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Structure of $\text{Co}(\text{H}_2)_n^+$ Clusters, for $n = 1-6$

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The geometries and H_2 binding energies have been determined for $\text{Co}(\text{H}_2)_n^+$, for $n = 1-6$. The binding energies are in good agreement with experiment. The shape of the clusters is used to explain the pairwise decrease in the binding energies. The bonding in CoH_2^+ and $\text{Co}(\text{H}_2)_2^+$ is very similar and is enhanced by $\text{sd}\sigma$ hybridization. The next two H_2 molecules add to the side of $\text{Co}(\text{H}_2)_2^+$. These two additional H_2 molecules cannot benefit from $\text{sd}\sigma$ hybridization and are less strongly bound. The addition of the fifth and sixth H_2 molecules eliminates $\text{sd}\sigma$ hybridization as a mechanism for reducing $\text{Co}-\text{H}_2$ repulsion. This coupled with the smaller Co to H_2 σ^* donation results in another decrease in the binding energies.

Introduction

Kemper, Bushnell, von Helden, and Bowers¹ (KBHB) have measured the successive H_2 binding energies to Co^+ . They found a pairwise decrease in the binding energies (D_0) for the first six H_2 molecules: 18.2, 17.0, 9.6, 9.6, 4.3, and 4.0 kcal/mol, respectively. They proposed structures for these $\text{Co}(\text{H}_2)_n^+$ clusters. On the basis of a preliminary report of these results, we studied² $\text{Co}(\text{H}_2)_n^+$, for $n = 1-3$. The donation from Co to the H_2 σ^* orbital and H_2 donation from the σ orbital to the Co are small but are important in accurately treating these systems. Electron correlation must be accounted for to correctly describe the interunit donation; we used the modified coupled-pair functional (MCPF) approach.³ Our first three binding energies (D_e) of 17.3, 17.7, and 10.7 kcal/mol were in reasonable agreement with experiment. CoH_2^+ was found to have a T structure as expected, on the basis of both the charge-quadrupole component of the bonding and maximizing the interunit donation. $\text{Co}(\text{H}_2)_2^+$ was found to have a staggered structure with D_{2d} symmetry. The eclipsed structure was 1.4 kcal/mol above the staggered. Since the two H_2 molecules shared the cost of $\text{sd}\sigma$ hybridization, the second ligand binding energy was larger than the first.

For $\text{Co}(\text{H}_2)_3^+$ it was impractical to fully optimize the structure at the MCPF level. While it was practical to optimize the structure at the self-consistent-field (SCF) level of theory, the result was not expected to be accurate because correlation was known to be important for this system. However, the SCF was used to determine the overall shape of $\text{Co}(\text{H}_2)_3^+$ and the geometry was then optimized at the MCPF level with the symmetry constrained to be that determined at the SCF level. The optimal structure for $\text{Co}(\text{H}_2)_3^+$ corresponded to adding an H_2 to the eclipsed form of $\text{Co}(\text{H}_2)_2^+$. We suggested² that this structure might be an artifact of the SCF treatment and that the true structure might correspond to adding an H_2 to the side of the staggered form of $\text{Co}(\text{H}_2)_2^+$.

While theory² found the D_e value of the second H_2 was larger than the first, experiment¹ found that the second D_0 value was smaller than the first. KBHB suggested this was not an inconsistency but that the zero-point effects accounted for this difference. Subsequent calculations⁴ using second-order Møller–Plesset (MP2) perturbation theory⁵ confirmed KBHB's suggestion. The MP2 geometries were in good agreement with the

MCPF results. Because analytic first and second derivatives are available for the MP2 approach, this appeared to offer a method of fully optimizing the $\text{Co}(\text{H}_2)_n^+$ clusters. We tried this, but unfortunately the CPU, disk space, and memory requirements make such MP2 calculations too expensive to be practical. More recently, we have found that density functional theory (DFT) yields geometries in even better agreement with higher levels of theory than MP2. Because it has significantly smaller computational requirements, it is practical to study $\text{Co}(\text{H}_2)_n^+$, for $n = 1-6$, with full geometry optimization at the DFT level. In this work we report on the optimal DFT structures for $\text{Co}(\text{H}_2)_n^+$.

Methods

We optimize the geometries and compute the harmonic frequencies and the binding energies using the DFT approach. We use a hybrid functional 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^{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,⁶ E_c^{LYP} is the correlation functional of Lee, Yang, and Parr,⁷ E_c^{VWN} is the correlation functional of Vosko, Wilk, and Nusair,⁸ and A , B , and C are the coefficients determined by Becke⁹ 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 functional⁹ is described in ref 10. This method is commonly denoted B3LYP.

The Co basis set used in the DFT calculations is an [8s4p3d] contraction of the (14s9p5d) primitive set developed by Wachters.¹¹ 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 function¹² and an f polarization ($\alpha = 1.6535$) are added. The final Co basis set is of the form (14s11p6d1f)/[8s6p4d1f]. The hydrogen basis set is the scaled (4s)/[2s] set of Dunning,¹³ 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 MCPF method at the DFT minima. The Co 1s–3p electrons are not correlated in the MCPF calculations. The Co basis set is the (20s15p10d6f)/[(6 + 1)s(5 + 1)p4d1f] averaged atomic natural

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TABLE 1: Summary of the Computed Results

	MCPF	DFT		expt ¹
	D_e	D_e	D_0	D_0
Co^+-H_2	15.96	20.65	18.56	18.2 ± 1.0
$\text{CoH}_2^+-\text{H}_2$	16.28	20.39	16.58	17.0 ± 0.7
$\text{Co}(\text{H}_2)_2^+-\text{H}_2$	10.53	10.94	8.43	9.6 ± 0.5
$\text{Co}(\text{H}_2)_3^+-\text{H}_2$	9.93	10.13	7.27	9.6 ± 0.6
$\text{Co}(\text{H}_2)_4^+-\text{H}_2$	5.55	5.23	3.10	4.3 ± 0.7
$\text{Co}(\text{H}_2)_5^+-\text{H}_2$		4.92	2.55	4.0 ± 0.7

orbital set described in ref 14. The hydrogen basis set is the s and p part of the augmented correlation-consistent polarized valence triple- ζ set.¹⁵ Only the pure spherical harmonic components of the basis functions are used. For CoH_2^+ and CoH_4^+ , this basis set yields results that are in good agreement with the larger basis sets used previously.^{2,4}

The DFT calculations were performed using Gaussian 92/DFT,¹⁶ while the MCPF calculations are performed using the SEWARD/SWEDEN program system.^{17,18} The calculations were performed on the NASA Ames Central Computer Facility CRAY C90 and Computational Chemistry IBM RISC System/6000 computers.

Results and Discussion

In all cases the bonding is derived from Co^+ with a $3d^8$ occupation, and hence all of the $\text{Co}(\text{H}_2)_n^+$ systems have triplet ground states. We summarize our computed binding energies in Table 1, and we show the optimized structures in Figures 1–5. Because there is some interest in the vibrational frequencies for interpreting the experiments, we have tabulated our vibrational frequencies in Table 2. We should note that for the larger systems the potentials are very flat, especially for rotation of the H_2 about a line connecting the H_2 bond midpoint to the Co. For example, while it takes 1.4 kcal/mol to rotate one of the H_2 molecules in $\text{Co}(\text{H}_2)_2^+$ by 90° , it takes only 0.14 kcal/mol to rotate atoms labeled H9 and H10 in Figure 4 by 90° .

We first note that the MCPF and DFT results are in reasonable agreement. The DFT results for the first two H_2 molecules are 4–5 kcal/mol larger than the MCPF results. Previous work^{2,4} on the first two binding energies has shown that using a larger basis set increases the MCPF value by up to 1 kcal/mol and that improved levels of correlation treatment increase the binding energy by about an additional 1 kcal/mol. Thus MCPF values for the first two H_2 molecules should be lower bounds, and we expect this to be true for all of the MCPF H_2 binding energies. The DFT D_0 values are in good agreement with experiment¹ and excluding the first are about 1 kcal/mol too small. Thus the computed results are consistent with the experimental binding energies. Given the good agreement between the computed and experimental binding energies, we have confidence that we have found the global minima.

CoH_2^+ has C_{2v} symmetry and a T structure—see Figure 1. The open-shell 3d orbitals are the $3d\sigma$ - and a $3d\delta$ -like orbitals.^{2,4} Singly occupying the $3d\sigma$ orbital minimizes the repulsion of the Co from the H_2 σ orbital, while singly occupying a $3d\delta$ orbital keeps Co^+ in its ground state. The repulsion is reduced further by $sd\sigma$ hybridization. $\text{Co}(\text{H}_2)_2^+$ has a staggered structure, as this allows two different 3d orbitals to donate to the H_2 molecules. The H_2 – H_2 repulsion is very small (0.13 kcal/mol), as expected. The H–H distance is shorter for $\text{Co}(\text{H}_2)_2^+$ than CoH_2^+ , suggesting that there is less Co to H_2 σ^* donation. While the donation may be less, the sharing of the cost of $sd\sigma$ hybridization leads to a slightly larger D_e value for the second H_2 .

In $\text{Co}(\text{H}_2)_3^+$ the third H_2 is added to the side of a staggered $\text{Co}(\text{H}_2)_2^+$. The “extra” H_2 has slightly longer Co–H bond

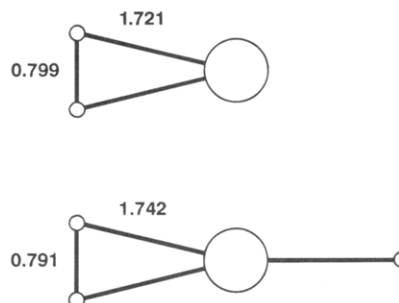


Figure 1. Optimal DFT structures for CoH_2^+ and $\text{Co}(\text{H}_2)_2^+$. The H–H distance in free H_2 is 0.745 Å at the same level of theory.

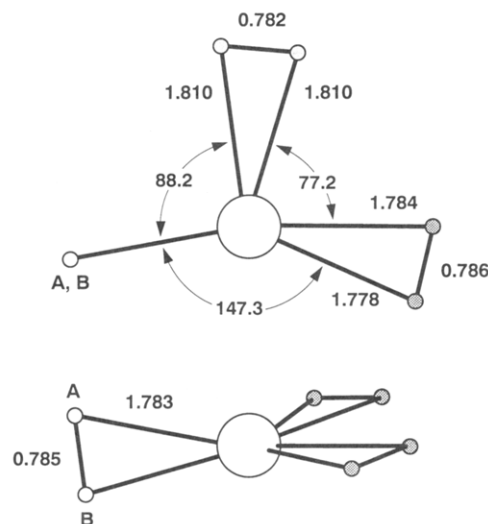


Figure 2. Optimal DFT structure for $\text{Co}(\text{H}_2)_3^+$. Note that the angles are given with respect to the plane containing H_A , H_B , and the Co atom.

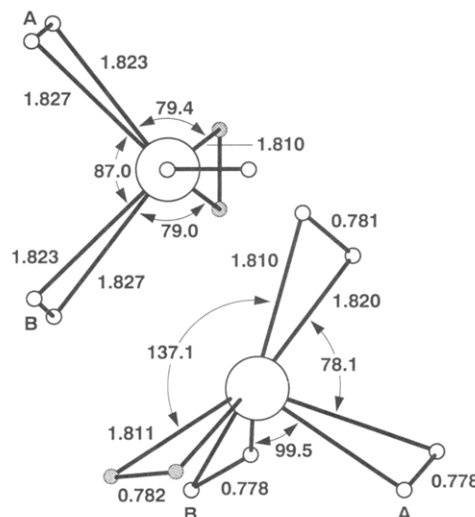


Figure 3. Optimal DFT structure for $\text{Co}(\text{H}_2)_4^+$.

distances than the first two H_2 molecules—see Figure 3. This structure is not what was found in our previous study² but is the structure that we speculated might be the lowest in an optimization that included electron correlation. It is apparent in Figure 3 that the H_2 molecules are not arranged in a manner that minimizes the H_2 – H_2 repulsion. The “original” H_2 molecules bend slightly away from the third H_2 molecule but retain mostly a linear arrangement to retain the $sd\sigma$ hybridization. The $4s$ – $3d\sigma$ hybrid orbital mixes in some $4p$ character to polarize away from the third H_2 molecule. A similar mechanism was observed¹⁹ for $\text{Sr}(\text{H}_2\text{O})_n^+$ for $n = 2$ and 3. While the $4p$ orbital is relatively high in energy, only a small

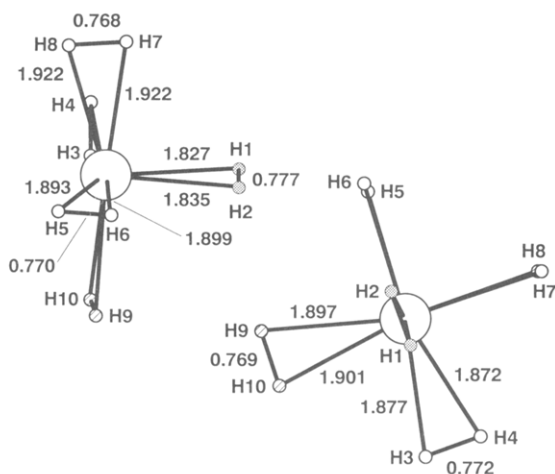


Figure 4. Optimal DFT structure for $\text{Co}(\text{H}_2)_5^+$.

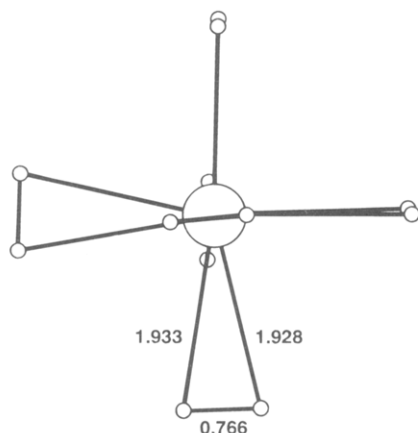


Figure 5. Optimal DFT structure for $\text{Co}(\text{H}_2)_6^+$.

mixing in of the 4p orbital significantly reduces the metal–ligand repulsion.²⁰ The 3d δ orbital is singly occupied, which also helps to minimize the Co–H₂ repulsion. The H–H bond distance is very similar to that in $\text{Co}(\text{H}_2)_2^+$, suggesting that Co to σ^* donation has not been significantly changed by the addition of the third H₂ molecule. The increase in the ligand–ligand repulsion with the addition of the third H₂ molecule is 1.45 kcal/mol at the computed minimum and only 1.65 kcal/mol if the Co–H distances are taken from $\text{Co}(\text{H}_2)_2^+$. Thus while ligand–ligand repulsion contributes to the reduction in the third H₂ binding energy, it is not the major factor. Polarization of the 4s–3d σ hybrid orbital is less efficient at reducing the repulsion for the third H₂ molecule than the sd σ polarization is for the first two. Thus the third H₂ binding energy is smaller than the first two.

Given the bonding in $\text{Co}(\text{H}_2)_3^+$, it might seem odd that the added H₂ molecule is not rotated by 90° about the H₂ bond midpoint–Co axis. This would allow this H₂ to have unshared Co to σ^* donation from the 3d(xy) orbital rather than to share 3d donation from one of the 3d π orbitals. We find this structure to be 1 kcal/mol above that shown in Figure 3. We speculate that the bending of the first two H₂ molecules away from the third polarizes the 3d π orbital toward the third H₂, which enhances the bonding for the structure shown in Figure 3.

KBHB speculated that $\text{Co}(\text{H}_2)_4^+$ would be an essentially planar molecule; that is, the Co and the H–H bond midpoints are all in a plane, with one pair of eclipsed H₂ molecules in this plane and a second pair out of the plane. The planar-like structure is a minimum, but it has a binding energy half that of the most favorable structure—see Figure 3. The optimal structure can be considered as being formed by adding two

TABLE 2: Summary of the Computed Harmonic Frequencies, in cm^{-1}

H_2				
4420				
		CoH_2^+		
944	1333	3609		
		$\text{Co}(\text{H}_2)_2^+$		
295	373	373	889	967
1317	1317	3720	3723	
		$\text{Co}(\text{H}_2)_3^+$		
57	262	296	333	368
449	745	787	853	1139
1210	1217	3791	3798	3843
		$\text{Co}(\text{H}_2)_4^+$		
14	200	214	259	318
362	381	435	442	699
717	745	790	1103	1110
1137	1142	3851	3859	3894
3903				
		$\text{Co}(\text{H}_2)_5^+$		
97	126	147	194	210
221	354	357	376	412
420	471	511	609	636
697	733	911	941	961
1001	1091	3914	3987	4009
4039	4059			
		$\text{Co}(\text{H}_2)_6^+$		
97	97	176	176	180
212	331	331	331	342
348	348	457	458	459
492	492	587	587	592
680	893	893	894	895
897	898	4061	4061	4070
4072	4077	4078		

molecules to the same side of a staggered $\text{Co}(\text{H}_2)_2^+$; one of the Co–H₂ bonds makes a 45° angle with the plane containing the Co and the bond midpoints of the first two H₂ molecules, and the second Co–H₂ bond has an angle of –45°. Thus like $\text{Co}(\text{H}_2)_3^+$, the molecule retains the very favorable staggered $\text{Co}(\text{H}_2)_2^+$ unit with its sd σ hybridization. The third and fourth H₂ molecules are on the same side, so that they both benefit from the polarization of the 4s–3d σ orbital. By singly occupying the other 3d δ -like orbital relative to $\text{Co}(\text{H}_2)_3^+$, the Co–H₂ repulsion is not significantly changed with the addition of the fourth H₂. The 90° angle between the third and fourth H₂ molecules could also suggest some H₂ σ donation to the Co 4p orbitals; unfortunately, due to population artifacts it is difficult to determine the importance of this effect. The bending of the first two H₂ molecules away from the third and fourth molecules and the rotation of the third and fourth molecules about the H₂–Co axis results in 3d orbitals that are strong mixtures of the atomic 3d orbitals; however, the bonding mechanism is similar to that in the smaller systems. Because the bonding mechanism is the same for $\text{Co}(\text{H}_2)_3^+$ and $\text{Co}(\text{H}_2)_4^+$ and the H₂–H₂ repulsion is small, the binding energies of the third and fourth H₂ molecules are very similar.

The bonding in $\text{Co}(\text{H}_2)_5^+$ is different from that in the smaller clusters. The Co–H distances are longer and the H–H distances are shorter than in the smaller clusters—see Figure 4. The molecule can be viewed as one H₂ molecule above a planar-like structure with two sets of staggered H₂ molecules. Since the Co is almost completely surrounded by H₂ molecules, sd σ hybridization cannot reduce the H₂–Co repulsion. In addition, the Co to σ^* donation per H₂ molecule is reduced. At the computed minimum, the increase in the ligand–ligand repulsion is 0.5 kcal/mol larger than that associated with adding the fourth ligand. If the Co–H distances in $\text{Co}(\text{H}_2)_5^+$ are set to the average of those in $\text{Co}(\text{H}_2)_4^+$, the H₂–H₂ repulsion is 2.0 kcal/mol larger

than that for adding the fourth ligand. These factors result in the reduction in the fifth H_2 binding energy relative to the fourth.

Given the structure of $\text{Co}(\text{H}_2)_5^+$, it is not surprising to find that $\text{Co}(\text{H}_2)_6^+$ is an octahedral-like molecule with three pairs of staggered H_2 molecules—see Figure 5. The Co–H and H–H distances are very similar to those found in $\text{Co}(\text{H}_2)_5^+$. If the H_2 molecules are aligned along the x , y , and z axes, the $3d\sigma$ and $3d(x^2 - y^2)$ orbitals are singly occupied to minimize the Co– H_2 repulsion and the other three $3d$ orbitals are doubly occupied and each donates to two H_2 molecules. The same bonding mechanism occurs for $\text{Co}(\text{H}_2)_5^+$. Clearly the bonding in $\text{Co}(\text{H}_2)_5^+$ and $\text{Co}(\text{H}_2)_6^+$ is very similar, and hence the H_2 binding energies are similar.

Conclusions

The $\text{Co}(\text{H}_2)_n^+$ structures are not those that minimize the H_2 – H_2 repulsion. For CoH_2^+ and $\text{Co}(\text{H}_2)_2^+$ the $sd\sigma$ hybridization enhances the bonding. $\text{Co}(\text{H}_2)_3^+$ and $\text{Co}(\text{H}_2)_4^+$ are best viewed as adding H_2 molecules to the side of $\text{Co}(\text{H}_2)_2^+$. The bonding in $\text{Co}(\text{H}_2)_5^+$ and $\text{Co}(\text{H}_2)_6^+$ is weaker than in the smaller clusters because the $sd\sigma$ hybridization is lost. The reliability of these proposed structures is supported by the good agreement between the computed and experimental H_2 binding energies.

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