The catalytic properties of gold nanoparticles are determined by their electronic and geometric structures. We revealed the geometries of several small neutral gold clusters in the gas phase by using vibrational spectroscopy between 47 and 220 wavenumbers. A two-dimensional structure for neutral $\text{Au}_{19}$ and a pyramidal structure for neutral $\text{Au}_{20}$ can be unambiguously assigned. The reduction of the symmetry when a corner atom is cut from the tetrahedral $\text{Au}_{20}$ cluster is directly reflected in the vibrational spectrum of $\text{Au}_{19}$.

The geometry of nanoparticles can also be studied in the gas phase. The advantages of this approach are the exact knowledge of the clusters’ size and the absence of any interaction with the surrounding environment. The properties of such well-defined species can thus be modeled very precisely with quantum-mechanical calculations. Different experimental techniques exist for the study of free clusters. By measuring the mobility of size-selected gold anions and cations in helium, a transition from 2D to 3D structures has been found (11, 12). This transition appears at different cluster sizes for cations and anions and is yet to be determined experimentally for neutral species. A combination of photoelectron spectroscopy and quantum-mechanical calculations has revealed fascinating structural changes of anionic gold species—for example, cages for clusters containing 16 to 18 atoms (13), a tetrahedral pyramid for $\text{Au}_{125}^-$ (14), and a possibly chiral structure for $\text{Au}_{34}^-$ (15). These structural motifs have been confirmed by measurement of the electron diffraction pattern of size-selected trapped anions (15, 16). Although ion mobility measurements, photoelectron spectroscopy...
py, and trapped-ion electron diffraction have all substantially added to the understanding of the geometric properties of free nanoparticles, these methods are restricted to the investigation of charged species.

We investigated neutral gold clusters in the gas phase by means of vibrational spectroscopy, which is inherently sensitive to structure. In infrared (IR) absorption spectroscopy, the number of allowed transitions is restricted by selection rules, and thus directly reflects the symmetry of the particle. Far-IR multiple-photon dissociation (FIR-MPD) spectroscopy is a proven technique for obtaining the vibrational spectra of gas-phase metal clusters and, hence, by comparison with calculated spectra, their geometries (17, 18). It is the only technique for determining the structure of free metal clusters that is not limited to charged species. We explored three representative sizes of neutral gold clusters. With Au19, we investigated the structure in a size region in which the anions and cations are known to adopt planar structures, and we thereby addressed a controversy in theoretical studies. With Au20, we confirmed that the neutral cluster retains the symmetrical pyramidal geometry established for the anion. With Au19, we directly observed the reduction of symmetry when one of the corner atoms is removed from Au20.

Details of the technique of FIR-MPD have been described elsewhere (17, 19). Neutral gold clusters are produced by means of laser vaporization from a gold rod in a continuous flow of He and Kr (1.5% Kr in He) at 100 K. Under these conditions, complexes of the bare metal clusters with one or two Kr ligands are formed. The molecular beam is overlapped with a pulsed FIR beam delivered by the Free Electron Laser for Infrared Experiments (FELIX) (20). The neutral complexes are ionized by an F2-eximer laser (7.9 eV per photon) and mass-analyzed in a time-of-flight mass spectrometer. Resonance of the FIR light with an IR-active vibrational mode of a given neutral cluster may lead to the absorption of several photons. The subsequent heating of the complex results in the evaporation of a loosely bound Kr ligand and a depletion of the corresponding mass spectrometric signal. Recording the mass-spectrometric signal while scanning the wavelength of FELIX leads to depletion spectra, from which absorption spectra \(\sigma(\tilde{v})\) are reconstructed (21).

Figure 1A shows the vibrational spectrum of neutral Au19 obtained with FIR-MPD of its complex with one Kr ligand. A number of bands were found in the region between 47 and 220 cm\(^{-1}\), usually having a full width at half maximum of less than 4 cm\(^{-1}\) (21). This is close to the spectral bandwidth of FELIX, which is about 2 to 3 cm\(^{-1}\) and nearly constant over the whole tuning range. The number of peaks implies a rather nonsymmetric structure for neutral Au7. The geometry of Au7 was established by comparing the experimental spectrum with the calculated vibrational spectra for multiple isomers predicted by density functional theory (DFT) calculations within the generalized gradient approximation (21, 22). We found a planar edge-capped triangle with \(C_3\) symmetry (Iso1) to be lowest in energy. This structure has been previously reported as the global minimum (23). A hexagonal planar structure (Iso2) (24) and a 3D structure (Iso3) (25) have been proposed as lowest-energy structures as well, but were computed to be higher in energy in the present study.

The experimental vibrational spectrum unambiguously tested the reliability of the theoretical methods. The calculated spectra were distinctive in the range between 150 and 220 cm\(^{-1}\). The peak positions of Iso1 fit with experimental absorptions at 165, 186, and 201 cm\(^{-1}\). Only the relative intensities of the bands did not agree completely; the central band at 186 cm\(^{-1}\) was much more pronounced in the experiment. Figure 1B shows the calculated absorption spectrum of the complex Iso1-Kr, in which Kr is bound to the energetically most favorable position of the Iso1 cluster with a bond dissociation energy of 0.09 eV. The positions of the resonances were not changed, but the relative intensities were substantially affected. The three bands were then in excellent agreement with the experiment, and, furthermore, all absorptions between 50 and 150 cm\(^{-1}\) became more pronounced (26). The calculations show that all of these vibrational modes are highly delocalized and involve the motion of all atoms in the cluster [see normal mode displacement vectors for the three highest-energy vibrations of Au19 (all in-plane) in fig. S3].

In principle, multiple isomers can be present in the molecular beam, in which case the spectrum would represent a superposition of their individual contributions. Iso2 has one strong absorption at
185 cm$^{-1}$, and its presence in the molecular beam could also explain the pronounced intensity of the central peak in the experimental spectrum. Ion mobility measurements, however, excluded the presence of major amounts of additional isomers for cationic and anionic Au$_{20}$. For experimental modes that were not present in the calculated spectrum of hexagonal Iso$_2$—for example, at 165 cm$^{-1}$ and 201 cm$^{-1}$—the mass-spectrometric intensity of Au$_7$Kr went down to below 30% of its original value when irradiated by FELIX, which set the upper limit for the abundance of other isomers. Therefore, although a minor contribution of Iso$_2$ could not be ruled out, the capped triangle could be assigned as the dominant structural isomer of neutral Au$_{19}$ present in our experiment.

On comparison with the experimentally determined structures of the corresponding ionic species, we found that Au$_{20}$ is a cluster size, which changes its geometries for each charge state. Although the cation is highly symmetric and corresponds to the $D_{2d}$ structure Iso$_2$ (12), the anion forms a threefold edge-capped square (11). We found this structure to be a saddle point in our calculations for neutral Au$_{19}$ that relaxes into Iso$_1$. The geometrical change as a function of cluster charge corresponds to a lessening of the average coordination as the electron density increases. Although the gold atoms in the cation have on average 3.43 nearest neighbors, this value decreases to 3.14 and 2.85 for the neutral and the anion, respectively. With additional electrons, the clusters favor more open structures.

Having shown that the experimental spectrum, in combination with theory, can be used to identify the geometry of the Au$_{19}$ cluster, we moved on to bigger sizes. Photoelectron spectroscopy and quantum-mechanical calculations have shown that anionic Au$_{20}$ is a pyramid and has $T_d$ symmetry (44). This structure has also been suggested to be the global minimum for neutral Au$_{20}$ (14). The FIR-MPD spectrum we measured of the Au$_{20}$Kr complex (Fig. 2A) was very simple, with a dominant absorption at 148 cm$^{-1}$, which already pointed to a highly symmetric structure. The calculated spectrum of tetrahedral Au$_{19}$Kr was in agreement with the experiment (Fig. 2C) and fig. S4 for the IR spectra of less stable isomers. In the FIR-MPD spectrum we measured of the Au$_{20}$Kr complex when the Kr ligands are included in the calculations, the main feature could not be ruled out, the capped triangle could be assigned as the dominant structural isomer of neutral Au$_{19}$ present in our experiment.

The search for electrolyte materials with high oxygen conductivities is a key step toward reducing the operation temperature of fuel cells, which is currently above 700°C. We report a high lateral ionic conductivity, showing up to eight orders of magnitude enhancement near room temperature, in yttria-stabilized zirconia (YSZ)/strontium titanate epitaxial heterostructures. The enhancement of the conductivity is observed, along with a YSZ layer thickness—indepedent conductance, showing that it is an interface process. We propose that the atomic reconstruction at the interface between highly dissimilar structures (such as fluorite and perovskite) provides both a large number of carriers and a high-mobility plane, yielding colossal values of the ionic conductivity.

Colossal Ionic Conductivity at Interfaces of Epitaxial ZrO$_2$.Y$_2$O$_3$/SrTiO$_3$ Heterostructures


The search for electrolyte materials with high oxygen conductivities is a key step toward reducing the operation temperature of fuel cells, which is currently above 700°C. We report a high lateral ionic conductivity, showing up to eight orders of magnitude enhancement near room temperature, in yttria-stabilized zirconia (YSZ)/strontium titanate epitaxial heterostructures. The enhancement of the conductivity is observed, along with a YSZ layer thickness—indepenent conductance, showing that it is an interface process. We propose that the atomic reconstruction at the interface between highly dissimilar structures (such as fluorite and perovskite) provides both a large number of carriers and a high-mobility plane, yielding colossal values of the ionic conductivity.

Solid oxide fuel cells (SOFCs) have emerged as a promising nonpolluting technology for the short-to-medium-term substitution of fossil fuels (1–4). The conversion efficiency of chemical into electrical energy is limited by the transport of oxygen anions through an elec-
Structures of Neutral Au$_7$, Au$_{19}$, and Au$_{20}$ Clusters in the Gas Phase
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Editor's Summary

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