Photofragmentation Patterns of Cobalt Oxide Cations $Co_nO_m^+$ (n = 5-9, m = 4-13): from Oxygen-Deficient to Oxygen-Rich Species

Nguyen Thi Mai,[†] Son Tung Ngo,^{‡,¶} Peter Lievens,[§] Ewald Janssens,^{*,§} and Nguyen Thanh Tung^{*,†}

†Institute of Materials Science and Graduate University of Science and Technology, Vietnam Academy of Science and Technology, Vietnam

‡Faculty of Applied Science, Ton Duc Thang University, Hochiminh, Vietnam

¶Laboratory of Theoretical and Computational Biophysics, Ton Duc Thang University, Ho Chi Minh City, Vietnam

§Quantum Solid-State Physics, Department of Physics and Astronomy, KU Leuven, 3001 Leuven, Belgium

E-mail: ewald.janssens@kuleuven.be; tungnt@ims.vast.ac.vn

Abstract

Cobalt oxide clusters, $\operatorname{Co}_n \operatorname{O}_m^+$ ($5 \le n \le 9$ and $4 \le m \le 13$), are produced by laser vaporization and studied by time-of-flight mass spectrometry. Specific stoichiometries are mass separated and photofragmented using 355 nm laser light. The preferred fragmentation channels of m = n-1, m = n-2, and $m \ge n$ species are investigated. Loss of oxygen molecules is the favorable dissociation channel of $m \ge n$ clusters. While $\operatorname{Co}_n \operatorname{O}_{n-2}^+$ clusters decay via the separation of a Co atom, the photofragmentation behavior of $\operatorname{Co}_n \operatorname{O}_{n-1}^+$ species interestingly can be divided into two regimes: the $n \le$ 6 clusters tend to lose an oxygen atom, but for n > 6 they favorably dissociate via the loss of a cobalt atom. The geometric structures of selected m = n-2 species are studied using density functional theory calculations. Dissociation energies for different evaporation channels are calculated and thermodynamically favorable channels are found to correspond to the experimental observations.

Introduction

Cobalt forms fascinating bulk oxide species. Their physical and chemical properties are useful for applications in electronic, magnetic, and catalytic materials.^{1,2} A cobalt oxide matrix can be used to stabilize the moments of embedded ferromagnetic nanoparticles, beating the "superparamagnetic limit" observed in isolated particles.³ Electrodes made of pure and doped cobalt oxides display an exceptionally high capacity and cyclability, even at a high charging rate.^{4,5} The unique catalytic behavior of cobalt oxides plays an active role in the water splitting reaction.⁶

Experimental and theoretical studies of the structure, stability, magnetism, and bonding of cobalt oxide clusters have received considerable attention recently.^{7–9} Although governed by the same fundamental laws, the chemical and physical properties of small clusters are strongly size and composition dependent and can be very different from and sometimes have superior properties as their macroscale analogues. For instance, reactions of neutral cobalt oxide clusters studied in a fast flow reactor indicated that the Co_3O_4 cluster has the highest overall rate constants for oxidation of CO and NO, suggesting a catalytic cycle for these oxidation reactions on a condensed-phase cobalt oxide catalyst.¹⁰ For larger metallic cobalt clusters, the Co_n^+O (n = 2-20) bond energies are found to be very close to the value for desorption of atomic oxygen from bulk cobalt.¹¹ A study of the size-dependent electronic structure of the oxide clusters implied that threshold binding energy features mainly originate from Co *d*-derived orbitals.¹² Antiferromagnetic behavior was found for $Co_nO_m^+$ cluster cations (n = 3-6 and m = 3-8) using combined IR vibrational spectroscopy and density-functional-theory (DFT) calculations.¹³ Small cobalt oxide clusters adapt a rich variety of geometric configurations. While bulk cobalt oxide crystals have a cubic rock-salt structure, a combined ion mobility mass spectrometry and computational study of $(CoO)_n$ with n = 2-7 hints to a geometrical transition from monocyclic ring shapes to compact cube/tower structures at $Co_6O_6^+$.¹⁴

Relative stability is often considered as an important measure for clusters. Insight into the size- and composition-dependent stability and possible growth mechanism of clusters may eventually allow to identify or to create chemically inert species with specific properties, which can be used as building blocks for advanced nanomaterials. However, the intensities of neighboring sizes in a mass spectrum do not necessarily reflect a high stability. This quantity is related to relative stability, but only if the size distribution in the source is obtained via processes in equilibrium. In case growth and evaporation are not in equilibrium, the relation between relative intensities and stability is not strict. The relative abundances of clusters, as produced directly in a laser ablation source, therefore should be treated with care concerning stability information.¹⁵

In this regard, mass spectrometry followed by mass-selected photodissociation measurements has been demonstrated as a reliable approach to investigate cluster stability.^{16–20} Favorable stoichiometries of Co oxide clusters have been determined by means of unimolecular fragmentation and their relative stability could be reliably measured. The collision-induced dissociation of $\text{Co}_n \text{O}_n^+$ and $\text{Co}_n \text{O}_{n-1}^+$ (n = 2-5) clusters was studied by Freas and coworkers.²¹ $\text{Co}_n \text{O}_n^+$ clusters tend to evaporate a CoO moiety. An important collision-induced fragmentation pathway for the oxygen-deficient species $\text{Co}_n \text{O}_{n-1}^+$ clusters is loss of a cobalt atom. Our earlier photodissociation and computational investigation of $\text{Co}_n \text{O}_m^+$ (n = 2-4,m = 4-8) clusters confirmed the high stability of $\text{Co}_2 \text{O}_2^+$, $\text{Co}_3 \text{O}_4^+$, and $\text{Co}_4 \text{O}_4^+$.²² Dibble and coworkers were the only ones who dealt so far with the photofragmentation of larger sizes of oxygen-equivalent and oxygen-rich cobalt oxide cations (n = 4-9, m = 4-12).²³ They revealed that oxygen-rich species dissociate preferentially via the loss of O_2 and the formation of daughter ions with a 1:1 stoichiometry is favored. For oxygen-equivalent clusters, probing the primary dissociation channel is even more challenging since multiple (large) fragment ions with comparable intensities were recorded simultaneously. It should be mentioned that a specific daughter with higher intensity does not always guarantee a higher stability. In addition, if too high excitation fluences are used, the detected daughter might result from sequential dissociation events. Experimental results on oxygen-deficient m < n clusters for n = 4-9 have not been reported yet and questions concerning their dissociation behavior remain unadressed.

In this work, we investigate the fragmentation patterns and discuss dissociation pathways of cobalt oxide cluster cations $\text{Co}_n \text{O}_m^+$ (n = 5-9, m = 4-13). Oxygen-deficient, -equivalent, and -rich species are produced in the gas phase and mass-selected before exposing to the fragmentation laser. Recorded fragments, dissociation behavior, and relative stabilities are analysed. We discuss possible structural information and compare with earlier experimental and theoretical studies.^{23,24}

Experimental method

The photofragmentation technique used in the current study has been described in detail elsewhere.^{22,25–27} In brief, cobalt oxide cluster cations $\text{Co}_n \text{O}_m^+$ are produced in a 10 Hz laser vaporization source²⁸ coupled to a dual-reflectron high-resolution $(m/\Delta m \sim 4000)$ time-offlight mass spectrometer.^{29,30} The species of interest are mass-selected by a wire-type mass gate.³¹ The mass gate is installed at the temporal focal point of the first reflectron, which is located between the first and the second reflectron.^{29,30} Right after the mass gate, selected clusters are exposed to the third harmonic of a Q-switched Nd:YAG laser (Spectra Physics GCR 150). The laser beam travels perpendicular to the clusters in the mass spectrometer. The length of the temporally focused cluster ion package is about 14 mm and its diameter is defined by a 15 mm diameter circular aperture in the metallic cage around the mass gate.



Figure 1: Photofragmentation time-of-flight spectra of $\operatorname{Co}_n \operatorname{O}_m^+$ $(n=5-9 \text{ and } n-2 \leq m \leq n)$ clusters (laser excitation: 355 nm, 80 mJ/cm²). Parent ion peaks are presented off-scale to highlight fragmentation peaks. $\operatorname{Co}_n \operatorname{O}_m^+$ fragments are labeled by n,m. Unidentified peaks are marked with '*'.

The laser is slightly defocused (laser fluence 80 mJ/cm²) and we estimate that about 75% of the clusters are exposed to the laser beam. After laser excitation, the fragment ions and the surviving charged parent clusters are mass separated in the second reflectron before reaching the microchannel plate detector. The timing of all sequential events is controlled by coupled Stanford DG535 delay generators. Each mass spectrum is accumulated for 3 minutes to obtain a good signal-to-noise ratio.

The energy required to dissociate smaller cobalt oxide clusters is of the order of 5-6 eV, which is considerably higher than the energy of a single photon at 355 nm.²² Multiple photon absorption is thus required to break the cluster bonds. After laser excitation, either a charged fragment or the surviving parent ion is detected. The fragment ions have the same velocity as the parent clusters in the free flight part of the mass spectrometer but they arrive earlier at the detector because they turn quicker in the reflectron given their lower kinetic energy. Because the potentials and the dimensions of the mass spectrometer as well as the kinetic energy of the clusters are known, the mass of fragment ions can be determined based on their arrival times.

Recorded dissociation channels

The photofragmentation spectra of $\operatorname{Co}_n \operatorname{O}_m^+$ clusters with $n-2 \leq m \leq n$ and n = 5-9 are shown in Fig. 1. Selected spectra of m > n species as well as a comprehensive overview of the identified fragment ions of $\operatorname{Co}_n \operatorname{O}_m^+$ (n = 5-9, m = 4-13) are given in the Supporting Information. An overview of the primary fragmentation channel of the $\operatorname{Co}_n \operatorname{O}_m^+$ clusters is summarized in Fig. 2. Circles filled with blue checkerboard, gray vertical, orange grid, and green solid correspond to the loss of O, O₂, Co, and the CoO, respectively. A purple borderline around the circles indicates an agreement with calculated results in Ref.²⁴ Oxygenrich species (m > n) favor the loss of oxygen molecules. We note that we were unable to identify the preferred fragment of $\operatorname{Co}_9 \operatorname{O}_{10}^+$ due to its low intensity after mass-selection.

m = n-2

As can be seen in the left column of Fig. 1, all $\text{Co}_n \text{O}_{n-2}^+$ n = 6-9 clusters have a similar fragmentation behavior. The main dissociation channel of those species is the loss of a Co atom. Other dissociation channels include the loss of an oxygen molecule (or two consecutive oxygen atoms) for Co_8O_6^+ and Co_9O_7^+ , the loss of a CoO molecule (or a Co and an O atom) for Co_7O_5^+ and Co_8O_6^+ , and the loss of an oxygen atom for Co_7O_5^+ . For n = 6, the loss of a single Co atom is less distinct. In particular, the intensity of the signal corresponding to CoO loss becomes more clear and comparable with that of Co atom loss. It is worth to mention that in principle we cannot distinguish the loss as a molecule (O₂ or CoO) or separated atoms. However, the energy required to sequentially evaporate a Co and O atom (or two oxygen atoms) is much higher than that of a CoO (or O₂) molecule.^{22,23} In the following, we only consider the evaporation of CoO and O₂ molecule since the loss of two sequential atoms is less likely.

$m = n - \mathbf{1}$

 $\operatorname{Co}_n \operatorname{O}_{n-1}^+$ (n = 7-9) clusters exhibit a similar photofragmentation behavior (middle column of Fig. 1) as the $\operatorname{Co}_n \operatorname{O}_{n-2}^+$ species. The most intense fragments from $\operatorname{Co}_7 \operatorname{O}_6^+$, $\operatorname{Co}_8 \operatorname{O}_7^+$, and $\operatorname{Co}_9 \operatorname{O}_8^+$ clusters correspond to Co atom loss, suggesting an enhanced relative stability of n= m species.²³ Other fragments with lower intensities are formed via the loss of CoO (for $\operatorname{Co}_7 \operatorname{O}_6^+$, $\operatorname{Co}_8 \operatorname{O}_7^+$, and $\operatorname{Co}_9 \operatorname{O}_8^+$), an oxygen molecule (for $\operatorname{Co}_9 \operatorname{O}_8^+$), and an oxygen atom (for $\operatorname{Co}_7 \operatorname{O}_6^+$). The $n \leq 6$ species are different. The fragmentation behavior of $\operatorname{Co}_6 \operatorname{O}_5^+$ shows a competition between two channels: evaporating a cobalt atom or an oxygen atom. $\operatorname{Co}_5 \operatorname{O}_4^+$ decays by elimination of an oxygen atom rather than by losing a cobalt atom, yielding $\operatorname{Co}_5 \operatorname{O}_3^+$ as the most prominent fragment ion. The second and third most intense fragments are $\operatorname{Co}_5 \operatorname{O}_2^+$, and $\operatorname{Co}_4 \operatorname{O}_4^+$), which correspond to the loss of an oxygen molecule and a Co atom, respectively.



Figure 2: Primary fragmentation channel(s) of the studied $\text{Co}_n \text{O}_m^+$ clusters. Circles filled with blue checkerboard, gray vertical, orange grid, and green solid correspond to the loss of O, O₂, Co, and CoO, respectively. The purple borderline of the circles indicates the agreement with calculated results in Ref.[24].

 $m \ge n$

The photodissociation behavior of $\operatorname{Co}_n \operatorname{O}_n^+$ (n = 5-9) clusters is presented in the right column of Fig. 1. Generally, losing an oxygen molecule is the most intense channel. For n=6, 7, and 9, the loss of CoO to form $\operatorname{Co}_{n-1}\operatorname{O}_{n-1}^+$ fragment ions is a parallel fragmentation channel. $\operatorname{Co}_8\operatorname{O}_8^+$ fragments solely by eliminating O_2 . Lower-intensity fragment ions are $\operatorname{Co}_n\operatorname{O}_{n-1}^+$ (for n = 6 and 7) and $\operatorname{Co}_{n-1}\operatorname{O}_{n-2}^+$ (for n = 7 and 9), and correspond to the loss of an oxygen atom and CoO_2 unit, respectively.

While the dissociation behavior of oxygen-poor species has not carefully been studied before, that of oxygen-equivalent and oxygen-rich clusters was reported elsewhere.^{23,24} For example, the 355 nm photofragmentation behavior of $\text{Co}_n \text{O}_m^+$ with n = 4-9 and $m \ge n$ has been studied by Dibble and coworkers.²³ Both our experimental data and theirs confirm that the most facile decay channel of $\text{Co}_n \text{O}_{n+1}^+$ and $\text{Co}_n \text{O}_{n+2}^+$ is the evaporation of O_2 units. However, in Dibble's experiments²³ smaller fragments are observed from the same parent clusters as in our work, which suggests that their clusters undergo (multiple) dissociation steps as a result of higher excitation energies compared to the current work. This different experimental condition is important to gain more insight in the dissociation behavior.

Discussions

The preferential loss of O_2 , seen for oxygen-rich m > n clusters, is also observed for $Co_nO_n^+$ species, but it is less distinct for $n \ge 6$. In particular, $Co_5O_5^+$ favorably dissociates via elimination of O_2 . The loss of a CoO unit is detected as the secondary channel. Similar dissociation pathways are suggested in the theoretical work by Toro *et al.*, whereas the experiments in the work of Dibble and coworkers indicated the loss of Co and CoO as the most facile channels. When *n* increases from 6 to 8, $Co_6O_4^+$, $Co_7O_5^+$, and $Co_8O_6^+$ are still the most intense fragments, in perfect agreement with the calculations.²⁴ However, the O_2 loss channels are recorded with much lower intensities, and comparable to that of other fragments for n = 6 and 7. The change of the fragmentation behavior of $Co_n O_n^+$ at n = 6 could be related to the predicted geometrical transition from ring to cube/tower-like structures.^{14,32} By comparing experimental and calculated collision cross-section of $Co_n O_n^+$ clusters (n = 2-7), it is found that $(CoO)_{3-5}^+$ have monocyclic-ring structures, while $(CoO)_{6.7}^+$ have compact cube/tower structures.¹⁴ DFT calculations also predicted that neutral Co₂O₂ and Co_4O_4 favor ring-type geometries whereas the cube/tower-based structure is the most stable motif for Co_6O_6 , Co_9O_9 , and $Co_{12}O_{12}$.³² For $Co_9O_9^+$, we notice a very strong signal of mass-selected $Co_9O_9^+$ parent clusters but the daughter intensities are low. A similar observation was reported in Ref. [23]. This could be due by an exceptionally low photoabsorption cross section (what is unlikely since also for other sizes the absorption process is likely non-resonant) or to a higher dissociation energy (implying less likely dissociation following photo-absorption) of $Co_9O_9^+$. Our results imply that the most facile channel of $Co_9O_9^+$ is the loss of a CoO molecule. The secondary dissociation pathway could be via either the elimination of O_2 or CoO_2 . A previous mass spectrometric study in combination with DFT calculations also suggests a relatively high stability for $Co_9O_9^+$, related to its cube/tower or cage structures. A similar cage structure has been predicted for Zn_9O_9 , which is relatively stable among $\text{ZnO}_{m=2-18}$ clusters.³³

Considering the $\operatorname{Co}_n \operatorname{O}_{n-1}^+$ (n = 5-8) clusters, the observed fragmentation patterns of $\operatorname{Co}_6 \operatorname{O}_5^+$ and $\operatorname{Co}_8 \operatorname{O}_7^+$ agree very well with the calculations of Aguilera-del-Toro and coworkers.²⁴ $\operatorname{Co}_7 \operatorname{O}_6^+$ fragments via the loss of Co and CoO, in disagreement with the calculations²⁴ that predict evaporation of O₂ and CoO₂. The structures of $\operatorname{Co}_6 \operatorname{O}_5^+$ and $\operatorname{Co}_7 \operatorname{O}_6^+$ are predicted as cube/tower-like geometries²⁴ and confirmed by collision cross-section measurements.¹⁴ The photofragmentation behavior of $\operatorname{Co}_5 \operatorname{O}_4^+$ is worth further discussion. Dible *et al.* reported that the most frequent dissociation channel of $\operatorname{Co}_5 \operatorname{O}_4^+$ is the loss of a Co atom,²³ whereas we clearly observe $\operatorname{Co}_5 \operatorname{O}_3^+$ as the most prominent fragment and the evaporation of a Co atom to form $\operatorname{Co}_4 \operatorname{O}_4^+$ is much less pronounced. Note that $\operatorname{Co}_5 \operatorname{O}_3^+$ is relatively more sta-fragment from $\operatorname{Co}_5 \operatorname{O}_5^+$ and $\operatorname{Co}_6 \operatorname{O}_4^+$ (see Fig. 1), indicating that $\operatorname{Co}_5 \operatorname{O}_3^+$ is relatively more sta-



Figure 3: Calculated structures of $\text{Co}_n \text{O}_{n-2}^+$ (with n = 6-8) and their possible $\text{Co}_n \text{O}_{n-3}^+$, $\text{Co}_n \text{O}_{n-4}^+$, $\text{Co}_{n-1} \text{O}_{n-2}^+$, and $\text{Co}_{n-1} \text{O}_{n-3}^+$ daughters. The black arrows indicate the fragmentation pathways and the dissociation energies (in eV) are listed. They correspond to the loss of O, O₂, Co, and CoO.

ble than $\operatorname{Co}_4\operatorname{O}_4^+$ under our experimental conditions. Computational results on the structure of $\operatorname{Co}_5\operatorname{O}_4^+$ are also different in many details. Ota *et al.* predicted the ladder-like structure for $\operatorname{Co}_5\operatorname{O}_4^+$ and it was matching well with the results from its measured collision cross section.¹⁴ Nevertheless, Aguilera-del-Toro and coworkers anticipated a square pyramid symmetry for $\operatorname{Co}_5\operatorname{O}_4^+$ which favorably decays via the loss of a Co atom or a CoO molecule. Similar as for the m = n species, an abrupt reduction in the intensity ratio between the most prominent and secondary fragment is observed at $n \ge 6$ in the fragmentation behavior of $\operatorname{Co}_n\operatorname{O}_{n-1}^+$ species. This transition at n = 6 in the fragmentation behavior coincides with the structural transition from 2D (linear, ring, ladder-type) geometries for n < 6 to 3D (cube/tower-like) geometries for $n \ge 6$.¹⁴

To the best of knowledge, there is no earlier experimental report about the dissociation of $\text{Co}_n \text{O}_{n-2}^+$ clusters and the fragmentation behavior of those species is far less documented as that of $\text{Co}_n \text{O}_n^+$ and $\text{Co}_n \text{O}_{n-1}^+$. Although the structure of $\text{Co}_6 \text{O}_4^+$, $\text{Co}_7 \text{O}_5^+$, and $\text{Co}_8 \text{O}_6^+$ have been reported elsewhere,^{14,24} their dissociation energies have not been calculated. In order to investigate the stability and validate the observed dissociation patterns of these specific clusters, we have performed DFT calculations³⁴ to explore their structures, dissociation energies, and Gibbs free energy changes of possible decay channels. The published lowest-energy isomeric structures for pure and oxide counterparts of cobalt were used as input structures.^{14,24,35} The B3LYP/6-31+G(d) level was selected for the calculations. The choice of this level resulted from reliable results previously reported for similar cobalt oxide systems.¹⁴

Figure 3 shows the computed structures of Co_6O_4^+ , Co_7O_5^+ , Co_8O_6^+ , as well as their possible daughters appearing in the fragmentation of O, O₂, Co, and CoO. Tower-like structures are identified for $\text{Co}_8\text{O}_{4-6}^+$ where the oxygen atoms tend bind to faces. $\text{Co}_7\text{O}_{3-6}^+$ and $\text{Co}_6\text{O}_{2-5}^+$ are most stable in the form of capped Co₇ and Co₆ cores, respectively. The first oxygen atoms likely bind to the triangular faces composed of three Co atoms while the next ones occupy bridge sites. This is presumably because of the tendency to maximize the number of

strong metal-oxygen bonds.²² The structure of Co_5O_4^+ is composed of a metal-oxygen-metal ladder-like Co_4O_4^+ frame capped by a Co atom. Meanwhile, Co_5O_3^+ favors a square pyramid symmetry with two oxygen atoms attaching to opposite triangular faces and another oxygen occupying a bridge site. It should be noted that all optimized structures are in excellent agreement with those reported by Toro *et al.*,²⁴ except for Co_5O_4^+ . In case of Co_5O_4^+ , we find that the ladder-like structure with an excess cobalt atom is preferred over the capped square pyramid. This is in line with the experimental collision cross section for Co_5O_4^+ .¹⁴

The stability and dissociation patterns of clusters can be reflected by their dissociation energy. It is common understanding that the higher the dissociation energy of the most facile dissociation channel, the more stable the cluster is. In addition, under the assumption that there are no barriers in the dissociation reaction, the evaporative rate constant $k_n(E)$ strongly depends on the dissociation $energy^{25,36}$ and the channel associated with the lowest dissociation energy is suggested to correspond to the preferred evaporation channel. Figure 3 includes the calculated dissociation energies of $\text{Co}_n \text{O}_{n-2}^+$ clusters (n = 6-8) for different fragmentation channels: (i) $\operatorname{Co}_{n}\operatorname{O}_{n-2}^{+} \to \operatorname{Co}_{n}\operatorname{O}_{n-3}^{+} + \operatorname{O}$; (ii) $\operatorname{Co}_{n}\operatorname{O}_{n-2}^{+} \to \operatorname{Co}_{n}\operatorname{O}_{n-4}^{+} + \operatorname{O}_{2}$; (iii) $\operatorname{Co}_{n}\operatorname{O}_{n-2}^{+} \to \operatorname{Co}_{n-1}\operatorname{O}_{n-2}^{+} + \operatorname{Co}$; (iv) $\operatorname{Co}_{n}\operatorname{O}_{n-2}^{+} \to \operatorname{Co}_{n-1}\operatorname{O}_{n-3}^{+} + \operatorname{CoO}$. These energies are defined as the total energy differences between the parent cluster and corresponding fragments obtained at their lowest-energy structures (at 0 K). Possible reverse barriers along the dissociation pathway have not been considered. The 0 K calculations strongly support the observed photofragmentation spectra that the most fragile channel of Co_6O_4^+ , Co_7O_5^+ , and $Co_8O_6^+$ is the evaporation of an Co atom. In particular, only 2.30 and 3.77 eV is needed for dissociation of Co_8O_6^+ and Co_6O_4^+ , respectively, while at least 4.20 eV is required to fragment Co_7O_5^+ . Their second favorable channel is the loss of CoO to form Co_7O_5^+ , Co_5O_3^+ , and $Co_6O_4^+$.

If two fragmentation channels would have the same dissociation energy, the channel with the largest entropy increase is favored. The entropy increase of the channels involving evaporation of a diatomic molecule, which has more possible conformations (vibration, translation, and rotation), is larger than those involving the loss of an atom, which has only three translational degrees of freedom and small electronic contributions to the entropy. If, for example, CoO and Co loss channels would have the same dissociation energy, CoO loss would be preferred because it generates a larger entropy increase. We note that the effect of the entropy depends on the temperature of the clusters after photo-excitation, which is not known. The higher the temperature, the more favored the channel with the larger entropy increases.

Conclusions

A dual-reflectron time-of-flight mass spectrometer combined with a pulsed cluster source has been utilized to investigate the photofragmentation of cationic cobalt oxide clusters, $Co_n O_m^+$ (n = 5-9 and m = 4-13). Oxygen-deficient, oxygen-equivalent, and oxygen-rich species are produced, mass-selected, and photofragmented. The loss of an oxygen molecules is the main dissociation channel of oxygen-rich and oxygen-equivalent clusters $(m \ge n)$. While $\operatorname{Co}_n \operatorname{O}_{n-2}^+$ clusters tend to decay via the evaporation of a Co atom, the photofragmentation behavior of $\operatorname{Co}_n \operatorname{O}_{n-1}^+$ species interestingly can be divided into two regimes: for $n \leq 6$ the loss of an oxygen atom is the most prominent, while for n > 6 the clusters' most intense decay channel is the loss of a cobalt atom. The observed size-dependent fragmentation could be related to the predicted 2D-to-3D structural transition of cobalt oxide clusters. In combination with available experimental and computed results, the lowest-energy fragmentation channels of m=n-1 and $m \ge n$, which could not be achieved in previous work, are identified in this study. DFT computations have been carried out for selected m=n-2 clusters. The comparison between the computed dissociation energies for different dissociation channels and photofragmentation spectra provides a clear picture of the dissociation behavior of oxygen-poor clusters. These results are important for understanding relative stabilities and dissociation pathways of cobalt oxide clusters. They also provide input for computational studies that deal with their growth mechanism.

SUPPORTING INFORMATION

Selected photofragmentation spectra of $\text{Co}_n \text{O}_m^+$ (n = 6-9, m > n) clusters recorded at 355-nm laser light with a fluence of 80 mJ/cm²; The list of all parent clusters and their corresponding fragments detected in our experiments and experimental and calculated results in literature for comparison; The contribution of conformational entropy to remove an atom or a molecule from a cobalt oxide cluster.

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