Structures and Magnetic Properties of Small Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) Clusters

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Abstract:

Small cobalt clusters Co_n^+ and their single chromium atom doped counterparts $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) were studied mass spectrometrically by measuring the infrared multiple photon dissociation (IRMPD) spectra of the corresponding argon-tagged complexes. The geometric and electronic structures of the Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters as well as their Ar complexes were optimized by density functional theory calculations. The obtained lowest energy structures were confirmed by comparing the IRMPD spectra of Co_nAr_m^+ and $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n = 3-5$, $m = 3$ and 4) with the corresponding calculated IR spectra. The calculations reveal that the doped clusters $\text{Co}_{n-1}\text{Cr}^+$ retain the geometric structures of the most stable Co_n^+ clusters. However, the coupling of the local magnetic moments within the clusters is altered in a size-dependent way: the Cr atom is ferromagnetically coupled in Co_2Cr^+ and Co_3Cr^+ , while it is antiferromagnetically coupled in Co_4Cr^+ .

Keywords: Cobalt cluster; Chromium doping; Infrared multiple photon dissociation; Mass spectrometry; Density functional theory; Magnetic coupling

1. Introduction

The study of small cobalt clusters is of scientific interest to obtain understanding about the evolution magnetic properties from single atoms to bulk materials [1-3]. For bulk hexagonal closed-packed (hcp) cobalt [4], x-ray magnetic circular dichroism (XMCD) experiments found spin and orbital magnetic moments per atom of 1.55 and 0.153 μ_B , respectively [5]. Several experimental studies have been performed to determine the magnetic moments of cobalt clusters in a broad size range ($\text{Co}_n^{0,+}$ with $n = 7-200$) [1-3, 6-10]. The obtained values per atom are larger for small clusters than for bulk and the magnetic moments vary in a non-trivial way with cluster size [1-3, 6-10]. Magnetic deflection experiments on small neutral Co_n clusters obtained, for $7 \leq n \leq 20$, total magnetic moments per atom in the range of 1.9–3.5 μ_B [2, 6-8]. Although it should be mentioned that the values determined in the different studies are not fully consistent with one another. A XMCD study on cationic cobalt clusters gave, for the same $7 \leq n \leq 20$ sizes, total and spin magnetic moments in the ranges of 2.6–3.7 μ_B and 1.9–2.8 μ_B , respectively [10].

The magnetic properties of cobalt clusters are also affected by details of the geometric and electronic structures [11-14]. In a photo-dissociation spectroscopy and theoretical investigation of Co_nAr^+ ($n = 3-5$) [15], the geometric and electronic structures of Co_3^+ and Co_4^+ have been proposed. The calculated average spin magnetic moments per atom are 2.0 μ_B for Co_3^+ (an equilateral triangle with a bond length of 2.00–2.25 Å) and 1.75 μ_B for Co_4^+ (a tetrahedron with a bond length of 2.00 Å). Infrared absorption spectra of argon tagged Co_n^+ ($n = 4-8$) clusters have been measured by infrared multiphoton dissociation (IRMPD) spectroscopy [16]. By comparison of the IRMPD spectra with simulated IR spectra obtained by density functional theory (DFT) calculations for different structural isomers, the geometric and electronic structures of cobalt clusters Co_n^+ ($n = 4-8$) were determined. For Co_4^+ and Co_5^+ , the reported lowest energy structures are a distorted tetrahedral with an average spin magnetic moment per atom of 1.75 μ_B and a distorted triangle bipyramid with an average spin magnetic moment per atom of 2.0 μ_B , respectively.

The elemental substitution of individual atoms in a material can dramatically change its properties and produce tailored materials with expected properties. The magnetic interactions in small cobalt particles can be tuned by variation of the chemical composition, which motivates the study of doped cobalt clusters [17-27]. Doped particles are also of interest for applications using customized magnetic materials [28-31]. The structural and magnetic properties of cobalt clusters can be modified by selection of the doping element, as demonstrated by various experimental and theoretical studies dealing with Co_nAu^+ and Co_nRh^+ [17], Co_nAu [18], Co_nRh_m [19, 26], Co_nV_m and Co_nMn_m [20, 22, 24], $M\text{Co}_{12}$ ($M = \text{Ti, V, Cr, Mn, Fe, Co, Ni, Ag, Pt, Au}$) [21, 23], Co_nCu_m [27], and Co_nRu_m [32]. A Stern–Gerlach magnetic deflection experiment on neutral Co_nMn_m ($n+m = 11-29$) clusters showed that, for most sizes, the measured magnetic moments of the alloy clusters Co_nMn_m are comparable to those of the pure cobalt clusters with the same number of atoms [25]. Interestingly, the measured magnetic moments of the Co_nMn_m clusters are significantly larger than expectations based on the corresponding bulk $\text{Co}_{1-x}\text{Mn}_x$ alloys [25]. For the icosahedral doped $M\text{Co}_{12}$ ($M = \text{Ti, V, Cr, Mn, Fe, and Ni}$) clusters, the magnetic moments were predicted to be reduced upon substitution of a Co atom by the dopant M atom [23]. For small Co_nRh ($n = 1-8$) clusters, theoretical investigations indicated that the induced magnetic moment of the dopant atom displays a ferromagnetic coupling in the most stable configuration, except for Co_3Rh . In addition, Rh doping influences the magnetic moment of the doped cobalt clusters in a size-dependent way. Compared with pure Co_n clusters, the average local magnetic moments on the Co atoms are noticeably enhanced for Co_nRh ($n = 1, 2, 5, 6, 7$, and 8), while they were predicted

to be reduced for $n = 3$ and 4. In larger Co_nRh_m ($n + m \approx 110$ and $n \approx m$) nanoparticles, the magnetic moment on the Rh atoms strongly depends on their position and environment [31].

Chromium is an interesting dopant material for tuning the magnetic properties of cobalt clusters, since bulk chromium is the only elemental solid that shows antiferromagnetic ordering at room temperature. A single Cr atom has a local spin magnetic moment of $6 \mu_B$. In the neutral Cr_2 dimer, the total magnetic moment is zero as a result of anti-ferromagnetic coupling of the local moments [33]. While, surprisingly, the local moments at the two Cr sites couple ferromagnetically in the cationic Cr_2^+ , resulting in a high-spin ground state $^1\Sigma$ ground state [34]. Non-zero average magnetic moments per atom have been measured for Cr_n ($n = 20\text{--}133$) clusters [35]. Those values quench if the particle size grows [36]. For example, the thin Cr films are antiferromagnetic and used for coating tips in scanning tunneling microscopy [37]. In a photofragmentation study, it was shown that Cr doping general destabilizes the cobalt clusters, with the exception of $\text{Co}_{12}\text{Cr}^+$ [38], which is relatively more stable than Co_{13}^+ and likely has an icosahedral structure [23]. We are not aware of dedicated studies dealing with the structure and magnetism of few-atom chromium doped cobalt clusters.

In the present work, we explore the effect of single Cr atom doping on the magnetic properties of small cobalt clusters Co_n^+ ($n = 3\text{--}5$). To this end, the geometric and electronic structures of Co_n^+ ($n = 3\text{--}5$) clusters and their single Cr atom doped counterparts $\text{Co}_{n-1}\text{Cr}^+$ are investigated by a combination of infrared multiple photon dissociation (IRMPD) spectrometry and density functional theory (DFT) calculations, from which information on their magnetic properties is obtained.

2. Experimental and Theoretical Methods

2.1. Experimental method

Pure cobalt clusters, Co_n^+ ($n = 3\text{--}5$), and their single Cr atom doped counterparts, $\text{Co}_{n-1}\text{Cr}^+$, were produced by a laser vaporization source [39] in a molecular beam instrument [40] that is connected to a beam line of the Free Electron Lasers for infrared eXperiments (FELIX) laboratory [41]. Two pulsed (10 Hz) Nd-YAG lasers were used to evaporate separate cobalt and chromium plate targets in the presence of a helium carrier gas mixed with 0.1% argon. Clusters were formed through collisions of the ablated metal atoms with the helium gas, and a fraction of the metal clusters formed cluster-argon complexes. Cooling the last part of the cluster source to temperatures between 130 and 160 K enhanced this process. After expansion into vacuum, the cluster-carrier gas mixture formed a molecular beam that was further collimated by a 2-mm diameter conical skimmer and a 1-mm diameter planar aperture, before entering the extraction zone of a reflectron time-of-flight mass spectrometer. Here, the clusters interacted with a counter propagating laser beam of infrared (IR) light from FELIX, where the collimation of the molecular beam assured that all detected clusters were exposed to comparable laser intensities. A few microseconds after interaction with the IR laser, all ions were pulse-extracted and mass-analyzed. The experiment was operated at twice the FELIX repetition rate, to obtain mass spectra as a function of wavenumber for both the situations with and without IR irradiation.

The IR laser frequency used covered the $100\text{--}300 \text{ cm}^{-1}$ range, and the spectral bandwidth was near-transform limited, and amounting to approximately 0.5% FWHM of the central frequency $\tilde{\nu}$. Pulse energies used amount to 2–20 mJ per pulse. If the IR frequency is in resonance with one of the vibrational modes of a specific cluster-argon complex and sufficient photons are absorbed, the cluster-argon bond will break. Indeed, argon detachment from cluster-argon complexes was detected in the mass spectra as a signal depletion of Co_nAr_m^+ and $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n =$

3–5, $m = 3$ and 4) and a simultaneous intensity increase of the corresponding $\text{Co}_n\text{Ar}_{m-1}^+$ and $\text{Co}_{n-1}\text{CrAr}_{m-1}^+$ mass channels. The amount of depletion depends not only on the photon absorption cross section, but also on the internal vibrational energy redistribution process and the cluster-argon binding energy [40]. Due to partial overlap of some of the peaks in the mass spectra, Gaussian peak shapes are fitted to obtain the abundances. By comparing mass spectra with and without laser excitation at a certain spectroscopic wavenumber $\tilde{\nu}$ and using the Lambert-Beer law, the relative IR adsorption cross section $\sigma_{exp}(\tilde{\nu})$ can be obtained:

$$\sigma_{exp}(\tilde{\nu}) = \frac{\ln(V_{OFF}/V_{ON})}{E(\tilde{\nu})}.$$

With E laser pulse energy and V_{ON} and V_{OFF} the mass intensity with and without laser excitation, respectively. The uncertainties on $\sigma_{exp}(\tilde{\nu})$ are obtained by standard error propagation of the fit uncertainties, which, due to the division, results in a larger error for runs with lower signal. The experiment is repeated for a total of twenty runs, with frequent wavelength calibrations using a grating spectrometer, as well as pulse energy measurements. The resulting values for $\sigma_{exp}(\tilde{\nu})$ are binned in 2 cm^{-2} intervals, and an average of the different runs is taken with the squared reciprocal standard error as weight.

2.2. Computational method

DFT calculations were performed with the Gaussian09 software package [42] to explore the geometric structures of the Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters and their Ar complexes. We tested 16 functionals in combination with the Def2TZVP basis set [43] by calculating the bond dissociation energy, bond length, and vibrational frequency of the cobalt dimer, Co_2 , and by simulating the IRMPD spectra of CoAr_6^+ and Co_3Ar_4^+ . The details of these benchmark calculations and the results are given in Table S1 and Figures S1–S2 in the supporting information (SI). It is found that the hybrid B3P86 exchange-correlation functional [44–46] performs very well to describe the Co_2 dimer as well as to reproduce the IRMPD spectra of CoAr_6^+ and Co_3Ar_4^+ . This is in accordance with findings in another study, where B3P86 was found to outperform other commonly used functionals to describe first row transition metals [47]. Therefore, we employed the B3P86 functional for the calculations in this work. The initial geometric structures of the metal clusters were built manually. For the Ar complexes, many configurations were tested by adding Ar atoms to the low-lying energy isomers of the metal clusters. To further confirm the obtained structures of the Ar complexes, global searching by the CALYPSO methodology [48] was performed. Geometry optimizations were conducted without symmetry constraints in a range of possible spin multiplicities. Harmonic vibrational frequencies were calculated at the same level of theory to ensure that all structures are local minima on the potential energy surface and to take into account zero-point energy (ZPE) corrections. Analytic second order derivatives were adapted to simulate the infrared adsorption spectra. All the calculated IR spectra are presented without frequency scaling. The wavefunction analyzer Multiwfn [49] was employed for the analysis of the density of states.

3. Results and discussions

3.1. Mass spectra

A part of the mass spectrum of Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ clusters and their Ar complexes is shown in Figure 1. The main observed species in this mass range are Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 6, 7$), Co_nAr_m^+ ($n-m = 3-4, 4-3, 5-2, 6-1, 4-4$, and $5-3$), $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n-m = 4-3, 6-1, 4-4$, and $5-3$) and CoAr_6^+ . In this size range the intensities of the single Cr doped

species are about four times smaller than those of the pure cationic cobalt clusters. The $n = 3-5$ cluster sizes readily bind-up multiple Ar atoms with the highest intensities for four Ar atoms on Co_3^+ and Co_4^+ and three Ar atoms on Co_5^+ . The larger clusters typically bind only one or two Ar atoms and the fraction of clusters that adsorb Ar is smaller. This size-depend Ar binding capacity was discussed in an earlier experimental study of cationic cobalt cluster-argon complexes [16]. Both the number of attached Ar atoms and the fraction of clusters that absorb Ar is comparable for Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$. So, the Ar adsorption capacity does not seem to be influenced significantly by the Cr for Co substitution. For the spectroscopy, we focus on clusters containing three to five metal atoms: Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$). Of those, only for Co_2Cr^+ no IRMPD spectrum could be recorded because the intensities of its Ar complexes are too low to be distinguishable from the noise. To avoid contaminations from ingrowth from larger dissociating complexes, only the clusters with the largest number of attached Ar atoms are considered for the IRMPD depletion spectra. These depletions result in ingrowth patterns for the sizes with less Ar atoms attached, which provide an independent confirmation of the IR absorption bands.

Figure 1 Mass spectrum of the produced clusters and cluster-argon complexes in the 295–420 u range. Colored labels are used for the pure cobalt (red) and the chromium doped (blue) cluster-argon complexes for which the IRMPD spectra are recorded.

3.2. Structures of Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters and their Ar complexes

The B3P86/Def2TZVP calculated lowest energy structures of bare Co_n^+ and doped $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters as well as their corresponding Ar complexes, Co_nAr_m^+ and $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n-m = 3-4, 4-4, \text{ and } 5-3$) are shown in Figure 2. The number of Ar atoms is selected based on the high intensity of these complexes in the mass spectra. More low-lying energy isomers for both the bare clusters (Figures S3–S8) and the Ar complexes (Figures S9–S14) are displayed in the SI. For Co_3^+ , the most stable structure is a triangle with C_s symmetry and a spin magnetic moment of $6 \mu_B$. The next two lowest-lying isomers are +0.19 and +0.23 eV higher in energy. They also have a triangular structure and a spin magnetic moment of $6 \mu_B$. The lowest energy structure of Co_4^+ is a distorted tetrahedron (C_1) with a magnetic moment of $7 \mu_B$. The second isomer, a strongly distorted tetrahedron with the same magnetic moment, is only +0.02 eV higher in energy. A rhombic isomer with D_{2h} symmetry is +0.19 eV

higher in energy and it has a magnetic moment of $11 \mu_B$. For Co_5^+ , the low-lying energy isomers are distorted trigonal bipyramids. The lowest energy structure has a spin magnetic moment of $10 \mu_B$. The second isomer is 0.07 eV higher in energy and has the same magnetic moment, while the third (+0.09 eV) and fourth (+0.13 eV) lowest energy isomers have magnetic moments of $6 \mu_B$ and $2 \mu_B$, respectively. The obtained structures of the Co_n^+ ($n = 3-5$) clusters are in good agreement with those reported in literature [15, 16].

The most stable geometric structures of the Cr doped clusters, $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$), can be obtained by Cr substituting one of the Co atoms in the lowest energy structures for Co_n^+ ($n = 3-5$). For Co_2Cr^+ , the low-lying energy isomers ($\Delta E \leq 0.55$ eV) have a magnetic moment of $9 \mu_B$. A higher energy (+0.69 eV) isomer has a magnetic moment of $7 \mu_B$. For Co_3Cr^+ , the lowest energy structure is a distorted tetrahedron (C_1) with a spin magnetic moment of $10 \mu_B$. With the same structural framework, the second (+0.02 eV) and third (+0.06 eV) low-lying isomers have the spin magnetic moment of 2 and $10 \mu_B$, respectively. Other isomers in the energy range of $0.15 \text{ eV} \leq \Delta E \leq 0.35 \text{ eV}$ are distorted tetrahedrons with exception of the fourth isomer (+0.20 eV), which is a rhombus. The spin magnetic moments of those isomers are $10 \mu_B$. The lowest energy structure of Co_4Cr^+ has a magnetic moment of $3 \mu_B$ and can be obtained by Cr substituting one of the Co atoms in the central triangle of the bipyramidal framework of Co_5^+ . The second lowest energy isomer (+0.04 eV) has the same connectivity and has a spin magnetic moment of $13 \mu_B$. The third isomer (+0.11 eV) has the same structural framework and spin magnetic moment with respect to the lowest energy structure. Other higher energy isomers ($0.11 \text{ eV} \leq \Delta E \leq 0.25 \text{ eV}$) have spin magnetic moments of 13, 3, 5, and $13 \mu_B$, respectively. The Cr dopant atom is located at top or middle bridge sites in those isomers.

Figure 2 B3P86/Def2TZVP calculated lowest energy structures of Co_n^+ ($n = 3-5$, first row), $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$, third row) as well as their corresponding Ar complexes Co_nAr_m^+ and $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n-m = 3-4, 4-4$, and $5-3$ in second and fourth row). The electronic states and point group symmetries are given.

To explore the correlation between the geometric structure and the magnetism of the $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters, the average Co–Co and Co–Cr bonds lengths of in Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) are summarized in Table 1. Although the connectivity of the clusters remains unchanged upon Cr for Co substitution, the Co–Cr distances are

significantly longer than the Co–Co distances. This can be attributed to the larger atomic (1.40 Å) and covalent (1.22 Å) radius of the Cr atom compared to that of the Co atom (1.35 and 1.11 Å, respectively) [50, 51]. Interestingly, it appears that the spin state has an influence on the bonds lengths. The low spin (LS) states of Co_3Cr^+ and Co_4Cr^+ have larger Co–Cr bond lengths than the high spin (HS) states. The average Co–Cr bond lengths are about 0.03 Å longer in the case of antiferromagnetic (AFM) coupling than in the case of ferromagnetic (FM) coupling. This bond length difference may have consequences for the energetic preference of the magnetic configuration. Considering the larger average Co–Co bond length for the pure Co_5^+ than for Co_3^+ and Co_4^+ , the substitution of Cr in Co_5^+ may imply less stress and may facilitate the AFM coupling of the Cr spin moment. While the shorter original Co–Co bond lengths in Co_3^+ and Co_4^+ may be correlated to the preference for FM coupling. In an earlier study of the neutral icosahedral Co_{12}Cr , the spin magnetic moment on the central Cr dopant atom was found to be AFM coupled [23].

Table 1 Average bond lengths of Co–Co and Co–Cr bonds for the lowest energy structures of Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters.

n	Cluster	Total spin (μ_B)	Co–Co ($r_e / \text{\AA}$)	Co–Cr ($r_e / \text{\AA}$)
3	Co_3^+	6	2.396	
	Co_2Cr^+	9	2.371	2.638
4	Co_4^+	7	2.422	
	Co_3Cr^+ (HS)	10	2.414	2.606
	Co_3Cr^+ (LS)	2	2.454	2.631
5	Co_5^+	10	2.458	
	Co_4Cr^+ (LS)	3	2.435	2.662
	Co_4Cr^+ (HS)	13	2.470	2.634

The connectivity of the Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) metal clusters remains unchanged upon Ar attachment. However, compared to the bare clusters, the bond lengths and bond angles are slightly modified. For Co_3Ar_4^+ , one of the three cobalt atoms binds two Ar atoms and the other two each bind one Ar atom. A similar Ar binding pattern is found for $\text{Co}_2\text{CrAr}_4^+$, in which there are two Ar atoms attached to the Cr dopant atom. For Co_4Ar_4^+ and $\text{Co}_3\text{CrAr}_4^+$, every metal atom binds one Ar atom. For Co_5Ar_3^+ and $\text{Co}_4\text{CrAr}_3^+$, one Ar atom is attached to each of the three metal atoms in the horizontal base of the triangular bipyramid.

3.3. The vibrational spectra of argon complexes Co_nAr_m^+ and $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n-m = 3-4, 4-4, \text{ and } 5-3$)

In Figures 3 and 4, the experimental IRMPD spectra of Co_nAr_m^+ ($n-m = 3-4, 4-4, \text{ and } 5-3$) and $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n-m = 4-4, \text{ and } 5-3$) are compared with the calculated IR spectra of the lowest energy structures of Co_n^+ ($n = 3-5$) and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 4,5$) and their corresponding Ar complexes. Calculated structures and IR spectra of additional isomers of the bare clusters (Figures S3–S8) and their Ar complexes (Figures S9–S14) are given in the SI. Due to the relatively low overall production of Co_nAr_m^+ and $\text{Co}_{n-1}\text{CrAr}_m^+$ complexes, the IRMPD spectra are relatively noisy, making it difficult to discern substructure in the bands observed. However, the width of the single absorption band in the Co_5Ar_3^+ spectrum (Figure 3, lower panel) amounts to 29 cm^{-1} FWHM, suggesting that the broader bands in the spectra of Co_3Ar_4^+ and Co_4Ar_4^+ result from multiple absorption bands.

The IRMPD spectra of Co_nAr_m^+ (Figure 3) have characteristic absorptions in the 100–225 cm^{-1} spectral range. The spectrum for Co_3Ar_4^+ is dominated by two bands with one narrower close to 120 cm^{-1} and one broader centered

around 180 cm^{-1} . Upon comparing the experimental spectrum with the calculated spectrum, it is clear that for such small species the Ar plays an important role: bare triangular Co_3^+ exhibits only a doublet band between 150 and 175 cm^{-1} . Upon complexation the doublet is blueshifted to 175 and 180 cm^{-1} , while a triad of bands appears in the $80\text{--}125\text{ cm}^{-1}$ range, thereby providing a favorable comparison to the experimental spectrum. In addition to the Co_3Ar_4^+ species, we also computationally tested the effect of the adsorption of one, two, and three Ar atoms on Co_3^+ . In Figure S15 the IRMPD spectrum of Co_3Ar_4^+ is compared with the calculated IR spectra of Co_3Ar_m^+ ($m = 0\text{--}4$). Generally, the frequencies shift to the blue and the intensities of the vibrational modes increase with the addition of Ar atoms. Similar effects have been found for Co_n^+ ($n = 4\text{--}8$) and were related to the nature of Ar bonding with the small clusters [16]. The authors stated that these effects are attributed to symmetry breaking, which enhances electron density polarization of the cobalt clusters induced by Ar tagging. This strong effect of Ar addition is markedly different from other, larger, metal clusters, such as cationic niobium, tantalum, and silver clusters, in which the influence of the rare-gas atoms on the IRMPD spectra was found to be small and limited to frequency shifts of a few wavenumbers only [52–54].

Figure 3 Comparison of the IRMPD spectra of Co_3Ar_4^+ , Co_4Ar_4^+ , and Co_5Ar_3^+ with the calculated IR spectra of the lowest energy structures of Co_n^+ ($n = 3\text{--}5$) and their corresponding Ar complexes obtained at B3P86/Def2TZVP level. The calculated IR spectra are unscaled.

Co_4^+ and Co_5^+ were previously studied by Fielicke and co-workers [16], who reported IRMPD spectra for $\text{Co}_4\text{Ar}_{1,2,4,5}^+$ and $\text{Co}_5\text{Ar}_{1,5}^+$. Their failure to report a spectrum for Co_5Ar_3^+ is likely due to the large abundances of Co_5Ar_4^+ and Co_5Ar_5^+ in their mass spectrum, whose loss of Ar would complicate the interpretation of a spectrum for Co_5Ar_3^+ . The current spectrum of Co_4Ar_4^+ is similar to the earlier reported spectrum [16], and compares well with that predicted for the octet tetrahedron with Ar on every Co atom. For Co_5Ar_3^+ , the IRMPD spectrum is consistent with the IR spectrum predicted for an 11-et bipyramid with all Ar on the pyramid base. However, it appears different to the one for Co_5Ar_5^+ published earlier by Fielicke et al.: here, the pronounced band around 200 cm^{-1} and the weak band over 100 cm^{-1} for Co_5Ar_3^+ are comparable to those corresponding two bands observed in the spectrum for Co_5Ar_5^+ , whereas they reported an additional band around 230 cm^{-1} [16]. Overall, we conclude that the calculated harmonic IR spectra agree well with the IRMPD spectra, with some room for improvement concerning the relative IR intensities (*e.g.*, calculated transitions for Co_4Ar_4^+ in the $100\text{--}125\text{ cm}^{-1}$ range are lower than in the experiment) or frequencies (*e.g.*, calculated transitions for Co_5Ar_3^+ in the $175\text{--}225\text{ cm}^{-1}$ range are redshifted compared to the experiment). However, it is imperative to include the Ar tagging atoms in the calculations. While the Ar messenger atoms do not significantly alter the cluster structure, they have a substantial impact on the IR spectrum by blue shifting bare cluster modes due to steric hindering, providing new bands corresponding to vibrations of Co–Ar bonds ($100\text{--}125\text{ cm}^{-1}$), and overall increasing the oscillator strengths of the transitions.

The IRMPD spectra of the Ar complexes $\text{Co}_3\text{CrAr}_4^+$ and $\text{Co}_4\text{CrAr}_3^+$ (Figure 4) have vibrational modes in the $100\text{--}130\text{ cm}^{-1}$ and $150\text{--}210\text{ cm}^{-1}$ ranges and appear relatively similar to the spectra of Co_4Ar_4^+ and Co_5Ar_3^+ . At first instance, one would be led to believe that this similarity implies only a little structural change; however, this is without taking into account the effect of spin. Upon comparing the calculated spectra for the high-spin (11-et) and low-spin (triplet) configurations of Co_3Cr^+ , one observes large differences in the vibrational fingerprints. As for the bare cobalt clusters, multiple Ar tagging has a pronounced amplifying effect on these differences. While it is difficult to give a definitive assignment, we judge that the high-spin configuration of $\text{Co}_3\text{CrAr}_4^+$ has a more favorable comparison to the experimental spectrum. This is mostly so in the $150\text{--}225\text{ cm}^{-1}$ spectral range, where the predicted triad of Co–Cr vibrations offers a good frequency match. The bands between $100\text{--}125\text{ cm}^{-1}$ offer a poorer match, mostly in terms of an underestimated IR intensity. An alternative, speculative explanation could be an efficient IRMPD process in the case of direct excitation of the metal–Ar vibrational modes.

For $\text{Co}_4\text{CrAr}_3^+$, we also find two structures with the same connectivity but different spin states (quartet and 14-et). Again, a marked difference is observed in the vibrational fingerprints for the two spin isomers, albeit less strong than for the $\text{Co}_3\text{CrAr}_4^+$ case. We nevertheless assign the experimental spectrum to the quartet lowest energy spin state. The two bands calculated in the $150\text{--}225\text{ cm}^{-1}$ spectral range for the high spin (14-et) isomer only 0.01 eV higher in energy are too blue-shifted to assign the spectrum to this isomer. Additionally, the calculated frequency difference between the two intense modes of the quartet state (168 and 186 cm^{-1} , respectively) reproduces the experiment (maxima of fitted Gaussians at $166 \pm 1.0\text{ cm}^{-1}$ and $184 \pm 1.4\text{ cm}^{-1}$) very well, while the splitting for the high spin state (modes at 172 and 200 cm^{-1}) is larger. The calculated IR spectrum of the $\text{Co}_4\text{CrAr}_3^+$ quartet state is thus in better agreement with the experiment than that of 11-et.

Despite the reasonable agreement between the measured IRMPD spectra and the calculated IR spectra for the lowest-energy isomers, there are several reasons to be critical concerning determination of the ground spin states. Firstly, one should take into consideration the multitude of different low-energy electronic states for the bare

clusters (Figures S7 and S8) and their Ar complexes (Figures S13 and S14). Several of those, corresponding to clusters with the same structural connectivity but different spin states, exhibit highly similar calculated IR spectra as the isomers shown in Figure 4. Secondly, in view of the small energy differences between the Ar complex isomers (also the bare cluster isomers) and the broad adsorption peaks in the IRMPD spectra, it is possible that those low-lying isomers coexist in the experiment. It was found that the IR spectra are sensitive to the structure changes with even only a slight adjustment of the bond lengths within the same framework and connectivity. This might be attributed to the multi-reference characters of the Co element [55]. Thirdly, the computational level tests in the SI for CoAr_6^+ and Co_3Ar_4^+ (Figures S1 and S2) demonstrate that the calculated IR spectra are sensitive to the used functionals.

Figure 4 Comparison of the IRMPD spectra of $\text{Co}_3\text{CrAr}_4^+$ and $\text{Co}_4\text{CrAr}_3^+$ with the calculated IR spectra of the lowest energy structures of Co_3Cr^+ and Co_4Cr^+ and their corresponding Ar complexes obtained at the B3P86/Def2TZVP level. The calculated IR spectra are unscaled. The relative energies of the bare clusters and their Ar complexes are given (bare cluster / Ar complex), respectively, with respect to the corresponding lowest energy structures.

3.4. Spin populations and size-dependent magnetic moments

To understand the magnetic properties of Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters, the Mulliken spin density distributions of the lowest energy structures are analyzed and shown in Figure 5. For Co_3Cr^+ and Co_4Cr^+ , an isomer with different spin configuration is included. Ferromagnetic ordering is identified for the lowest energy structures of Co_n^+ ($n = 3-5$), $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3$ and 4), and the high spin isomer of Co_4Cr^+ , while an antiferromagnetic coupling is preferred for the lowest energy structure of Co_4Cr^+ and the low spin state isomer of Co_3Cr^+ . In these two structures, the spin on the Cr atom is anti-parallel to those on the Co atoms. For $n = 3$ and 4, the spin of the ground states increases upon Cr doping, while it decreases for $n = 5$. The local spin magnetic moments on each of the Co atoms in Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) are around $2.0 \mu_B$. The Cr dopant atom has little influence on the magnitude of the local moments on the Co atoms. The magnitude of the local spins on Cr atoms in $\text{Co}_{n-1}\text{Cr}^+$ are much larger and amount to around $5 \mu_B$. Therefore, the magnetism of Co_n^+ ($n = 3-5$) clusters is enhanced by Cr doping for $n = 3$ and 4, while it is attenuated for $n = 5$. This intriguing size-dependence is illustrated in Figure 6, where the average spin magnetic moments per atom are plotted for the lowest energy structures. For Co_n^+ , the average spin magnetic moment per atom decreases from $2.0 \mu_B$ ($n = 3$) to $1.75 \mu_B$ ($n = 4$) and increases again to $2.0 \mu_B$ for $n = 5$. Those average magnetic moment values are in line with earlier computational results of small neutral cobalt clusters [56, 57]. For $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$), the average spin magnetic moment per atom decreases monotonically.

Figure 5 B3P86/Def2TZVP calculated spin density distributions (in unit of μ_B , isovalue = 0.02 e/au^3) for low-energy structures of Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$). The relative energies (ZPE included) with respect to the lowest energy structures are given for the isomers of Co_3Cr^+ and Co_4Cr^+ .

To gain more insight into the magnetic structures, the total and d -projected partial density of states (PDOS) of the Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters are plotted in Figure 7. Clearly, the d -projected PDOSs dominates the magnetism of the clusters. This is consistent with the physical sense that electrons from the incompletely filled d shells are mainly responsible for the magnetism of the clusters. The number of occupied spin-up states near the

Fermi level is much larger than the number of spin-down states for Co_n^+ ($n = 3-5$) and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3$ and 4), which results in high magnetic moments in these clusters. While for Co_4Cr^+ , the spin-up electrons are largely offset by spin-down electrons, resulting the low magnetic moment of this cluster.

Figure 6 Calculated average spin magnetic moments per atom ($\mu_{\text{spin}}/\text{atom}$) of the lowest energy structures of Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$).

4. Conclusion

The effect of single Cr doping on the properties of small cobalt clusters Co_n^+ ($n = 3-5$) was investigated by a combination of IRMPD spectroscopy and DFT calculations. The geometric and electronic structures of Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) are determined by comparisons of the experimental IRMPD spectra of their Ar tagged complexes, Co_nAr_m^+ ($n = 3-5$, $m = 3$ and 4) and $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n = 4$ and 5 , $m = 3$ and 4), with the corresponding calculated IR spectra. It is found that chromium doping has a minor effect on the geometry of clusters but does change the magnetic coupling in a size dependent way. That is, the total spin magnetic moment increases upon Cr doping for $n = 3$ and 4 , while it decreases for $n = 5$. The density of states analysis reveals that the incomplete filled *d*-shells play an important role to the magnetism of the clusters. The enhanced magnetism for $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3$ and 4) clusters is because of the ferromagnetic coupling of the Cr atom with the Co atoms, while the decreased magnetism for $n = 5$ attributes to the antiferromagnetic coupling of the Cr atom. The different magnetic configuration of the Cr dopant could be correlated with the geometry of the corresponding pure cobalt clusters. Pure clusters with a larger (smaller) average Co–Co bond length, like Co_5^+ (Co_3^+ and Co_4^+) seem to favor AFM (FM) coupling of the spin moment of the Cr dopant atom because the optimized bond distances in AFM (FM) coupled Co–Cr are larger (shorter).

Figure 7 Total (TDOS) and d -projected partial density of states (PDOS) of Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) clusters. The curves are obtained by Gaussian broadening of the discrete energy levels. The vertical dashed line (has been shifted to zero) indicates the Fermi level.

Supporting Information

Additional calculation results, including calibration of DFT functionals; B3P86/Def2TZVP calculated low-lying isomers and IR spectra for Co_n^+ and $\text{Co}_{n-1}\text{Cr}^+$ ($n = 3-5$) and $\text{Co}_2\text{CrAr}_4^+$; comparisons of the IRMPD spectra of Co_nAr_m^+ ($n-m = 3-4$, $4-4$ and $5-3$) and $\text{Co}_{n-1}\text{CrAr}_m^+$ ($n-m = 4-4$ and $5-3$) with the corresponding calculated IR spectra of the low-lying energy isomers; and comparison of the IRMPD spectrum for Co_3Ar_4^+ with the calculated IR spectra of Co_3Ar_m^+ ($m = 0-4$). This material is available free of charge via the Internet at

<http://iopscience.iop.org>.

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