frequency modes correspond to the H-H stretches, the next  $n$  to the antisymmetric  $V-H_2$  stretches, and the next  $n$  to the symmetric  $V-H_2$  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,<sup>3,4</sup> this structure is favored by both the electrostatic charge-quadruple interaction and the dative interactions, namely,  $H_2$   $\sigma$  donation to  $V^+$  and  $V^+$  donation to the  $H_2$   $\sigma^*$  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  $V(H_2)_4^+$ .

is lower than those (0.745 Å and 4420  $\text{cm}^{-1}$ ) in free  $H_2$  due to the V to  $\sigma^*$  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

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

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  $sd\sigma$  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

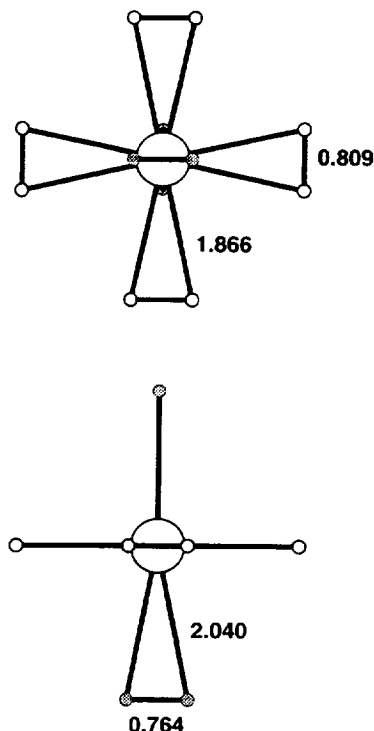


Figure 7. The optimal DFT structure for triplet state of  $V(H_2)_6^+$ .

to minimize the metal– $H_2$  repulsion and the  $3d_{xy}$  orbital is doubly occupied to allow for donation into the four  $H_2$   $\sigma^*$  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<sup>5</sup> 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 bipyramidal 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  $3d_{z^2-y^2}$  and  $3d\sigma$  orbitals mix. That is, rather than retain the  $3d_{z^2-y^2}$  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 MCPFF 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 MCPFF binding energy that is 1.76 kcal/mol larger than the MP2 geometry for  $V(H_2)_5^+$  (see Table 1). Thus the MCPFF 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  $3d_{z^2-y^2}$  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  $\Delta S$  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  $\Delta S$  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 MCPFF 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 MCPFF 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 MCPFF 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  $\Delta S$  (see Table 3) as is observed experimentally<sup>1</sup> for the sixth  $H_2$ .

The binding energies are in reasonable agreement with experiment<sup>1</sup> (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)<sup>a</sup>**

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

<sup>a</sup> 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. <sup>b</sup> The values in parentheses use the MP2 geometries, while the others use the DFT geometries. <sup>c</sup> 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  $cm^{-1}$ )<sup>a</sup>**

		$H_2$		
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)		

<sup>a</sup> The intensities, in  $km/mol$ , are given in parentheses.

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<sup>3</sup> at the MCPF level

**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 <sup>a</sup>	expt <sup>l</sup>
1	19.0	$19.1 \pm 1.1$
2	23.0	$22.2 \pm 1.3$
3	23.4	$21.7 \pm 1.4$
4	25.2	$26.1 \pm 1.5$
5	27.1 (39.4)	$26.1 \pm 1.5$
6	37.8 (25.6)	$40.9 \pm 2.8$

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

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<sup>32</sup> 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  $\Delta S$  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

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  $H_2$  molecules 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  $H_2$   $\sigma$  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<sup>33</sup> 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.*<sup>34</sup> 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  $\Delta S$  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  $\Delta S$  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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