Determining the size-dependent structure of ligand-free gold-cluster ions

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Ligand-free metal clusters can be prepared over a wide size range, but only in comparatively small amounts. Determining their size-dependent properties has therefore required the development of experimental methods that allow characterization of sample sizes comprising only a few thousand mass-selected particles under well-defined collision-free conditions. In this review, we describe the application of these methods to the geometric structural determination of Au_{n}^{+} and Au_{n}^{-} with n = 3–20. Geometries were assigned by comparing experimental data, primarily from ion-mobility spectrometry and trapped ion electron diffraction, to structural models from quantum chemical calculations.

Keywords: gold clusters; structure; electron diffraction; ion mobility; optical properties

1. Introduction

Gold nanoparticles, with sizes much below the wavelength of visible light, were first inferred in aqueous colloidal gold suspensions (Faraday 1857). More recently, monodispersed gold clusters with less than 1000 gold atoms have become a focus of attention in fields ranging from synthetic chemistry to solid-state physics and nanotechnology. A significant part of this work has concerned ligand-stabilized clusters (Schmid et al. 1981). These have been prepared and structurally characterized by X-ray diffraction methods with core sizes of up to 102 gold atoms (Jadzinsky et al. 2007). While inorganic chemistry can access molar quantities of such substances, not all atom counts or charge states are available. Furthermore, even the largest gold-cluster cores synthesized so far are still significantly modified by the ligand shell (Lopez-Acevedo et al. 2009).

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Corresponding changes to electronic and geometric structures are still only poorly understood—in part because of missing information concerning the ‘reference state’: ligand-free clusters.

In contrast to their ligand-stabilized congeners, bare gold clusters can be made in all sizes and many charge states (from multiply positive through neutral to (multiply) negative), but typically in very small quantities. Over the last 20 years, physical characterization methods have however been developed, which are sensitive enough to allow detailed studies, even on such small sample sizes. As a result, two old questions can now be experimentally addressed: (i) how and why do ligand-free gold-cluster properties (such as structure and colour) change with the number of cluster atoms and (ii) what happens when the charge on a cluster of a given size is varied.

In order to determine the size- and charge-dependent properties of ligand-free clusters, they must first be generated in the form of atomically monodispersed samples. This typically involves production of a cluster size distribution within a collision-free molecular/ion beam (Foster et al. 1969), as well as some form of mass selection. Furthermore, these monodispersed clusters must then be characterized under conditions ensuring minimal (or at least uniform) environmental perturbation of the inherent electronic and geometric structure. This is done either: (i) directly in the gas phase (typically within the molecular beam itself or after electrostatic extraction and trapping of cluster ions from the beam), (ii) within a cryogenic inert gas matrix after cluster co-deposition (Harbich & Felix 2002), or (iii) on a clean, single-crystal surface also after fragment-free cluster deposition from a low kinetic energy ion beam (Dicenzo et al. 1988). In particular, the first approach has been extensively pursued and has yielded results for a wide range of monodispersed gold-cluster sizes. This review primarily concerns such gas-phase studies.

The first molecular-beam experiments on gold clusters were performed using a liquid metal ion source to generate small singly (and doubly) charged cluster cations, which were detected mass spectrometrically (Sudraud et al. 1979). Significantly larger Au$^{+}$$_n$ clusters were found some years later in experiments using a sputter ion cluster source (Katakuse et al. 1985). The ion-intensity distributions that were recorded showed a size-dependent structure, which was interpreted in terms of the spherical jellium model (Knight et al. 1984). This model was put forward to rationalize observations originally made for sodium clusters (Kappes et al. 1982b). It approximates the electronic structure of simple s$^1$-electron metal clusters in terms of the quantum mechanics of uncorrelated electrons moving in a spherical uniformly positively charged potential box (one valence electron per constituent atom). The model predicts a series of ‘magic numbers’, stability islands at specific valence-electron counts corresponding to successive electronic-shell closings. Many of these magic numbers were also observed in the gold experiment—as discontinuities in the ion-abundance distributions (offset by one atom because of the overall positive charge). Following these pioneering mass spectrometric studies (also for singly charged anions: Katakuse et al. 1986), ionization energies and adiabatic/vertical electron affinities were acquired for a whole range of gold-cluster sizes (Ho et al. 1990; Jackschath et al. 1992). By 1992, more detailed electronic structure information had become available from anion photoelectron spectroscopy—notably from a study using a magnetic-bottle spectrometer for cluster monoanions up to 223 atoms.
Review. Structures of gold-cluster ions (Taylor et al. 1992). Near-predictive-level quantum chemical calculations were not yet possible, and consequently spectra were interpreted in terms of the spherical jellium model. In particular, characteristic structure in the ‘valence’ regions of the spectra was interpreted in terms of the jellium energy-level sequence and corresponding degeneracies. In addition, an ‘s–d band-splitting’ feature was assigned in the spectra at higher binding energies, and its size-dependence mapped. In one case (planar hexamer anions; Taylor et al. 1990; Ganteför et al. 1992), vibrational fine structure was resolved allowing tentative geometric inferences. Beyond photoelectron spectroscopy, other spectroscopic methods were also brought to bear on characterizing free gold clusters. Resonant two-photon ionization spectroscopy was applied to Au$_3$ (triangular) (Bishea & Morse 1991). Additionally, visible-near UV photodepletion spectra were recorded for various neutral and cationic gold clusters up to 13 atoms—complexed to one or two xenon atoms (Collings et al. 1994). The latter were thought to act as weakly bound (and hopefully non-perturbing) tracers for the absorption of single photons. Again, the implementation status of theory (particularly for electronically excited states) precluded detailed structural inferences. Infrared multi-photon depletion spectroscopy was also used to study gold clusters complexed to one or more methanol molecules (Knickelbein & Koretsky 1998). In particular, the pioneering study on Au$_n^+$CH$_3$OH, $n \leq 15$, (Rousseau et al. 1998) provided the complete experimental size-dependence of the methanol C–O stretching frequency, as well as Car–Parrinello calculations of vibrational frequencies and structures (for specific cluster sizes). From these, it was inferred that Au$_n^+$CH$_3$OH has a planar gold-cluster core for $n \leq 7$, whereas larger clusters are three-dimensional.

In parallel to probes of physical properties, studies of chemical reactivity quickly followed the first cluster beam mass spectra. These ranged from Penning-trap measurements of the reactivity of small cluster cations with N$_2$O (Dietrich et al. 1994), through flow-tube studies of the uptake of diatomic molecules onto clusters of various charge states (Cox et al. 1991; Salisbury et al. 2000) to probes of unimolecular dissociation following collisional excitation (Becker et al. 1994). Generally, these experiments uncovered strongly particle-size-dependent phenomena, which were interpreted either in terms of the spherical jellium model, electron spin-pairing phenomena (‘even–odd effects’) and/or size-dependent variations in electron affinities and ionization potentials. However, detailed understanding was limited by the lack of knowledge concerning structural details.

By about 2000, when we began our own work on gold clusters (which is to be the focus of this review), this situation had begun to change, due in part to observations that led to a surge of interest in these systems. First, it was shown that small supported gold particles were surprisingly active oxidation catalysts (Haruta 1997). This inspired work to explore the (strongly size-dependent) reactivity of mass-selected gold clusters deposited onto single crystal surfaces under ultrahigh-vacuum (UHV) conditions (Sanchez et al. 1999). Following up on earlier synthetic work (Brust et al. 1994), it became possible to prepare, separate and then physically characterize a wide size range of thiol-terminated gold-cluster compounds (Whetten et al. 1996). These ligand-stabilized species were shown to have interesting potential applications in nanoscience (Chen et al. 1998). At the same time, quantum chemistry was making great strides towards accurately describing the ground states of both bare and ligand-stabilized clusters.

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Consequently, the time appeared ripe for us to attempt more detailed structural probes of the bare gold-cluster reference states. Below we describe the results, focusing primarily on the structures of singly positively and negatively charged gold clusters ranging in size of up to 20 atoms (Furche et al. 2002; Gilb et al. 2002, 2004; Weis et al. 2002b; Schweizer et al. 2003; Neumaier et al. 2005; Lechtken et al. 2007, 2008, 2009; Gloess et al. 2008; Johansson et al. 2008). At the same time, several other groups also worked on structural determination of gold clusters (in various charge states) using complementary/identical experimental methods. In particular, structures were assigned via comparison of quantum chemical calculations to: (i) high-resolution photoelectron spectra of cluster anions (Häkkinen et al. 2003; Li et al. 2003; Bulusu et al. 2006; Yoon et al. 2007), (ii) infrared multi-photon-dissociation spectra of neutral gold clusters complexed to one or two krypton atoms (Gruene et al. 2008), and (iii) trapped ion electron diffraction (TIED) measurements on mass-selected gold-cluster anions (Xing et al. 2006). We compare our results to these experiments as necessary.

2. Methods

We begin by describing experimental and theoretical methods used in Karlsruhe for structural determination. Resulting structural assignments are discussed in §3.

(a) Cluster-ion sources

The field of refractory element clusters can be traced back to the development of suitable cluster-ion sources. Critical issues that needed to be tackled were sufficient cluster intensity, variable size distributions, low vibrational temperatures and long-term stability. Two types of cluster (ion) sources were found to be most suitable and were systematically developed. We used both source types and our findings were independent of cluster source type.

(i) Laser-vaporization cluster source

The laser-vaporization cluster-ion source dates back to the early 1980s (Smalley 1983). It combines the generation of a metal vapour/plasma by pulsed laser heating and the subsequent rapid quenching by a pulsed supersonic expansion of an inert gas (Bondybey & English 1981; Dietz et al. 1981). In the original design, the output of a ns-pulsed laser (Nd:YAG laser or excimer laser) was directed onto a target rod that rotated and translated through the laser (focus) to ensure smooth surface ablation and stable conditions for cluster formation. The metal vapour is entrained in a pulse of helium, and the mixture undergoes a nozzle expansion. The associated rapid adiabatic cooling causes the (mostly atomic) vapour to form clusters by multiple collisions. This design was later improved to remedy the shortcomings such as coating of laser windows, gas leakage through the motional feedthrough and unstable motion of the target rod (de Heer & Milani 1991). The laser-vaporization cluster source used for our studies was based on a further improved design (Heiz et al. 1997). It has a disc target (O’Brien et al. 1986) of approximately 50 mm diameter and a planetary gear motion.
(Gangopadhyay & Lisy 1991), which yields an increased usable surface of approximately 15 cm$^2$. The counter-propagating vaporization laser (20–40 mJ pulse$^{-1}$ at 532 nm) enters the expansion nozzle along the primary beam axis and is focussed onto the perpendicularly oriented disc target. The source yields stable ion currents for metal clusters of up to approximately 1 nA for a mass-selected cluster size at a repetition rate of 100 Hz. For a typical mass spectrum, see figure 1.

(ii) Magnetron cluster source

The magnetron cluster source (MCS; Haberland et al. 1994) is a variant of an inert gas aggregation cluster source (Sattler et al. 1980) and is based on a DC magnetron sputtering device (Cuomo & Rossnagel 1986; Hahn & Averback 1990). The source comprises a DC sputter head in a liquid-nitrogen-cooled aggregation tube filled with a mixture of Ar and He (approx. 1:10) to a pressure of approximately 1 mbar. Energetic argon ions generated in the plasma, which is confined in front of the magnetron head, sputter atoms from the gold target. These atoms are subsequently cooled by collisions with He, leading to nucleation and growth of clusters along their route to the exit of the aggregation tube. A considerable fraction of the clusters generated are positively or negatively charged. The size distribution can be tuned (e.g. by the gas pressures or aggregation length) from the monomer to several thousands of atoms per cluster. A more detailed description of the MCS can be found in Xirouchaki & Palmer (2004) and Kamalou et al. (2008).

The MCS is a continuous cluster source. However, in the TIED application described below, the source is only switched on for several seconds per measurement cycle to minimize material consumption and deposition along the ion path. This ‘quasi-pulsed’ operation allows stable cluster-ion intensities for up to several days.

(b) Direct structural-determination methods

We distinguish between ‘direct’ and ‘indirect’ structural-determination methods. Here, direct refers to collision cross section or diffraction pattern measurements that require comparison with structural models for geometry assignment. Indirect methods rely on thermochemical or spectroscopic data.

(i) Collision cross sections from ion-mobility spectrometry

Ion-mobility spectrometry (IMS) is a method to obtain structural information for cluster ions in gas phase via their reduced mobility $K_0$ in a buffer gas (often helium). The mobility can be obtained by measuring the drift time $t_D$ of the ions pulled by an electrical field $E_D$ through a cell that is filled with the buffer gas at a pressure $p$ and temperature $T$,

$$K_0 = \frac{L}{t_D E_D} \frac{p}{1013 \text{ mbar}} \frac{273.2 \text{ K}}{T}.$$
Figure 1. Typical gold-cluster cation mass spectra obtained using the laser-vaporization disc source as interfaced to a 7T-FT-ICR mass spectrometer. The data shown were assembled from partial mass spectra for which cluster source, ion optics and Penning trap were optimized for maximal signals around cluster sizes \( n \sim 12, 35, 60 \) and 90.

From the mobility, the experimental collision cross section \( \Omega_{\text{exp}} \) can be easily calculated (Mason & McDaniel 1988) by

\[
\Omega_{\text{exp}} = \frac{3q}{16N_0K_0}\sqrt{\frac{2\pi}{\mu k_B T}},
\]

where \( q \) is the ion charge, \( N_0 \) the number density of the buffer gas and \( \mu \) the reduced mass of helium and the ion. The interaction between a neutral molecule and an ion comprises two parts: the attractive \((1/r^4)\) charge-induced dipole interaction, which scales with the polarizability of the neutral, and the repulsive interaction owing to the van der Waals radii of the ion and neutral. When using helium with its extremely small polarizability as the buffer gas, the attractive interaction can be neglected, and the measured collision cross section essentially corresponds to the geometrical (hard sphere) cross section. This significantly facilitates comparison with theory. For a calculated candidate structure (obtained by geometry optimization at density functional theory (DFT) level, see below), a theoretical cross section \( \Omega_{\text{theo}} \) can be calculated either by the projection approximation (PA; Von Helden et al. 1993b) or the exact hard-spheres scattering (EHSS; Shvartsburg & Jarrold 1996) model, which both treat the cluster ion as comprised of hard-sphere atoms with element (and charge) specific radii. If experimental and theoretical cross sections differ by more than the combined uncertainty (typically 2%, see below), a candidate structure can be ruled out. Note, however, that the method cannot strictly ‘prove’ a candidate structure.

The instrument used to determine the ion mobilities has been described in detail elsewhere (Weis et al. 2002c). Briefly, the setup comprises a laser-vaporization source (see above), a time-of-flight mass spectrometer with...
Figure 2. Schematic of the ion-mobility instrument. The setup comprises a laser-vaporization cluster source, a time-of-flight mass spectrometer with a mass gate, a helium-filled, temperature-variable drift cell and a quadrupole mass filter (see text).

a pulsed mass gate to select a specific cluster mass, a deceleration lens, the helium-filled drift cell and a quadrupole mass filter to remove possible fragmentation products (figure 2). The deceleration lens allows us to adjust the injection energy, i.e. the energy of the ions entering the drift cell (typically 100–300 eV laboratory frame).

The drift cell is 110 mm long, it has 0.5 mm entrance and exit orifices and is filled with typically 8 mbar helium. The gas temperature in the cell can be varied between 77 and 400 K. The guiding electrical field is varied in the range between 0.5 and 3 V mm$^{-1}$. After leaving the cell, the ions pass the quadrupole mass filter and are detected by a channeltron electron multiplier. The detector signal is fed into a multi-channel scaler and recorded as a function of time. The maximum of the arrival-time distribution is directly connected to the drift time $t_D$ plus a small offset owing to the time the ions spend in the quadrupole mass filter and therefore to the reduced mobility $K_0$ and cross section $\Omega_{\exp}$ (see above). The resolution of the instrument is between 25 and 40, dependent on applied drift voltage, pressure and temperature. For all ions, the arrival-time measurements have been reproduced several times to within 2 per cent. For the absolute error, we estimate 5 per cent, mainly owing to errors in temperature, pressure and voltage readings. Note that recently the drift cell has been modified and an electrodynamic ion funnel has been installed, which increased the transmission roughly by a factor of five without significantly reducing the resolution.

(ii) Trapped ion electron diffraction

Gas-phase electron diffraction is a well-established method to obtain the structure of neutral molecules (Brockway 1936). Ten years ago, a variant of this approach was developed for measurements on $>10^5$ mass-selected ions stored in a variable temperature quadrupole ion (Paul) trap (Maier-Borst et al. 1999; Krückeberg et al. 2000). The Karlsruhe TIED setup is based on this design. A schematic is shown in figure 3. Preformed ions are injected into the Paul trap, which is contained in a UHV (diffraction) chamber. Within this UHV chamber, all components (ion detector, ion trap and electron detector) are mounted on a three-rod system centred on the exit of a collinear electron gun.
Figure 3. Schematic of the trapped ion electron diffraction setup. CCD is charge-coupled device.

to maintain cylindrical symmetry. Ions from an MCS are guided by electrostatic steering and focusing elements into the radio-frequency (RF) quadrupole ion trap. The ion trap (300 kHz RF, up to 7000 V\textsubscript{pp}) is used for ion capturing, mass selection, ion storage and detection. The trap temperature can be regulated between 100 and 650 K; for the experiments described here, it was set to approximately 100 K. High-energy electrons (40 keV, approx. 2 μA) from a long-focal-length electron gun cross the trapped ion cloud. Scattered electrons are detected on a phosphor-screen assembly, optimized to detect electrons in this energy range. The (unscattered) main electron beam is captured by an on-axis Faraday cup.

The TIED experimental cycle comprises a sequence of individual steps. A TIED sequence starts with capturing cluster ions from the ion beam. To maximize the capture rate, the ion trap is simultaneously filled with several 10\textsuperscript{−3} mbar He. About 10\textsuperscript{5}–10\textsuperscript{6} cluster ions are then trapped, size-selected by applying a stored wave inverse Fourier transformation (SWIFT) waveform dipolar to the end caps of the ion trap, and cooled by (>10\textsuperscript{6}) He collisions to the trap temperature. After pumping down to UHV conditions, the electron beam is switched on, and the diffraction pattern as imaged by the phosphor screen is integrated by an external charge-coupled device camera for approximately 30 s. After camera readout, the remaining clusters in the trap are detected. To remove the experimental background, exactly the same sequence is repeated without cluster ions in the trap. This generates a reference measurement. This cycle is then repeated several hundred times, until a sufficient signal to noise ratio is achieved. The overall measurement time is typically 14–16 h.

For data reduction, the reference-corrected difference picture is centred and radially averaged yielding the total scattering intensity as a function of the electron momentum transfer \( s = 4\pi/\lambda \sin(\theta/2) \). \( \lambda \) denotes the electron de Broglie wavelength (0.0602 pm) and \( \theta \) the scattering angle. The experimental molecular scattering function is calculated as \( sM^\text{exp} = s(I_{\text{tot}}/(I_{\text{back}}I_{\text{nat}}) - 1) \). \( I_{\text{nat}} \) is the atomic scattering function (Prince 2004) and \( I_{\text{back}} \) an unspecified, flat and \textit{a priori} unknown additional background that is determined within the

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fitting procedure described below. $I_{\text{back}}$ has the form $I_{\text{back}}(s) = A \exp(-\alpha s) + \sum_i^4 a_i s^i$. The theoretical modified scattering function is approximated by $sM_{\text{theo}} = S_{c}/N \exp(-L^2 s^2/2) \sum_i^N \sum_{j \neq i}^N \sin(r_{ij}s')/r_{ij}$, with $s' = k_{s} s$. $N$ is the number of gold atoms in the cluster, $S_{c}$ and $k_{s}$ are scaling factors and $r_{ij}$ is the distance between two atoms. $L$ is the mean vibrational amplitude averaged over all distances in the cluster and accounts for thermal vibrations. To include the finite sizes of electron beam and ion cloud, the theoretical molecular scattering function is smooth by a running average over $\Delta s = 0.39 \text{Å}^{-1}$. Comparison of the experimental and theoretical scattering function is achieved by a $\chi^2$-fit minimizing the differences of experimental and theoretical scattering function by variation of $S_{c}$, $k_{s}$, $L$ and the parameters of the background function. The quality of the fit, i.e. the level of agreement between $sM_{\text{expt}}$ and $sM_{\text{theo}}$, is characterized by a weighted $R$-value of the form $R_w = \sqrt{\sum_i w_i (sM_i^{\text{theo}} - sM_i^{\text{expt}})^2 / \sum_i w_i (sM_i^{\text{expt}})^2}$. The sums go over all experimental and corresponding theory data points. The weighting factors $w_i$ are calculated from the (error-propagated) standard deviation of $I_{\text{tot}}$. Because of this dependence on the experimental data, comparisons of different $R_w$ are only meaningful within a single experimental dataset.

For a given material, the cluster size range accessible to TIED is limited at its lower end by the atomic scattering intensity. This scales (in a crude approximation) with the square of the atomic number (Hargittai & Hargitta 1988) and increases linearly with $N$, the number of atoms in the cluster. The upper cluster size limit is determined by the maximum mass-to-charge ratio detectable in the ion trap (approx. 40 000 atomic mass units for singly charged species). In the current configuration, this translates to an accessible size range of $n = 10$–200 for gold-cluster ions.

The good reproducibility of the TIED data has been demonstrated by a study of clusters of very similar structure but different charge states (i.e. Ag$_{55}^+$ and Ag$_{55}^-$), where fitting parameters were found to be identical within experimental error (Schooss et al. 2005).

In fitting the diffraction data to a theoretical model, the only structural variation that is carried out is a uniform compression (or expansion) of the calculated coordinates via the $s$-scaling factor $k_{s}$. In effect, this allows an experimental verification of the mean bond length of a model structure (Blom et al. 2006). In cases where a single isomer describes the TIED data very well, deviation of $k_{s}$ from unity can be mapped onto mean bond-length deviations of the model structures. The maximum systematic error in $k_{s}$ is estimated to be 1–2 per cent. For gold-cluster ions using TPSS/7s5p3d1f, a consistent value of $k_{s} \approx 1.03$–1.04 was found. Hence, TPSS/7s5p3d1f leads to a weak overestimation of the mean bond lengths by 1–2 per cent, in good agreement with benchmark calculations for smaller gold clusters (Johansson et al. 2008).

As the molecular scattering function is the Fourier transformation of the (modified) radial distribution function (Hargittai & Hargitta 1988), TIED is a sensitive measure of the atomic distance distribution. Consequently, in the case of an isomer mixture, the TIED experiment measures the mean distance distribution averaged over all isomers. Distinguishing different isomers can therefore be difficult, if the isomers constituting the mixture belong to the same structure family. Additionally, the $s$-range accessible to our TIED apparatus in its current configuration is restricted to $s_{\text{max}} \sim 12 \text{Å}^{-1}$. This leads to limited contrast in

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distinguishing similar isomers. Nevertheless, in cases where isomeric structures in a mixture belong to different motifs (e.g. $\text{Au}_{12}^-$, $\text{Au}_{18}^-$, $\text{Au}_{20}^+$, see below) contributions from different isomers can be clearly identified, as indicated by a significant reduction of the profile factor in a mixture fit compared with fitting just one structure.

(c) Model structures from theory for comparison to experiment

Extensive surveys of the previous quantum chemical literature for gold clusters and related systems can be found in reviews by Pyykkö (2004, 2005, 2008). All quantum chemical calculations carried out for the gold-cluster ions of interest here were performed with the TURBOMOLE program package (Ahlrichs et al. 1989) using the DFT level of theory with the resolution of identity RI-J (Eichkorn et al. 1995, 1997). Ground-state cluster geometries were optimized using either the Becke–Perdew-86 functional BP86 (Becke 1988; Perdew et al. 1996) or the meta-generalized gradient approximation of Tao, Perdew, Staroverov and Scuseria (TPSS; Tao et al. 2003) in combination with the ‘7s5p3d1f’ basis set ((9s7p5d1f)/[7s5p3d1f]), which was specifically devised for gold clusters (Gilb et al. 2002). This basis set includes a scalar relativistic effective core potential that leaves 19 electrons per atom in the valence space.

The performance of ‘TPSS/7s5p3d1f’ has been validated for small gold-cluster anions in a large-scale benchmark study including coupled cluster (CC) methods up to CCSD(T), a Møller-Plesset (MP) perturbation series up to MP4, as well as different variants of DFT (Johansson et al. 2008). For $\text{Au}_{17}^-$, TPSS predicts the same energy ordering as CCSD(T) and performs better than MP2, MP4 or the traditional generalized gradient functionals (GGAs). For the two-dimensional–three-dimensional transition region (Au$_{11}^-$ to Au$_{13}^-$), the same study showed that GGAs such as B3LYP, BP86 or PBE are significantly biased towards two-dimensional structures (see §4 below).

For the larger gold-cluster cations $\text{Au}_{n}^+$, $n = 14–19$, a DFT-based genetic algorithm (GA) has been employed to help find the global minima (Sierka et al. 2007). Given the large number of geometry optimizations inherent in such a procedure, a more modest basis set [def-SV(P)] had to be used. For $\text{Au}_{14}^+$ and $\text{Au}_{15}^+$, TPSS was used together with this basis. For the larger clusters, the BP86 functional was applied. While geometries are expected to be well described by this approach, it is associated with energy errors of several tenths of an electronvolt. In order to take this into account without loss of speed, we evaluated the ‘fitness’ of a cluster structure based not only on its energy, but also on agreement with the experimental diffraction data (in terms of its profile factor $R_w$). Further tests and detailed calculations show that experimental structures can be found very efficiently using such a modified GA (Neiss & Schooss in preparation). The final output structure of the GA procedure, i.e. lowest energy structures and/or isomers that optimally fit the diffraction data were re-optimized using TPSS/7s5p3d1f. Independent of the structure search method, a vibrational frequency analysis was conducted in each case to verify true (local) minimum structures for the assigned isomers.

To illustrate the procedure of structure assignment using TIED, figure 4 shows simulated scattering functions obtained for the lowest energy isomers of $\text{Au}_{20}^-$ in comparison with the experimental data. The structure of $\text{Au}_{20}^-$ has been inferred
Figure 4. (a) Minimum energy structures of Au$_{20}^-$ (two views rotated by 90°), together with structural motif, point-group symmetry, relative energy and profile factor $R_w$. The lighter atoms are visual aids to indicate the relative positions of the two views. (b) Comparison of the experimental (open circles) and simulated (red lines) reduced molecular scattering function $sM$ from DFT structures (1)–(5) for Au$_{20}^-$. The blue traces show the residuals.

Our results are fully consistent with these findings: the slightly (Jahn–Teller) distorted tetrahedron, a segment of the gold face-centred cubic (fcc) structure, is the ground-state structure according to TPSS/7s5p3d1f. The best agreement with our experimental data ($R_w = 2.3\%$) is found for this tetrahedral structure (1). The remaining differences between experimental and simulated scattering function (figure 4) are probably owing to incomplete consideration of vibrational effects such as (bond-dependent) vibrational amplitudes and anharmonicities. As indicated by their high(er) $R_w$-values, other structural motifs such as icosahedral (3), or decahedral (5) can be clearly ruled out. Even the singly defective tetrahedral isomer (2) or the distorted fcc structure (4) shows significantly higher profile factors and are unlikely to contribute considerably to the cluster ensemble probed.

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Indirect structural-determination methods

(i) Radiative association kinetics and adsorption equilibria

Ion cyclotron resonance (ICR) mass spectrometry makes use of a Penning ion trap to probe near-thermal energy ion-molecule reactions at pressures well below $10^{-6}$ mbar. Concomitantly, long trapping times of $> 1$ ms are routinely attained. ICR work on atomic metal cation chemistry under such single collision conditions dates back more than 30 years (Staley & Beauchamp 1975). For example, complete cycles of metal ion-catalysed oxidation reactions have been studied (Kappes & Staley 1981) or thermochemical information like gas-phase acidities/basacidities or relative ligand-binding energies (‘thermochemical ladder’) has been obtained by way of quantifying exchange equilibria (Kappes et al. 1982).

More recently, it was recognized that absolute binding energies of metal-ion/ligand systems may be obtained by modelling the low-pressure kinetics of the corresponding bimolecular association reactions (Kofel & McMahon 1988; Dunbar et al. 1996). This radiative association kinetics model is based on a mechanism that can be written as

$$\begin{align*}
M^+ + L & \overset{k_f}{\underset{k_b}{\rightleftharpoons}} [M(L)^+]^* \\
[M(L)^+]^* & \overset{k_r}{\underset{k_c}{\rightarrow}} M(L)^+ + hv \\
[M(L)^+] & \underset{k_c[L]}{\rightarrow} M(L)^+,
\end{align*}$$

wherein the initially formed energized complex $[ML^+]^*$ releases its excess energy by photon emission (with a rate constant $k_r$) rather than by collisional relaxation. By making further assumptions concerning the $[ML^+]^*$ formation rate, $k_f$ (=Langevin capture cross section) and by modelling the transition state and its dissociation rate $k_b$ (Rice–Ramsperger–Kassel–Marcus (RRKM) theory or phase-space theory), an expression can be derived that may, in turn, be used to fit the kinetic data of $ML^+$ formation with the $M^+\text{-}L$ binding energy as the sole free-fit parameter (for more details, see Wu & McMahon 2009).

Apart from providing thermochemical information (which can then be compared with predictions from structural models), adsorption/desorption experiments can, in principle, also be used to obtain more direct information on isomer content. For monodispersed cluster ions with two (or more) coexisting isomers having significantly different chemical properties, there are several consequences (assuming slow interconversion rate): (i) the adsorption kinetics will deviate from the single-exponential decay behaviour expected for a single-isomer parent species. Note, that such isomer-specificity has often been observed for the ‘inverse’ process of radiatively induced dissociation/depletion ‘BIRD’ (Dunbar 2004), e.g. for electron autodetachment (Arnold et al. 2003) and for radiatively induced dissociation (Schnier & Williams 1998). In order to obtain reliable results, such experiments and their kinetic modelling have to be performed at several temperatures owing to the generally rather poor robustness of the corresponding multi-parameter fits (ii) Two different saturation coverages may be observable: under certain conditions of pressure and temperature it is possible to follow physio- and/or chemisorption kinetics to a steady state (‘saturation’), e.g. allowing ‘titration’ of strongly binding apex sites and thus structural inferences. This
latter methodology was extensively employed in flow-tube studies on neutral Ni\textsubscript{n} (n ≤ 60) with N\textsubscript{2}, CO and H\textsubscript{2}, in the group of Riley at Argonne (Kerns et al. 2000; Parks et al. 2000). In our experiments, a Fourier-transform ICR (FT-ICR) mass spectrometer (Bruker Daltonics, APEX II) equipped with a 7 T magnet and a laser-vaporization source was used. Ions are trapped using a homogenous magnetostatic and superimposed quadrupolar electrostatic field inside an ICR cell under UHV conditions. Ion-molecule reactions can be studied under few collision conditions at reactive gas pressures of 10\textsuperscript{−7} to 10\textsuperscript{−8} mbar. Under these conditions, radiative processes, e.g. spontaneous photon emission, may have to be taken into account when analysing kinetic data (radiative association model, see above).

(ii) Electronic photodissociation spectroscopy

Measurements of the energies of electronically excited states, as well as corresponding absorption cross sections, can be directly related to cluster structures if: (i) excitation energies can be calculated to sufficient accuracy (typically to within 0.1 eV) and (ii) possible structural isomers can be clearly distinguished on the basis of predicted spectra (Schweizer et al. 2003).

Owing to the low particle densities, direct absorption measurements cannot normally be performed on mass-selected cluster beams. One solution is to couple photoabsorption to a change in cluster-ion intensity. The simplest version of this is photodissociation as detected by parent ion intensity depletion. Unfortunately, dissociation energies of gold-cluster ions are comparable with visible photon energies (Becker et al. 1994; Spasov et al. 2000). Therefore, even if the (one) photon energy is rapidly and completely converted into ground-state vibrational excitation, unimolecular dissociation rates are often too slow for complete fragmentation on the experimental time scale—particularly for larger clusters. Consequently, depletion cross sections can be significantly smaller than the one-photon absorption cross sections (further complicated by unknown fluorescence quantum yields). The inert-gas-tracer method offers (a partial) solution. Instead of bare gold-cluster ions, inert-gas adducts Au\textsubscript{x}Rg\textsuperscript{y+}/\textsuperscript{−} are photodissociated. The method presupposes that the inert-gas binding energy is small enough to yield complete one-photon dissociation on the experimental time scale and that the optical properties of the bare cluster are essentially unperturbed by complexation. Both assumptions were tested in our experiments.

The experimental setup used has been previously described (Schooss et al. 2000). Briefly, Au\textsubscript{x}Rg\textsuperscript{y+}/\textsuperscript{−} (Rg = Ar or Xe) were generated using a Smalley/Heiz-type pulsed laser-vaporization source. The gold vapour was expanded together with a helium/inert gas mixture to yield a seeded supersonic beam. Cluster ions were extracted from this primary beam into a perpendicularly oriented reflectron time-of-flight mass spectrometer. For several experiments, this mass spectrometer was equipped with custom ion-extraction optics that allowed setting the first space focus to a comparatively small distance of ca. 1 cm from the primary beam axis. This allowed essentially simultaneous irradiation of a wide range of extracted ion masses, while at the same time ensuring mass-specific detection of depletions and ensuing fragment ions (Schooss et al. 2000). As a result, it was possible to carry out spectroscopic measurements on several cluster ions at once, thus enhancing the throughput of the experiment. Cluster ions were
photodissociated using a Nd-YAG-pumped, tuneable, pulsed optical parametric oscillator (OPO) laser. One-photon dissociation conditions were ensured by also determining depletions as functions of laser fluence. Details concerning laser/ion beam overlap and the relations used to determine cross sections from measured depletions can be found in Schweizer et al. (2003) and Gloess et al. (2008).

3. Structures

(a) Singly charged cluster ions

IMS was the first direct method used to obtain information on gold-cluster structures (see figure 5). It was applied to singly charged cations and anions ranging in size up to 13 atoms. Subsequently, cluster sizes from 11 atoms to beyond 20 were studied by TIED. We discuss these efforts in sequence. The resulting geometries are shown in figures 6 and 7. The corresponding atomic coordinates are given in the electronic supplementary material.

(i) Ion-mobility measurements

A summary of the collision cross sections as determined by IMS is shown in figure 5. Anions generally have larger cross sections than cations of the same nuclearity—due essentially to electron spillout. For structural assignments, individual cross sections were analysed in terms of model calculations as described below.

\( \text{Au}_3^{+/-} \): according to the DFT calculations, the lowest energy structure for the trimeric cation is triangular (\( D_{3h} \) symmetry, bond length 2.640 Å), while the anion is linear (bond length 2.587 Å; figure 6). These assignments can be confirmed by ion-mobility data (for details see Furche et al. 2002; Gilb et al. 2002).

\( \text{Au}_4^{+/-} \): the DFT global minimum for the tetrameric cation is a planar rhombic \( D_{2h} \) structure, in agreement with the ion-mobility data. For the anion, a zig-zag chain is lowest in energy, a Y-shaped structure is however only 0.02 eV higher in energy. On the basis of our ion-mobility measurements (\( \Omega_{\text{exp}} = 58.6 \text{ Å}^2 \)), we can rule out the zig-zag structure (\( \Omega_{\text{theo}} = 62.0 \text{ Å}^2 \)) and confirm the Y-shaped structure (\( \Omega_{\text{theo}} = 58.5 \text{ Å}^2 \)).

\( \text{Au}_5^{+/-} \): DFT predicts the cation to be a planar, X-shaped (\( D_{2h} \)) structure symmetry. The anion is planar as well; however, the symmetry is reduced to a W-like (\( C_{2v} \)) structure.

\( \text{Au}_6^{+/-} \): the lowest energy structure for both charge states is planar triangular. For the anion, it is an isosceles triangle (\( D_{3h} \) symmetry), the cation is slightly Jahn–Teller-distorted (\( C_{2v} \) symmetry).

\( \text{Au}_7^{+/-} \): the DFT global minimum for the cation is a highly symmetric hexagon with one central atom (\( D_{6h} \) symmetry). The anion is planar as well; however, it is lower in symmetry. It can be thought of as a square with three of its edges bridged by additional gold atoms (\( C_{2v} \); figure 5). All of these structures are confirmed by ion-mobility data.
Figure 5. Ion-mobility measurements: experimental cross sections for gold-cluster cations (black circles) and anions (grey circles) at 300 K. Note that the small gold-cluster anions have significantly larger cross sections than the corresponding cations. For $\text{Au}^{-12}$, a bimodal arrival-time distribution is obtained, indicative of two different isomers. This is the only cluster size where we observe two peaks of comparable intensities in the room-temperature measurements.

Figure 6. Structures of gold-cluster anions $\text{Au}_n^-$ ($n = 3$–$20$). Shown are the isomers fitting the experimental data best, together with their corresponding point-group symmetry. In cases where the experimentally assigned structure is different from the calculated global minimum, the relative energy is given. For $\text{Au}^{-12}$ and $\text{Au}^{-18}$, two isomers are shown in each case, as here a two-component isomer mixture has been identified.

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Figure 7. Structures of gold-cluster cations Au\(^{+}\)_n (n = 3–20). Only the isomers that optimally fit the experimental data are shown, together with their point-group symmetries. In cases where the experimentally assigned structure is different from the calculated global minimum, the relative energies are given. For Au\(^{+}\)_9 and Au\(^{+}\)_20, two isomers are shown in each case, as two-component isomer mixtures have been identified for these sizes.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Structure</th>
<th>Symmetry</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
</tr>
<tr>
<td>Au(^{+})_4</td>
<td>C(_{3v})</td>
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<td></td>
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<td></td>
</tr>
<tr>
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<td>C(_{3v})</td>
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<td></td>
</tr>
<tr>
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<td>D(_{3h})</td>
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<td></td>
</tr>
<tr>
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<td>C(_{4v})</td>
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<td></td>
</tr>
<tr>
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</tr>
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</tr>
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<td>Au(^{+})_20</td>
<td>D(_{2d})</td>
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**Au\(^{+/-}\)_8:** for the cation, DFT predicts a planar structure to be lowest in energy (basically the Au\(^{+}\)_7 hexagon with one additional bridging atom, C\(_{2v}\)). A three-dimensional structure with completely different topology is found only 0.06 eV higher in energy. Based on the ion-mobility data, we can rule out the planar global minimum structure and confirm the isomeric three-dimensional structure (C\(_{6}\) symmetry). The anion on the other hand turns out to be planar and highly symmetric (D\(_{4h}\)), its structure consists of a square with all edges bridged. This structure can be confirmed experimentally—the energetically closest three-dimensional structure is almost 1 eV higher and has a cross section that is 10 percent below the experimental value and can therefore be ruled out.

**Au\(^{+/-}\)_9:** the cation has a three-dimensional structure (C\(_{2v}\)) that basically represents a segment of the gold-crystal lattice. In our ion-mobility measurements at room temperature, we observe one single peak in the arrival-time distribution, low-temperature studies reveal however the coexistence of isomer (C\(_{3v}\); figure 5). Both structures interconvert at room temperature (see below). Planar structures can be ruled out both on the basis of cross section and relative energies. The favoured structure for the anion, however, is planar, in agreement with the ion-mobility data.
The cations are three-dimensional (figure 7). For the anions, DFT predicts planar structures. This can be confirmed by ion mobility only for $\text{Au}^{-10}$ and $\text{Au}^{-11}$. For $\text{Au}^{-12}$, we find a bimodal arrival-time distribution (figure 5). The first peak can be identified as a three-dimensional isomer, while the second corresponds to a planar structure. For $\text{Au}^{-13}$, we find only a three-dimensional structure, planar candidate structures can be ruled out on the basis of the ion-mobility data.

(ii) Trapped ion electron diffraction measurements: $\text{Au}^{-n}$, $n = 11–20$

The smallest gold-cluster anion studied by TIED was $\text{Au}^{-11}$ (Johansson et al. 2008). It is a flat $C_s$ structure in good agreement with theoretical prediction. For $\text{Au}^{-12}$, an isomer mixture was found: the three-dimensional $C_{2v}$ isomer together with a smaller contribution (approx. 15%) of a planar $D_{3h}$ isomer. This is in contrast to the theoretical prediction; the GGA functionals PBE and BP86 predict the planar structure to be the global minimum 0.4–0.6 eV lower than the three-dimensional structure. Even TPSS predicts a slight bias towards the planar structure (0.17 eV). Spin-orbit coupling (SOC) significantly affects the relative energies. Incorporation of SOC into the calculations leads to a stabilization of the three-dimensional structure by more than 0.1 eV. Contrary to previous PES studies (Bulusu et al. 2006) and (Koskinen et al. 2007), which have suggested that $\text{Au}^{-13}$ has a two-dimensional structure, we found it to have a flat three-dimensional structure ($C_{2v}$). This is also in agreement with theory; at TPSS level, the two-dimensional isomer is 0.2 eV higher in energy. The assignments based on TIED for $\text{Au}^{-11}$ to $\text{Au}^{-13}$ are in perfect agreement with the room temperature IMS results described above.

For $\text{Au}^{-14}$, again a flat three-dimensional structure ($C_2$) fits the experimental data best. Interestingly, its energy is 0.22 eV above the two-dimensional ground-state structure suggested by TPSS/7s5p3d1f (Lechtken et al. 2009). To our knowledge, neither the $C_2$ nor the planar structure has been considered for $\text{Au}^{-14}$ before. In former TIED (Xing et al. 2006) and PES (Häkkinen et al. 2003; Bulusu et al. 2006) studies, a $C_{2v}$ structure was assigned, which is a saddle-point rather than a minimum-energy structure using TPSS/7s5p3d1f. For $\text{Au}^{-15}$, a flat-layered structure ($C_{2v}$) closely related to the $\text{Au}^{-14}$ structure is the best-fitting isomer, in agreement with previous TIED measurements.

At $\text{Au}^{-16}$, the structural motif changes: the ground state and also the best-fitting structure is now a slightly distorted tetrahedral ($D_{2h}$) cage structure. This structure can be constructed from the tetrahedral $\text{Au}^{-20}$ by removing four corner atoms and moving out each of the centre atoms of the four faces. This structure comprises a sizeable hollow of 5.1 Å diameter, large enough to accommodate a heteroatom, as was shown recently for Cu@Au$^{-16}$ (Wang et al. 2007) and Fe/Co@Au$^{-16}$ (Wang et al. 2009). $\text{Au}^{-17}$ also has a cage structure ($C_{2v}$).

For $\text{Au}^{-18}$, a mixture of structures was found. The dominating isomer (approx. 80%) is again a cage-like structure ($C_{2v}$-2), while the minor component ($C_{2v}$-1) (TPSS/7s5p3d1f ground state) is an fcc-like structure. It can be derived from the $\text{Au}^{-20}$ tetrahedron by removing two corner atoms. Finally for $\text{Au}^{-19}$ and $\text{Au}^{-20}$, tetrahedral fcc-like structures have been found in good agreement with the former TIED and PES measurements.
(iii) *Trapped ion electron diffraction measurements: \((Au_n^+, n = 11–20)\)

The structures of \(Au_{11}^+–Au_{13}^+\) (previously studied by IMS—see above) have also been studied by TIED. For this, the three-dimensional structures found by IMS were re-optimized using TPSS/7s5p3d1f, and the resulting simulated scattering functions were found to be in close accordance to the TIED data (Lechtken \textit{et al.} in preparation).

For \(Au_{14}^+\), the best agreement between experiment and theory is found for a layered structure \((C_1)\) decorated with an additional atom. This motif is continued for \(Au_{15}^+\) \((C_1)\) and \(Au_{16}^+\) \((C_{2v})\). \(Au_{17}^+\) is an interesting case. Among the low-energy structures, only layered structures are able to explain the experimental data. Neither the calculated high-symmetry ground state (Lechtken \textit{et al.} in preparation) nor structures based on the \(Au_{20}\) tetrahedron are in agreement with the experimental data. Within the layered structure family, the lowest-energy isomer we have found (figure 7) is 0.36 eV above the TPSS/7s5p3d1f ground state. Additional support for this assignment results from IMS measurements, as only flat-layered structures have simulated cross sections close to the experimental value (Weis \textit{et al.} 2002a).

At \(Au_{18}^+\), the structural motif changes: a decorated cage that is isoenergetic with the fcc-like ground-state structure is found to fit the TIED data best. The hollow in this star-like configuration has a diameter of 5.9 Å and exceeds the hollow in \(Au_{16}^-\). \(Au_{19}^+\) is found in the experiment to again have a decorated cage structure, while calculations predict a defected \(Au_{20}\) tetrahedron as the ground state.

For \(Au_{20}^+\), a mixture of two isomers was found (Lechtken \textit{et al.} 2008). The predicted minimum-energy structure is similar to \(Au_{20}^-\), a slightly distorted \((D_{2d})\) tetrahedral structure. The next higher lying isomer (0.27 eV) is a distorted icosahedral structure of \(C_3\) point-group symmetry. None of the calculated structures alone is able to explain the experimental scattering function. However, a 2:3 mixture of \(D_{2d}\) and \(C_3\) structures fits the scattering data very well.

\((b)\) *Comparison of experiment and theory and rationalization of structures*

The overall agreement between TIED experiment and theoretical prediction using TPSS/7s5p3d1s is remarkably good. For most clusters (anions and cations) in this size range, the best-fitting structures correspond either to the tentative ground states or to energetically close-lying isomers. However, there are exceptions, most notably for \(Au_{12}^-\), \(Au_{14}^-\), \(Au_{18}^-\), \(Au_{17}^+\), \(Au_{19}^+\) and \(Au_{20}^+\). This discrepancy may be owing to (i) the possibility that the correct global minimum-energy isomer was not yet found/considered, (ii) significant changes in free-energy ordering of isomers occurs at the experimental temperature (100 K) relative to the sequence of vibration-less total energies, or (iii) systematic errors in theory that yield the incorrect energy ordering of isomers (or perhaps even incorrect structures). To rule out (i), we have conducted more extensive structure searches (e.g. via \textit{ab initio} molecular dynamics for \(Au_{11}^-\) to \(Au_{13}^-\) and GA for \(Au_n^+\)). However, no lower-energy isomers were found. To test the finite-temperature effect, we have calculated free-energy differences, i.e. differences in zero-point energies as well as thermal corrections in the harmonic approximation. These corrections turn out to be small (e.g. approx. 0.01 eV for \(Au_{12}^-\) and \(Au_{20}^+\) at 100 K, leaving the relative energies virtually unchanged. Additionally, the TIED experiment probes clusters
thermalized in a He bath on second time scales. It is therefore unlikely that isomer distributions are dominated by metastable species. This leaves (iii) as the likely explanation.

The predicted ground-state structures for $\text{Au}^-_{12}$ and $\text{Au}^-_{14}$ are planar and tetrahedral for $\text{Au}^-_{18}$, $\text{Au}^+_{18}$ to $\text{Au}^+_{20}$. Both comprise exclusively segments of the gold (111) surface. Cluster geometries containing this structural element appear to be overestimated in stability by the DFT calculations. Note, however, that this systematic error in DFT can only be (experimentally) detected for those clusters in which a different structural motif is comparable in energy to the (111) segment geometries.

In order to rationalize the assigned structures, it is helpful to contrast these structures to the ones of copper and silver clusters. In recent work, we have studied the structural properties of $\text{Cu}^{+/-}_{20}$, $\text{Ag}^{+/-}_{20}$ and $\text{Au}^{+/-}_{20}$ (Lechtken et al. 2008). As already pointed out by Häkkinen et al. (2002) and Fernandez et al. (2006), Cu and Ag are quite similar, whereas Au prefers different structures. It is well known that relativistic contraction of the inner electronic shells of gold atoms stabilizes the 6s valence electrons, while the lower-lying 5d electrons are raised in energy. This leads to smaller s–d separation and significant s–d hybridization. In contrast, for Cu and Ag, the corresponding effects are much smaller. The extent of s–d hybridization in gold clusters also depends on the actual structural motif/symmetry. As a result, for some cluster sizes, notably at the two-dimensional/three-dimensional structural transition, enhanced s–d hybridization can lead to relative stabilization of planar structures and even compensate for decreased average coordination numbers. Also, s–d hybridization is more pronounced for tetrahedral than for icosahedral structures. Compact icosahedral structures in gold clusters require stretching of interatomic distances compared with the (111) microfacets in tetrahedral structures. Such deviations from optimal Au–Au bond distances involve a large energy penalty, caused in part by the relativistic contraction of the 6s orbital. Altogether, these effects lead to non-compact, planar, flat or cage-like structures instead of icosahedral structures as seen for copper and silver.

It is important to note that the minimum-energy structures determined for a given cluster size depend strongly on the charge state. This might appear surprising for a metallic cluster. In fact, calculations show that cations and anions do have common structural isomer types with only minor charge state-dependent geometry differences. However, the relative energies of different structural isomers can change significantly upon changing charge, thus yielding different global minima. This effect can be rationalized if one considers that the clusters have structure-dependent highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gaps, which can be quite large (e.g. 1.81 eV for $\text{Au}_{20}$). Consequently, ionization energies and electron affinities are quite distinct for different isomer geometries. Only for (larger) clusters for which band gaps approach zero, would one expect that the energetic ordering of the isomers no longer depends on the charge state.

(c) Isomer distributions, interconversion kinetics and thermodynamic equilibrium

The IMS data resolved isomer mixtures for $\text{Au}^{+}_{12}$ and $\text{Au}^{-}_{12}$. For $\text{Au}^{-}_{12}$, we observed two well-separated peaks in the arrival-time distribution at room temperature (figure 5). This indicates that any interconversion between the two
isomers is significantly slower than the drift time through the cell (1 ms), i.e. the rate is smaller than $10^3$ s$^{-1}$. Given an internal vibrational energy of ca 0.65 eV for Au$_{12}^-$ at room temperature, this translates into an interconversion barrier of >0.4 eV based on a RRKM calculation (Forst 1973) using DFT-derived vibrational frequencies. For Au$_9^+$, we observed two peaks in the arrival-time distribution only for $T < 120$ K. Near 140 K, one broad peak is seen. Above 160 K, we observed one narrow peak. Its width corresponds to the instrumental resolution (figure 8). These observations can be interpreted in terms of two interconverting isomers—with a temperature-dependent half-life. This is significantly larger than the average arrival time (1 ms) for temperatures below 120 K and significantly smaller above 160 K. The corresponding temperature-dependent rate translates into a barrier height of 0.1–0.2 eV (for details, see Weis et al. 2002b). Based on their cross sections, we can assign structures for the two isomers (figures 5 and 8). They differ basically by the position of one atom and correspond to the DFT global minimum and the structure closest in energy, respectively. These observations are independent of source
parameters such as vaporization laser intensity, timing and injection energy, indicating that the experiment probes thermodynamically controlled isomer distributions. Similar conclusions, i.e. near-thermal equilibrium conditions, can be drawn for those TIED cases that require a mixture of lowest energy isomers to optimally fit the measurements (Au$_{12}^-$, Au$_{18}^-$ and Au$_{20}^-$). Note however, that equilibrium isomer distributions are not always observed in cluster experiments: carbon clusters made by laser vaporization of graphite, for example, coexist in several non-interconverting isomeric forms, such as chains, rings and cages, and can be completely annealed into the most stable form upon injection into the drift cell (Von Helden et al. 1993a). Carbon clusters have much higher binding energies and interconversion barriers than gold clusters do. Consequently, thermodynamically limited isomer distributions are more difficult to achieve.

(d) Structural determinations for other cluster charge states

Experimental information on the structure of Au$_n^q$ in charge states other than $q = \pm 1$ is very scarce. So far, the only direct structure assignments for neutral clusters were obtained in a messenger IR multi-photon dissociation study of Au$_n$Kr, $n = 7, 19$ and $20$. The vibrational spectra showed a convincing consistency with theoretical predictions (Gruene et al. 2008): Au$_7^0$ is planar, but differs from the highly symmetric $D_{6h}$ structure prevailing for the cation. Au$_{19}^0$ and Au$_{20}^0$ conform to tetrahedral structures with the 19-atom cluster being truncated at one corner of the pyramid—both being closely related to the structures observed for the respective anions.

Highly charged metal clusters have enjoyed considerable interest in cluster science because of novel properties deriving primarily from competing cohesive and repulsive Coulombic interactions (Näher et al. 1997). Stability criteria and concomitant appearance cluster sizes have been predicted for many metallic systems in pioneering theoretical work based in part on a liquid-drop model (Yannouleas & Landman 1993, 2000).

Au$_3^{2+}$ (Sudraud et al. 1979) was the first multiply charged cluster to be experimentally observed. Subsequent more extensive studies of the properties of Au$_n^{2+}$ ($9 \leq n \leq 18$) concerned their dissociation by fission (Saunders 1990, 1992). Generation of Au$_n^{-}$ (Herlert et al. 1999; Schweikhard et al. 1999) and Au$_n^{3-}$ (Yannouleas et al. 2001) was first achieved by electron attachment to trapped gold-cluster anions for which appearance sizes of $n \geq 12$ (dianions) and $n \geq 51$ (trianions) were established (Herlert & Schweikhard 2003). Another source to produce gold-cluster dianions was found to be UV laser ablation from a metal target under high-vacuum conditions (Stoermer et al. 2001).

Essentially, the only information on the geometric structure of multiply charged gold clusters derives from quantum chemical computations. Recently, the most stable isomer of Au$_6^{2-}$ has been calculated to have octahedral symmetry rather than planar topology. The same authors have made structural predictions for Au$_{10}^{2+}$ ($D_{kl}$ symmetry) and Au$_{14}^{4-}$ ($D_{2d}$ symmetry; Chen et al. 2006). Au$_{16}^{2-}$ is thought to have a hollow cage structure with full $T_d$ symmetry (similar to the cage found for Au$_{16}^{-}$). This structure was computed to be electronically stable with a positive second electron affinity of 0.92 eV (Walter & Häkkinen 2006).
4. Consequences of structure for ion chemistry and electronic spectroscopy

(a) Carbon monoxide chemisorption

Knowledge of the geometric structures of gold clusters helps to rationalize their ion chemistry. To illustrate this, we discuss the CO chemisorption (which is also the most extensively studied chemisorption process on single-crystal gold surfaces) and revisit some of the previous experimental results on clusters ‘in retrospect’. As outlined in §1, these were mostly analysed in terms of electronic structure when first published. In the meantime, one can consider these observations in terms of a more ‘holistic’ approach, which incorporates interdependent electronic and geometric structure.

Absolute bimolecular rate constants for the adsorption of CO on gold-cluster anions \( \text{Au}_n^- \) were determined with a guided-ion-beam setup for \( n \leq 7 \) (Lee & Ervin 1994). These rates increase with increasing cluster size and show a pronounced step between \( n = 4 \) (a quasi-one-dimensional Y-shaped cluster with a singly connected gold atom) and \( n = 5 \), which adopts a planar W-shaped structure. The relative CO adsorption reactivities of \( \text{Au}_n^- \) \((n = 4–19)\) as determined in a flow-tube study (Wallace & Whetten 2002) revealed local maxima at \( n = 11, 15 \) and \( 19 \). Early accounts of CO reactivity with \( \text{Au}_n^+ \) included a preliminary FT-ICR mass spectrometric study (Nygren et al. 1991) for \( n \leq 21 \), which displayed local reactivity maxima at \( n = 7 \) and \( n = 18/19 \). More recently, we have systematically studied the chemisorption kinetics of CO reacting with \( \text{Au}_n^+ \) \((n < 65)\) trapped in an ICR cell at room temperature (Neumaier et al. 2005). Sequential CO uptake of up to four carbon monoxide molecules is observed. The corresponding quasi-unimolecular rate constants are summarized in figure 9a. The rate constants for the first CO have been analysed by the radiative-association model to give the binding energies (‘heats of adsorption’) that are shown in figure 9b. For some of the larger cluster sizes \((n > 20)\), this kinetic modelling was complemented by measurements of the steady-state ion abundance equilibria resulting from competing absorption and desorption kinetics. Analyses of equilibrium constants yielded reaction enthalpies in excellent agreement with the binding energies from the kinetic model. These decrease with cluster size from 1.09 eV for \( \text{Au}_{20}^+ \) to below 0.65 eV for \( n > 26 \), with notable exceptions at \( n = 30, 31, 32 \) and \( 48, 49 \).

Note that experiments on gold surfaces (Lemire et al. 2004), as well as quantum-chemical calculations (Neumaier et al. 2008), indicate \( \mu_1 \)-type bonding of CO to (charged) gold clusters or gold surfaces, i.e. an atop Au–CO bond. Given this information, can our observations from ion chemistry be used as a local probe for the surface structure of a gold-cluster educt? As previously pointed out, the simplest approach derives from saturation kinetics. \( \text{Au}_{20}^+ \) is capable of adsorbing four CO molecules with virtually identical efficiency (figure 9a). A fifth CO is not observed to bind under experimental conditions. This behaviour may be attributed to the four equivalent vertices of a tetrahedral cluster structure. However, this simple picture fails as soon as the cluster significantly restructures upon CO adsorption. Our quantum chemical calculations indicate that lowest-energy structures for some gold carbonyl species deviate from the structures of the bare cluster ions. In particular, the size range of the
two-dimensional–three-dimensional transition is affected: Au$_7$CO$^+$ is calculated to have a three-dimensional structure, whereas Au$_8$CO$^+$ adopts a planar geometry (Neumaier et al. 2005). This also means that the radiative association model is too simple for these cluster sizes—an (activated) cluster core interconversion step must be additionally invoked. Along the same lines, interpretation of adsorption kinetics is complicated by significant reactant isomer interconversion. At room temperature, Au$_9^+$ reacts readily and sequentially with four CO molecules. This is associated with single exponential kinetics (and virtually identical reaction rates) in each case. One possible interpretation is that the cluster has a high symmetry (four equivalent adsorption sites). This is not borne out by IMS structural determination. Alternatively, the reactivity may reflect a fluxional core—consistent isomer-interconversion at room temperature as observed in IMS.

Figure 9. Quasi-unimolecular rate constants ($k_1, \ldots, k_4$) of sequential carbon monoxide (CO) chemisorption on gold-cluster cations at room temperature versus cluster size ($a$) and binding energy for Au$_n^+$–CO, i.e. the first CO molecule ($b$), see text for details. ($a$) Dark green squares, $k_1$; red circles, $k_2$; blue stars, $k_3$; light green triangles, $k_4$. ($b$) Dark green squares, radiative association model; black inverted triangles, B3LYP calculations.
Single adsorbate-induced restructuring (and large-scale isomer interconversion) is expected to become less pronounced with increasing cluster size. Correspondingly, interaction energies derived from radiative association kinetics are more likely to reflect the strongest adsorption sites—which are in turn related to those gold atoms with the lowest electron density, as our recent calculations have shown (Neumaier et al. 2008). Then, our observations for Au$^{+}_{20}$ indicate a CO binding energy of 0.75 eV to the potentially tetrahedral apex sites, still significantly higher than for a single-crystal gold surface—e.g. the surface binding energy for a (reconstructed) Au(110)…CO amounts to 0.55 eV (Gottfried et al. 2003). Note that in contrast to Au$^{+}_{20}$, Au$^{+}_{21}$ shows a pronounced affinity to the first CO molecule—the rate constant for attaching a second one being two orders of magnitude smaller. Here, it is tempting to postulate a closed-shell structure with one additional reactive gold ad-atom. For this (still hypothetical) Au$^{+}_{21}$ structure, density-functional computations show that the atoms with the smallest electron density, here the gold ad-atom, form the strongest CO bond.

In future, it will be of interest to rationalize local maxima in CO binding energies at $n = 30, 31, 32$ and $48, 49$ in terms of the actual cluster structures.

(b) Electronically excited states versus charge and topology

Three inert-gas-tracer depletion spectroscopic studies were performed in order to obtain information on optically excited states and corresponding geometric structures of Au$_x$Rg$^+/−$ (Rg = Ar and Xe). First, depletion spectra were recorded for Au$_4$…Ar$^+$, $n = 0–4$, in the photon energy range of 2.14–3.35 eV (Schweizer et al. 2003). The molecule is small enough such that direct one-photon dissociation is fast on the experimental time scale—throughout the experimental photon energy range. This is consistent with the calculated dissociation energy (into Au$^+$ + Au) of ca 2.1 eV. Consequently, Au$^+$ can be used as a reference to gauge the spectral effect of inert-gas complexation (which can be regarded as upper limits to analogous effects for larger clusters). Overall, the spectra recorded for Au$_4$…Ar$^+$, $n = 0–2$ had similar shapes. We found that argon-induced shifts in the positions of electronic absorption bands were of the order of 0.1 eV for adducts with one and two argon atoms, respectively. Component oscillator strengths of the complexes were modified by at most ±50 per cent relative to the corresponding transitions in the bare cluster ions. In contrast, complexation of three or more argon atoms led to significant changes in the spectral shapes. We modelled the experimental observations in terms of DFT-B3LYP (and RI-MP2) calculations for ground and time-dependent density functional theory (TDDFT) for excited states, respectively. Argon binding energies were 0.1–0.2 eV, depending on computational method, adsorption isomer and argon coverage. The geometric structure of the planar rhombic Au$^+$ core remained essentially unchanged upon complexation of one and two argon atoms. TDDFT calculations for the lowest-energy-adsorption isomers can roughly describe the measured spectral bands—although a systematic blue shift of features (by about 0.15 eV) was observed superimposed on scatter of ±0.1 eV. Transition strengths were typically not well-enough described to allow fingerprint assignments.

Next, we studied Au$_n$Xe$^−$, $n = 7–11$ (spectral range 2.1–3.4 eV; Gilb et al. 2004). Fluence dependencies showed the necessity for inert-gas-tracer measurements at Au$_{10}$ and by inference also at $n = 7$. Whereas the bare clusters...
required two or more visible-region photons to dissociate on the experimental time scale, AuXe showed a one-photon fluence dependence. Generally, agreement between depletion spectra of monoxenon adducts and TDDFT predictions for the corresponding bare-cluster anions using structures determined in our IMS study was good but better for odd \( n \) species. Even \( n \) species have lower vertical-detachment energies than their odd \( n \) neighbours, and direct electron detachment is possible within the wavelength range probed (but not taken into account in TDDFT calculations of dipolar allowed excitations). The excitation energies predicted for odd \( n \) species were typically within 0.1–0.2 eV of experimental features. Spectra were therefore consistent with planar cluster cores. However, the level of agreement was not good enough to allow fingerprint identification/differentiation of energetically close-lying planar isomers.

Finally, we have recorded the depletion spectra of \( \text{Au}_m\text{Ar}_n^+ \), \( m = 7 \); \( n = 0–3 \) and \( m = 8, 9 \); \( n = 0, 1 \) (Gloess et al. 2008). In the case of the bare clusters, the spectra were deconvoluted under the assumption that two-photon absorption (with identical cross sections for first and second photon) is required in order to obtain dissociation on the experimental time scale. Spectral features recorded for argon adducts can be described with TDDFT calculations for the most stable adsorption isomers—to within ca 0.25 eV. They show a slight blue shift with increasing argon complexation (smaller than that observed for \( \text{Au}_4^+ \)). Overall, for \( n = 0 \) and 1, there is a change in the centroid of the spectral distributions between \( m = 7 \) and \( m = 8 \). This can be rationalized on the basis of TDDFT calculations as reflecting a corresponding change in topology from planar to three-dimensional. DFT calculations indicate, as before, that the ground-state cluster core geometries do not measurably change upon inert-gas complexation.

With regard to geometric structural determination, the direct tools previously discussed are presently superior to electronic depletion spectroscopy. The corresponding spectra contain many comparatively weak electronic bands that cannot yet be calculated routinely to predictive accuracies. Furthermore, several adsorption isomers differing slightly in optical spectra may be simultaneously probed. For further advances in understanding electronic transitions, it is necessary to: (i) obtain more highly resolved spectra (e.g. using low-temperature ion traps), as well as (ii) more accurately calculate ground and excited states, e.g. by incorporation of spin-orbit coupling as well as a better description of inert-gas bonding.

5. Outlook

(a) Determining the structures of larger clusters

This review has discussed gold clusters with up to 20 atoms. With the experimental methods now available, significantly larger clusters can be addressed. The present limitation lies in the ability of theory to rapidly and accurately identify model structures. Whereas, we have acquired TIED data for clusters with more than 90 atoms, the largest gold-cluster ion we have been able to assign a structure to is \( \text{Au}_{34}^- \) (Lechtken et al. 2007). We find a chiral \( C_3 \) structure, in agreement with the lowest energy structure predicted by theory. In addition to the TIED data, photoelectron spectra were simulated and compared with experimental PES data. In both experiments, the \( C_3 \) structure gives best agreement among the model structures considered—including different structural
motifs and morphologies. The $C_3$ structure comprises a slightly distorted inner tetrahedron, of which three faces are covered by a nearly planar arrangement of six atoms, respectively. The chirality of the structure is most apparent in the helical arrangement of the edge atoms, as shown in the top view of figure 10.

An intuitive way to rationalize this structure is to start with a 38-atom truncated octahedron, remove a seven-atom hexagonal plane from the bottom of the truncated octahedron, and then add a triangle on the top, such that an ABAC stacking results. The resulting $C_{3v}$ structure is then transformed into the $C_3$ structure by twisting the planes of the cluster with respect to each other and by repositioning the surface atoms perpendicular to the planes (both steps under maintaining the $C_3$ symmetry). The transformation removes the (100) facets of the truncated octahedron and leads to an increased surface density with a higher coordination number. This ‘surface reconstruction’ leads to a substantial energy gain (approx. 0.96 eV) and reveals another strategy to minimize the (surface) energy of a gold cluster, while retaining a dense packing and an optimal bond length.

(b) Structure-dependent properties: some open experimental questions

Experiments on Au$_{10}$ have recently demonstrated that two non-interconverting isomers simultaneously present can be separated by means of their widely different reactivities—the more reactive isomer being in this case ‘titrated’ with O$_2$ to product (Huang & Wang 2009). Resolution of isomers by temperature-controlled IMS is also feasible as we have demonstrated above. Recent improvements of ion transmission through mobility cells suggest that IMS-based preparation of pure isomers for further (e.g. spectroscopic) study is now possible. Among other things, this will allow detailed studies of isomer interconversion, e.g. by means of selective vibrational excitation (or rapid thermal heating). It will also facilitate TIED and infrared multi-photon dissociation measurements (IR-MPD) on pure isomers—leading to better structural data at specific sizes/charges. Along the same lines, adsorbate positional isomers may also be separable by IMS—depending on binding energies.

Related to structural determinations of adsorbate positional isomers is the question of restructuring of the cluster core as a result of adsorbate binding. As discussed above, restructuring has been inferred from calculations of Au$_7$CO$^+$...
and Au₈CO⁺ equilibrium geometries, cf. the bare clusters. It has also been seen in IR-MPD probes of neutral gold-cluster carbonyls (Fielicke et al. 2005), and is in fact expected to be quite common for strongly bound adsorbates. Clearly, information on such structural changes, as well as the associated thermochemistry and dynamics, are necessary in order to understand the adsorption reactions/kinetics. Beyond the, as yet only partially understood CO chemisorption system, adsorbate-induced cluster restructuring is of present interest for: (i) oxidation catalysis involving supported gold clusters (which could be modelled via structural characterization of possible intermediates in the gas phase) and (ii) gold/thiol surface chemistry (structural probes of S–H cleavage and H₂ desorption upon reaction of gold-cluster ions with alkanethiols).

Most of the structural assignments in this paper refer to experiments at temperatures between 100 and 300 K. In particular, measurements at higher temperatures are also required, perhaps resolving the transition regime between few isomer interconversion to more rapid transitions between many local minima. So far, only neutral and singly charged clusters have been structurally characterized. More highly charged species should also be looked at. Are structural isomer types retained or does charge localization lead to dramatic distortions? What are the global minima and does experiment still deliver them? Dications are the most easily accessible higher charge-state clusters for the direct structural-determination methods described above.

With regard to optical properties, apart from the general need for more highly resolved electronic spectra, it is presently not known to what extent gold-cluster ions luminesce. Fluorescence quantum yields and emission spectra need to be acquired as functions of particle size, charge state and adsorbates. A recent time-resolved pump-probe photoelectron spectroscopy study has shown that Au₆⁻ has a surprisingly long excited state lifetime—suggesting that fluorescence may, in fact, be significant (Stanzel et al. 2007). Sufficiently sensitive trapped ion laser-induced fluorescence (TLIF) setups have recently been developed to allow analogous experiments on gold clusters (Iavarone et al. 2006).

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