

Interaction of Co_mO^- ($m = 1-3$) with water: Anion photoelectron spectroscopy and density functional calculations

Ren-Zhong Li, Hong-Guang Xu, Guo-Jin Cao, Yu-Chao Zhao, and Wei-Jun Zheng^{a)}*Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

(Received 8 July 2011; accepted 10 September 2011; published online 4 October 2011)

We investigated the reactions between cobalt-oxides and water molecules using photoelectron spectroscopy and density functional calculations. It has been confirmed by both experimental observation and theoretical calculations that dihydroxide anions, $\text{Co}_m(\text{OH})_2^-$ ($m = 1-3$), were formed when Co_mO^- clusters interact with the first water molecule. Addition of more water molecules produced solvated dihydroxide anions, $\text{Co}_m(\text{OH})_2(\text{H}_2\text{O})_n^-$ ($m = 1-3$). Hydrated dihydroxide anions, $\text{Co}_m(\text{OH})_2(\text{H}_2\text{O})_n^-$, are more stable than their corresponding hydrated metal-oxide anions, $\text{Co}_m\text{O}(\text{H}_2\text{O})_{n+1}^-$. © 2011 American Institute of Physics. [doi:10.1063/1.3644897]

I. INTRODUCTION

The interactions between transition metal-oxides and water have attracted increasing interest because of their important applications in oxidation catalysis and materials.¹⁻³ Metal oxides interacting with H_2O can form hydrated metal-oxides or undergo hydrogen-transfer to render the corresponding dihydroxides. The hydrated metal-oxide ions and dihydroxide isomers have been investigated by many research groups.⁴⁻¹¹ The relative stabilities between hydrated metal-oxide and dihydroxide species and the interconversions between them have received special attention. Schröder *et al.* conducted collision-induced dissociation experiments and density functional calculations to investigate the structure of $[\text{MO}_2\text{H}_2]^+$ ($M = \text{Fe}, \text{Co}, \text{and Ni}$).⁸ They found that the relative stability of hydrated metal-oxide cations ($\text{MO}^+(\text{H}_2\text{O})$) compared to the dihydroxide isomers ($\text{M}(\text{OH})_2^+$) increases from Fe to Ni, whereas the dihydroxide structure is favorable for FeO_2H_2^+ while the hydrated metal-oxide structure is more stable for NiO_2H_2^+ . The flow tube experiments⁹ and density functional calculations¹⁰ show that the hydrated metal-oxide species such as $\text{NbO}_3(\text{H}_2\text{O})^-$ and $\text{NbO}_5(\text{H}_2\text{O})^-$ can undergo hydrogen migration processes to produce dihydroxide species $\text{NbO}_2(\text{OH})_2^-$ and $\text{NbO}_4(\text{OH})_2^-$, respectively. The dihydroxide species $\text{NbO}_2(\text{OH})_2^-$ and $\text{NbO}_4(\text{OH})_2^-$ are more stable than their corresponding hydrated metal-oxide species. Ricca *et al.* studied the structures of $\text{M}(\text{OH})_n^+$ ($n = 1-3$, $M = \text{Sc}, \text{Ti}, \text{V}, \text{Co}, \text{Ni}, \text{Cu}$) with B3LYP method and calculated their successive OH bond energies at CCSD(T) level.¹¹ More interestingly, it has been found that the tautomerization processes between $\text{MO}(\text{H}_2\text{O})^+$ and $\text{M}(\text{OH})_2^+$ ($M = \text{V}, \text{Nb}, \text{and Ta}$) can be catalyzed by water molecules.¹² Therefore, investigating the interactions between metal oxides and water is important for understanding the relative stabilities between hydrated oxides and dihydroxides as well as for providing useful information about catalysis processes. We are especially interested in the interactions between cobalt

oxide and water because cobalt oxide and cobalt hydroxide are important materials for energy conversion and storage devices such as batteries and supercapacitors.¹³⁻¹⁵ Recent studies show that α -cobalt hydroxide is a potential high performance electrode material for redox-supercapacitors.^{16,17} In this work, we investigated the interactions between cobalt-oxide and water in the gas phase by conducting photoelectron spectroscopy experiments and density functional calculations on $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($m = 1-3$, $n < 3$) clusters. As we will show later, the $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ clusters are not equivalent to $\text{Co}_m\text{O}(\text{H}_2\text{O})_{n+1}^-$.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. 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. The details of the experimental apparatus have been described previously.¹⁸ Briefly, the $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ cluster anions were produced in a laser vaporization source. The second harmonic (532 nm) light pulses of a Nd:YAG laser ablated a rotating, translating Co target with residual surface layers of oxygen. 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 oxides with water generated the resultant cluster anions. The cluster anions were mass-analyzed by the time-of-flight mass spectrometer. After mass-selection and deceleration, the $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$) and $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($m = 2-3$, $n = 0-1$) clusters were photodetached with a second Nd:YAG laser. The electrons resulting from photodetachment were energy-analyzed by the magnetic-bottle photoelectron spectrometer. The photoelectron spectra were calibrated using the known spectrum of Cu^- . The resolution of the photoelectron spectrometer was approximately 40 meV at 1 eV kinetic energy.

^{a)} Author to whom correspondence should be addressed. Electronic mail: zhengwj@iccas.ac.cn. Tel: +86 10 6263 5054. Fax: +86 10 6256 3167.

B. Computational methods

The theoretical calculations were performed with the density-functional theory employing BPW91 (Refs. 19 and 20) method and the 6-311+G(d,p) basis set. The geometries of all complexes were determined by optimizing the structures at several multiplicities using different initial geometries. Optimizations were performed without imposing symmetry constraints, and the calculated energies were corrected by the zero-point vibrational energies. Harmonic vibrational frequency calculations were performed to verify that the optimized structures correspond to real local minima. The vertical electron detachment energies (VDEs) were calculated as the energy difference between the neutrals and anions at the geometry of the anionic species. All the calculations were conducted with the GAUSSIAN 09 program package.²¹

III. RESULTS AND DISCUSSION

The photoelectron spectra of $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$), $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$), and $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$) taken with 266 nm photons are presented in Figures 1-3, respectively. For comparison, the spectra of CoO^- , Co_2O^- , and Co_3O^- are also presented in these figures.

The optimized ground-state geometries of the typical low-lying isomers of $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$), $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$), and $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$) are shown in Figures 4-6, respectively, with the most stable structures on the left. The calculated ADEs and VDEs are compared with the experimental values in Table I. We have also calculated the ADEs and VDEs of CoO^- , Co_2O^- , and Co_3O^- and included them in Table I. The theoretical ADEs and VDEs of CoO^- , Co_2O^- , and Co_3O^- are in reasonable agreement with the experimental values, indicating that the theoretical method used here is suitable for the $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ systems.

A. $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$)

As seen in Figure 1, the spectrum of CoO^- has three major features in the range of 1.4-1.8, 2.1-2.5, and 3.1-4.0 eV. Each of these major features has fine structures. However, the spectrum of CoO_2H_2^- has only two broad feature centered at 1.92 and 3.41 eV. It is quite obvious that the spectrum of CoO_2H_2^- is very different from that of CoO^- spectrum, indicating that CoO_2H_2^- and CoO^- have very different structures and electronic properties. CoO_2H_2^- cannot be simply considered as a hydrated CoO^- although it has the same chemical composition as $\text{CoO}^-(\text{H}_2\text{O})$. Indeed, our theoretical calculations show that CoO_2H_2^- in the form of $\text{CoO}^-(\text{H}_2\text{O})$ is much more unstable. We identified three typical low-lying isomers for CoO_2H_2^- (Figure 4). Isomer 1A and 1B are nearly degenerate with 1B higher than 1A by only 0.01 eV. Isomer 1A is a C_{2v} symmetry chain structure at 3A state, in which the two OH groups locate on the opposite sides of the Co atom and in *cis* positions. The calculated VDE for isomer 1A is about 1.71 eV, in agreement with the experimental VDE of 1.92 eV. Isomer 1B is a C_{2h} symmetry chain structure at 3A electronic state with the two OH groups in *trans* positions. The calcu-

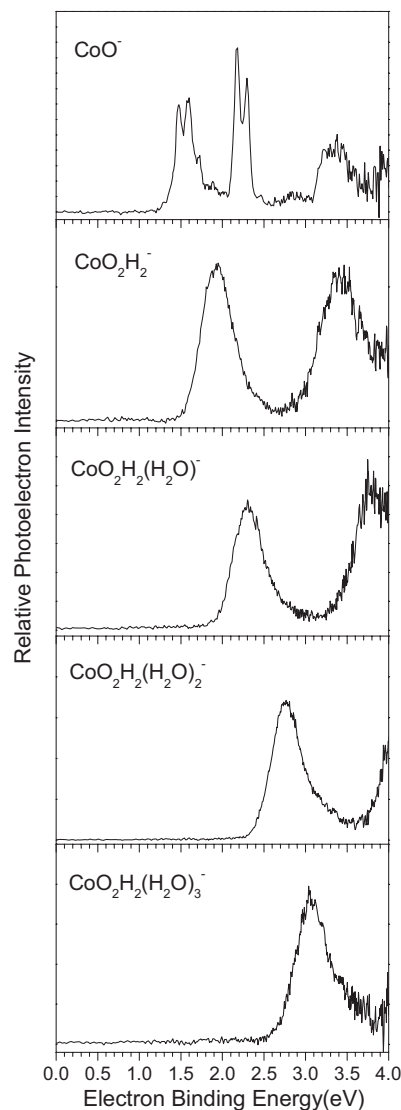


FIG. 1. Photoelectron spectra of CoO^- and $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$) taken with 266 nm photons.

lated VDE (1.61 eV) and ADE (1.39 eV) of isomer 1B are also close to the experimental values. Our calculations show that the energy barrier between isomer 1A and 1B is about 0.16 eV. Both isomers 1A and 1B are dihydroxide anions in the form of $\text{Co}(\text{OH})_2^-$. They probably both contribute to the photoelectron spectrum of CoO_2H_2^- measured in our experiment. Isomer 1C, the hydrated metal-oxide species $\text{CoO}(\text{H}_2\text{O})^-$, is higher than isomer 1A by ~ 1.79 eV in energy, much more unstable than isomer 1A and 1B. Thus, the dihydroxide anion $\text{Co}(\text{OH})_2^-$ is energetically preferred over the hydrated cobalt-oxide, $\text{CoO}(\text{H}_2\text{O})^-$.

The photoelectron spectra of $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 1-3$) are very similar to that of CoO_2H_2^- except that the first peaks of these spectra shift to higher electron binding energy with increasing number of water molecules. The VDEs of $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ for $n = 1, 2$, and 3 are 2.31, 2.76, and 3.04 eV, respectively. The similarities between the spectra of $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 1-3$) and CoO_2H_2^- indicate that the addition of water molecules to CoO_2H_2^- is a simple solvation effect. This can also be verified by our

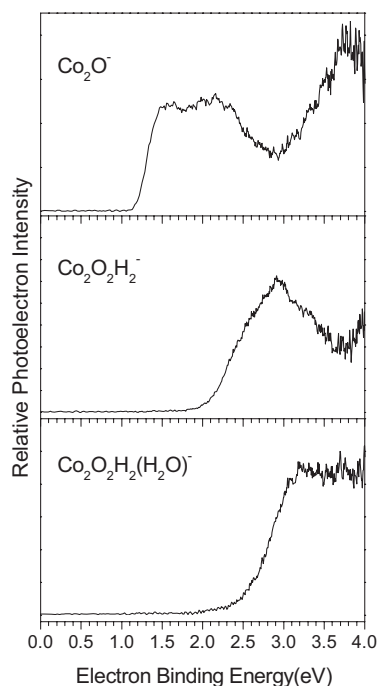


FIG. 2. Photoelectron spectra of Co_2O^- and $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$) taken with 266 nm photons.

theoretical calculations. As seen in Figure 4, our calculations show that the $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ clusters in the form of $\text{Co}(\text{OH})_2(\text{H}_2\text{O})_n^-$ are much more stable than those in the form of $\text{CoO}(\text{H}_2\text{O})(\text{H}_2\text{O})_n^-$.

For $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})^-$, the most stable isomers 2A and 2B are nearly degenerate in energy. They are both in the form of $\text{Co}(\text{OH})_2(\text{H}_2\text{O})^-$ with the $\text{Co}(\text{OH})_2$ anion solvated by a water

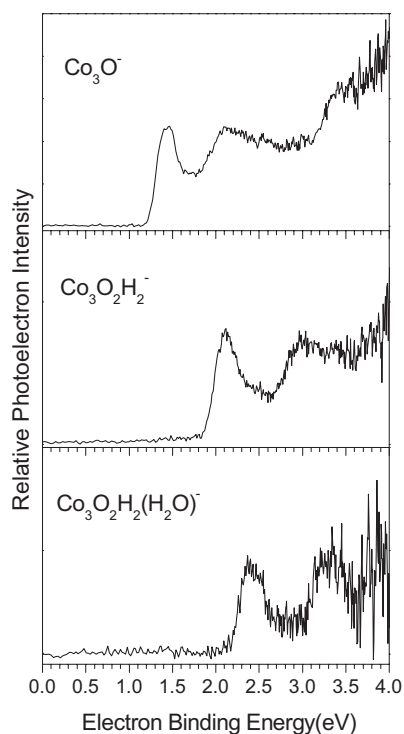


FIG. 3. Photoelectron spectra of Co_3O^- and $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$) taken with 266 nm photons.

TABLE I. Relative energies, VDEs and ADEs of the typical low-lying isomers of $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$) and $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($m = 2-3$, $n = 0-1$) calculated at the BPW91 level of theory as well as the comparison with the experimental VDEs and ADEs. (The isomers labeled with bold are the most probable ones observed in the experiments.)

Isomer	ΔE (eV)	ADE (eV)		VDE (eV)	
		Theo.	Expt.	Theo.	Expt.
CoO^-		1.35	1.54 (± 0.08)	1.36	1.54 (± 0.08)
Co_2O^-		1.17	1.29 (± 0.10)	1.19	1.43 (± 0.10)
Co_3O^-		1.32	1.36 (± 0.10)	1.35	1.42 (± 0.10)
CoO_2H_2^-	1A	0.00	1.41	1.58 (± 0.10)	1.71
	1B	0.01	1.39		1.61
	1C	1.79	1.90		2.0
$\text{CoO}_2\text{H}_2(\text{H}_2\text{O})^-$	2A	0.00	1.62	1.98 (± 0.10)	2.21
	2B	0.004	1.61		2.24
	2C	1.68	1.54		1.97
$\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_2^-$	3A	0.00	1.89	2.38 (± 0.10)	2.67
	3B	0.002	1.88		2.72
	3C	1.67	1.34		2.38
$\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_3^-$	4A	0.00	2.54	2.69 (± 0.10)	3.29
	4B	0.009	1.75		3.16
	4C	1.70	1.37		2.77
$\text{Co}_2\text{O}_2\text{H}_2^-$	5A	0.00	1.91		2.06
	5B	0.10	1.83	2.09 (± 0.20)	2.50
	5C	0.13	1.81		2.55
	5D	1.26	1.65		3.21
	6A	0.00	2.25		2.47
$\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$	6B	0.05	2.04	2.50 (± 0.20)	2.95
	6C	0.08	2.15		2.97
	6D	1.42	1.03		1.96
	7A	0.00	1.90	1.89 (± 0.10)	2.08
$\text{Co}_3\text{O}_2\text{H}_2^-$	7B	0.004	1.90		2.10
	7C	1.52	1.57		1.67
	8A	0.00	2.06	2.19 (± 0.10)	2.47
$\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$	8B	0.002	1.83		2.44
	8C	0.009	2.16		2.43
	8D	1.60	0.95		1.91

molecule. Isomer 2C, the hydrated metal-oxide type of structure, is much more unstable than isomer 2A and 2B. Therefore, it is unlikely to be present in our experiment. Isomer 2A has one of the water hydrogens involved in a strong hydrogen bond with one oxygen of the unit $\text{Co}(\text{OH})_2^-$ and the $\text{O}\cdots\text{H}$ distance is ~ 1.675 Å. The addition of the water molecule to $\text{Co}(\text{OH})_2^-$ weakened the Co–O bond slightly, therefore, the Co–O bond near the water molecule is slightly longer than the Co–O bonds in free $\text{Co}(\text{OH})_2^-$. Isomer 2B has C_1 symmetry and 3A electron state. The calculated VDEs of isomer 2A and 2B (2.21 and 2.24 eV) are in excellent agreement with the experimental measurement. Thus, we believe that both isomers 2A and 2B contribute to the experimental photoelectron spectrum of $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})^-$.

Similarly, for $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_2^-$, the $\text{Co}(\text{OH})_2(\text{H}_2\text{O})_2^-$ type of isomers, 3A and 3B are also nearly degenerate. They are much more stable than the $\text{CoO}(\text{H}_2\text{O})(\text{H}_2\text{O})_2^-$ type of isomer, 3C. The theoretical VDEs of isomer 3A and 3B (2.67 and 2.72 eV) are in agreement with the experimental measurement (2.76 eV). For $\text{CoO}_2\text{H}_2(\text{H}_2\text{O})_3^-$, the $\text{Co}(\text{OH})_2(\text{H}_2\text{O})_3^-$ type of isomers, 4A and 4B, are the most stable isomers. Their

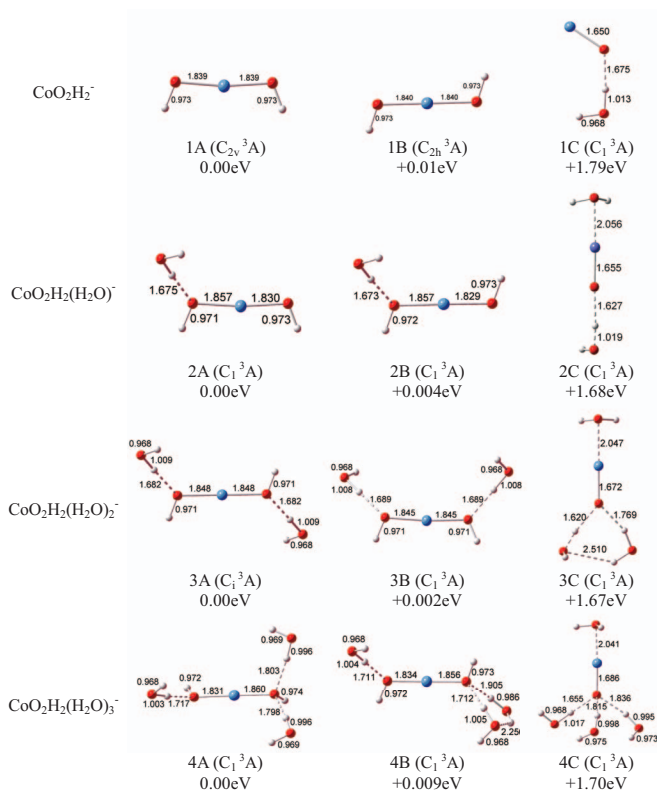


FIG. 4. Optimized geometries of the typical low-lying isomers of $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$) clusters. The unit of the bond lengths is angstrom.

theoretical VDEs are calculated to be 3.29 and 3.16 eV, respectively, in agreement with the experimental measurement. Isomer 4C, the $\text{CoO}(\text{H}_2\text{O})(\text{H}_2\text{O})_3^-$ type of structure, is higher than isomer 4A by ~ 1.70 eV, much more unstable than isomer 4A and 4B.

B. $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$)

As can be seen from Figure 2, the photoelectron spectral features of Co_2O^- , $\text{Co}_2\text{O}_2\text{H}_2^-$, and $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$ are very broad. The VDEs of $\text{Co}_2\text{O}_2\text{H}_2^-$ and $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$ shift toward higher electron binding energy compared to Co_2O^- .

The theoretical calculations identified four low-lying isomers for $\text{Co}_2\text{O}_2\text{H}_2^-$ (Figure 5). The most stable isomer of $\text{Co}_2\text{O}_2\text{H}_2^-$, isomer 5A is an anchor shaped structure with C_{2v} symmetry. The calculated VDE of isomer 5A is about 2.06 eV, much lower than the experimental value. Isomer 5B and 5C are chain structures, with the OH groups bound to different Co atoms. Isomer 5B and 5C are nearly degenerate and are higher than isomer 5A by 0.10 and 0.13 eV, respectively. The energy barrier between isomer 5B and 5C is determined to be only 0.05 eV. The theoretical VDEs of isomer 5B and 5C are calculated to be 2.50 and 2.55 eV, respectively, in good agreement with the experimental measurement (2.55 eV). Thus, we suggest that both isomers 5B and 5C contribute to the photoelectron spectral features of $\text{Co}_2\text{O}_2\text{H}_2^-$ observed in our experiment. Isomer 5D is a hydrogen bounded chain structure with a water molecule connecting to the oxygen end of Co–Co–O. It is much less stable than isomer 5A, 5B,

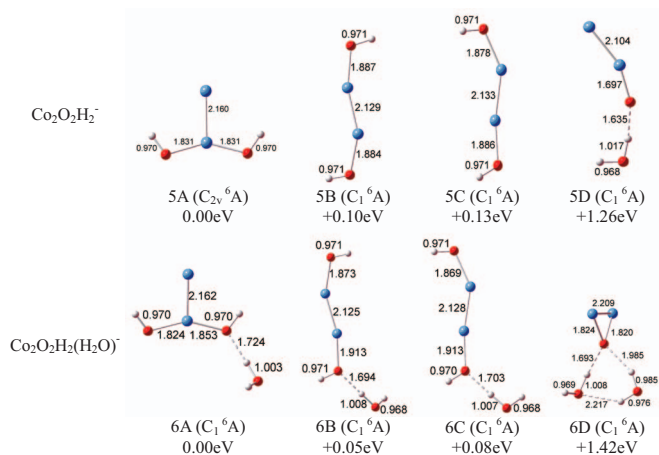


FIG. 5. Optimized geometries of the typical low-lying isomers of $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$) clusters. The unit of the bond lengths is angstrom.

and 5C. The calculated VDE of isomer 5D is about 3.21 eV, much higher than our experimental value. That indicates it is unlikely for isomer 5D to be present in the experiment. Both isomers 5B and 5C are dihydroxide anions, while isomer 5D can be considered as hydrated metal-oxide. Thus, the combination of the experiment and theoretical calculations show again that the dihydroxide anion structures are preferred in $\text{Co}_2\text{O}_2\text{H}_2^-$. Although isomer 5A is slightly more stable than isomer 5B, it has not been detected in the experiments. We suspect that there is a fairly large energy barrier for the formation of isomer 5A. When H_2O interacts with Co_2O^- , the H_2O molecule and the existent O atom prefer to bind to different Co atoms. Then, $\text{Co}_2\text{O}_2\text{H}_2^-$ undergoes hydrogen-transfer to form isomer 5B.

According to the theoretical calculations, the most stable structure of $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$, isomer 6A, can be viewed as isomer 5A solvated by a water molecule. Although isomer 6A is the most stable one, its VDE (2.47 eV) is much lower than the experimental VDE of $\text{Co}_2\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$. Therefore, isomer 6A probably does not exist in our experiments. The non-detection of isomer 6A in the experiments more likely is due to the same reason as that of isomer 5A. Isomers 6B and 6C are higher than isomer 6A by only 0.05 and 0.08 eV, respectively. They are evolved from isomers 5B and 5C by interacting with a water molecule via hydrogen bond. Therefore, they are dihydroxide anions solvated by water molecule. The calculated VDEs of isomers 6B and 6C are consistent with the experimental measurement (3.07 eV). Isomer 6D is a hydrated metal-oxide species, $\text{Co}_2\text{O}(\text{H}_2\text{O})_2^-$, much less stable than the dihydroxide isomers $\text{Co}_2(\text{OH})_2(\text{H}_2\text{O})^-$ (6B and 6C).

C. $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$)

In the spectrum of Co_3O^- (Figure 3), three major features are observed at 1.42, 2.11, and above 3.0 eV. The spectrum of $\text{Co}_3\text{O}_2\text{H}_2^-$ shows two major bands at 2.10 and 3.00 eV. Although the spectrum of $\text{Co}_3\text{O}_2\text{H}_2^-$ looks similar to that of Co_3O^- , its VDE is higher than that of Co_3O^- by about

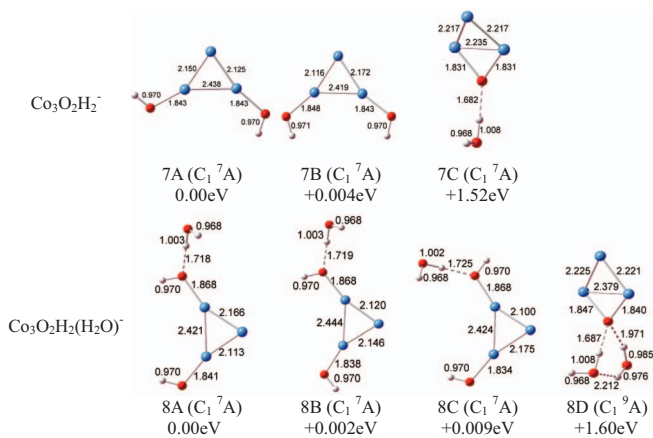


FIG. 6. Optimized geometries of the typical low-lying isomers of $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$) clusters. The unit of the bond lengths is angstrom.

0.68 eV. The difference of the VDEs is quite large, indicating that $\text{Co}_3\text{O}_2\text{H}_2^-$ cannot be simply considered as Co_3O^- solvated by a water molecule. The spectrum of $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$ is similar to that of $\text{Co}_3\text{O}_2\text{H}_2^-$ except that it shifts to higher electron binding energies. Two major bands are observed at 2.40 and 3.30 eV. It indicates that a single water molecule stabilizes the negative ion $\text{Co}_3\text{O}_2\text{H}_2^-$ by ~ 0.30 eV. We would like to mention that the original $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$ spectrum is contaminated by the photoelectron signals from $\text{Co}_3\text{O}_3\text{H}_3^-$. The spectrum presented here is obtained by subtracting the $\text{Co}_3\text{O}_3\text{H}_3^-$ signals from the original spectrum.²²

Three low-lying isomers are identified for $\text{Co}_3\text{O}_2\text{H}_2^-$ (Figure 6). Isomers 7A and 7B are energetically degenerate. The energy barrier between them is found to be only ~ 0.04 eV. They are formed by attaching two OH groups to two Co atoms in the Co_3 triangle. The theoretical VDE of isomers 7A and 7B are calculated to be 2.08 and 2.10 eV, respectively, in excellent agreement with the experimental value (2.10 eV). Isomer 7C corresponds to a hydrated metal-oxide structure $\text{Co}_3\text{O}(\text{H}_2\text{O})^-$, which is much higher in energy than isomers 7A and 7B ($\text{Co}_3(\text{OH})_2^-$) in energy. Isomer 7C is unlikely to be populated in the experiments. Mulliken charge analysis shows that the excess electron mainly localizes on Co_3 in both Co_3O^- and $\text{Co}_3\text{O}_2\text{H}_2^-$ (isomer 7A and 7B). That probably can explain why the spectra of Co_3O^- and $\text{Co}_3\text{O}_2\text{H}_2^-$ look similar.

As shown in Figure 6, the first three isomers of $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$, isomers 8A, 8B, and 8C, all consist of a $\text{Co}_3(\text{OH})_2^-$ unit and H_2O moiety, in which a H atom of the water molecule interacts with one oxygen of the $\text{Co}_3(\text{OH})_2^-$ unit to form a hydrogen bond. Isomers 8A, 8B, and 8C are very close in energy. Their calculated VDEs are 2.47, 2.44, and 2.43 eV, respectively, in good agreement with the experimental VDE of $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$. For the above reason, we suggest that isomers 8A, 8B, and 8C probably all contribute to the experimental photoelectron spectrum of $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$. On the other hand, the hydrated metal-oxide species, isomer 8D, is much less stable than isomers 8A, 8B, and 8C. Its VDE deviates from the experimental measurement as well. Thus, the dihydroxide anion structures are preferred in $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$.

IV. CONCLUSIONS

$\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($m = 1-3$) cluster anions were investigated using photoelectron spectroscopy and density functional calculations. It is observed that the VDEs of the $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($m = 1-3$) clusters shift toward higher electron binding energy with increasing number of water molecules. The possible structures of the $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$) and $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($m = 2-3, n = 0-1$) clusters were determined by comparison of theoretical calculations with experimental measurements. It is confirmed that $\text{Co}_m(\text{OH})_2^-$ ($m = 1-3$) exists as a distinct structural unit in all the solvated clusters. That implies that dihydroxide anions, $\text{Co}_m(\text{OH})_2^-$ ($m = 1-3$), were produced when Co_mO^- ($m = 1-3$) interact with the first water molecule. These results might be useful for understanding the phenomena involved in cobalt oxides and water in energy conversion and storage devices such as batteries and supercapacitors.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC) (Grant No. 20933008). We are grateful to Professor Zhen Gao for valuable discussion. The theoretical calculations were conducted on the ScGrid and Deepcomp7000 of the Supercomputing Center, Computer Network Information Center of Chinese Academy of Sciences.

- ¹B. Meunier and W. Adam, *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations* (Springer, Berlin/New York, 2000).
- ²Y. Zhang, Y. Chen, P. Westerhoff, K. Hristovski, and J. C. Crittenden, *Water Res.* **42**, 2204 (2008).
- ³V. M. Aroutiounian, V. M. Arakelyan, and G. E. Shahnazaryan, *Sol. Energy* **78**, 581 (2005).
- ⁴D. Vukomanovic and J. A. Stone, *Int. J. Mass Spectrom.* **202**, 251 (2000).
- ⁵D. Schröder and H. Schwarz, *Int. J. Mass Spectrom.* **227**, 121 (2003).
- ⁶D. Schröder, J. Roithová, and H. Schwarz, *Int. J. Mass Spectrom.* **254**, 197 (2006).
- ⁷D. Schröder, *J. Phys. Chem. A* **112**, 13215 (2008).
- ⁸D. Schröder, S. O. Souvi, and E. Alikhani, *Chem. Phys. Lett.* **470**, 162 (2009).
- ⁹S. W. Sigsworth and A. W. Castleman, *J. Am. Chem. Soc.* **114**, 10471 (1992).
- ¹⁰J. R. Sambrano, L. Gracia, J. Andrés, S. Berski, and A. Beltrán, *J. Phys. Chem. A* **108**, 10850 (2004).
- ¹¹A. Ricca and C. W. Bauschlicher, *J. Phys. Chem. A* **101**, 8949 (1997).
- ¹²J. R. Sambrano, J. Andrés, L. Gracia, V. S. Safont, and A. Beltrán, *Chem. Phys. Lett.* **384**, 56 (2004).
- ¹³A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. van Schalkwijk, *Nature Mater.* **4**, 366 (2005).
- ¹⁴D. H. Buss, J. Bauer, W. Diembeck, and O. Glemser, *J. Chem. Soc., Chem. Commun.* **81** (1985).
- ¹⁵J. Bauer, D. H. Buss, H. J. Harms, and O. Glemser, *J. Electrochem. Soc.* **137**, 173 (1990).
- ¹⁶V. Gupta, T. Kusahara, H. Toyama, S. Gupta, and N. Miura, *Electrochem. Commun.* **9**, 2315 (2007).
- ¹⁷V. Gupta, S. Gupta, and N. Miura, *J. Power Sources* **177**, 685 (2008).
- ¹⁸H.-G. Xu, Z.-G. Zhang, Y. Feng, J. Y. Yuan, Y. C. Zhao, and W. J. Zheng, *Chem. Phys. Lett.* **487**, 204 (2010).
- ¹⁹A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ²⁰J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- ²¹M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 09, Gaussian, Inc., Wallingford, CT, 2009.
- ²²See supplementary material at <http://dx.doi.org/10.1063/1.3644897> for the original photoelectron spectra of $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})^-$ and $\text{Co}_3\text{O}_3\text{H}_3^-$ and their subtraction, as well as the Cartesian atomic coordinates of the typical low-lying isomers of $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-3$), $\text{Co}_m\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$), and $\text{Co}_3\text{O}_2\text{H}_2(\text{H}_2\text{O})_n^-$ ($n = 0-1$).