Size-Dependent Association of Cobalt Deuteride Cluster Anions $\text{Co}_3\text{D}_n^-$ ($n = 0–4$) with Dinitrogen

Li-Hui Mou, Zi-Yu Li, Qing-Yu Liu, Sheng-Gui He

Abstract. Dinitrogen ($\text{N}_2$) activation by metal hydride species is of fundamental interest and practical importance while the role of hydrogen in $\text{N}_2$ activation is not well studied. Herein, the structures of $\text{Co}_3\text{D}_n^-$ ($n = 0–4$) clusters and their reactions with $\text{N}_2$ have been studied by using a combined experimental and computational approach. The mass spectrometry experiments identified that the $\text{Co}_3\text{D}_n^-$ ($n = 2–4$) clusters could adsorb $\text{N}_2$ while the $\text{Co}_3\text{D}_n^-$ ($n = 0$ and 1) clusters were inert. The photoelectron imaging spectroscopy indicated that the electron detachment energies of $\text{Co}_3\text{D}_{2–4}^-$ are smaller than those of $\text{Co}_3\text{D}_{0,1}^-$, which characterized that it is easier to transfer electrons from $\text{Co}_3\text{D}_{2–4}^-$ than from $\text{Co}_3\text{D}_{0,1}^-$ to activate $\text{N}_2$. The density functional theory calculations generally supported the experimental observations. Further analysis revealed that the H atoms in the $\text{Co}_3\text{H}_{n}^-$ ($n = 2–4$) clusters generally result in higher energies of the Co 3d orbitals in comparison with the $\text{Co}_3\text{H}_{n}^-$ ($n = 0$ and 1) systems. By forming chemical bonds with H atoms, the Co atoms of $\text{Co}_3\text{H}_{2–4}^-$ are less negatively charged with respect to the naked $\text{Co}_3^-$ system, which leads to higher $\text{N}_2$ binding energies of $\text{Co}_3\text{H}_{2–4}^–\text{N}_2^-$ than that of $\text{Co}_3^–\text{N}_2^-$. Keywords: Ion-molecule reactions, Mass spectrometry, Photoelectron imaging spectroscopy, $\text{N}_2$ activation, Cobalt, Density functional theory

Introduction

Mild, energy-saving approaches for conversion of $\text{N}_2$ into available nitrogenous species are highly desirable in view of enormous energy consumption and greenhouse gas production in industrial Haber–Bosch process [1, 2]. Although the thermodynamically stable and kinetically inert $\text{N}=\text{N}$ bond renders its utilization a typically challengeable issue [3], some remarkable progress has been made on the daunting road of $\text{N}_2$ fixation in different research areas [4–8]. One thing in common is that the $\text{N}_2$ molecule should interact with a metal system [4, 8], in most cases, with multiple metal sites [5–7]. Recently, the transition metal hydride complexes have attracted extensive attentions owing to the potential in direct reduction of $\text{N}_2$ avoiding the use of extra strong reducing agents and proton sources [9–12]. For example, a trinuclear titanium polyhydride complex found by Hou et al. can induce $\text{N}_2$ cleavage and hydrogenation at ambient conditions [10]. Besides, it is significant to study $\text{N}_2$ activation by hydride species because they are related to the Haber–Bosch process and biological nitrogen fixation [9, 13].

Gas-phase clusters are ideal models to mimic the active sites of related condensed-phase systems [14–18]. Homonuclear metal clusters such as $\text{M}_3^-$ ($\text{M} = \text{Ni, Pd, Pt}$) [19], $\text{Nb}_n^-$ ($n = 2–7$) [20], $\text{W}_n$ ($n = 4–26$) [21], $\text{Co}_n$ ($n = 4–28$) [22], $\text{Co}_n^-$ ($n = \ldots$)
1–18) [23, 24], and TaN− [25] have been reported to adsorb N2 in either a molecular or a dissociative way. The size-dependent reactivity and donation/back-donation of electrons in N2 activation were uncovered. There have been some reports and knowledge of N2 activation by metal clusters doped with ancillary main group atoms (C, S, etc.) in gas-phase investigations [26, 27]. However, to the best of our knowledge, there has been no report about the N2 activation by gas-phase metal hydride species that have already been studied to activate other very stable molecules such as CO2 [28–31] and CH4 [32–35].

In this work, we studied the gas-phase reactions between polynuclear cobalt deuteride clusters anions Co3Dn− (n = 0–4) and N2 via mass spectrometry, photoelectron imaging spectroscopy, and quantum chemical calculations. Cobalt is a cheap, abundant, and monoisotopic (beneficial for mass spectrometry) late transition metal. Pure cobalt is less competitive than the very stable molecules such as CO2 [28–31] and CH4 [32–35].

The photoelectron spectroscopy of Co− has been investigated by Wang and his coworkers [39].

Experimental and Computational Methods

Experimental Methods

Details of the experimental setup can be found in our previous studies [40, 41], and only a brief outline of the experiments is given below. In the reactivity experiments, the Co3Dn− (n = 0–4) cluster anions were generated by laser ablation of a rotating and translating cobalt metal disk in the presence of 10% D2 seeded in a He carrier gas with a backing pressure of about 4 atm. The cluster anions of interest were mass-selected by a quadrupole mass filter (QMF) [40] and then entered into a linear ion trap (LIT) reactor [41], in which they were confined and thermalized by collisions with a pulse of He gas for about 1.4 ms. The thermalized cluster anions subsequently reacted with a pulse of N2 for about 8.6 ms. The pressures of N2 were in the range of 1–2 Pa. The reactant and product ions ejected from the LIT were transferred into a reflectron time-of-flight mass spectrometer (TOF-MS) for mass and intensity measurements [41].

The photoelectron imaging spectroscopy (PEIS) experiments were carried out with a separate apparatus of tandem TOF-MS coupled with an optical parametric oscillator (OPO) laser source and a PEIS system [42]. The Co3Dn− (n = 0–4) clusters were generated according to the procedure described in the reactivity experiments with 5% D2 (for n = 3 and 4) and 0.6% D2 (for n = 0–2) seeded in He. The temperature of the cluster source was 298 K. The generated cluster anions from the supersonic expansion were skimmed into the tandem TOF-MS and were mass-selected by the primary TOF-MS with a mass gate to interact with a 550 nm laser beam delivered from the OPO system. The photodetached electrons were accelerated to the PEIS detector where the electron velocities were imaged. The two-dimensional images were transformed into three-dimensional electron velocity distributions. The photoelectron kinetic energies and angular distribution were obtained [43, 44]. The resolution of the photoelectron spectrometer was found to be around 30 meV for electrons with 1 eV kinetic energy in the test experiment with the gold anions [42].

Computational Methods

Density functional theory (DFT) calculations using Gaussian 09 program [45] were carried out to investigate the structures of Co3Hn− (n = 0–4) as well as the mechanistic details for the size-dependent reactivity with N2. There is a long-standing controversy on the most stable geometry of Co3−. The reported DFT calculations predicted either a linear or a triangular structure, depending on the functionals and basis sets adopted [46–51]. To find an appropriate functional for the polynuclear cobalt hydrides, the experimental values of electron detachment energies of Co3− [39], bond length of Co–Co [52], and bond dissociation energy of Co–H [53] were used to test various functionals (Table S1). It turned out that the TPSS functional [54] is the best overall with the def2-TZVP basis set [55]. The low-lying structure isomers for each of Co3Hn− (n = 0–4) were determined by the TPSS calculations for different spin multiplicities. The electron adiabatic detachment energies (ADEs) and vertical detachment energies (VDEs) were calculated. Based on the structures of Co3Hn− (n = 0–4), the structures and N2 adsorption energies of Co3Hn(N2)− (x = 1, 2, or 3) were calculated. The reported relative energies of the cluster isomers were corrected with zero-point vibrations. The molecular orbital (MO) analysis and natural bond orbital (NBO) analysis were performed to further interpret the experimental results.

Results

Reactivity of Co3Dn− (n = 0–4) with N2

The TOF mass spectra for the interactions of Co3Dn− (n = 0–4) with N2 are shown in Figure 1. It is obvious that in the reactions of Co3− (Figure 1a) and Co3D− (Figure 1b) with N2, no product peaks were generated. In contrast, under similar experimental conditions, the interactions of Co3D− (Figure 1c), Co3D− (Figure 1d), and Co3D− (Figure 1e) with N2 generated product peaks that can be assigned as Co3D2−N2−, suggesting the following reaction channels:

\[\text{Co}_3\text{D}_2\text{D}^- + \text{N}_2 \rightarrow \text{Co}_3\text{D}_2\text{D}^- \text{N}_2^- \]  

(1)
As shown in Figure 2, the $k_1$ values for the reactions of Co$_3$D$_{2-4}$ with N$_2$ were determined to be $(3.4 \pm 0.7) \times 10^{-13}$, $(5.9 \pm 1.2) \times 10^{-14}$, and $(9.3 \pm 1.9) \times 10^{-14}$ cm$^3$ molecule$^{-1}$s$^{-1}$, respectively. The $k_1$ value of Co$_3$D$_2^-$ with N$_2$ is about six and four times larger than those of Co$_3$D$_3^-$ and Co$_3$D$_4^-$ systems, respectively.

**DFT Calculated Structures and N$_2$ Adsorption Energies**

The DFT calculated structures of the Co$_3$H$_n^-$ ($n = 0$–$4$) clusters and the N$_2$ adsorption products are presented in Figure 3 (see Figures S1 and S2 for more details). For clarity, the $i$th isomer of Co$_3$H$_n^-$ is denoted as $n$-$i$. For example, 0–1 denotes the most stable structure of Co$_3^-$. Similarly, N$_2$ adsorption complex Co$_3$H$_n$(N$_2$)$_i^-$ is denoted as $n$-C$X$-$i$. The DFT calculated lowest-lying isomer of Co$_3^-$ (0–1) has an equilateral triangular structure with the bond length of 226 pm and the nonet spin state, while the linear structure of Co$_3^-$ (0–2) has the sepeet state that is 0.38 eV higher in energy than the triangular one. For Co$_3$H$^+$, the lowest-lying isomer (1–1) has the octet spin state and the $C_3$ symmetry. The H atom in isomer 1–1 is bridgingly bonded with two Co atoms. The isomer 1–2 with a terminal H atom and the isomer 1–3 with the $C_{2v}$ symmetry were calculated to be 0.11 and 0.19 eV higher in energy than the 1–1 structure, respectively. All of the H atoms in the lowest-lying isomers of Co$_3$H$_4^-$ (2–1) and Co$_3$H$_3^-$ (3–1) are bridgingly bonded. One of the four H atoms in Co$_3$H$_4^-$ (4–1) is terminally bonded. Each of the Co$_3$H$_n^-$ ($n = 1$–$4$) clusters has one or two isomers that are very close in energy (within 0.2 eV) to the lowest-lying isomers. These isomers are possible candidates that could be populated in the cluster source. It is noteworthy that test calculations indicated that the cluster structures with an unbroken H–H bond such as (H$_2$)Co$_3$H$^+$ and (H$_2$)Co$_3$H$_2^-$ are all high in energy (isomers 3–6 and 4–6 in Figure S1).

For the N$_2$ adsorption complexes, several N$_2$ binding modes were considered and it turned out that the end-on coordination is the most favorable mode. The most stable structures of the
while the N-N bond order is decreased from 3.0 in free N\textsubscript{2} to significant chemical bonding between N and Co atoms. Mean-

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \text{Co}<em>{2}H</em>{n}^- (n = 0 - 4) )</th>
<th>( \text{N}_2 ) adsorption products</th>
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Figure 3. DFT calculated low-lying isomers of \( \text{Co}_{2}H_{n}^- (n = 0 - 4) \) and their \( \text{N}_2 \) adsorption products. The relative energies with respect to the lowest-lying isomers (\( n \)-1) for isomers (\( n \)-4) and the \( \text{N}_2 \) binding energies for adsorption products (\( n \)-Cx-\( i \)) in units of eV. Some selected bond lengths are given in pm. The superscripts indicate the spin multiplicities. The calculated ADE/VDE values of \( \text{Co}_{2}H_{n}N_{2}^- (n-C1-1, n = 2 - 4) \) are listed in the brackets. The bond orders of Co–N are listed in the square brackets.

adsorption products \( \text{Co}_3H_2N_2^- \) remain the same spin multiplicities as the reactant clusters while that of \( \text{Co}_3H_0N_2^- \) have different spin multiplicities with respect to the reactants. As shown in Figure 3, the most stable structure of \( \text{Co}_3N_2^- (0-C1-1) \) has the septet spin state and the \( \text{N}_2 \) adsorption energy (1.15 eV) is larger than that of the isomer (0-C1-4) with nonet spin state by 0.61 eV. For \( \text{Co}_3H^+ \), the low-lying isomers (1-1, 1-2, and 1-3) can bind \( \text{N}_2 \) to generate the most stable adsorption structure (1-C1-1) with the sextet spin state which has a larger adsorption (1.30 eV) energy than the isomer in the octet spin state (1.16 eV). For \( \text{Co}_3H_2^- \), the low-lying isomers (2-1, 2-2, and 2-3) can adsorb \( \text{N}_2 \) to form the most stable adsorption structure (2-C1-1). For \( \text{Co}_3H_3^- \), the \( \text{N}_2 \) adsorption onto 3-1 and 3-3 can produce the most stable complex 3-C1-1 while the complex formed from 3-2 with \( \text{N}_2 \) is higher in energy by 0.70 eV (3-C1-3, Figure S2). The most stable adsorption complex of \( \text{Co}_3H_2N_2^- (4-C1-1) \) can be formed from 4-1 and 4-2 with \( \text{N}_2 \). In the adsorption complexes \( \text{Co}_3H_2N_2^- (2-C1-1), \text{Co}_3H_3N_2^- (3-C1-1), \) and \( \text{Co}_3H_4N_2^- (4-C1-1) \), the bond orders (Figure 3, square brackets) between \( \text{N}_2 \) and the related Co atoms are around 0.83–0.87, which indicates that there is significant chemical bonding between N and Co atoms. Meanwhile the N-N bond order is decreased from 3.0 in free \( \text{N}_2 \) to about 2.5 in the association complexes. Therefore, the N-N bond was significantly activated in the adsorption complexes. The structures of the complexes with two and three \( \text{N}_2 \) molecules were also determined and all of the \( \text{N}_2 \) units are end-on coordinated (Figure 3, bottom right). The \( \text{N}_2 \) adsorption energy of \( \text{Co}_3H_2N_2^- (n-C1-1) \) generally increases as the increase of the number (\( n \)) of H atoms, which is qualitatively consistent with the experimental result that \( \text{Co}_3H_2.4^- \) absorbed \( \text{N}_2 \) while \( \text{Co}_3H_0.4^- \) did not (Figure 1).

**Photoelectron Spectra and Structure Assignments**

For most of the \( \text{Co}_3H_n^- (n = 0 - 4) \) clusters, the DFT calculations predicted more than one isomeric structure that are close in energy (Figure 3, left). The PEIS experiment can be helpful to assign the cluster structures. The photoelectron spectra of \( \text{Co}_{0.4}D_0.4^- \) are presented in Figure 4, and the experimental and DFT calculated ADE/VDE values are listed in Table 1. The simulated photoelectron spectra of the low-lying isomers of \( \text{Co}_3H_n^- (n = 0 - 4) \) based on the generalized Koopmans’ theorem [57], named as density of states (DOS) spectra, are presented in Figures S4–S8.

For \( \text{Co}_3^- \) (Figure 4a), the spectrum is dominated by a band ranging from about 1.40 to 1.80 eV, with a band center at the electron binding energy (EBE) of 1.62 eV, which determines the VDE value. The ADE value of \( \text{Co}_3^- \) was estimated to be 1.41 eV by extrapolating the lower EBE side of the band to zero photoelectron intensity. The ADE and VDE values (1.41/1.62 eV) of \( \text{Co}_3^- \) are in line with those (1.40/1.60 eV) of Wang...
with respect to that of Co3−, the spectral bands of Co3D2−,4 (Figure 4c–e) are all broad and the ADE values of those clusters are all red-shifted (Table 1). For Co3D2−, the isomers 2-1 and 2-2 are almost degenerate in energy (Figure 3). The combination of the DOS spectra of isomers 2-1 and 2-2 can fit most of the experimental features (Figure S6). Thus, isomers 2-1 and 2-2 are suggested to be coexist in the cluster source. Notably, the isomer 2-3 may have minor contribution because its DOS spectrum resembles the high EBE peaks in the experimental spectrum. Similarly, the broad spectral bands of Co3D− by the experiment and the DOS spectra of several low-lying isomers (Figure S7) suggest that isomers 3-1 and 3-3 may be the major structures contributing to the experimental spectrum and isomer 3-2 may have the minor contribution. For Co3D4−, the combination of the DOS spectra of isomers 4-1 and 4-2 (Figure S8) can match the experimental spectrum. The isomer 4-3 was unlikely to be touched in the PEIS experiments because the ADE/VDE values (2.72/3.06 eV) deviate largely from the experimental values (1.00/1.76 eV).

**Discussion**

**Size-Dependent Reactivity of Co3Dn− (n = 0–4) with N2**

The relaxed potential energy surface scans revealed that the processes of N2 adsorption onto Co3D2−,4 are exothermic and barrier-free and the N2 adsorption energies of Co3D2−,4N2− are generally larger (1.31–1.55 eV, Figure 3) than those of Co3N2− and Co3DN2−. In addition, the spin conversions [58] have to take place in order to form the most stable structures of Co3N2− (0-C1-1) and Co3DN2− (1-C1-1). The relatively low N2 binding energies of 0-C1-4 (0.54 eV) and 1-C1-2 (1.16 eV) and the possibly low-spin conversion efficiencies can lead to relatively weak N2 adsorption, which is in agreement with no observation of Co3N2− and Co3DN2− in the experiment (Figure 1). Interestingly, the rate constant for the reaction of Co3D3− with N2 is the smallest among Co3D2−,4 reaction systems while Co3D3N2− has a larger N2 adsorption energy (1.55 eV) than Co3D2N2− (1.38 eV) and Co3D4N2− (1.31 eV). The DFT calculations indicated that the ADE (1.40 eV) and VDE (1.49 eV) values (Figure 3, in brackets) of Co3D2N2− are smaller than the N2 adsorption energy (1.55 eV), which means that associative electron detachment (AED) could take place in the experiment Co3D+ + N2 → (Co3D2N2−)→ Co3D2N2− + e−. Note that the AED process was often observed in the reactions of small molecules with negative ions [59, 60]. In contrast, the AED process for the Co3D− and Co3D4− reaction systems would not take place because the ADE values of Co3D2N2− and Co3D4N2− are significantly higher than the corresponding N2 adsorption energies. In other words, Co3D3− could be the most reactive cluster towards N2 but exhibited the smallest reaction rate among Co3D2−,4 due to

![Figure 4. Photoelectron spectra of (a) Co3−, (b) Co3D−, (c) Co3D2−, (d) Co3D3−, and (e) Co3D4− taken with 550 nm (2.254 eV) photons. The structures shown are the most probable isomers in the experiments](Image)
the undetectable adsorption products (the \( T_f \) value in Eq. (4)) could be underestimated for \( \text{Co}_3\text{D}_4^-+\text{N}_2 \).

The size-dependent reactivity of the \( \text{Co}_3\text{D}_n^- \) \((n=0-4)\) clusters with \( \text{N}_2 \) is also supported by the PEIS experiment. The increased ADE of \( \text{Co}_3\text{D}^- \) (1.57 eV) with respect to that of \( \text{Co}_3^- \) (1.41 eV) indicates that it is more difficult for \( \text{Co}_3\text{D}^- \) to lose electrons to activate and then absorb \( \text{N}_2 \). In contrast, the decreased ADEs of \( \text{Co}_3\text{D}_2^- \) (1.00–1.18 eV) mean that \( \text{Co}_3\text{D}_2^- \) can lose electrons more easily to activate and then absorb \( \text{N}_2 \) than \( \text{Co}_3^- \) and \( \text{Co}_3\text{D}^- \). Therefore, the different ADEs by the PEIS can generally interpret the size-dependent reactivity of the \( \text{Co}_3\text{D}_n^- \) \((n=0-4)\) clusters with \( \text{N}_2 \) in the mass spectrometry experiment.

### MO Analysis

To further understand the differences in electron detachment and \( \text{N}_2 \) adsorption energies of the \( \text{Co}_3\text{D}_n^- \) \((n=0-4)\) clusters, the MO analysis has been performed. The highest occupied MOs (HOMOs) were considered to lose electrons in the electron detachment. The HOMOs of selected isomers of \( \text{Co}_3\text{H}_4^- \) (note that the electronic structures of \( \text{Co}_3\text{H}_0^- \) and \( \text{Co}_3\text{D}_0^- \) are identical) are given in Figure 5. Note that both isomers 1-1 and 1-2 are listed for a comparison although the isomer 1-2 is assigned as the experimental species. It can be seen that both the number and the bonding mode of H atoms can influence the energies of HOMOs that are primarily composed of the Co 3d orbitals. A terminally bonded H atom (denoted as \( \text{H}_t \)) in \( \text{Co}_3\text{H}_3 \) (1.22 eV) lowers down the HOMO energy with respect to that of \( \text{Co}_3^− \), which leads to a larger ADE of \( \text{Co}_3\text{H}_3^- \) (1.57 eV) than \( \text{Co}_3^- \) (1.41 eV). In contrast, the HOMO energy increases if the H atom is bridgingly bonded (denoted as \( \text{H}_b \)) in \( \text{Co}_3\text{H}_2 \) (1.41 eV). For \( \text{Co}_3\text{H}_2^- \), the HOMO energies are all higher than that of \( \text{Co}_3^- \), leading to smaller ADEs (1.00–1.18 eV) of \( \text{Co}_3\text{D}_2^- \) than that of \( \text{Co}_3^- \). The increased HOMO levels of \( \text{Co}_3\text{H}_2^- \) can also facilitate back-donation bonding with the \( \pi^* \) orbitals of \( \text{N}_2 \) due to the decreased energy gap. Interestingly, for each of the \( \text{Co}_3\text{H}_n^- \) \((n=1-4)\) clusters, the isomers with more \( \text{H}_b \) atoms tend to have higher HOMO levels.

### NBO Analysis

The NBO analysis was performed to further interpret the bonding between \( \text{N}_2 \) and \( \text{Co}_3\text{H}_n^- \) \((n=0-4)\) clusters, and the results are presented in Table 2. It turned out that the less negatively charged Co atom functions as the preferred trapping site to anchor \( \text{N}_2 \) molecule (hereafter called active-Co), while the other two Co atoms and the H atoms serve as indirect electron donors for the active-Co atom and \( \text{N}_2 \) molecule. The active-Co atoms in \( \text{Co}_3\text{H}_{0.1}^- \) (1-1 and 1-2) have relatively large negative charges (–0.333 and –0.290 e, respectively) and more 4s electron occupancies (4s\(^{1.32}\) and 4s\(^{1.51}\), respectively), which give rise to an unfavorable approach and relatively high \( \sigma \)-repulsion to the \( \text{N}_2 \) molecule. Upon bonding of two H atoms on the Co\(^{−} \) cluster to form \( \text{Co}_3\text{H}_2^- \) (2-1), the natural charge on the active-Co increases to –0.099 e; meanwhile, more 3d and less 4s electron occupancies are located, which can result in an easier approach of \( \text{N}_2 \) to the cluster and a larger adsorption energy (1.38 eV). The above changes of charge on the active-Co and the electron occupancies in 3d and 4s orbitals are further enhanced when three H atoms are bonded with \( \text{Co}_3^- \) to form \( \text{Co}_3\text{H}_3^- \) (3-1), which leads to a further larger \( \text{N}_2 \) adsorption energy (1.55 eV). For \( \text{Co}_3\text{H}_4^- \), the natural charges on the active-Co and the four H atoms are +0.134 e and –1.225 e, respectively, and electron configuration of the 3d orbital reduces to 3d\(^{7.83}\)). Such a positive Co site tends to compete with \( \text{N}_2 \) for electron densities. It turns out that the active-Co of \( \text{Co}_3\text{H}_4^- \) gains –0.250 e while the \( \text{N}_2 \) unit only gains –0.212 e which becomes smaller than the corresponding value (–0.259 e) of \( \text{Co}_3\text{H}_3^- \) (3-1) reaction system. As a result, the \( \text{N}_2 \) is less activated in \( \text{Co}_3\text{H}_4^- \) (4-1) than in \( \text{Co}_3\text{H}_3^- \) (3-1-1), which is consistent with the larger \( \text{N}_2 \) adsorption energy of the latter (1.55 eV) versus the former (1.31 eV). One can conclude that the H atoms on the metal cluster (\( \text{Co}_3^- \)) significantly manipulate the charge/electron distribution (and the electronic structure), and an appropriate number of H atoms can enhance and maximize the cluster reactivity in \( \text{N}_2 \) activation.

### Table 1. Experimental and DFT calculated ADE/VDE values of \( \text{Co}_3\text{D}_n^- \) \((n=0-4)\)

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<tr>
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<td>1.19/1.75 (4–1)</td>
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*The isomers labeled in italics are the most probable isomers in the experiments.

Figure 5. HOMO levels of selected \( \text{Co}_3\text{D}_n^- \) \((n=0-4)\) cluster isomers that lose electrons to form the corresponding neutral counterparts. The up and down arrows denote the \( \alpha \) and \( \beta \) electrons, respectively.
Table 2. Natural charge and electron occupancy analysis

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<td>4(^1\text{1.32}; 2\text{p}^{83})</td>
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<tr>
<td>1-2</td>
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<td>4(^1\text{3.003}; 2\text{p}^{89})</td>
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<td>−0.007</td>
<td>−0.963 – 0.259 − 0.047</td>
<td>4(^1\text{3.161}; 2\text{p}^{86})</td>
<td></td>
</tr>
<tr>
<td>4-1</td>
<td>+0.134</td>
<td>−1.225 – 0.212 − 0.250</td>
<td>4(^1\text{3.085}; 2\text{p}^{83})</td>
<td></td>
</tr>
</tbody>
</table>

*The ith isomer of Co₃H₄⁺ (n = 0–4)
*The natural charges on the active-Co (N₂ trapping site) and the H atoms
*The natural charges gained by the N₂ unit and the active-Co upon the process of N₂ adsorption
*The electron occupancy on the active-Co atom

Conclusion

The structures of Co₃D₄⁻ (n = 0–4) clusters and their reactions with N₂ have been studied by mass spectrometry, photoelectron imaging spectroscopy, and density functional theory calculations. The Co₃D₂₋₄⁻ clusters were observed to adsorb N₂ molecules in an ion trap reactor while Co₃⁻ and Co₃D⁻ were inert. The photoelectron spectra indicated that Co₃D⁻ and Co₃D₂₋₄⁻ have blue- and red-shifted adiabatic electron detachment energies with respect to Co₃⁻, which interprets the size-dependent abilities to transfer electrons from the cluster anions to activate and then absorb N₂ molecules. The density functional theory calculations revealed that (i) the disagreement of the largest N₂ adsorption energy and the smallest reaction rate of Co₃D₃⁻ among Co₃D₂₋₄⁻ reaction systems may be resulted from the exothermic process of the associative electron detachment, leading to the undetectable neutral product in the mass spectrometry experiment and the underestimate of the rate constant; (ii) the highest occupied molecular orbitals of Co₃H₂₋₄⁻ (primarily Co 3d orbitals) are pushed higher in energy upon the bonding of H atoms on the Co₃⁻ cluster, which facilitates electron detachment as well as N₂ adsorption; and (iii) the bonding of H atoms on the Co₃⁻ cluster can also lead to less negatively charged Co sites with more 3d electron occupancies that are more effective to make π-back-donation bonding with N₂ molecules. An appropriate number of H (or D) atoms on a metal cluster such as Co₃⁻ can enhance and maximize the cluster reactivity in N₂ activation.

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References
