Probing cluster structures with sensor molecules: methanol adsorbed onto gold clusters

R. Rousseau a, G. Dietrich b, S. Krückeberg c, K. Lützenkirchen b,1, D. Marx a,1, L. Schweikhard c, C. Walther b

a Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany
b Institut für Kernchemie, Universität Mainz, Fritz Strassmann Weg 2, 55099 Mainz, Germany
c Institut für Physik, Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany

Received 11 July 1998

Abstract

Structural, dynamical and electronic properties of the adducts formed by adsorbing methanol onto size-selected gold clusters are investigated using infrared multiple-photon dissociation spectroscopy of trapped AuqCH3OH, n ≤ 15, in conjunction with Car–Parrinello calculations. The C–O stretching vibration of the attached sensor molecule changes discontinuously as a function of cluster size, which is traced back to a change in dimensionality of the cluster structure.

Clusters bridge the gap between the molecular level and bulk behavior [1]. They also pave the way to study and design materials that are neither truly microscopic nor macroscopic in nature and thus combine aspects of both [2]. One emerging paradigm in the realm of nanoscience is the tunability or control of properties simply by changing the cluster’s size [2]. Thus, size-selectivity is a prerequisite of paramount importance. One of the chief quests is to determine the real-space structures of these clusters [1,2], which has been proven possible by comparing experimental to calculated spectra [3–6].

Much more scarce are analogous investigations that probe interactions between individual molecules and size-selected clusters as a function of cluster size [1,7,8]. Of course, the behavior of these adducts is diverse and one is flooded by a host of intriguing questions: how do the molecules adsorb, what is the nature of their bonding, do the properties of the attached molecule change as the cluster grows, and many others? Stimulated by these considerations, we focus the present joint experimental/theoretical study onto this emerging field. In particular, we use a rather weakly attached molecule, methanol, as a sensor to probe properties of size-selected gold clusters Auq+ that span the range from a single gold atom to n = 15. We find that the C–O vibrational frequency is tuned as a function of cluster size. Most interestingly, it is sensitive to a change in dimensionality from two-dimensional (2D) to three-dimensional (3D) structures.

A technique that is capable of probing the inter- and intramolecular binding of a cluster–molecule
adduct is vibrational infrared (IR) spectroscopy. Here, we induce dissociation of the adducts by IR photons which allows photoabsorption to be detected through a measurement of product masses \[9±18\]. In the present case, we employ a combination of a Penning ion trap for storage and ion cyclotron resonance for mass selection of adducts, multiple-photon dissociation, and time-of-flight (TOF) mass spectrometry \[17,19\]. In particular, Au\(_n^+\) clusters are produced by pulsed-laser vaporisation and are focused into a low-energy ion beam in ultra-high vacuum. After injection into a Penning trap, Au\(_n^+\)CH\(_3\)OH adducts with a well-defined \(n\) are prepared \[2\]. Subsequently the C–O stretching mode of methanol is excited by absorption of IR photons (\(\approx 0.12\) \text{eV each}) from a pulsed line-tunable CO\(_2\) laser. Vibrational predissociation leads to a rupture of the cluster–molecule bond and desorption of neutral methanol. The photodissociation products Au\(_n^+\) are then identified by axial ejection of all ions out of the trap and TOF mass analysis with a resolution of \(M/\Delta M = 100\).

As an example, we show for Au\(_5^+\)CH\(_3\)OH the relative number of produced Au\(_n^+\) fragment ions in Fig. 1. In order to derive a centroid frequency these photodissociation spectra are fitted by Lorentzians. For clusters with \(n = 3–7\) the peak of the resonance is located in the frequency range near the Q-branch of CO\(_2\) where no laser lines are available \[956–966\] \text{cm}^\text{–1}\). For these cases, the centroid frequencies could still be determined from the low- and high-frequency tails of the resonances; however, with somewhat larger systematic uncertainties of at most \(+3\) \text{cm}^\text{–1}. For \(n = 1,2\) photodissociation was not observed at any of the frequencies studied, but for \(n = 1\) we could still determine a clear upper frequency bound from photoabsorption data of Au\(^+(\text{CH}_3\text{OH})_2\).

As an example, we show for Au\(_5^+\)CH\(_3\)OH the relative number of produced Au\(_n^+\) fragment ions in Fig. 1. In order to derive a centroid frequency these photodissociation spectra are fitted by Lorentzians. For clusters with \(n = 3–7\) the peak of the resonance is located in the frequency range near the Q-branch of CO\(_2\) where no laser lines are available \[956–966\] \text{cm}^\text{–1}\). For these cases, the centroid frequencies could still be determined from the low- and high-frequency tails of the resonances; however, with somewhat larger systematic uncertainties of at most \(+3\) \text{cm}^\text{–1}. For \(n = 1,2\) photodissociation was not observed at any of the frequencies studied, but for \(n = 1\) we could still determine a clear upper frequency bound from photoabsorption data of Au\(^+(\text{CH}_3\text{OH})_2\).

Despite tremendous progress in handling individual molecules or size-selected clusters, it is not possible to address experimentally questions relating directly to cluster geometries, binding sites, etc. \[1\]. Here we use ab initio simulations to complement experiment. We performed ab initio molecular dynamics, simulated annealing and geometry optimization in the Car–Parrinello scheme \[20,21\]. In particular we use the local density approximation of Kohn–Sham density functional theory \[22\] supplemented by gradient corrections \[23,24\], represent the core electrons by pseudopotentials \[3\], and expand the valence orbitals in a 26 au non-periodic cubic box using plane waves with a cutoff of 50–90 \text{Ry}. We have studied the bare Au\(_n^+\) (with \(n = 1, 3, 5, 7, 9\) and 15, including two isomers for \(n = 7\) and 15) and Au\(_4^+\) clusters as well as their adducts with one CH\(_3\)OH molecule. The unknown structures of the bare Au\(_n^+\) clusters were determined as unbiased as possible by performing high temperature ab initio molecular dynamics runs followed by simulated annealing down to at least 10 \text{K} using different protocols, initial configurations and 50 \text{Ry}. In a second step, a methanol molecule was added to the pre-optimized Au\(_n^+\) clusters followed by molecular dynamics

\[2\] Formation of Au\(_n^+\) (CH\(_3\)OH)\(_n\) is achieved by pulsed inlet of methanol at a peak pressure of \(= 10^{-3}–10^{-4}\) \text{mbar}. After \(= 0.5\) \text{s reaction and equilibration time, the well-defined adduct Au\(_n^+\)CH\(_3\)OH (\(\approx 20–30\) ions for one experimental cycle) is mass-separated for the selected cluster size, \(n = 1–9, 15\). All other ions are radially ejected through excitation of their cyclotron motions at frequencies \(\omega = qB/M\) (\(q\), ion charge; \(B\), magnetic field of 5 \text{T}; \(M\), ion mass). Due to collisions the clusters may well be expected to be in thermal equilibrium with the gas molecules at 300 \text{K}.

\[3\] The pseudopotential for Au is scalar-relativistic with 11 valence electrons; see Ref. [25]
at 300 K and simulated annealing at 70 Ry. Finally, all clusters and adducts were fully optimized using local geometry optimization and 90 Ry. Harmonic vibrational frequencies were extracted for all Au₃CH₃OH as well as their per-deuterated analogues using static finite-differences. These frequencies are estimated to be converged to within about 5 cm⁻¹. In addition, we estimated anharmonic corrections by performing (after equilibration) 2.3 ps ab initio molecular dynamics runs for CD₃OD and the two representative adducts Au₃CD₃OD and Au₃CD₂OD at the experimental temperature 300 K. The relevant frequencies were obtained from the power spectra of the C–O stretch autocorrelation function. All reported frequency shifts Δν = νₓ−νₚ are based on the harmonic frequencies that were approximately corrected for the isotope effect and anharmonicity.

We first concentrate on the experimental findings (filled squares in Fig. 2): the gross picture is that the C–O frequency is lower in the adducts than in free methanol signalling a weakening of the C–O bond. The largest red shift Δν, which exceeds 100 cm⁻¹, is observed in the limit of n = 1. Increasing the cluster size to n = 3 the red shift is observed to drop significantly and to reach a plateau around 75 cm⁻¹ up to n = 7. Here, a second less pronounced step-like change occurs and the frequency shift seems to level off at about 60 cm⁻¹ for n ≥ 8 up to n = 15. This behavior is in contrast to neutral Mₙ-methanol adducts (Mₙ = Fe₃−ₐ₁₅, Cu₃−₁₁, Ag₃−₂₂ and Au₃−₁₃) where n-independent constant red shifts (in the range of 15–40 cm⁻¹) were observed [16,18]. The calculated frequency shifts Δν for the most stable adducts (open circles in Fig. 2) parallel the experimental findings. Based on odd-n clusters, we confirm essentially quantitatively the significant drop from n = 1 to 3 ≤ n ≤ 7 as well as the less pronounced step between 3 ≤ n ≤ 7 and n ≥ 9. Finally, we note that our neutral Au₃CH₃OH adduct leads to a shift of about 30 cm⁻¹, which is again in accord with experiment (25 cm⁻¹ using CD₃OH and 30 cm⁻¹ for CD₂OD) [18].

Having reproduced phenomenologically the measured frequency shifts, we are now confident of going beyond experiment and analysing these findings in microscopic detail. A central finding is that the step-like discontinuity at n ≥ 7 coincides with a change of dimensionality of the underlying cluster structure. The lowest energy isomer of the n = 7 adduct is 2D, whereas that of the n = 9 adduct is 3D. As a check, we optimized an Au₃CH₃OH isomer, but now 3D, which turned out to be 7.3 kcal/mol higher in energy. Its frequency shift (Δν, Fig. 2) does not fit the experimental trend as well as the planar isomer. For n = 15 we stabilized another isomer that was 22.1 kcal/mol higher in energy, which again does not follow the overall experimental picture. This suggests that we analyzed in the experiment low-energy isomers, which means that the adducts are well thermalized in the Penning trap prior to photofragmentation.

The cluster–molecule interaction is mediated via a direct Au*–O bond between one atom Au* of the gold cluster and the methanol molecule (see Fig. 3a for the representative case Au₃CH(OH). The adsorption site Au* turns out to be the lowest-coordinated gold atom that is available in each cluster, which is two for the 2D (n ≤ 7) and three or four for the 3D (n ≥ 9) clusters. This goes hand in hand with the dimensionality change of the cluster structure at n ≥ 7. In addition, the Au*–O bond distance in the lowest-energy adducts is shortest for n = 1 with 2.04 Å, increases to 2.09–2.10 Å for the 2D n = 3, 5, 7
species, and finally levels off to about 2.13–2.14 Å for the 3D n = 7, 9, 15 clusters. As with the measured vibrational frequencies, we uncover a clear discontinuous relationship between the cluster–methanol bond distance and the change of dimensionality. By far the longest distance 2.17 Å is found for the more weakly bound neutral Au₄(CH₃)OH adduct. In this case, the cluster–molecule interaction is too weak to turn the molecule into a sensor of the cluster’s structure, which explains the constant C–O frequency shifts found for various neutral adducts [16,18].

What remains to be understood is what type of interaction holds methanol and gold clusters together? This is achieved with the help of the electron localization function (ELF) [26,27] supplemented with its topological bifurcation analysis [28]. This function \( \eta(r) \) is large in regions where two electrons with antiparallel spin are paired in space, whence its maxima can be associated with attractor positions due to electron pairing and corresponding attractor basins. Thus, higher ELF values correspond to more tightly localized electron pairs in space and can be used to locate and interpret chemical bonding.

The ELF cut and the set of isosurfaces in Fig. 3b–f give a flavor of how this function looks for the Au₄(CH₃)OH adduct. For pure methanol we find that the ELF (not shown here but similar to Fig. 3) displays three attractors associated with the methyl C–H bonds (with high values \( \eta^{\text{max}} = 0.99 \) at their maxima), one attractor stemming from the alcohol O–H bond (\( \eta^{\text{max}} = 0.97 \)) and two attractors ascribed to the two lone pairs of electrons of the hydroxyl group (\( \eta^{\text{max}} = 0.93 \)). At \( \eta^{\text{max}} = 0.85 \) emerges the signature of the C–O bond, the attractor being located on the C–O bond axis but slightly displaced towards the more electronegative oxygen atom. At a bifurcation value of about \( \eta^{\ast} = 0.78 \) the four attractor basins around the hydroxyl group merge and form one basin and the corresponding confluence of the methyl moiety basins is established at \( \eta^{\ast} = 0.73 \). The merging of the methyl and hydroxyl ELF basins occurs at \( \eta^{\ast} = 0.55 \). This bifurcation hierarchy [28] is best summarized by the diagrammatic representation in Fig. 4a. The corresponding analysis of the isolated Au₄⁺ cluster in Fig. 4b is much less involved as all attractor maxima occur at essentially the same \( \eta^{\text{max}} = 0.41 \) followed by the coalescence of all basins at about \( \eta^{\ast} = 0.25 \).

The chemical bonding in the Au₄(CH₃)OH adduct can now be rationalized by comparing its ELF topology to that of the isolated Au₄⁺ and CH₃OH fragments with the help of Fig. 3 and Fig. 4. One can directly infer that the methanol molecule is arranged such that one of the hydroxyl lone pairs points directly towards the Au⁺ site. A corresponding attractor appears on the line connecting Au⁺ with O very close to the oxygen atom (see Fig. 3c). It has a less pronounced maximum electron pairing as the unperturbed lone pair in the free methanol (\( \eta^{\text{max}} = 0.88 \) versus \( \eta^{\text{max}} = 0.93 \)). This transmutation of one
particular lone pair into an Au\(^*\)--O bond leaves the electronic structure of the rest of the methanol molecule qualitatively untouched. As for the gold atoms, we see that the methanol adsorption localization at Au\(^*\) (\(\eta_{\text{max}} = 0.43\) versus \(\eta_{\text{max}} = 0.41\)), whereas the rest of the cluster remains essentially unperturbed. However, the increased pairing at Au\(^*\) is not spherical suggesting its polarization within the cluster due to the cluster--molecule interaction. This indicates that the bonding is made by charge transfer from methanol to the cluster, but such that the electrons within the cluster are redistributed making the bonding site Au\(^*\) the most positively charged gold atom; note that the positive charge is essentially equally distributed over all atoms in the pure Au\(_{\text{w}}\) clusters. Finally, we stress that we found this pattern to be generic for all species.

We interpret this scenario as being indicative of a classical coordination bond between methanol and the cluster where the ligand molecule partially donates electrons to a positively charged metal atom. Thus, the Au\(_{\text{w}}\)CH\(_2\)OH cluster adduct can be viewed as a gold complex compound. This goes hand in hand with the observation that generic coordination compounds typically have Au--O bonds similar in length to the Au--O bonds studied here. This identification allows one to make contact between the chemistry of gold clusters and that of coordination chemistry \(^{29}\), and may be a key to develop novel metal--organic junctions and interfaces.

**Acknowledgements**

It is a pleasure to acknowledge P. Ballone, J. Hutter, M. Kaupp, and T.P. Martin for insightful discussions. RR would like to thank NSERC Canada for financial support. We thank DFG and MWFZ Mainz for support of the experiment. The calculations were performed on the CRAY-T3E/816 of the Max-Planck-Gesellschaft.

**References**