Hydrogenated gold clusters from helium nanodroplets: displacement of \( \text{H}_2 \) by \( \text{H}_2\text{O} \)

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Abstract. Cationic clusters of gold, containing up to 8 atoms, and decorated with molecular hydrogen and water, were investigated with mass spectrometry. The clusters were grown as neutrals in superfluid helium nanodroplets that were ionized by electron impact. The resulting gas phase cluster cations exhibit magic sizes corresponding to the number of \( \text{H}_2 \) molecules that form the first solvation layer, consistent with previous findings. The presence of water is found to efficiently displace hydrogen, one \( \text{H}_2 \) molecule for each \( \text{H}_2\text{O} \). Our calculations show that the binding energy of water to the charged gold clusters is about twice as large as for hydrogen, though this depends on the charge of the clusters. This suggests that residual water could reduce the efficiency for metal particles to chemically store hydrogen gas, a promising technique for hydrogen fuel storage.

1 Introduction

The use of metal nanoparticles for high density \( \text{H}_2 \) storage is becoming increasingly relevant in modern fuel technology. Storing hydrogen gas in quantities required for, e.g. fuel cells, traditionally requires storing large amounts of the flammable gas in high pressure vessels, which involves undesired risks in commercial applications. An alternative approach involves chemical storage of hydrogen in a reversible fashion, so that the bound \( \text{H}_2 \) molecules can be released back into the gas phase before being extracted for use [1]. Particles of transition metals and their alloys are promising in this regard because of their moderate bond strengths with \( \text{H}_2 \) [2], which allows the bonds to be formed and broken by small changes in temperature and pressure [1,3]. A disadvantage of purely metallic matrices for hydrogen storage is the weight and cost of the (often precious) metals used [1], but this can be, at least partially, overcome by doping other materials with metal nanoparticles. Examples of this include the doping of carbon matrices with metal particles, as small as one or a few atoms, that act as nucleation sites for binding \( \text{H}_2 \) [4–6]. In this light, nanosize effects have become an important research focus as has nanoparticle protection against oxidation by \( \text{O}_2 \) and \( \text{H}_2\text{O} \), for example by using semipermeable protective layers that still allow \( \text{H}_2 \) to easily penetrate [1,7]. While platinum group metals have received much attention in hydrogen storage applications [1,5,6], gold too has become of interest as a substrate for \( \text{H}_2 \) storage because of its catalytic activity [8].

Previous experiments in our laboratory [9] have shown that \( \text{H}_2 \) molecules readily attach to gold clusters with up to at least 8 gold atoms when captured by superfluid helium nanodroplets. Helium nanodroplets are miniature cryo-vessels with equilibrium temperatures of 0.37 K that are extremely versatile for growing cold clusters from atomic and molecular building blocks [10,11]. Their high thermal conductivity and low temperatures mean that any captured dopants will be efficiently cooled to the temperature of the liquid and readily condense into clusters [10,11]. Using this technique to form hydrogenated gold clusters, the clusters were readily ionized by the presence of electron acceptors such as \( \text{He}^+ \) or proton donors such as \( \text{HeH}^+ \) following electron impact on the doped droplets, after which some \( \text{H}_2 \) elimination ensued due to the high excess energy of these processes [9]. There was no evidence for the dissociation of adsorbed \( \text{H}_2 \) molecules in that there was no indication of \( \text{H} \) elimination that might result from dissociation. The hydrogenated gold cluster ion distributions exhibited “magic” features that appear to reflect special stabilities for certain numbers of adsorbed \( \text{H}_2 \) molecules depending on the structure of the underlying (most often computed to be flat) Au cluster skeleton and the number of \( \text{Au} \) atoms exposed on the periphery. Shifts in magic numbers were suggested to reflect transitions
from 2D to 3D structures as the cluster size increases. The computed \( H_2 \) affinities of the cationic clusters were as high as 1.1 eV, but weakened with increasing cluster size [9].

Interestingly, we noted in these experiments that some residual water molecules became embedded in the hydrogenated gold clusters, apparently displacing more weakly bound hydrogen molecules. This led to an observed shift in the “magic” numbers corresponding to the reduction of the number of adsorbed hydrogen molecules by one for each additional water molecule. These observations provided an opportunity to investigate the “poisoning” of \( H_2 \) storage by water molecules and this is the focus of the experimental and theoretical study reported here.

2 Methods

2.1 Experimental details

An overview of the procedures involved in our experiments is provided schematically in Figure 1. A continuous beam of neutral He droplets was formed by the expansion of pre-cooled He gas (Messer, 99.9999% purity) with a backing pressure of 22.5 bar into vacuum through a nozzle with an inner diameter of 5 \( \mu \)m that was cooled to 9.55 K by a two stage, closed circuit helium cryocooler (SRDK-415D-F50H, Sumitomo Heavy Industries Ltd.). Under these conditions, droplets were formed following a broad log-normal size distribution and with a mean size on the order of 10\(^6\) He atoms. The central part of the beam then passed through a 0.8 mm diameter skimmer located 8 mm downstream from the nozzle before traversing a pair of sequentially pumped pickup chambers. In the first pickup chamber, molecular hydrogen gas (Messer Austria GmbH, purity 99.999%) was introduced by a gas line controlled with a needle valve. H\(_2\) molecules along the flight path of the He droplet beam were captured by the droplets where they were cooled to the 0.37 K equilibrium temperature of the liquid and could condense into clusters. Residual water molecules in the hydrogen gas line and from the walls of the pickup chamber were incorporated in the droplets too. The second pickup chamber, located 115 mm after the first one, housed an oven with a heating power of 118 W for evaporating solid gold at a temperature of approximately 950°C. The design of this oven is similar to the one reported by Feng et al. [12]. The gold vapor, mostly consisting of individual Au atoms, was picked up by the He droplets to condense together with the \( H_2/H_2O \) mixture already present therein. The vapor pressures in the two pickup cells were both on the order of 10\(^{-6}\) mbar.

The doped droplets were ionized by the impact of 85 eV electrons in a Nier-type ion source. When the droplets are struck by an electron, He\(^+\) is the main initial product. This charge then migrates through the droplet via resonant hole-hopping, on average about 10 times, until a He\(_2^+\) is expected to be formed (unless a dopant is encountered first) [13]. This ion may then be attracted by the dopants, which have higher polarizabilities than the surrounding He. Since the ionization energy of He is much higher than most dopants, the interaction between the He\(_2^+\) (or He\(^+\)) ion and the dopant will lead to a highly exothermic charge transfer reaction. The excess energy will heat the dopant cluster and have a strong influence on their final structures as they then cool. The measurable properties of the final products thus represent primarily their cationic forms, e.g. with regard to magic numbers, with the precise structures of their neutral precursors being of lesser importance. This method of ionizing He droplets typically deposits several charges to the droplets [14]. Charges in excess of the stability limit of the droplets will be expelled into the gas phase as the multiply charged droplets stabilize [14]. It is these gas phase charge carriers that we detect in our measurements.

Positively charged products were analyzed using a reflector time-of-flight mass spectrometer (Tofwerk AG, model HTOF) with a rated resolution of \( m/\Delta m = 5000 \). The recorded mass spectra were evaluated using the IsotopeFit software [15]. IsotopeFit is a tool for analyzing mass spectra that corrects for isotopic distributions and can deconvolute overlapping cluster distributions, allowing the user to extract the corrected abundances of different species. Additional experimental details can be found in references [16–18].

2.2 Theoretical details

Cluster geometries were determined using electronic structure calculations with the Gaussian 16 software package [19]. Second order Möller-Plesset (MP2) perturbation theory was used together with a def2-TZVP triple zeta basis set. For the Au atoms, core potentials belonging to this basis set were used for the inner electron shells that contain corrections for relativistic effects and speed up the
Fig. 2. Mass spectrum of cationic clusters formed from helium nanodroplets doped with H₂, atomic Au, and residual H₂O molecules and ionized by electron impact at 85 eV. The start of each cluster group is labeled by the number of gold atoms they contain. The dominating species are AuₙHₓ⁺ clusters. At masses up to about 500 u, the tail of the Heₙ⁺ cluster series is clearly visible. The inset is a close-up in which the water content of the clusters is easily seen.

3 Results and discussion

Figure 2 shows the intensity distribution obtained mass-spectrometrically for hydrogenated gold cluster cations with trace amounts of residual water content. The dominant species in the mass spectrum are Heₙ⁺ clusters, fragments of the large droplets from which the clusters are formed, and the series of hydrogenated gold clusters. However, substantial peaks are also observed for AuₙHₓ(H₂O)⁺ ions (with y = 1 and 2) among the many peaks for AuₙHₓ⁺ ions. An example of this is shown (for n = 5) in the inset of Figure 2. We do see some evidence of 3 water molecules binding to the AuₙHₓ⁺ clusters as well, but the weak signal and overlap with systems containing fewer water molecules and more hydrogen (with the same mass) make it difficult to reliably determine their abundances.

The panels in Figure 3 present measured size distributions extracted from the mass spectrum in Figure 2. Three series are shown for each gold cluster size from n = 1–8: purely hydrogenated AuₙHₓ⁺ clusters for x from 1 up to 20 (from Ref. [9]), and hydrogenated cationic gold clusters containing one and two water molecules, AuₙHₓ(H₂O)⁺ and AuₙHₓ(H₂O)₂⁺, respectively. The presence of oscillations and intense “magic” numbers in the distributions of the AuₙHₓ⁺ cluster sizes have been discussed previously [9]. The deviating trend in magic numbers with respect to hydrogenation for clusters containing 7 or more Au atoms were in the previous study suggested to reflect transitions from 2D to 3D structures as the cluster size increases. The addition of water molecules to the clusters shift the magic numbers of H atoms by 2 for each molecule that is added, at least for clusters sizes of n < 7. For n = 7 and 8, the trend is less clear but suggests that the effect of adding water to the clusters is weakened, although the increasing statistical uncertainties make it prohibitive to draw any strong conclusions.

For cluster sizes up to n = 6, the shift in the magic number of H atoms by two indicates that the water is effectively replacing one H₂ molecule. The process appears to be rather strong since the amount of water present in the experiment is expected to be considerably lower than the amount of hydrogen. Despite this, the yield of clusters containing a single water is of the same order of magnitude as the purely hydrogenated gold clusters. Another feature of the water-containing clusters is the enhancement of sizes larger than the magic numbers. This is most clear for larger systems (higher n) in which a second maximum is present in the range of 10 ≤ x ≤ 15. The magic numbers shown in Figure 3 signify the saturation of the gold clusters with hydrogen, effectively closing the first and most tightly bound solvation layer [9]. The second hump could be indicative of a second solvation layer, but calculations. The optimized structures were also evaluated with a vibrational analysis to determine that real potential energy minima were obtained and to determine the zero-point energy corrections. The initial structures of the studied clusters were based on geometries determined for pure gold clusters and complexes of gold and hydrogen, previously calculated at the same level of theory, which were re-optimized following the addition of water molecules [9]. Other tested structures did not result in more energetically favorable structures.
the role of water is not clear from the experimental data. One possibility is that the permanent dipole moment of
the H₂O molecules allows for a stronger interaction of the
outer solvation layers with the ionic cores of the clusters
compared to the non-polar H₂. This would presumably
only play a role if water molecules were present in the
outer solvation layer.

3.1 Computed structures of hydrogenated and
hydrated gold cluster cations

Figures 4 and 5 display the calculated structures for some
of the most abundant “magic” clusters of AuₙHₓ⁺ with
n = 1–3 and n = 4–6, respectively, in which up to 3
H₂ molecules are sequentially displaced by H₂O. All the
structures that are shown are planar in regard to the posi-
tions of the Au atoms. The calculations suggest that H₂O
molecules, like H₂, bind directly to Au atoms of the gold
cluster “skeleton” and that the extra H atom in the even-
numbered gold clusters (n = 2, 4, and 6) simply bridges
two Au atoms, giving a closed shell electron structure.
The geometries of the protonated, even-numbered clusters
show a strong resemblance to the next larger gold cluster
size (except for differences in the Au–H vs. Au–Au bond
distances). This is consistent with the similarities seen in
Au and H chemistry, where gold atoms often behave as
“large” hydrogen atoms [20–25]. The structures in which
H₂O molecules have displaced H₂ units show essentially no
change in their overall geometries; the water is effectively a
1:1 replacement for the hydrogen. From a structural stand-
point this explains the shift by 2H atoms seen in the clus-
ter yields in Figure 3 for each additional water molecule.
In the limit of fully hydrated clusters, these results are in
good agreement with previous results [26,27].
Table 1. The binding energy of an H$_2$O molecule bound to different sized gold-hydrogen clusters. The values in parenthesis are the ratios between the binding energy of H$_2$O and that of H$_2$: BE(H$_2$O)/BE(H$_2$).

| B.E. of H$_2$O to: | X = – | X = H | X = H$_2$ | X = H$_3$ |
|-------------------|-------|-------|----------|----------|
| AuX$^+$ | 1.65 eV (1.83) | 3.50 eV (1.56) | 2.26 eV (2.01) | – |
| Au$_2$X$^+$ | 2.25 eV (1.41) | 1.74 eV (2.02) | 1.15 eV (2.89) | 1.75 eV (2.00) |
| Au$_3$X$^+$ | 1.44 eV (1.96) | 1.69 eV (1.85) | 1.42 eV (1.92) | 1.34 eV (2.66) |
| Au$_4$X$^+$ | 1.27 eV (1.95) | 1.51 eV (1.97) | 1.16 eV (2.00) | 1.44 eV (2.02) |
| Au$_5$X$^+$ | 1.23 eV (1.88) | 0.99 eV (2.99) | 1.24 eV (1.82) | 1.55 eV (1.79) |
| Au$_6$X$^+$ | 1.35 eV (1.64) | 1.29 eV (2.44) | 0.99 eV (2.57) | 1.04 eV (2.73) |

As has been seen for other cationic gold-ligand complexes [28], our calculations indicate that the gold clusters preferentially form bonds with the one of the lone electron pairs on the O atom of the water molecules. For the structures studied here, the binding energy of the water molecule is on average 2.1 ± 0.4 times higher than the equivalent binding energy of an additional hydrogen molecule (see Tab. 1 and the lower panel of Fig. 6). Among these values there are some individual outliers, e.g., Au$_2$H$_2^+$ and Au$_3$H$^+$ where the binding energy of H$_2$O is close to three times higher than for H$_2$. Similarly, the ratio for Au$_5^+$ is only 1.4. These deviations appear mostly for open shell systems, which in general have weaker binding energies and larger relative fluctuations in the interaction energies between complex sizes. The structures of the Au skeletons are also more readily distorted by the attachment of ligands for the open shell systems. A similar effect was also seen for Au clusters interacting with imidazole [28] molecules, where open shell systems often had the loss of Au atoms as their lowest dissociation pathway instead the loss of ligand molecules. For the closed shell systems (i.e. odd numbers of Au atoms matched with even numbers of H atoms and vice versa), we instead see more consistent binding energies of both H$_2$O and H$_2$ adducts for all cluster sizes.

For comparison, we have also performed test calculations (for a few select geometries, not an exhaustive survey) of neutral gold dimers and trimers interacting with H$_2$ or H$_2$O. These showed that the binding energies are significantly lower than for the charged clusters, between 0.5 eV and 0.8 eV depending on the structure. As for the charged clusters, the water forms a stronger bond with the gold cluster than the hydrogen, but the ratio of binding energies is lower, with the highest being 1.3 for the neutral gold dimer. The relative interaction energies of water and hydrogen are thus dependent on the partial charges of the gold atoms in the cluster, which could potentially be tuned for metal particles in matrices.

Table 1 summarizes our computed values for the H$_2$O affinity for small Au clusters that are hydrogenated to varying degrees, Au$_n$H$_x$(H$_2$O)$^+$. We show graphically in the top panel of Figure 6 the variation of the H$_2$O affinity, BE(H$_2$O), the values displayed in Table 1. In the lower panel of Figure 6 we also show the calculated magnitude of the H$_2$O affinity relative to the H$_2$ affinity, BE(H$_2$O)/BE(H$_2$), for different extents of hydrogenation. Much like the binding energies of hydrogen atoms and molecules to gold clusters [9], the binding energy of water is highest for small gold clusters. For a single Au$^+$ the binding energies range between 1.32 eV and 3.50 eV depending on the degree of hydrogenation. The spread in binding energies decreases with increasing cluster size. For the largest clusters calculated in this study, containing 6 Au atoms, the energies range between from 0.99 eV for Au$_6$H$_2^+$ and 1.35 eV for Au$_6^+$ when interacting with a single H$_2$O molecule.

As has been seen for other cationic gold-ligand complexes [28], our calculations indicate that the gold clusters preferentially form bonds with the one of the lone electron pairs on the O atom of the water molecules. For the structures studied here, the binding energy of the water molecule is on average 2.1 ± 0.4 times higher than the equivalent binding energy of an additional hydrogen molecule (see Tab. 1 and the lower panel of Fig. 6). Among these values there are some individual outliers, e.g., Au$_2$H$_2^+$ and Au$_3$H$^+$ where the binding energy of H$_2$O is close to three times higher than for H$_2$. Similarly, the ratio for Au$_5^+$ is only 1.4. These deviations appear mostly for open shell systems, which in general have weaker binding energies and larger relative fluctuations in the interaction energies between complex sizes. The structures of the Au skeletons are also more readily distorted by the attachment of ligands for the open shell systems. A similar effect was also seen for Au clusters interacting with imidazole [28] molecules, where open shell systems often had the loss of Au atoms as their lowest dissociation pathway instead the loss of ligand molecules. For the closed shell systems (i.e. odd numbers of Au atoms matched with even numbers of H atoms and vice versa), we instead see more consistent binding energies of both H$_2$O and H$_2$ adducts for all cluster sizes.

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4 Conclusions

Previously we demonstrated experimentally that H$_2$ molecules readily attach to cationic gold clusters with up to at least 8 gold atoms that are formed from neutral parents grown in a He environment near zero K. Here we see that trace amounts of ambient water molecules can displace the adsorbed H$_2$. The computed H$_2$ affinities of the cation clusters are as high as 1.1 eV, but the equivalent...
H₂O affinities are here shown to be on average about two times higher for all cluster sizes. Despite the higher interaction energies, the water molecules do not significantly alter the structures of the hydrogenated gold clusters. In both cases, all of the lowest energy structures containing up to at least 6 gold atoms are found to be planar (with regard to the gold “skeleton”). In the experiments, the displacement of hydrogen molecules by water is evident from the shift in magic numbers associated with the closure of the first solvation shell by 2H atoms for each additional water molecule. This is true for cluster size up to 6 Au atoms, after which the trend is less clear. This switch occurs at the same size as the previously reported [9,29] transition from 2D structures of the Au “skeletons” to 3D geometries with increasing cluster size. These findings are also consistent with previous studies on gold-water complexes [26,27].

Our findings show that even trace amounts of water can interfere with the binding of molecular hydrogen to metal nanoparticles, and that this effect is charge dependent. For applications in hydrogen storage, our results indicate that nucleation sites used for binding H₂ could be susceptible to “poisoning” by much more tightly bound H₂O molecules, limiting the amount of hydrogen that can be stored in the presence of water. Technologies are available to alleviate this potential problem [7]. However, this also opens the possibility for applications in which the displacement of hydrogen by water is exploited. For example, water could be used to extract hydrogen stored on metal nanoparticles, where H₂O spontaneously triggers the release of H₂ from the surface. This process could then later be reversed by baking the system to evacuate the water before replenishing the storage device with hydrogen.

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Author contribution statement
The measurements were performed by P. Martini and M. Goulart. The calculations were performed by L. Lundberg. The data were evaluated and visualized by L. Lundberg and M. Gatchell. The manuscript was written and reviewed by M. Gatchell, D. K. Bohme, and P. Scheier. All the authors have read and approved the final manuscript.

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