Growth mechanisms for doped clusters

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Abstract
Structural growth mechanisms for metal doped nanoclusters are investigated in combined experimental and theoretical studies. In particular, silicon, copper and gold clusters incorporating a transition metal dopant atom are investigated: Si$_n$X ($X = \text{Cu, V}$), Cu$_n$Sc$^+$ and Au$_n$Y$^+$ with $n < 20$. The doped clusters are produced with a dual-target dual-laser vaporization source. Structural information about the doped nanoclusters is provided by infrared multi-photon dissociation spectroscopy. Their size and composition dependent stability is studied with photofragmentation and mass spectrometry. A detailed understanding of the role of the dopant atom in the structural growth and in the electronic structure of the clusters is obtained by comparison with quantum chemical computations using density functional theory.

Keywords: photofragmentation, infrared spectroscopy, metal clusters, silicon clusters, density functional theory, electronic shell model

Classification number: 4.02

1. Introduction

Tuning the properties of atomic clusters by their composition has been a long standing challenge in cluster science, and has over the years been realized by the synthesis and study of a wide variety of bimetallic, binary and also some ternary clusters [1, 2]. One specific asset of studying bimetallic clusters is the possibility of tailoring independently the cluster geometry (number of atoms) and the cluster electronic properties (determined by the number of delocalized electrons). Indeed, while geometry and symmetry are crucial for the description of small clusters, the properties of metal clusters are largely determined by a finite number of valence electrons essentially confined to zero dimensions. Various approaches of electronic shell models have emerged, leading to a successful description of cluster properties and their dependences on size [3, 4].

Doped clusters show a wide range of structural and electronic features depending on the dopant atom. For specific sizes, the dopant atom not only alters properties, such as ionization energy, electron affinity and dissociation energy, but also the magnetic characteristics of the cluster. This has been pointed out before; for example, in the case of gold and silver clusters doped with transition metal atoms [5–7].

For a number of years now, detailed studies of selected cluster species have been undertaken to gather insight into the growth mechanisms for small clusters. Indeed, while di- and tri-atomic molecule-like systems and their bulk counterparts are fairly well understood using common chemical and solid-state physics concepts, respectively, the intermediate size regime of several up to thousands of atoms is less well understood. For these sizes, the ratio of surface to total atoms is very large. There is no onset yet of periodicity and the itinerant electrons essentially sense a zero-dimensional background potential. All of this leads to properties that vary in a non-trivial and a non-scalable way with the number of constituent atoms.

So far, the focus of investigations of nanocluster growth mechanisms and properties has been on homogeneous cluster species, mainly of simple metals (alkali, trivalent metals and coinage metals) and semiconductors (in particular, silicon). Our goal has been to elaborate this work towards species that are altered, often in a significant way, by incorporating one or a few dopant atoms. In particular, we focus on doping...
coinage metal clusters (gold, silver, copper) on the one hand, and on the doping of semiconductor and semimetal clusters (silicon, germanium, tin, lead) with other metal atoms (mainly transition metals) on the other.

Here, we review our recent work on the growth mechanisms of small (less than 20 atoms) copper- and vanadium-doped silicon clusters, on scandium-doped copper clusters, and on yttrium-doped gold clusters. For all of these systems, the focus of our research is to exploit the interplay between structure and geometry versus the electronic structure, whereby the dopant atom is instrumental in both triggering specific geometries, often with high symmetry and related electronic properties.

2. Methods

The clusters are produced with a dual-target dual-laser vaporization source, which is described extensively elsewhere [8]. Two independent pulsed Nd:YAG lasers vaporize the surface of two translating rectangular plate targets. Helium gas is introduced into the source by a pulsed supersonic valve. Subsequently, the mixture of atoms, clusters and inert gas expands into the vacuum, resulting in a cold molecular cluster beam. The source parameters are optimized to make clusters containing only one or a few dopant atoms. After passage through a skimmer, the cluster beam enters the extraction region of a reflectron time-of-flight mass spectrometer.

Structural information is obtained by infrared (IR) spectroscopy. With infrared multi-photon dissociation (IRMPD) spectroscopy, either the depletion of parent ions or the formation of photofragments is monitored to probe the absorption process. However, tunable table-top laser systems do not provide sufficient fluence in the IR to excite strongly bound clusters to a point where fragmentation occurs. Only with access to powerful free-electron lasers, like the Free Electron Laser for Infrared eXperiments (FELIX), situated at the FOM Institute for Plasma Physics in Rijnhuizen, the Netherlands [9], did gas-phase IR spectroscopy become possible. Even with the high laser power that is provided by a free electron laser, IRMPD of silicon and noble metal clusters (typical bond dissociation energies of 2–4 eV) at energies corresponding to their vibrational modes (typically in the 5–60 meV range) has not been observed. This problem can be overcome by using the so-called messenger method, in which a loosely bound ligand that is supposed to have a negligible influence on the structure and vibration properties is attached to the species to be analyzed [10]. Such a ligand is typically an inert gas atom (Ar, Xe). This can be attached to clusters by adding a small fraction of the messenger gas to the carrier gas in the cluster source and cooling the cluster source to about 100–150 K.

The size-dependent cluster stability is investigated by means of photofragmentation. The cluster beam is irradiated by an intense laser beam (> 5 mJ pp cm\(^{-2}\)) stemming from an ArF excimer laser (\(h\nu = 6.43\) eV). The clusters are heated by multiphoton absorption, and cooling occurs through fast sequential evaporation of atoms and eventually larger fragments. The resulting photofragments reveal a size distribution with higher abundances of clusters with enhanced stability. The preferred fragmentation channels of the excited clusters can also be analyzed after size selection with a mass gate [11].

Quantum chemical calculations were carried out using density functional theory (DFT). The geometries of clusters were optimized with the pure exchange–correlation BP86 generalized gradient functional [12, 13] as implemented in the Gaussian03 software package [14]. For each cluster, different isomeric structures in different spin multiplicities were considered. The isomers presented in the remainder of this work are the lowest energy isomers found. Comparison of experimental IRMPD spectra with the calculated harmonic vibrations of the different isomers allows for the deduction of the cluster-size-specific structures. The BP86 functional reliably predicts the vibration frequencies of transition metal atom containing systems when compared with IR spectroscopy data [15].

3. Results

3.1. Vanadium and copper doped silicon cluster cations, \(\text{Si}_n\text{V}^+\) and \(\text{Si}_n\text{Cu}^+\) (\(n = 6–11\)).

Silicon clusters have been studied extensively in recent years, in part due to the dominant role of silicon nanostructures in the semiconductor industry. The structural motif of silicon clusters is dissimilar from pieces of the bulk material [16]. In contrast to carbon, silicon favours sp\(^3\) hybridization and thus tetrahedral coordination, which leads to rather asymmetric and reactive structures. A recent combined gas-phase IRMPD and DFT study unambiguously assigned the structures of cationic \(\text{Si}_n^+\) (\(n = 6–21\)) clusters [17].

Silicon clusters can be stabilized by proper metal doping [18]. The doping leads to specific sizes in the formation of stable, symmetric and unreactive caged structures, which are potential building blocks in future nanotechnological devices. The structures and properties of such endohedral structures have been addressed in a number of theoretical and experimental studies [19, 20]. Here, we focus on the influence of a transition metal atom on the structural properties of small silicon clusters, where the number of silicon atoms is too small to fully encapsulate the dopant atom, i.e. exohedrally doped silicon clusters.

3.1.1. Structural identification of exohedrally doped silicon clusters. Argon binds to exohedrally doped silicon clusters at a cluster source temperature of 80 K [21]. Therefore, the vibration spectra of \(\text{Si}_n\text{V}^+\) and \(\text{Si}_n\text{Cu}^+\) have been obtained by IRMPD of the corresponding argon complexes. The vibrational transitions of doped silicon clusters lie in the far-infrared, typically between 150 and 600 cm\(^{-1}\), which corresponds to an energy per photon of only 20–75 meV. In case of resonant absorption of several IR photons, the cluster heats up. This eventually leads to evaporation of the loosely bonded argon atom and depletion of the complex in the mass spectrum. The IR absorption cross section is constructed by recording the ion intensity of the cluster-rare gas complex as a function of the FELIX wavelength. Figure 1 shows the experimental IRMPD spectra of \(\text{Si}_n\text{X}^+\) (\(n = 7, 8\) and \(X = \text{Cu}, \text{V}\)). These spectra have been compared with calculated
vibrational spectra of low-lying isomers at the BP86/6-311 + G(d) level. Typically, many isomers are found close in energy, of which only one agrees with the experiment. Figure 1 also shows the calculated harmonic spectra of the best fitting isomers. In general, peak positions are in good agreement while peak intensities might deviate between theory and experiment.

3.1.2. Growth mechanism of Si\textsubscript{n}V\textsuperscript{+} and Si\textsubscript{n}Cu\textsuperscript{+} (n = 6–11). Figure 2 gives an overview of the structures of cationic Si\textsubscript{n}V\textsuperscript{+} and Si\textsubscript{n}Cu\textsuperscript{+} (n = 2–10) as assigned, except for the smallest sizes (n = 2, 3 for V and n = 2–5 for Cu), on the basis of the experimental IRMPD spectra [21, 22]. Starting with n = 2, both doped silicon clusters have the same triangular shape. The third silicon atom is added to Si\textsubscript{2}V\textsuperscript{+} to form a trigonal pyramid (3.V) as the ground state of Si\textsubscript{3}V\textsuperscript{+}, whereas it bridges copper and a silicon atom on the molecular plane to generate the lowest-lying planar structure 3.Cu of Si\textsubscript{3}Cu\textsuperscript{+}. n = 3 is the only size where the vanadium atom adsorbs to the bare cluster Si\textsubscript{3}\textsuperscript{+}, while the copper atom substitutes to the Si\textsubscript{3}\textsuperscript{+} rhombus to form Si\textsubscript{3}Cu\textsuperscript{+}. Copper keeps the doped silicon clusters planar up to n = 4, at which size the bare silicon cluster is also planar, whereas Si\textsubscript{4}V\textsuperscript{+} clusters already favor 3D structures. Comparison with the bare clusters shows that 4.Cu is an adsorptive derivative of the rhombus Si\textsubscript{4}\textsuperscript{+}, while 4.V is a substitutive derivative of the trigonal bipyramid Si\textsubscript{5}\textsuperscript{+}. At n = 5, both dopants modify the bare silicon cluster in a similar way. In particular, both transition metal atoms substitute a silicon atom at the axial position of the fluxional Si\textsubscript{5}, leading to slightly different structures. While 5.V has a shape analogous to the neutral Si\textsubscript{5}, 5.Cu has a shape similar to that of the bare cation Si\textsubscript{5}. The structure of Si\textsubscript{6}V\textsuperscript{+}, 6.V, results from a silicon by vanadium substitution at an equatorial position of the pentagonal bipyramid Si\textsubscript{7}. From Si\textsubscript{7}V\textsuperscript{+} to Si\textsubscript{10}V\textsuperscript{+}, vanadium occupies an apex of the pentagonal bipyramid. There also exists an obvious growth path as the size of the cluster increases. Indeed, 8.V is obtained by adding one more silicon atom to a Si–Si–V face of the ground state of Si\textsubscript{7}V\textsuperscript{+} (7.V). A consecutive addition of the ninth silicon atom to the adjacent Si–Si–V face builds up the ground state of Si\textsubscript{10}V\textsuperscript{+} (9.V). Adding an extra silicon atom to a Si–Si–Si face of Si\textsubscript{10}V\textsuperscript{+} results in the best fitting isomer of Si\textsubscript{11}V\textsuperscript{+} (10.V), which is, however, 0.18 eV higher in energy than the calculated ground state.
For \( n = 6 \)–11, the single copper cation or copper atom prefers to cap a face or an edge of the ground state structure of the bare Si\(_n^+\) or Si\(_n^{10+}\), respectively, leading to Si\(_n^+\)Cu\(^+\). The Mulliken charge distribution helped to reveal how the copper and silicon framework combine to form Si\(_n^+\)Cu\(^+\) [22]. In particular, the ground state of Si\(_6^+\)Cu\(^+\) (6.Cu) is formed by adding copper to a face of the distorted octahedron Si\(_8^+\). Si\(_6^+\)Cu\(^+\) is formed by adding Cu to a face of the bicapped pentagonal bipyramid Si\(_9^+\) but the structure is strongly distorted. 7.Cu is formed by adding copper to an equatorial edge of the pentagonal bipyramid Si\(_{11}^+\) and 11.Cu is produced by adding Cu\(^+\) to an edge of the pentacapped trigonal prism Si\(_{11}^+\). In the ground state structures of Si\(_9^+\)Cu\(^+\) and Si\(_{10}^+\)Cu\(^+\) (8.Cu and 10.Cu, respectively), the copper atom is added on an edge and also bridges two apexes of the cationic bare clusters, namely the monocapped pentagonal bipyramid Si\(_{12}^+\) and tetracapped trigonal prism Si\(_{10}^+\).

3.2. Scandium doped copper clusters, Cu\(_n^+\)Sc\(^0\), \( n = 6 \)... 11.

Copper clusters have been investigated extensively, starting from the early years of metal cluster physics [23]. Also, transition metal doped copper clusters are intensively studied, mainly because of interest in the local magnetism in dilute systems of magnetic impurities in nonmagnetic metals [24, 25].

The phenomenological shell model of metal clusters, proposed 25 years ago by Knight et al. [26], is a useful tool to interpret the variation in the stability and other properties with the number of atoms. This model basically assumes that the valence electrons are delocalized over the whole cluster. In its simplest version, the electrons are treated as moving in a simple mean-field potential, whereas the nuclei expose only a constant background term [3]. The valence s atomic orbitals (AO) form molecular orbitals (MO) having similar shapes to that of the s, p and d AOs. These MOs are labeled hereafter S, P and D. Enhanced stability of metal clusters is expected if the number of delocalized electrons corresponds to closed electronic shells. In the case of a spherical arrangement of atoms, a shell closing occurs if the cluster has 2, 8, 18, 20...itinerant electrons, corresponding to the filling of (1S\(^2\)(1P\(^0\)(1D\(^0\)...2S\(^2\)... electron shells. A reduction in the symmetry of the cluster changes the shell closure sequence, due to splitting of the energy levels. For cylindrically shaped clusters or for planar circular clusters, the magic numbers 2, 6, 10... appear corresponding to the sequential filling of (1S\(^2\)(1P\(^4\)(1D\(^4\)... electron shells [4].

3.2.1. Photofragmentation of cationic Cu\(_6^+\)Sc\(^+\). The abundance spectrum of Cu\(_6^+\)Sc\(^+\) after photofragmentation shows enhanced abundances for Cu\(_6^+\)Sc\(^+\) and Cu\(_{10}^+\)Sc\(^+\) [27]. Assuming that each copper atom, as for pure Cu\(_n^+\) clusters, delocalizes its 4s valence electron, these sizes agree with the magic numbers 8 and 18 corresponding to filled (1S\(^2\)(1P\(^0\)(1D\(^0\)...) and (1S\(^2\)(1P\(^4\)(1D\(^4\)... electron shells, provided that the scandium atom delocalizes its three valence electrons (Sc = [Ar]3d\(^4\)4s\(^2\)).

This was indeed confirmed by quantum chemical calculations. Cu\(_6^+\)Sc\(^+\) has a tricapped tetrahedral oblate shape within the D\(_{3h}\) point group [28]. It has 8 electrons in 4 delocalized MOs, which are shown in figure 3. The electronic structure of Cu\(_6^+\)Sc\(^+\) can be described by a (1S\(^2\)(1P\(^4\,... configuration. Cu\(_{10}^+\)Sc\(^+\), on the other hand, is a Frank–Kasper tetrahedron (T\(_d\) symmetry) [27]. It has a caged structure with 16 copper atoms encapsulating the scandium atom in a highly coordinated position. In

Figure 3. The geometry of the lowest energy isomer of Cu\(_6^+\)Sc\(^+\), Cu\(_7^+\)Sc\(^0\) and Cu\(_{16}^+\)Sc\(^+\) at the BP86/LANL2DZ level. These clusters have, respectively, 8, 10 and 18 delocalized electrons whose corresponding molecular orbitals are plotted and assigned using the nomenclature of the phenomenological shell model. The orbital energies are given in eV.
addition, Cu16Sc+ accommodates 18 itinerant electrons in a (1S)2(1P)6(1D)10 electron shell structure. The corresponding MOs are shown in figure 3.

### 3.2.2. Growth mechanism of neutral CuₙSc (n =1–10).

The growth mechanism of neutral CuₙSc⁰ clusters (n = 1–16) was investigated with density functional theory [29]. Figure 4 shows the most stable CuₙSc clusters of each size up to ten copper atoms. Their relative energies compared to the lowest energy structure and the proposed growth mechanism are indicated.

CuSc is triplet ¹Δ with a bond distance of 2.53 Å (1.1CuSc). The scandium atom takes the central position in the nonlinear Cu₂Sc (2.1CuSc) and the rhombohedral Cu₃Sc (3.1CuSc). The energy of the three-dimensional Cu₄Sc (4.1CuSc) is, within the computational accuracy, equal to that of the planar 4.2CuSc. For larger clusters, the located most stable isomers are non-planar. The octahedral Cu₅Sc (5.1CuSc) is the only exception from maximal coordination of a central scandium atom. 5.1CuSc is stabilized by an eight electron shell closure [28]. The most stable Cu₅Sc structure is a pentagonal bipyramid, 6.1CuSc, obtained by adding an extra copper atom to the square copper unit of the octahedral 5.1CuSc. However, other structures, such as 6.2CuSc, are quasi-degenerate. A planar, six-membered copper ring is a transition state, which relaxes to the hexagonal pyramid structure 6.7CuSc. The strain due to the small interatomic scandium–copper distances is the reason for the non-planarity of this cluster. By adding an additional copper atom, the ring is enlarged and the strain can be released.

This results in the planar D₃h symmetric cluster, 7.1CuSc⁺, which is the global minimum on the potential-energy surface of Cu₇Sc. The central scandium is surrounded by a seven-membered ring of copper atoms [30]. Cu₇Sc has ten itinerant electrons that, based on the phenomenological shell model for metal clusters, is a magic number in the case of cylindrical and (planar) circular clusters [4]. Indeed, the analysis of the MOs showed that Cu₇Sc has a (1S)²(1P)²(1D)²(1Dₓ₂₋₃)² electron configuration in line with the shell model expectations. The MOs of 7.1CuSc are shown in figure 3.

The most stable Cu₈Sc cluster, 8.1CuSc⁺, is based on 7.2CuSc and is a fraction of the Frank–Kasper Cu₁⁰Sc⁺ cluster. The scandium has a maximal coordination here. Capping of 7.1CuSc leads to the substantially less stable 8.3CuSc cluster, in which the seven-membered ring is still nearly planar. The most stable Cu₉Sc clusters, 9.1CuSc and 9.2CuSc, can be obtained from 8.1CuSc, whereas 9.3CuSc is a bicapped derivative of the planar Cu₃Sc seven-membered ring. A growth path from 9.1CuSc leads to the most stable Cu₁₀Sc cluster (10.1CuSc). The overall growth process indicates that filling of the first copper shell around the scandium atom is a kinetically favored process. For CuₙSc with n = 7–15, the obtained ground state isomer has an incomplete copper shell around a central scandium atom [29]. The copper shell around scandium is complete at Si₁₆Sc. Clusters derived from the planar 7.1CuSc (such as 8.3CuSc, 9.3CuSc and 10.2CuSc) are significantly less stable than the ground state structures.

### 3.3. Yttrium doped gold clusters, AuₙY⁰⁺

Bare gold clusters favor planar structures up to surprisingly large sizes [31]. Neutral Auₙ clusters have a 2D–3D transition at size n = 11–12 [32]. The structures of cationic Auₙ⁺ and anionic Auₙ⁻ have been found experimentally and theoretically to be planar up to n = 7 and n = 11, respectively [32, 33]. The preference of gold clusters for 2D structures is a consequence of relativistic effects in gold atoms, which cause shrinking of the atomic s orbitals and subsequent enhancement of the s–d hybridization and the d–d interaction, resulting in a preference for more directional Au–Au bonds [34, 35]. Larger gold clusters also have unexpected geometries, such as tetrahedral Au₂₀ [36] and fullerene-like Au₃₂ [37].

A single transition metal atom can strongly interact with a small gold cluster and, for certain cluster sizes and numbers of valence electrons, it has a strong influence on the electronic shell structure and/or the cluster geometry. It was shown in combined mass spectrometric and DFT studies on Auₙ clusters doped with an open 3d shell transition metal atom that the planar structure can be stabilized by a dopant atom and that, in particular, six electron species are more stable [38, 39]. It was also predicted that a central transition metal atom stabilizes a golden fullerene if the number of valence electrons satisfies the 18-electron rule [40].
### 3.3.1. Photofragmentation of cationic Au\textsubscript{n}Y\textsuperscript{+}. The size-dependent stability of cationic Au\textsubscript{n}Y\textsuperscript{+} (n = 2–40) clusters was studied with photofragmentation [11, 41]. Also, the delayed fragmentation of metastable clusters was investigated using a mass gate, which allowed determination of the evaporation channels of mass selected clusters [11].

Photofragmentation reveals a size distribution with higher abundances for clusters with enhanced stability (see figure 5). Enhanced intensities, with respect to neighboring Au\textsubscript{n}Y\textsuperscript{+} cluster sizes, are found at n = 6, 16 and 32. In particular, Au\textsubscript{16}Y\textsuperscript{+} appears to be a very stable configuration as evidenced by a much larger amplitude than neighboring sizes. In addition, an odd–even alternation in the intensity is seen, where clusters with an even number of gold atoms are more stable. Assuming that each gold atom delocalizes its 6s valence electron, as for pure gold clusters, these cluster sizes correspond to 8, 18 and 34 itinerant electrons, provided that the three yttrium valence electrons can be considered itinerant (Y = [Kr]4d\textsuperscript{1}5s\textsuperscript{2}). Also, the observation that odd n Au\textsubscript{n}Y\textsuperscript{+} species give a larger monomer decay fraction can be explained as an electronic odd–even effect [11]. Dimer decay was only observed after Au\textsubscript{6}Y\textsuperscript{+} and Au\textsubscript{16}Y\textsuperscript{+}. The inset shows the geometry of Au\textsubscript{16}Y\textsuperscript{+}, identified upon comparison of the experimental IRMPD spectrum with DFT calculations. Au\textsubscript{16}Y\textsuperscript{+} has eight delocalized electrons in the plotted four MOs that are assigned as S, P\textsubscript{x}, P\textsubscript{y} and P\textsubscript{z}, using the nomenclature of the phenomenological shell model.

These observations point to the importance of electronic shells to explain the size-dependent stability. This was also seen in mass spectrometric studies of Au\textsubscript{n}X\textsuperscript{+} (X = Sc, Ti, V, Cr, Mn, Fe, Co and Ni) clusters where the observed stability patterns could be explained on the basis of a phenomenological shell model that takes into account the electronic structure of the dopant atom [38].

### 3.3.2. Electronic shells in Au\textsubscript{n}Y\textsuperscript{+}.0–. The geometry of Au\textsubscript{6}Y\textsuperscript{+} and the role of the charge state on the cluster’s stability were studied. Here, the experimental IRMPD spectrum of Au\textsubscript{6}Y\textsuperscript{+} was recorded. Its geometry was assigned by comparing the IRMPD spectrum with harmonic vibration spectra of different isomers found at the BP86/cc-pVDZ-PP DFT level [42]. The lowest energy isomer of Au\textsubscript{6}Y\textsuperscript{+} has a 3D oblate eclipsed C\textsubscript{3v} shape, in contrast to the quasi-planar C\textsubscript{2v} and planar D\textsubscript{3h} shapes for the neutral and anionic counterparts, respectively. The cationic Au\textsubscript{6}Y\textsuperscript{+} possesses an eight electron 1S\textsuperscript{2}(1P\textsubscript{x}, 1P\textsubscript{y})\textsuperscript{2}1P\textsubscript{z}\textsuperscript{2} closed shell structure and the contributions of local s-like AOs are predominant in the chemical bond formation (see inset in figure 5). Comparing Au\textsubscript{6}Y\textsuperscript{+} (8 valence electrons) with Au\textsubscript{16}Y\textsuperscript{+} (10 valence electrons), a transition from a 3D to a 2D geometry is observed as the most probable structure. While 8 is a magic number for a spherical symmetry in the phenomenological shell model for metal clusters, 10 corresponds to a shell closure for planar circular clusters. The cluster thus seems to seek the shell closing that is closest or easiest to match, even if this implies a change in the dimensionality. This demonstrates the importance of electronic shells in the stability of small bimetallic clusters.

### 3.3.3. Growth pattern of neutral Au\textsubscript{n}Y (n = 1–9). The growth mechanisms of small neutral yttrium-doped gold clusters, Au\textsubscript{n}Y with n = 1–9, were explored by IRMPD spectroscopy in conjunction with DFT calculations [43, 44]. The IR spectra are recorded on the corresponding cluster–xenon complexes, where isotopically enriched \textsuperscript{129}Xe is used as messenger atom. The recorded spectra are interpreted with DFT at the BP86/cc-pVDZ-PP level. The number of structural isomers dramatically increases with increasing cluster size. In the discussion below, we only describe the two lowest energy isomers found for each size. More isomers are given in [44]. Good agreement between calculated harmonic vibration spectra and experimental results supports the structural assignment. Figure 6 gives an overview of the assigned Au\textsubscript{n}Y (n = 1–9) isomers.

Au\textsubscript{2}Y has a triangular form (C\textsubscript{2v}), \textit{2.1AuY}, which is created by adding a second gold atom to the diatomic \textit{1.1AuY}. Binding a third gold atom to the yttrium atom of \textit{2.1AuY} leads to the \textit{D\textsubscript{3h}} symmetric \textit{3.1AuY}. Because of a strong Jahn–Teller effect arising from the degenerate orbital occupancy due to the unpaired electron, the geometry of Au\textsubscript{4}Y is distorted from an ideal \textit{T\textsubscript{d}} point group symmetry and a lower-symmetry \textit{C\textsubscript{2v}} structure. \textit{4.1AuY}, results. A \textit{C\textsubscript{2v}} isomer \textit{4.2AuY} of comparable energy is not observed in the experiment. Attaching a fifth gold atom to the central yttrium atom of \textit{4.1AuY} leads to two low-lying \textit{Au\textsubscript{5}Y} forms with the same energy but different geometries. \textit{5.1AuY}, agreeing best with the experiment, is planar (\textit{C\textsubscript{2v}}), whereas \textit{5.2AuY} keeps the \textit{C\textsubscript{4}} structure of \textit{4.1AuY}.  

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**Figure 5.** Mass abundance spectra of photofragmented Au\textsubscript{n}Y\textsuperscript{+} for n = 3–30. The grid lines mark the bare Au\textsubscript{n} clusters that are produced in the source together with the yttrium doped clusters. Peaks corresponding to Au\textsubscript{n}Y\textsuperscript{+} are connected by a solid red line. Intensity drops are observed after Au\textsubscript{6}Y\textsuperscript{+} and Au\textsubscript{16}Y\textsuperscript{+}. The inset shows the geometry of Au\textsubscript{16}Y\textsuperscript{+}, identified upon comparison of the experimental IRMPD spectrum with DFT calculations. Au\textsubscript{16}Y\textsuperscript{+} has eight delocalized electrons in the plotted four MOs that are assigned as S, P\textsubscript{x}, P\textsubscript{y} and P\textsubscript{z}, using the nomenclature of the phenomenological shell model.
which quasi-degenerate singly occupied molecular orbitals [43], stretching isomers is a consequence of the partially filled 5 kJ mol$^{-1}$ to only 0. Also, the bond stretching isomerization is a highly facile process with the corresponding energy barrier amounting to only 1.9 kJ mol$^{-1}$.

Figure 6. Growth pattern of neutral Au$_n$Y with $n = 1$–9. For sizes $n = 4$–9, the two lowest energy isomers found are shown. The electronic states and relative energy for the second isomer (in eV, at the BP86/cc-pVDZ-PP level of theory) are given. The underlined isomer is the one that is assigned by comparing the calculated harmonic vibration spectrum with the experimental IRMPD spectrum.

Binding a sixth gold atom to the yttrium center of 5.1AuY or 5.2AuY produces the quasi-planar 6.1AuY (C$_{2v}$) and a structure with one out of plane gold atom 6.2AuY (C$_s$), respectively. Again, the lowest energy isomer, 6.1AuY, corresponds well with the experimental IRMPD spectrum, although the experimental bands show a pronounced line broadening. This can be attributed to the quasi-planar structure and fluxional behavior of 6.1AuY [43]. A study of the potential energy surface shows that 6.1AuY easily distorts along different axes. In fact, the barrier of inversion through a planar transition structure amounts to only 1.9 kJ mol$^{-1}$. Also, the bond stretching isomerization is a highly facile process with the corresponding energy barrier amounting to only 0.5 kJ mol$^{-1}$. The existence of the different bond stretching isomers is a consequence of the partially filled quasi-degenerate singly occupied molecular orbitals [43], which are degenerate in the planar $D_{6h}$ symmetry. The highly anharmonic potential with several degenerate minima on the potential energy surface, separated by very low barriers, is expected to yield fluxional behavior of Au$_n$Y on picosecond timescales, which in turn explains the broadening of the experimental IRMPD peaks.

The attachment of a seventh gold atom to the 6.1AuY isomer gives rise to two different species; the planar 7.1AuY (C$_{2v}$) and non-planar 7.2AuY (C$_s$). The 7.2AuY isomer (+0.01 eV at the BP86/cc-pVDZ-PP level but the ground state at the CCSD(T)/cc-pVTZ-PP level) was shown to be the main carrier in the molecular beam. The addition of an eighth gold atom to 7.1AuY and 7.2AuY yields several structures for Au$_n$Y with similar energies. The two most stable isomers, 8.1AuY (C$_1$) and 8.2AuY (C$_2$), bear rather low symmetry. By comparing the computed harmonic vibration spectra to the experimental results, 8.2AuY (+0.02 eV at the BP86/cc-pVDZ-PP level) is seemingly the dominant isomer present in the molecular beam. The lowest-energy isomer of Au$_n$Y (C$_2$) can be constructed by introducing a ninth gold atom into 8.2AuY.

A consistent feature that emerges from the set of assigned Au$_n$Y structures is that the yttrium atom prefers high coordination. Except for Au$_2$Y and Au$_3$Y, the yttrium doped gold clusters Au$_n$Y ($n = 3$–9) adopt very different structural patterns from those of Au$_{n+1}$. In other words, doping one yttrium atom into pure gold clusters induces a full reconstruction of the structure for Au$_2$Y ($n = 3$–9). Furthermore, we find that a small Au$_n$Y cluster can already adopt 3D shapes (see figure 6), with the smallest 3D isomer being Au$_5$Y, whereas the pure Au$_n$ clusters prefer a planar form up to $n = 11$ [32]. Charge analysis shows that the yttrium atom is always positively charged in Au$_n$Y, which suggests that there is an effective charge transfer from yttrium to gold.

4. Conclusion

We have unraveled the growth mechanism of small cationic copper- and vanadium-doped silicon clusters, neutral and cationic scandium-doped copper clusters, and neutral yttrium-doped gold clusters. Hereto, the interplay between experimental observations (photofragmentation studies and infrared spectroscopy) and quantum chemical calculations was crucial. It is shown that a single dopant atom can significantly modify the cluster geometry. Vanadium substitutes a highly coordinated silicon atom in Si$_{n+1}^+$ to form Si$_n^+$Y$^+$, whereas copper favors a lower coordination number and adsorbs to the neutral or cationic bare silicon clusters. Cu$_n$Sc clusters grow by completion of a shell of copper atoms around a central scandium atom. The shell formation is completed at Cu$_{16}$Sc. Yttrium prefers a highly coordinated position in neutral Au$_n$Y clusters. The yttrium dopant atom induces a full reconstruction of the structure and triggers a 2D to 3D transition.

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