



# Theoretical study of hydrogen adsorption on Co clusters



Fernando Buendía, M.R. Beltrán\*

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, A.P. 70-360, C.P. 04510, Col. Copilco Universidad, México D.F., Mexico

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## ABSTRACT

We present results of a systematic study of the adsorption of one to five hydrogen atoms on  $\text{Co}_n$ ,  $n = 1-5$  neutral clusters. The density functional (DFT) formalism has been adopted to perform this study with the use of the hybrid functional B3LYP. We present results for their binding, vertical and adiabatic detachment energies, magnetic moments, HOMO–LUMO gaps and their infra red spectra. The results show that by the use of a hybrid functional we obtain different ground state geometries as well as magnetic moments than some of the previous theoretical studies. We test the methodology comparing the calculated Infra Red (IR) spectra for the cationic clusters:  $\text{Co}_4\text{Ar}^+$ ,  $\text{Co}_5\text{Ar}^+$ ,  $\text{Co}_4\text{H}_2^+$  and  $\text{Co}_5\text{H}_6^+$  with the available Far Infra Red Multiple Adsorbed Photon (FIR-MPD) experimental spectra, and we obtained a good agreement. We found the adsorption of  $\text{H}_2$  exclusively dissociative for all neutral  $\text{Co}_n\text{H}_m$ ,  $n = 1-5$ ,  $m = 1-5$  clusters. The twofold bridge site is identified to be the most favorable for adsorption on neutral  $\text{Co}_n$  ( $n > 2$ ). Therefore hydrogen adsorption in clusters is different than it is on surfaces, where it is known that hydrogen adsorbs in high coordination sites. We found that as we add H atoms: first, a structural transition from three to two dimensions occur in the cluster geometry, second an enhanced but non-monotonic change in their magnetic moments is observed, and finally the stability of the system is greatly increased.

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## 1. Introduction

Transition metals have been intensively studied for several decades, and in recent years, nanoscaled systems have renewed attention due their interesting properties such as super paramagnetism, surface enhanced magnetism, optical and new electronic properties. Another important aspect is their role in catalysis. In particular, clusters of transition metal elements attract attention, as they provide a unique opportunity to study the behavior of the 3d electrons as a function of the cluster size. Those 3d electrons are the ones that play an important role in the emerging of both, magnetism [1,2] and their catalytic activity [3], perhaps because of the significant exchange interaction and electron correlation of its 3d band. On the other hand, hydrogen adsorption on metal surfaces and clusters is another very important subject of study, as it brings up the opportunity to understand many interesting problems such as catalytic process, and hydrogen storage. Although hydrogen adsorption on transition metal clusters has been studied extensively (see for example the review articles by Knickelbein and Armentrout [4–6]). Nevertheless, there is hardly any structural information on the hydrogen binding sites on transition metal clusters with only a small number of metal atoms [9], only indirect information on bonding geometries is available from hydrogen uptake measurements on small clusters. On the contrary,

for extended metal surfaces it is well known that hydrogen binds preferably in high coordination sites. A systematic study on hydrogen saturated transition metal clusters that allows for an understanding of the interaction between metal and hydrogen ligands is thus highly desirable.

The study of cobalt clusters in the gas phase has been addressed in the past by many groups, both theoretically as well as experimentally. From the experimental side, we will emphasize the experiments done by Bloomfield and his group [1]. He determined that the magnetic moment of small Co clusters through Stern–Gerlach deflection, for sizes that range from 13 to 200 atoms reveal that their magnetic moments are larger than the value for bulk cobalt. Finding evidence that the reduced dimensionality and increased surface-to-volume ratio of clusters leads to enhanced magnetism. The next experimental work we reviewed because of its relevance to our work are the experiments done by Wang and his group [10] and those by Yoshida et al. [11]. The first group has done High Resolution Photo Electron Spectroscopy studies on  $\text{Co}_n$  for  $n = 1-108$  atoms studying the electronic affinity dependence with the cluster size. The second group studied cobalt clusters with 3–70 atoms, by Photo Electron Spectroscopy (PES) they also studied the electron affinity dependence with the cluster size, observing a metal–nonmetal transition for clusters with around 7 atoms. The next relevant experimental studies have been performed by Fielicke and his group [7,9]. These are combined Infrared Spectroscopy–DFT study of small cobalt clusters and their interaction with both, argon and  $\text{H}_2$  adsorption on transition metal clusters. By means of vibrational

\* Corresponding author. Tel.: +52 556224624.

E-mail address: [mbeltran@unam.mx](mailto:mbeltran@unam.mx) (M.R. Beltrán).

spectroscopy, combined with quantum chemical calculations. We have also sustained our calculations through a direct comparison of our results with those obtained in earlier theoretical studies of Sebetci [12], Liu and Armentrout [6], Jones et al. [2], Barden et al. [13], Pereiro et al. [14], Castro et al. [15] and Siegbahn et al. [16]. All of which all together give a very sound combined effect of how the different approaches that one can explore within the DFT framework can affect the results.

The focus of this work is precisely a systematic study on hydrogen adsorption on cobalt clusters. Our approach combines pre-existing experimental results on negative ion Photo Electron Spectroscopy (PES) with our first-principles electronic structure calculations. Proceeding in this way, we obtain a precise way of determining the ground state geometries for both neutral and anionic clusters, and have achieved fundamental knowledge of their structural, electronic and magnetic properties.

To double verify our methodology, we will focus on a couple of cases that have also been studied by [9,7]. They provide detailed information on adsorption geometries for several cluster complexes, amongst them  $\text{Co}_{4-5}^+ \text{Ar}$ , and  $\text{Co}_{4-5}^+ \text{H}_{2-6}$  clusters, which we conveniently used for comparison. Our two main focuses were to identify the ground state structure of these clusters and by that, understand their electronic and magnetic behavior. With regards to their magnetic properties, we found that the magnetic moment varies non-monotonically with size. As to the hydrogen bonding, we found that it binds in a dissociative manner. This paper is organized as follows: the details of the method are described in Section 2, the results and discussions are presented in Section 3, and the summary in Section 4.

## 2. Computational methods

A QZVP-based basis set [17] within the all electron approximation by means of the Gaussian 09 package [18] has been used while the exchange–correlation energy is calculated using the B3LYP [19–21] hybrid functional which considers a 20% Hartree–Fock [22]. This gives a binding energy ( $E_b$ ) and the dimer bond length of 0.86 eV and 1.95 Å, respectively, while the value for the vibrational frequency is 426  $\text{cm}^{-1}$ . This result is very similar the one obtained in a previous study [15]. Our calculated electron affinity is 0.86 eV, this value is in good agreement with the experimental data 1.00 eV in [10]. A good analysis of the results of these quantities obtained earlier by other groups, both experimentally as well as theoretically can be seen for example in reference [12] Table 1. In the

**Table 1**  
Comparison between the present  $\text{Co}_2$  results with previous studies of the binding energies, nearest neighbor distance, Ionization Potentials (IP) adiabatic and vertical detachment energies. All energies are in eV and the bond lengths are in Å.

	$E_b$	$D_{\text{Co-Co}}$	IP	ADE	VDE
<i>Experimental</i>					
Ref. [25]	<1.32				
Ref. [26]	0.7–1.4				
Ref. [27]	$1.69 \pm 0.26$	2.31			
Ref. [29]			$6.26 \pm 0.16$		
Ref. [10]				0.8	1.1
Ref. [11]				1.0	
<i>Theory</i>					
Ref. [2]	2.57	1.99			
Ref. [12]	1.71	2.13	6.84		
Ref. [14]	0.87	1.96	5.97		
Ref. [13]	1.50	2.41			
<i>Present work</i>					
(PBE)	2.54	2.01	7.10	0.91	0.93
(PBE1)	0.37	1.99	7.02	0.83	0.85
(B3LYP)	0.86	1.95	7.28	0.84	0.86

first part of this study cobalt clusters for sizes  $n = 1-5$  atoms were calculated. At each cluster size have been considered a number of initial structures, each of them relaxed in the redundant internal coordinates, until the forces on all the atoms become smaller than a threshold of  $1.0 \times 10^{-7}$  hartrees. All possible spin configurations were considered and the vibrational analysis has been performed in all cases to identify the local minima. This procedure was implemented for the anionic, the neutral and the hydrogenated clusters. Once the ground state structure and spin multiplicity  $M$  ( $M = 2S + 1$ ), of the anion were obtained, the energy of the neutral cluster at the anion geometry was calculated with a multiplicity  $M \pm 1$ . This is because if the anion has a multiplicity  $M$ , the neutral cluster at the same geometry will have a multiplicity of one more or less, depending on whether the electron is removed from the minority or the majority spin manifold. The lower of these two energies was then used to calculate the vertical detachment energy (VDE) as described below. The Gaussian 09 [18] code was used for all our calculations. In this work we calculated the spin magnetic moment, and neglected spin–orbit coupling (SOC). For the second part of this study the adsorption of hydrogen atoms has been considered by adding one H atom at a time for  $H = 1-5$  according to the system. At each stage, several configurations for the adsorption H site have been studied until the minimum energy configuration was found, and verified through the frequency analysis. In this part, only neutral clusters have been studied, and the whole range of spin configurations has been systematically explored.

## 3. Results

### 3.1. Cobalt clusters

Our calculations for the  $\text{Co}_n$  clusters ( $n = 1-5$ ) were obtained under the density functional theory (DFT) approximation by means of the B3LYP hybrid functional and with the use of a QZVP basis set. We summarize and compare results for the dimmer  $\text{Co}_2$  which has a symmetry group ( $D_{\infty h}$ ) with the available experimental data, as well as other theoretically previously reported results in Table 1, where the binding energies, the bond lengths, the ionization potentials as well as both, the adiabatic and vertical detachment energies are listed. The calculated binding energy defined as:

$$E_b = -[E(\text{Co}_n) - nE(\text{Co})] \quad (1)$$

has been evaluated with three different functionals namely the PBE [23] which gives a value  $E_b = 2.54$  eV, the PBE1 [24]  $E_b = 0.37$  eV and for the B3LYP hybrid functional  $E_b = 0.86$  eV, being the later (B3LYP) the closest to the experimental value [25,26]. Nevertheless, another experimental value by Kant et al. [27] report a different binding energy  $E_b = 1.69 \pm 0.26$  eV. Another result we have calculated is the dissociation energy for  $\text{Co}_2^+$ -deuterium which gives 2.22 eV in very good agreement with the experimental result 2.21 eV reported in [6]. As for the vibrational frequency, we obtained a value of 426  $\text{cm}^{-1}$  which is similar to the value 421  $\text{cm}^{-1}$  theoretically obtained by Castro et al. [15] by means of a PBE functional. The calculated ionization potential (IP) has also been studied with the three functionals, but in this case, we noticed few differences with the chosen methodology. For B3LYP we obtain an IP = 7.28 eV, PBE gives IP = 7.10 eV, and for PBE1 we obtain IP = 7.02 eV, while the only experimental value of Hales et al. [25] is IP = 6.42 eV.

Our values for the adiabatic detachment energy 0.84 eV and the vertical detachment energy 0.86 eV match those obtained experimentally by Leopold and Lineberger [28] and Liu et al. [10]. The spin multiplicities obtained for the ground state neutral dimer is a quintet. The electronic symmetry state is ( ${}^5\Sigma_g^+$ ) for the highest occupied molecular orbital. Our results compare with previous theoretical studies [2,12–15]. and are summarized in Table 1.

For  $\text{Co}_3$  the ground state is a very open triangle which corresponds to a ( $C_{2v}$ ) symmetry group. This result has been obtained after an extensive search for the global minima, where many initial configurations have been considered. The linear ground state proposed by [12] is not the global minima, nor stable under the methodology proposed in this study. The structures proposed in [2,13–15] turned out to be higher in energy than the result here exhibited. With regards to the multiplicity of the ground state, we found it to be an octet with an electronic state  $^8A_1$ . This agrees with most theoretical studies other than Jones et al. [2] who obtained an isosceles triangle in a sextet state as global minimum. The geometries for all the calculated ground state structures are shown in Fig. 1. The  $\text{Co}_3$  binding energy is 1.25 eV per atom, the average atomic distance is 2.31 Å and the energy of the HOMO–LUMO (H–L) gaps for both, the neutral and the anion are: 2.18 and 1.93 eV respectively, (see Table 2 columns 4–7) making them stable. We would like to remark their non-metallic characteristic behavior also discussed by Yoshida et al. [11]. The Photo Electron Spectroscopy (PES) results are close to our calculated values. Table 3 shows our calculated (ADE) and (VDE) in columns 2 and 3, with the experimental results of both Liu et al. [10] in columns 4 and 5 and Yoshida et al. [11] in columns 6 and 7. The simulated infra red spectra can be seen in Fig. 2 which reveals a single peak at  $272.2\text{ cm}^{-1}$  for the neutral cluster and for the anion a peak at  $201.8\text{ cm}^{-1}$ .

The ground state for  $\text{Co}_4$  is an out-of plane rhombus with group symmetry ( $C_s$ ) (see Fig. 1) the electronic state of the highest

**Table 2**

Structure, symmetry, spin multiplicity, binding energies per atom, average nearest neighbor distances (given in Å) and HOMO–LUMO gaps of  $\text{Co}_n$  and  $\text{Co}_n^-$  ( $n=1-5$ ) clusters. All energies are in eV.

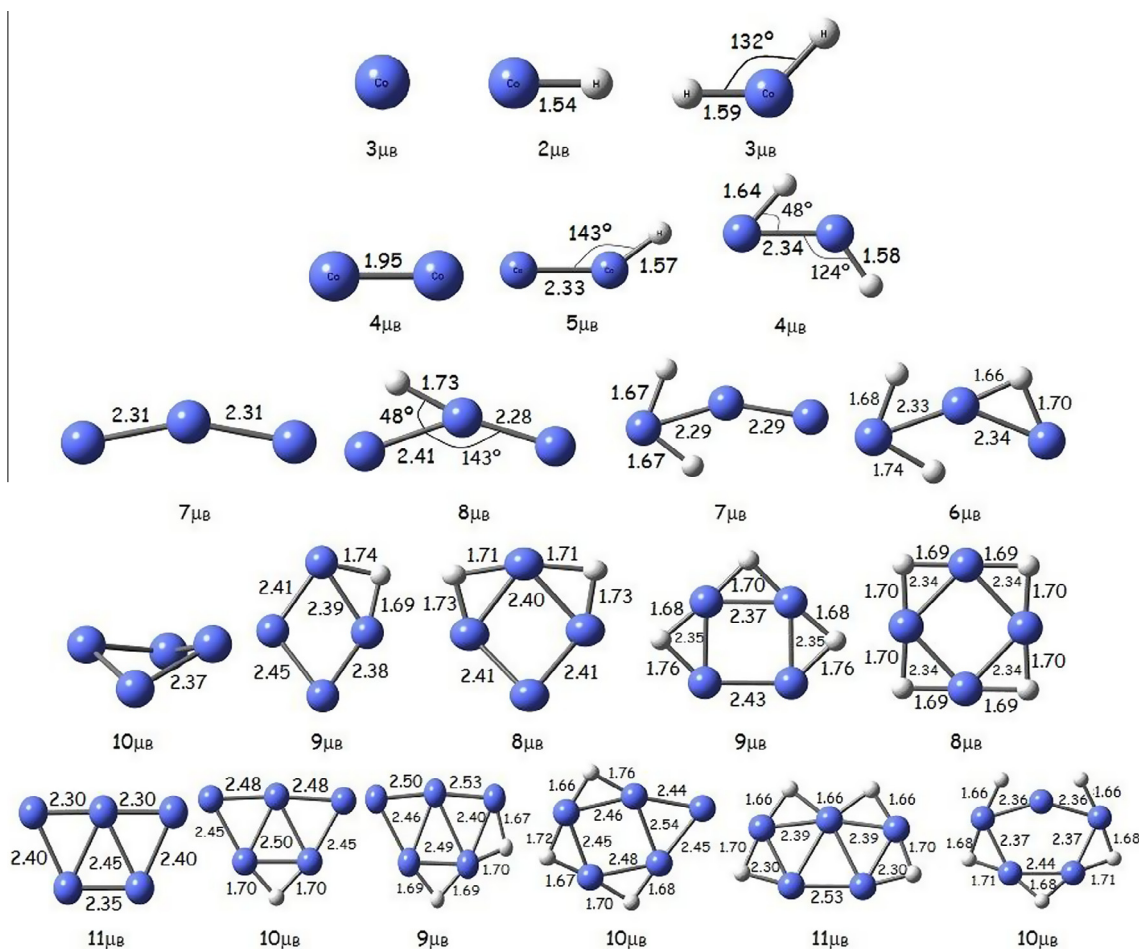
Cluster	Symmetry	$2S+1$	Eb/atom	$\bar{R}_{\text{Co-Co}}$	(H–L) <sup>0</sup>	(H–L) <sup>-</sup>
Co	–	4	–	–	1.48	1.91
Co <sub>2</sub>	$D_{\infty h}$	5	0.43	1.95	1.51	1.01
Co <sub>3</sub>	$C_{2v}$	8	1.25	2.31	2.18	1.93
Co <sub>4</sub>	$C_s$	11	1.42	2.37	2.01	1.48
Co <sub>5</sub>	$C_{2v}$	12	1.47	2.38	1.45	0.28

**Table 3**

Calculated and experimental [10,11] adiabatic detachment energy and vertical detachment energy of  $\text{Co}_n$  ( $n=1-5$ ) clusters. All energies are in eV.

Structure	Calculated		Shu-Rong et al.		Yoshida et al.	
	ADE	VDE	ADE	VDE	ADE	VDE
Co	1.00	1.00	1.00	–	0.70	–
Co <sub>2</sub>	0.84	0.87	0.80	1.10	1.00	–
Co <sub>3</sub>	1.38	2.45	1.50	1.60	1.30	1.80
Co <sub>4</sub>	1.55	1.99	1.80	1.90	1.60	2.00
Co <sub>5</sub>	0.97	1.69	1.70	1.90	1.40	1.90

occupied orbital is  $^1A_1$ . The simulated IR spectra for this cluster can be seen in Fig. 2 the peaks are situated one at  $25.9$  and a double peak at  $179.88$  and  $179.89\text{ cm}^{-1}$  due to the symmetry of this



**Fig. 1.** Calculated structures of neutral  $\text{Co}_n$  clusters and its corresponding multiplicities: on the right column  $\text{Co}_3$  and  $\text{Co}_4$  are an isosceles triangle and out-of plane rhombus respectively,  $\text{Co}_5$  is a W-like structure. To the left, the ground state structures as they adsorb 1–5 hydrogen atoms. For all cases the bond lengths are shown in Å. The coordinates for all structures can be found in [30].

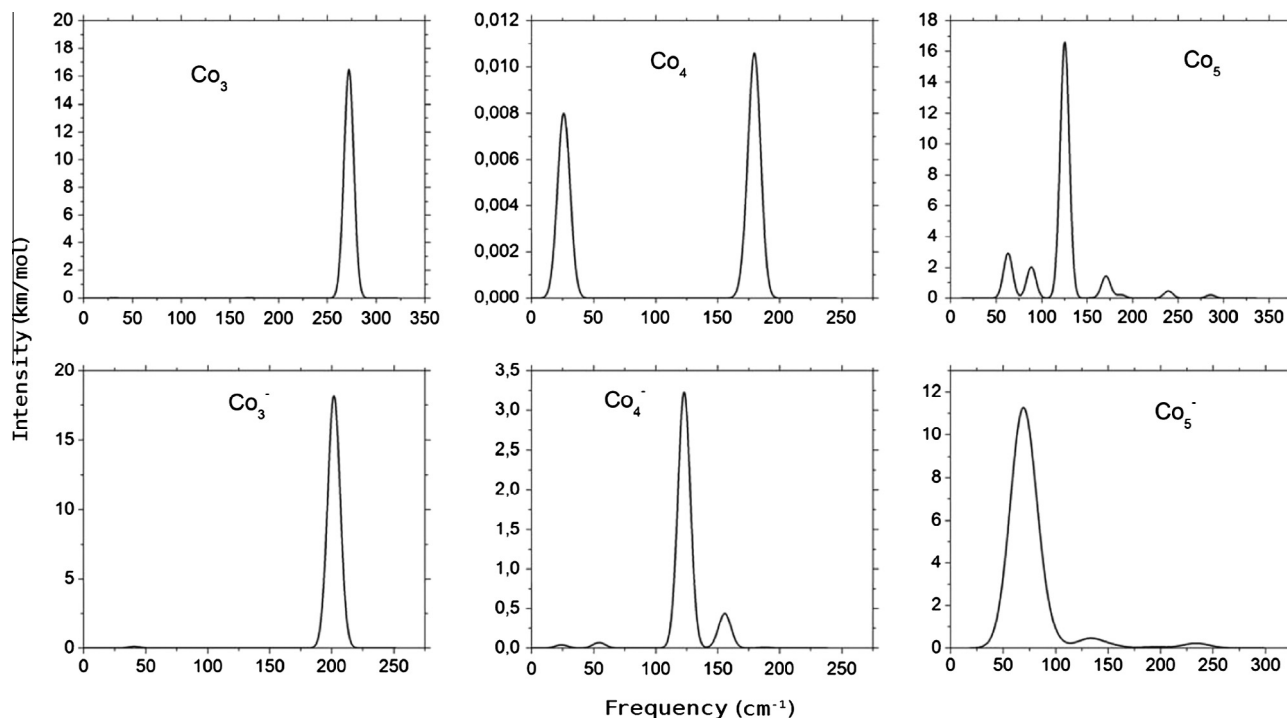


Fig. 2. Calculated Infra Red (IR) spectra of neutral  $\text{Co}_n$  and anion  $\text{Co}_n^-$  clusters a for  $n = 3-5$ .

system in the case of the neutral cluster, while the most intense peaks for the anion are located at 122.9, and 155.8  $\text{cm}^{-1}$ . The cation  $\text{Co}_4^+\text{Ar}$  has been studied earlier by Gehrke et al. [7] both theoretically and experimentally. They have found that for small Co clusters there is an unusually high value of the binding energy (0.3 eV) between Co and the argon atom used in the FIR-MPD technique, leading to the appearance of new IR-active modes, shifts in the frequency spectra, splittings of existing peaks and an increase in the absorption intensity. This makes it altogether a very difficult task to assign the IR spectra to the structure of  $\text{Co}_4^+$  and  $\text{Co}_4^+\text{Ar}$  DFT-IR calculations, as we have also found it to be true [8].

The binding energy in the  $\text{Co}_4$  neutral cluster is 1.42 eV per atom, and the average inter-atomic distance is 2.37 Å. The H–L energy gaps for both, the neutral and anionic clusters are 2.01 and 1.48 eV respectively as can be seen in Table 2. The next isomer higher in energy is a tetrahedron with multiplicity  $M = 11$  and lies 0.16 eV above the ground state. Our ground state coincides with all the previous theoretical results found in the literature. Our calculated ADE and VDE are 1.55 and 1.97 eV respectively and are compared with the experimental data available [10,11] in Table 3.

Finally the  $\text{Co}_5$  cluster case has been found after several initial configurations such as the triangular bi-pyramid, the square pyramid, the capped tetrahedron, a pentagon and several others. The resulting ground state turned out to be a W-like structure as the one found by Sebetci [12], with a  $C_{2v}$  symmetry group. The electronic state of the highest molecular orbital is  ${}^{12}B_1$  and the simulated IR spectra can be seen in Fig. 2. The main peaks are located at 62.9, 88.5, 125.2 and 170.7  $\text{cm}^{-1}$  followed by less intense peaks at 62.3, 154.6, 187.2, 239.4 and 285.93  $\text{cm}^{-1}$  for the neutral cluster, for the anion the main peaks are at 68.6, 85.1, 131.8 and 233.7  $\text{cm}^{-1}$ . The cationic  $\text{Co}_5^+\text{Ar}$  cluster case has been studied earlier by Gehrke et al. [7]. They found a distorted trigonal bipyramid as global minimum but the assignment as we mentioned in the previous case, is not clear because the IR is greatly modified by the presence of the Ar atom, making inaccurate a direct comparison with pure  $\text{Co}_5^+$  DFT results [8]. The W-like lowest energy structure for the cationic case has also been found after an intense

global search, and has been verified through a frequency analysis. In the next section we show how as it adsorbs H atoms the binding energy increases substantially and therefore the Ar atom cases to be of importance for the IR spectra and in this case the calculated IR spectra matches the experimental one quite accurately.

This structure has a 1.47 eV binding energy per atom, an average atomic distance of 2.38 Å, the energy H–L gaps for both, the neutral and the anionic cluster are 1.45 and 0.28 eV respectively (see Table 2). Notice that the  $\text{Co}_5^-$  anion already starts to observe a semi-metallic like behavior. The calculated adiabatic and vertical detachment energy are 0.97 eV, and 1.69 eV, both in good agreement with the available experimental data which is summarized in Table 3.

### 3.2. Hydrogenated Cobalt clusters

The main objective of this work is to understand the electronic behavior of neutral Co clusters after the adsorption of hydrogen atoms. For this reason we will add one hydrogen atom at a time for 1–5 hydrogen atoms. For the CoH dimer the binding energy is 2.83 eV which compares well to the value 2.63 eV obtained previously by Jones et al. [2] for the same system, where a PBE approach was implemented. Both studies found a triplet electronic state with  $C_v$  symmetry. We found the frequency for the mixed CoH dimer to be 1769  $\text{cm}^{-1}$ , as can be seen in Fig. 3, this high frequency is due to the difference in mass between the two atoms involved. As we add hydrogen atoms to the system all adsorption sites must be, and have been explored, i.e. top, bridge and hollow positions. All the lowest minima turned out to adsorb the hydrogen in the bridge site (not so for the dimer and trimer), and in a dissociative manner for all cases. This result is considerably different than the well known behavior in macroscopic systems, where cobalt surfaces adsorb molecular  $\text{H}_2$ , and in high coordination sites and in the adsorption of  $D_2$  (deuterium) in  $\text{Co}_n^+$  clusters [6]. Fig. 1 shows the geometries for the ground state hydrogenated  $\text{Co}_n\text{H}_m$  clusters, corresponding to  $n = 1-5$  and  $m = 1-5$  with their corresponding magnetic moment. Where we can clearly see how the structures

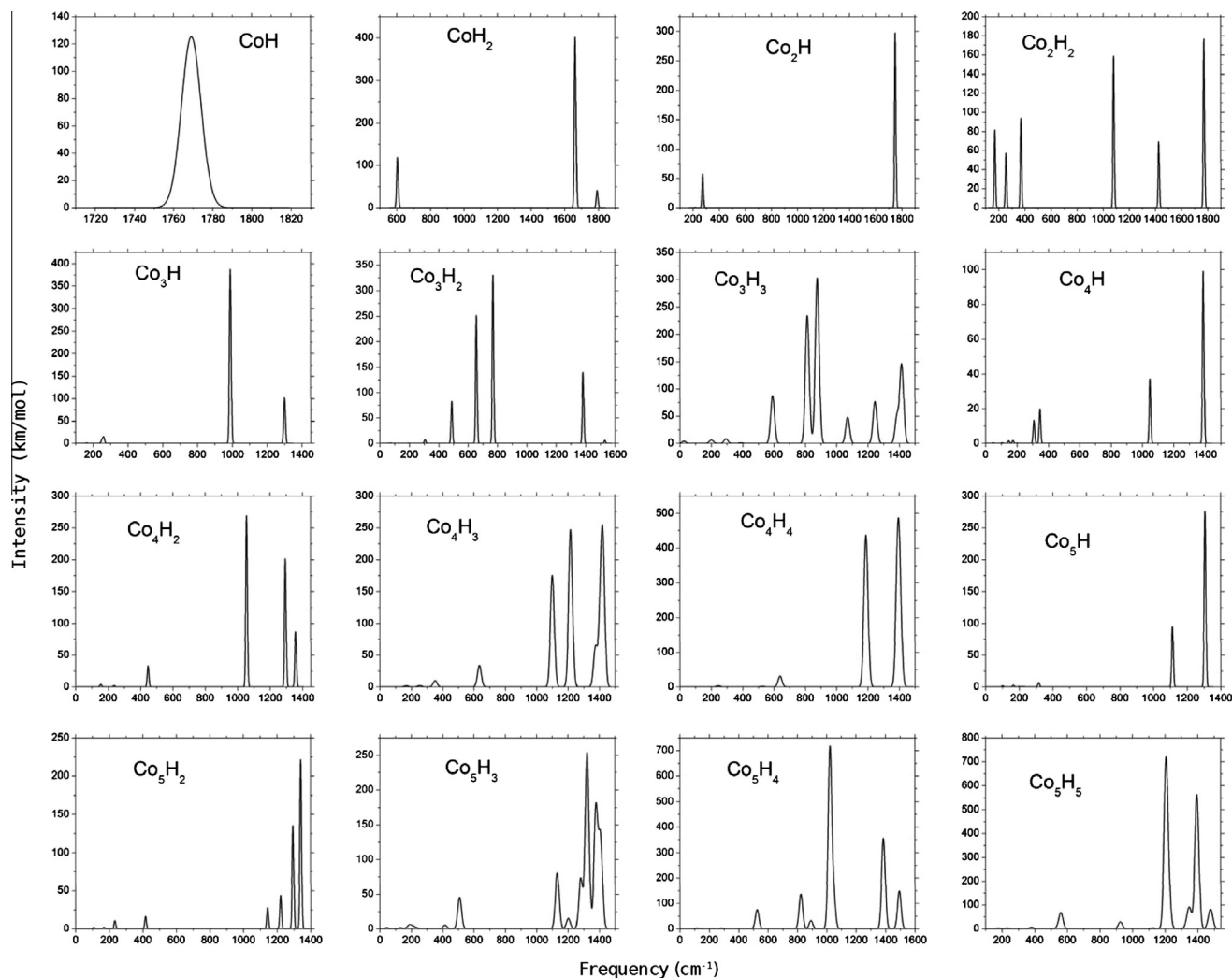


Fig. 3. Calculated Infra Red (IR) spectra of neutral  $\text{Co}_n\text{H}_m$  for  $n = 1-5$  and  $m = 1-5$  clusters.

become more planar as more H is added, and is taken mostly at bridge positions. In particular the  $\text{Co}_5$  structure suffers a topological transformation with the H intake, until it turns from W-like to a pentagonal geometry slightly off the X–Y plane. These results summarize the global minimum found for each case, after an intense search for different geometries configurations as well as the whole range of spin multiplicities.

Fig. 3 shows the calculated IR spectra, in a progressive manner as an H atom is added one by one. One can see that the peaks shift consistently towards higher frequencies, and subsequently adds more features to the spectra. Another important effect introduced is that for each hydrogen included, the magnetic moment is modified, for example going from  $\mu = 4 \mu_B$  for  $\text{Co}_2$  to  $\mu = 5 \mu_B$  for  $\text{Co}_2\text{H}$  (see Table 2 column 3 and Table 4 column 2). This effect has actually been reported earlier by one of us [2]. The change in the magnetic moment due to the presence of an hydrogen atom is quantified by:

$$\Delta\mu_H = [\mu(\text{Co}_n\text{H}_x) - \mu(\text{Co}_n\text{H}_{x-1})] \quad (2)$$

This quantity can be either positive or negative according to the newly added electron. If it has gone to the majority or the minority spin manifold, the changes in magnetic moment upon adsorption of H successive atoms lead to an oscillatory behavior. It increases for  $\text{Co}_n\text{H}_m$  for  $n=2$  upon the addition of the first H atom, while for the rest of the  $\text{Co}_n$   $n = 1, 3, 4, 5$  clusters, it decreases. The

Table 4

Structure, calculated spin multiplicities, gain in magnetic moment, binding energies, gain in binding energy and HOMO–LUMO gaps for  $\text{Co}_n\text{H}_m$  ( $n = 1-5$ ,  $m = 1-5$ ) clusters. All energies are in eV.

Cluster	$\mu$	$\Delta\mu_H$	$E_b$ (eV)	$\Delta E_{bH}$
$\text{CoH}$	2	–1	2.83	2.83
$\text{CoH}_2$	3	+1	5.10	2.26
$\text{Co}_2\text{H}$	5	+1	4.56	3.70
$\text{Co}_2\text{H}_2$	4	–1	6.91	2.35
$\text{Co}_3\text{H}$	6	–1	6.22	2.46
$\text{Co}_3\text{H}_2$	7	+1	9.11	2.89
$\text{Co}_3\text{H}_3$	6	–1	13.09	3.98
$\text{Co}_4\text{H}$	9	–1	8.87	3.20
$\text{Co}_4\text{H}_2$	8	–1	11.98	3.11
$\text{Co}_4\text{H}_3$	9	+1	14.91	2.93
$\text{Co}_4\text{H}_4$	8	–1	18.33	3.42
$\text{Co}_5\text{H}$	10	–1	11.23	3.18
$\text{Co}_5\text{H}_2$	11	+1	13.59	2.36
$\text{Co}_5\text{H}_3$	10	–1	17.18	3.59
$\text{Co}_5\text{H}_4$	11	+1	19.41	2.23
$\text{Co}_5\text{H}_5$	10	–1	23.06	3.65

successive addition of hydrogens changes the picture, enhancing the magnetic moment yet again for the next adsorbed H atom, as can be seen in Table 4 columns 2 and 3.

This result is contrary to the case on surfaces where the H adsorption reduces the magnetic moment [16]. Showing that the

behavior of small particles can be very different from thin layers, or bulk. This can be understood within a model that has been proposed earlier [2]: If we consider that each additional H atom is nothing else but a proton and an electron where the proton is screened, and the electron enters the lowest spin manifold available. This consideration may not hold when the LUMO of the majority and minority spin states are close in energy. This is because if the LUMO of the preceding cluster that belongs to the minority manifold, and the LUMO of the minority is only slightly higher in energy. The additional electron may still go to the majority manifold, since the exchange coupling could lead to a rearrangement of the manifolds. It is the difference  $\delta E$  defined by:

$$\delta E = [E_{\text{LUMO}}(\alpha) - E_{\text{LUMO}}(\beta)]. \quad (3)$$

That measures the change between the LUMO of the majority ( $\alpha$ ) and the minority ( $\beta$ ) spin manifolds, when the hydrogen atoms enters the system. This quantity is summarized for all our systems in Table 5, column 7. And it is precisely  $\delta E$  that controls the change in the magnetic moment. When it is positive the magnetic moment increases, while if it is less than  $-0.40$  eV, the addition of an H atom would decrease the magnetic moment. This model works for all cases considered in this study as it is shown in Table 5.

The next quantities studied are the binding energy ( $E_b$ ) shown in Table 4, column 4 and the gain in binding energy ( $\Delta E_{bH}$ ) as an H atom is added shown in Table 4, column 5. And have been calculated according to:

$$E_b = -[E(\text{Co}_n\text{H}_m) - (nE(\text{Co}) + mE(\text{H}))]. \quad (4)$$

And

$$\Delta E_{bH} = -[E(\text{Co}_n\text{H}_x) - (E(\text{Co}_n\text{H}_{x-1}) + E(\text{H}))]. \quad (5)$$

Note that the hydrogen binding energies increase with clusters size and vary from 0.86 eV to 4.56 eV upon the addition of one H atom (for example, in the  $\text{Co}_2$  dimer). As it can be seen in Tables 2 and 4 in columns, 2 and 4 respectively. We can see that the addition of H greatly enhanced the binding energy, adding stability to all cases. Another very important result of this study is the following: notice how as H is adsorbed, for example from the cluster  $\text{Co}_4\text{H}_2$  and onwards, the structures become planar. The enhanced binding energy is sufficient to modify the geometry of the cluster. This effect is very interesting and worth to be remarked, as even after the

**Table 5**  
Structures multiplicity HOMO and LUMO levels (hartrees) of the majority and minority spin states and  $\delta E$  (eV) in  $\text{Co}_n$  and  $\text{Co}_n\text{H}_m$  clusters

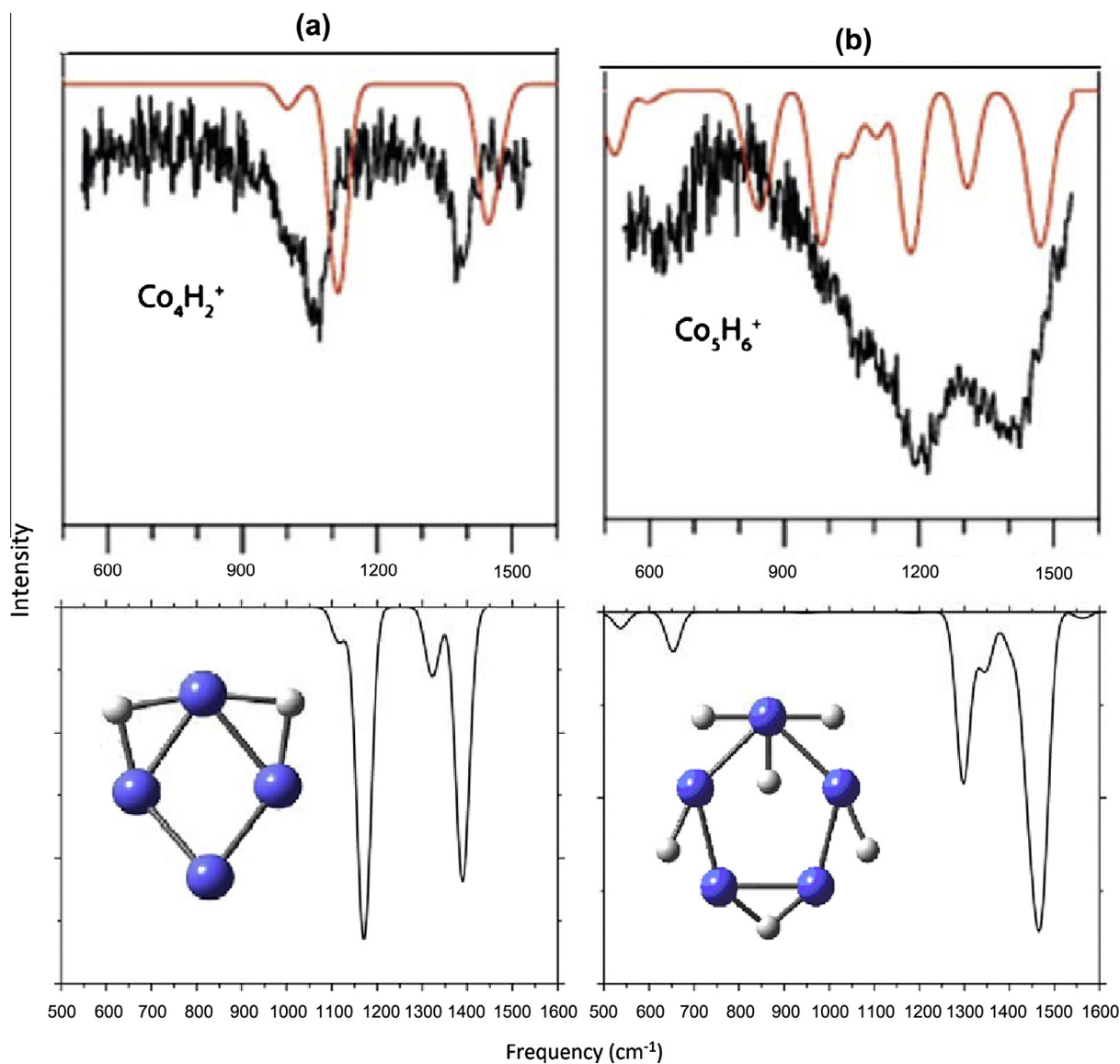
Cluster	2S + 1	Majority ( $\alpha$ )		Minority ( $\beta$ )		$\delta E$
		HOMO	LUMO	HOMO	LUMO	
Co	4	-0.18916	-0.02567	-0.16395	-0.10976	-2.29
CoH	3	-0.22567	-0.07963	-0.19695	-0.08897	-0.25
CoH <sub>2</sub>	4	-0.26304	-0.06880	-0.27263	-0.13078	-1.69
Co <sub>2</sub>	5	-0.21094	-0.09145	-0.1362	-0.08044	0.29
Co <sub>2</sub> H	6	-0.21253	-0.07652	-0.2093	-0.11935	-1.16
Co <sub>2</sub> H <sub>2</sub>	5	-0.22566	-0.10631	-0.19722	-0.10013	0.16
Co <sub>3</sub>	8	-0.18437	-0.08625	-0.18215	-0.10033	-0.38
Co <sub>3</sub> H	7	-0.16206	-0.05632	-0.16307	-0.06368	-0.20
Co <sub>3</sub> H <sub>2</sub>	8	-0.20327	-0.08577	-0.19546	-0.10221	-0.44
Co <sub>3</sub> H <sub>3</sub>	7	-0.19230	-0.08776	-0.17890	-0.08064	-0.53
Co <sub>4</sub>	11	-0.1726	-0.08536	-0.17968	-0.10597	-0.56
Co <sub>4</sub> H	10	-0.1682	-0.08523	-0.17387	-0.09978	-0.40
Co <sub>4</sub> H <sub>2</sub>	9	-0.20332	-0.08322	-0.16307	-0.07889	0.12
Co <sub>4</sub> H <sub>3</sub>	10	-0.18197	-0.06639	-0.19949	-0.10366	-1.01
Co <sub>4</sub> H <sub>4</sub>	9	-0.2471	-0.06427	-0.19468	-0.1061	-1.14
Co <sub>5</sub>	12	-0.17365	-0.0866	-0.14896	-0.09581	-0.40
Co <sub>5</sub> H	11	-0.20059	-0.0856	-0.1757	-0.08318	-0.25
Co <sub>5</sub> H <sub>2</sub>	10	-0.17775	-0.08582	-0.18189	-0.100389	-0.39
Co <sub>5</sub> H <sub>3</sub>	11	-0.18313	-0.08756	-0.22121	-0.08272	0.13
Co <sub>5</sub> H <sub>4</sub>	12	-0.19712	-0.08125	-0.19821	-0.09843	-0.46
Co <sub>5</sub> H <sub>5</sub>	11	-0.24024	-0.08984	-0.19064	-0.10936	0.19

adsorption of 5 hydrogen atoms by the cluster:  $\text{Co}_5\text{H}_5$ , the structures remains almost 2 dimensional (One can see the successive geometries of this cluster in Fig. 1), and even more importantly with the hydrogen bound in a dissociative manner.

The results in this study do not agree with a previous similar work in which one of us was involved [2] because by using a different exchange and correlation functional (PBE) the coinciding geometries ( $\text{Co}_{1-4}$ ) are substantially different, in both studies, therefore lead to different electronic and magnetic properties. Even the H adsorption for the  $\text{Co}_2\text{H}_2$  case in [2] is non-dissociative. To justify the methodology here exposed, we have studied the cationic  $\text{Co}_4\text{H}_2^+$  and  $\text{Co}_5\text{H}_6^+$  clusters separately to be compared with the experimental FIR-MPD spectra published by Swart et al. [9]. A similar procedure has been applied for the search of the lowest minimum, exploring different geometries, and the spin manifold. The lowest structure we found for the  $\text{Co}_4\text{H}_2^+$  corresponds to their almost 2-D rhombus. But the  $\text{Co}_5\text{H}_6^+$  structure here calculated, corresponds to a slightly off plane pentagonal structure with hydrogens in bridge positions, as opposed to their 3-D pyramid. Nevertheless the experimental FIR-MPD spectra [9] is in excellent agreement to our calculated IR for both  $\text{Co}_4\text{H}_2^+$  and  $\text{Co}_5\text{H}_6^+$ , as can be seen in Fig. 4.

#### 4. Summary

To summarize, the present work we have performed a comprehensive study of the electronic, magnetic and structural properties of small cobalt clusters  $n = 1-5$  atoms, and the effect of hydrogen adsorption on its surfaces, by using a synergistic approach. We compare our results with the most relevant PES and FIR-MPD experimental data available in these systems [9,7,10,11]. An important outcome of the present study is that, in all cases here studied the best agreement between experimental and calculated spectra was found for the geometry corresponding to the putative global minima. Our studies show that the effect of hydrogen adsorption in small clusters can be significantly different than in macroscopic samples. As it is known that in surfaces, the adsorption of  $\text{H}_2$  first it bounds in highly correlated sites, and secondly it invariably leads to a quenching of the magnetic moment. In small clusters, however, hydrogen bounds dissociatively, and in low coordinated sites (bridge). The calculated IR spectra for both cases, before and after the adsorption of H reveals first, a marked shift of the peaks to much higher frequencies, and the appearances of more features in the spectra as there is a symmetry loss for the combined species. Furthermore the magnetic moment can increase upon adsorption of one single H atom. It is shown that the progression in the magnetic moment can be understood within a model involving the unoccupied electronic states in the parent cluster. The effect of adding H can effectively be looked upon as adding an electron to the unfilled states of the parent cluster. The calculated infra red spectra of the ground state geometries for the cationic clusters:  $\text{Co}_4\text{H}_2^+$  and  $\text{Co}_5\text{H}_6^+$  here obtained are in excellent agreement with the experimental far-infrared multiple photon dissociation spectroscopy [9]. In this work we demonstrate the reliability of hybrid exchange–correlation functionals in identifying the correct ground state geometry. Some small differences in the spin manifold have been observed though, when comparing the calculations in [2] at the same ground state geometries with our own. This difference is due to the fact that we use B3LYP that incorporates 20% Hartree–Fock (HF) exchange, while [2] used the PBE functional with no HF exchange. Therefore despite the achieved certitude in the geometry between for both cations and anions between theory and experiment, obtained by means of the inclusion of such hybrid functionals, it is clear that a reliable description of the spin multiplicity and electronic structure for these highly open shell systems remains a challenge. It is clear that a more decisive



**Fig. 4.** Experimental (black) and simulated (red) IR depletion spectra of  $\text{Co}_4\text{H}_2^+$  in (a) and of  $\text{Co}_5\text{H}_6^+$  in (b) shown at the top, both taken from [9]. Our corresponding calculated IR and corresponding geometries are shown directly below. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

EPR type experiment is required to appropriately determine the factors underpinning the performance of the hybrid functional for 3d transition metals in general.

IR spectra, adiabatic and vertical detachment energies, binding energies, magnetic moments as well as the HOMO–LUMO gaps have been calculated. The stability and dependence of these properties on the cluster sizes has been analyzed. It has been shown that they are very stable, if we judge their stability by their enhanced binding energy. Even more, as they adsorb hydrogen, they become planar, and at the same time they enhance their magnetic properties substantially. Now, if we extrapolate, this result it correlates well with earlier Stern–Gerlach experiments [1] in bigger size clusters. Work to extend such studies to larger cluster sizes is in progress. Finally we hope that through the presented study, more FIR-MPD experiments on these systems may appear in the literature.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2013.07.012>.

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