



Photoelectron spectroscopy and density functional study of Co_nOH^- ($n = 1-3$)



Ren-Zhong Li^{a,b}, Hong-Guang Xu^b, Xi-Ling Xu^b, Wei-Jun Zheng^{b,*}

^a College of Electronics and Information, Xi'an Polytechnic University, Xi'an 710048, China

^b Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:

Received 14 April 2014

In final form 19 May 2014

Available online 24 May 2014

ABSTRACT

We investigated Co_nOH^- ($n = 1-3$) clusters with photoelectron spectroscopy and density functional theory calculations. The vertical detachment energies of Co_nOH^- ($n = 1-3$) were measured to be 1.41 ± 0.04 , 1.22 ± 0.08 , 1.62 ± 0.08 eV, respectively. The electron affinity and term energy of CoOH neutral were determined to be 1.33 ± 0.04 and 0.25 ± 0.04 eV, respectively. The most probable geometries of CoOH^- and Co_2OH^- were determined to be L-shaped structures, and that of Co_3OH^- can be considered as one of the Co atoms of Co_3 triangle bonded to the oxygen atom of OH group. The excess electron of the Co_nOH^- anion is mainly localized on the Co_n site.

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1. Introduction

Transition metal hydroxides have many important applications such as battery electrode materials [1–3] and heterogeneous catalysts [4–6]. Many studies on transition metal hydroxides have been carried out. Kauffman et al. [7,8] studied a number of hydroxides formed by reaction of the first row transition-metals with water in argon matrices at 15 K and found that the structures of HMOH (M = transition metal) are nonlinear in all cases, which is similar to covalent molecule H_2O but different from highly ionic molecules like KOH and RbOH [9,10]. Zhou et al. [11–15] explored the reactions of Mn, Fe, Sc, Ti, V with H_2O using matrix-isolation FTIR and quantum chemical calculations, and found that the MOH_2 type of structures for Mn and Fe are stable while the MOH_2 type of structures for Sc, Ti, and V are metastable and rearranged to form HMOH type of structures. Wang et al. [16–20] investigated the reactions of transition metals with H_2O_2 or with H_2/O_2 mixtures in argon matrices and found that $\text{M}(\text{OH})_2$ molecules can be formed. Schröder et al. [4] investigated the thermochemistry of FeOH and $\text{Fe}(\text{OH})_2$ neutrals and their cations using mass spectrometry. Zheng et al. [21] studied AuOH^- and Au -water clusters with photoelectron spectroscopy. The structures of CuOH and AgOH were found to be bent [22–27], indicating that the Cu–O and Ag–O bonds have some characters of covalent bonds.

Previously, we investigated Co_nO^- ($n = 1-3$) clusters [28] and the interactions between Co_nO^- ($n = 1-3$) and water [29] using photoelectron spectroscopy and density functional theory. The

results revealed that dihydroxides $\text{Co}_n(\text{OH})_2^-$ ($n = 1-3$) were formed when Co_nO^- clusters interact with water. In this work, we carried out a combined photoelectron spectroscopy and density functional theory study on Co_nOH^- ($n = 1-3$) cluster anions. Cobalt hydroxides can be used as an additive to electrode materials [30]. Understanding the bonding properties of cobalt hydroxides may provide valuable information of reaction mechanism for their applications.

2. Experimental and computational methods

2.1. Experimental

The experiments were carried out using a home-built apparatus consisting of a time-of-flight mass spectrometer and a magnetic-bottle photoelectron spectrometer, which has been described elsewhere [31]. In brief, a rotating and translating Co target was ablated with the second harmonic (532 nm) light pulses of a Nd:YAG laser. Helium gas with 4 atm. backing pressure seeded with water vapor was allowed to expand through a pulsed valve over the target. The reaction of cobalt with water generated the Co–water adducts and Co_nOH^- ($n = 1-3$) cluster anions. The produced cluster anions were mass-analyzed by the time-of-flight mass spectrometer, and then the Co_nOH^- ($n = 1-3$) clusters were each mass-selected and decelerated before being photodetached. The photodetachment of the selected cluster anions was performed using the 532 or 266 nm beams from another nanosecond Nd:YAG laser. The electrons resulting from the photodetachment were energy-analyzed by the magnetic-bottle photoelectron spectrometer. The photoelectron spectrum was calibrated using the

* Corresponding author. Fax: +86 10 62563167.

E-mail address: zhengwj@iccas.ac.cn (W.-J. Zheng).

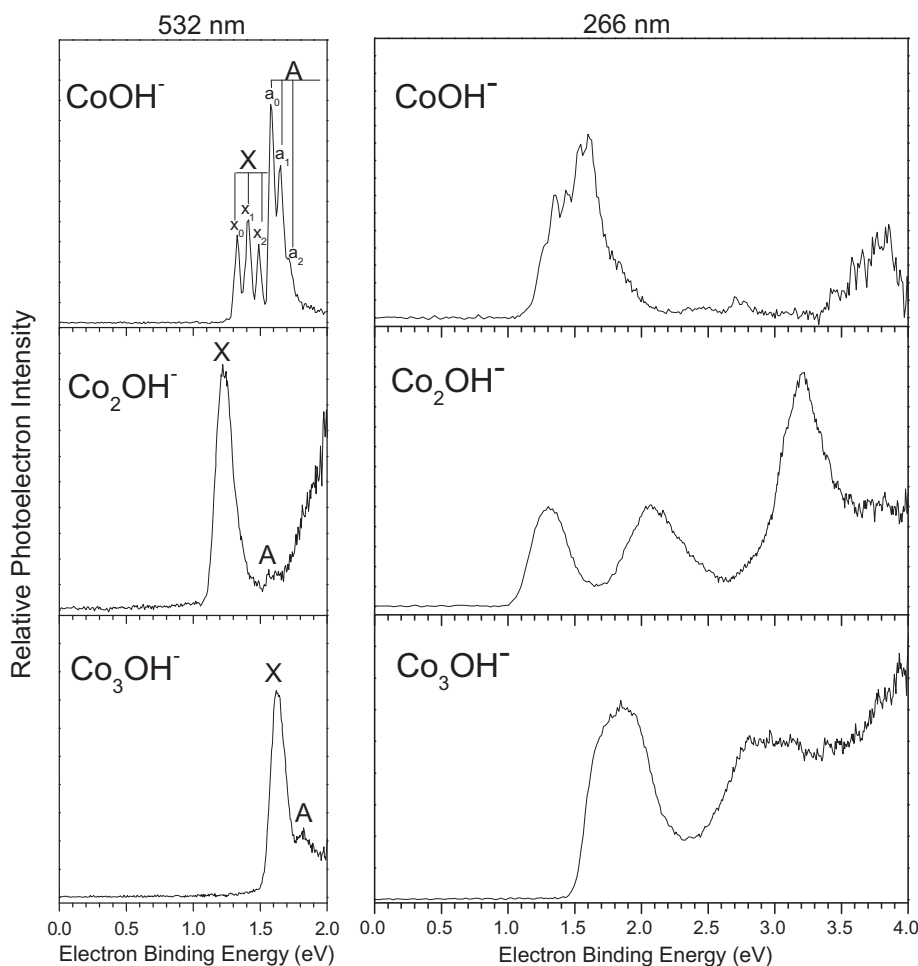


Figure 1. Photoelectron spectra of Co_nOH^- ($n = 1-3$) taken with 532 and 266 nm photons.

spectrum of Cu^- taken at similar conditions. The instrumental resolution was approximately 40 meV for electrons with 1 eV kinetic energy.

2.2. Computational methods

The theoretical calculations were performed using the BPW91 functional with a combination of Beck's exchange [32] and Perdew-Wangs' correlation [33]. The standard 6-311+G** basis set was used for the Co, O and H atoms. The geometric structures of the anionic and the neutral species were determined by optimizing different initial geometries at several multiplicities. The optimizations were performed without imposing symmetry constraints and the calculated energies were corrected with the zero-point vibrational energies. Harmonic vibrational frequencies were calculated to confirm that the optimized structures correspond to real minima. The theoretical vertical detachment energies (VDEs) were calculated as the energy differences between the neutrals and anions both at the geometries of the anionic species. The theoretical adiabatic detachment energies (ADEs) were obtained as the energy differences between the cluster neutrals and the anions with the neutral structures relaxed to the nearest local minima using the geometries of the corresponding anions as initial structures. In addition, the term energy $T(\tilde{A} \leftarrow \tilde{X})$ of CoOH neutral was calculated with TD-DFT [34–35] and SAC-CI [36–38] methods. All calculations were conducted using the GAUSSIAN09 program package [39].

3. Experimental results

The photoelectron spectra of Co_nOH^- ($n = 1-3$) taken with 532 and 266 nm photons are shown in Figure 1. The adiabatic detachment energies (ADEs) and vertical detachment energies (VDEs) of Co_nOH^- measured from their photoelectron spectra are listed in Table 1.

3.1. CoOH^-

At 266 nm, the photoelectron spectrum of CoOH^- has two major broad bands in the ranges of 1.26–1.79 and 3.38–3.97 eV.

Table 1

Relative energies, VDEs and ADEs of the low energy isomers of Co_nOH^- ($n = 1-3$) calculated at the BPW91 level of theory as well as the comparison with the experimental VDEs and ADEs.

Isomer	ΔE (eV)	ADE (eV)		VDE (eV)	
		Theo.	Exp.	Theo.	Exp.
CoOH^-	1A ($^4A'$)	0.00	1.11	1.33 $\pm$ 0.04	1.17
	1B ($^2A'$)	0.27	0.64	0.75	1.41 $\pm$ 0.04
Co_2OH^-	2A ($^5A'$)	0.00	1.25	1.14 $\pm$ 0.08	1.35
	2B ($^3A''$)	0.64	1.49	1.66	1.22 $\pm$ 0.08
	2C (7A)	0.69	0.94	0.97	
Co_3OH^-	3A (8A)	0.00	1.47	1.56 $\pm$ 0.08	1.54
	3B (6A)	0.69	0.77	0.78	1.62 $\pm$ 0.08
	3C (2A)	0.74	1.29	1.53	

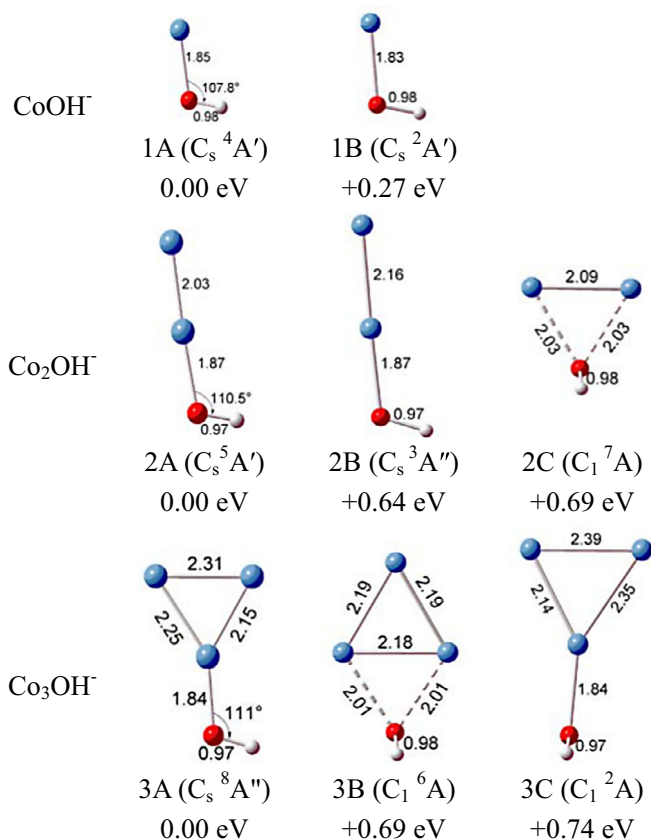


Figure 2. Optimized geometries of the low-lying isomers of Co_nOH^- ($n = 1-3$) clusters. The bond lengths are in angstroms.

With 532 nm photons, the vibrationally resolved photoelectron spectrum was obtained, and more details of the low electron binding features can be seen. There are two sets of peaks, X and A, in the 532 nm photoelectron spectrum, corresponding to the transitions from the anion to two electronic states of CoOH neutral. The first one (X) at the low electron binding energy side presents a vibrational progression which is produced due to the transition to the electronic ground state of CoOH. The measured energy spacing between the vibrational states is ~ 0.08 eV. The electron affinity of CoOH neutral is determined to be 1.33 eV from the $0 \leftarrow 0$ transition. The $(1,0,0) \leftarrow (0,0,0)$ transition at 1.41 eV corresponds to vertical transition and yields VDE of 1.41 eV for CoOH^- . The second one (A) at higher electron binding energy represents the transition to the first electronic excited state of CoOH ($\tilde{A}(\text{CoOH}) \leftarrow \tilde{X}(\text{CoOH})$) with vibrational frequency of 0.07 eV. The term energy ($\tilde{A}(\text{CoOH}) \leftarrow \tilde{X}(\text{CoOH})$) is determined to be 0.25 eV based on the spacing between x_0 and a_0 (see Figure 1).

3.2. Co_2OH^-

The photoelectron spectrum of Co_2OH^- taken with 266 nm photons has three broad features in the ranges of 1.12–1.58, 1.82–2.45, and 2.94–3.58 eV. The 532 nm photoelectron spectrum shows an intense peak at 1.22 eV. Its VDE and ADE were measured to be 1.22 and 1.14 eV, respectively.

3.3. Co_3OH^-

Three unresolved broad bands in the ranges of 1.55–2.23, 2.54–3.20, and 3.62–4.0 eV are showed in the 266 nm photoelectron spectrum of Co_3OH^- . Two discernible features at 1.62 eV (X) and 1.83 eV (A) are observed in the 532 nm spectrum.

4. Theoretical results and discussion

The optimized geometries of the typical low-lying isomers of Co_nOH^- ($n = 1-3$) anions are presented in Figure 2, and their corresponding neutral isomers are presented in Figure 3. The calculated ADEs and VDEs are summarized in Table 1 and compared with the experimental values.

4.1. CoOH^- and CoOH

For CoOH^- , the structure with the lowest energy is isomer 1A, which is an L-shaped bent structure in $^4A'$ state with the Co atom attached to the O atom of OH. The angle $\angle_{\text{CoOH}}$ is about 107.8° and the bond lengths of Co–O and O–H are 1.85 and 0.98 Å, respectively. The Co–O bond length is 0.23 Å longer than that in CoO^- [28]. It is noteworthy that the bond angle of CoOH^- is slightly larger than that of H_2O ($\angle_{\text{HOH}} = 104.5^\circ$) [40], meaning that electrostatic repulsion between Co and H is larger than that between the two H atoms of H_2O . The theoretical VDE and ADE of isomer 1A are 1.17 and 1.11 eV respectively, in agreement with the experimental values. Cobalt hydroxide has three vibrational modes: Co–O stretching, O–H stretching, and Co–O–H bending. The calculated Co–O stretch frequency of CoOH is about 629 cm^{-1} after a scale factor of 0.96 [41], consistent with the vibrational spacing of 0.08 eV (645 cm^{-1}) for $\tilde{X}(\text{CoOH}) \leftarrow \tilde{X}(\text{CoOH}^-)$ observed in the 532 nm spectrum of CoOH^- . Isomer 1B is 0.27 eV higher than isomer 1A in energy, and its ADE (0.64 eV) and VDE (0.75 eV) is much lower than the experimental values (Table 1). Therefore, the existence of isomer 1B in the experiments can be ruled out. The lowest energy geometry for neutral CoOH molecule is isomer 1A' in $^3A''$ state, with C_s symmetry, which is also an L-shaped bent structure and the bond angle $\angle_{\text{CoOH}}$ is 110° , slightly larger than that of CoOH^- . We noted that covalent molecule H_2O has a strongly bent structure, but highly ionic molecules KOH and RbOH are found to be linear [9,10]. It is interesting that the previous studies found that the structures of

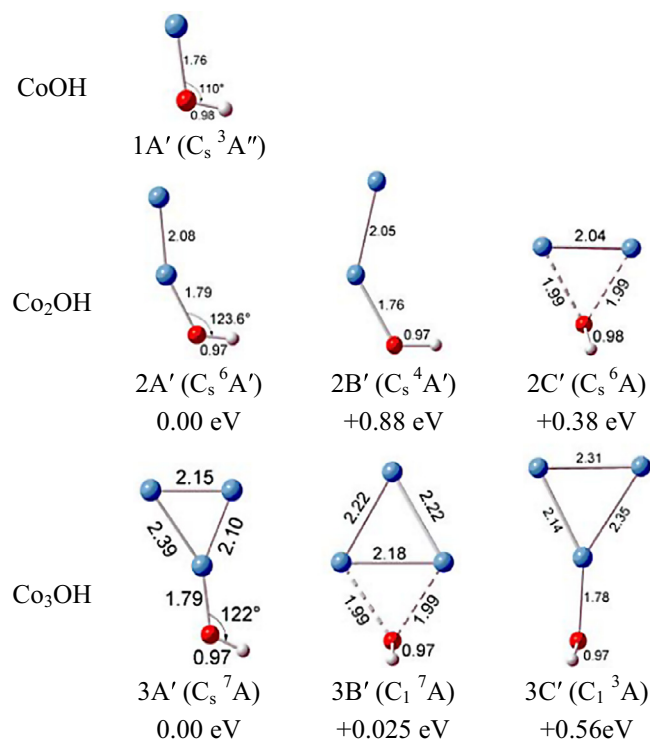


Figure 3. Optimized geometries of the low-lying isomers of neutral Co_nOH ($n = 1-3$) clusters. The bond lengths are in angstroms.

Table 2

Mulliken charges, atomic magnetic moments (μ_A), and total magnetic moments (μ_T) of the most stable isomers of Co_nOH^- ($n = 1-3$).

Cluster	Atom	Mulliken charges (e)	μ_A (μ_B)	μ_T (μ_B)
CoOH^-	Co_1	−0.54	2.80	3
	O_2	−0.62	0.20	
	H_3	0.16	−0.003	
Co_2OH^-	Co_1	−0.43	2.08	4
	Co_2	−0.10	1.87	
	O_3	−0.66	0.03	
	H_4	0.19	0.002	
Co_3OH^-	Co_1	−0.32	2.47	7
	Co_2	−0.34	2.42	
	Co_3	0.10	2.03	
	O_4	−0.66	0.08	
	H_5	0.22	0.002	

Table 3

Mulliken charges, atomic magnetic moments (μ_A), and total magnetic moments (μ_T) of the most stable isomers of Co_nOH ($n = 1-3$).

Cluster	Atom	Mulliken charges (e)	μ_A (μ_B)	μ_T (μ_B)
CoOH	Co_1	0.28	1.84	2
	O_2	−0.51	0.17	
	H_3	0.23	−0.007	
Co_2OH	Co_1	0.10	2.09	5
	Co_2	0.18	1.87	
	O_3	−0.55	0.03	
	H_4	0.27	0.002	
Co_3OH	Co_1	0.08	2.47	6
	Co_2	0.10	2.42	
	Co_3	0.15	2.03	
	O_4	−0.58	0.08	
	H_5	0.25	0.002	

CuOH and AgOH are also bent and the $\text{Cu}-\text{O}$ and $\text{Ag}-\text{O}$ bonds present considerable covalent interactions [22–27,42]. That indicates that the $\text{Co}-\text{O}$ bond of $\text{CoOH}^{-/0}$ has covalent characters similar to the $\text{Cu}-\text{O}$ and $\text{Ag}-\text{O}$ bonds. In addition, we calculated the term energy of CoOH with TD-DFT and SAC-CI methods. The term energy of the transition $A \leftarrow X$ of CoOH is calculated to be 0.24 eV with both methods, in good agreement with the experimental value of 0.25 eV.

4.2. Co_2OH^- and Co_2OH

The most stable structure of Co_2OH^- is isomer 2A in quintet state, with C_s symmetry. Similar to CoOH^- , isomer 2A is also an L-shaped structure with the bond angle $\angle_{\text{CoOH}} = 110.5^\circ$. The three atoms $\text{Co}-\text{Co}-\text{O}$ could be considered as quasilinear because of the bond angle $\angle_{\text{CoCoO}} = 177^\circ$. Its $\text{Co}-\text{Co}$, $\text{Co}-\text{O}$, $\text{O}-\text{H}$ bond lengths are 2.03, 1.87 and 0.97 Å, respectively. The $\text{Co}-\text{O}$ bond length in Co_2OH^- is slightly longer (0.02 Å) than that of CoOH^- , and the $\text{O}-\text{H}$ bond length is almost the same as that of CoOH^- . The calculated VDE and ADE of isomer 2A are 1.25 and 1.35 eV, respectively, which are consistent with the experimental values listed in Table 1. Isomer 2B is also an L-shaped structure in triple state with C_s symmetry. Isomer 2C has no symmetry with 7A state. Both isomers 2B and 2C are much less stable than isomer 2A. So it is unlikely for isomers 2B and 2C to be presented in the experiments. For the neutral Co_2OH , isomer 2A' presents a sextet $^6A'$ ground state and C_s symmetry, with the bond angles $\angle_{\text{CoCoO}} = 158^\circ$ and $\angle_{\text{CoOH}} = 123.6^\circ$. Isomers 2B' in $^4A'$ state and 2C' in 6A state are higher in energy than isomer 2A' by 0.88 and 0.38 eV, respectively.

4.3. Co_3OH^- and Co_3OH

The most stable structure of Co_3OH^- is found to be isomer 3A in $^8A'$ state with C_s symmetry. It is formed by attaching the oxygen

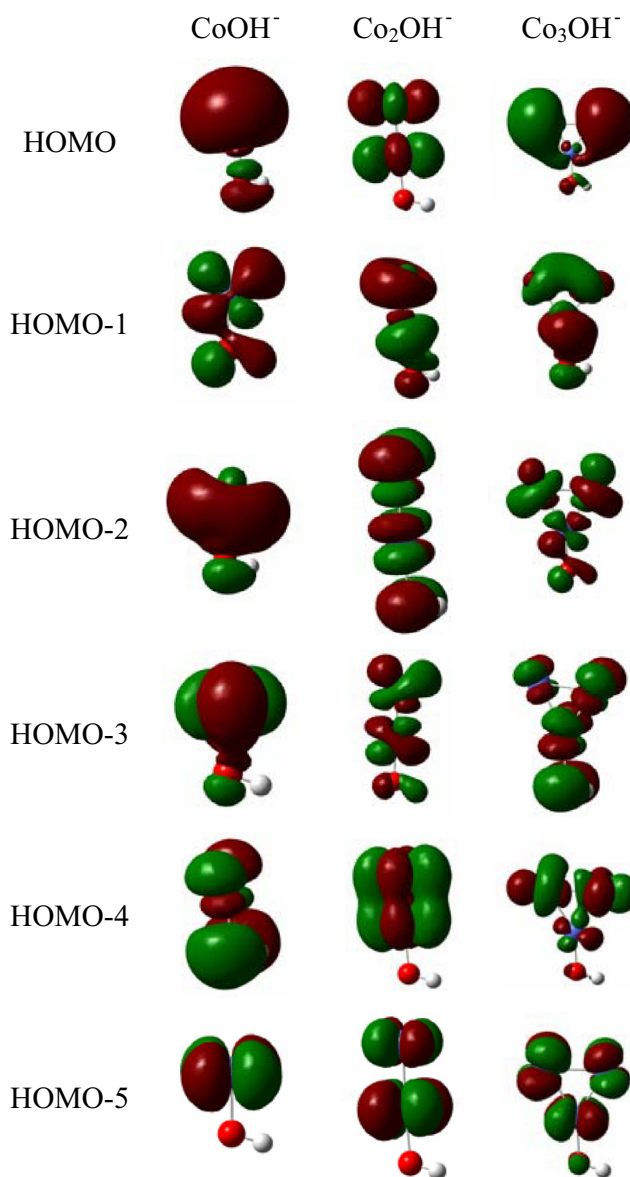


Figure 4. Diagrams of the molecule orbitals of the most stable isomers of Co_nOH^- ($n = 1-3$). The orientations of the clusters are the same as the ones in Figure 2.

atom of OH group to one of the Co atoms in Co_3 triangle with the bond angle $\angle_{\text{CoOH}} = 111^\circ$. The bond lengths of $\text{Co}-\text{O}$ and $\text{O}-\text{H}$ are 1.84 and 0.97 Å, respectively. The $\text{O}-\text{H}$ bond length of Co_3OH^- is nearly the same as those of CoOH^- and Co_2OH^- described above. The calculated VDE (1.47 eV) and ADE (1.54 eV) of isomer 3A agree well with the experimental values. Isomer 3B presents 6A electron state and no symmetry. The energy of isomer 3B is higher than that of isomer 3A by 0.69 eV. The VDE (0.78 eV) and ADE (0.77 eV) of isomer 3B are much lower than the experimental values. The energy of isomer 3C is much higher than that of isomer 3A. Therefore, the existence of isomers 3B and 3C in the experiments can be excluded. For the neutral Co_3OH , isomer 3A' has the lowest energy in state 7A with C_s symmetry, and it is similar to the anion structure isomer 3A.

Mulliken population and magnetic properties analysis were performed to investigate the charges and magnetic moments of Co_nOH^- ($n = 1-3$) and their corresponding neutrals as presented in Tables 2 and 3. For Co_nOH^- ($n = 1-3$), the sum of negative charges on the cobalt atoms increased by 0.81e–0.89e compared to their neutral counterpart, suggesting that the excess electron

is mainly localized at the Co sites. As for the magnetic moments, the calculated values for Co_nOH ($n = 1-3$) neutral are 2, 5, and 6 μ_B while those of Co_nOH^- ($n = 1-3$) are 3, 4, 7 μ_B respectively. The magnetic moments of CoOH^- and Co_3OH^- are higher than those of their corresponding neutrals by 1 μ_B , whereas for Co_2OH^- , its magnetic moment is lower than that of its neutral counterpart by 1 μ_B . In addition, we also conducted molecular orbital analysis of Co_nOH^- ($n = 1-3$). As shown in Figure 4, it is found that the highest occupied molecular orbitals of these clusters are mainly localized over Co_n , which is similar to that of Co_nO^- ($n = 1-3$) [28].

5. Conclusions

We report a combined photoelectron spectroscopy and density functional calculations study on Co_nOH^- ($n = 1-3$) clusters. Based on the vibrationally resolved photoelectron spectrum of CoOH^- , the electron affinity and term energy of CoOH were determined to be 1.33 and 0.25 eV, respectively. By comparing the calculated VDEs with the experimental results, we found that CoOH^- and Co_2OH^- have L-shaped structures and the angles $\angle_{\text{CoOH}}$ of them are 107.8° and 110.5°, respectively. Co_3OH^- corresponds to a structure where one Co atom of Co_3 triangle bonded to the oxygen atom of OH group, and the angle $\angle_{\text{CoOH}}$ is calculated to be 111°. The excess electrons are mainly localized at Co sites.

Acknowledgments

W.-J. Zheng acknowledges the National Natural Science Foundation of China (NSFC, Grant No. 20933008) for financial support. R-Z Li acknowledges the National Natural Science Foundation of China (NSFC, Grant No. 21301134) and Scientific Research Program Funded by Shanxi Provincial Education Department (Grant No. 2013JK0655). The theoretical calculations were conducted on the ScGrid and DeepComp 7000 of the Supercomputing Center, Computer Network Information Center of Chinese Academy of Sciences.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2014.05.051>.

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