

Activation of molecular oxygen by anionic gold clusters

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Nano and sub-nano particulate materials have been the subject of much recent theoretical and experimental study owing to their novel physical and chemical properties, often quite unlike those of the bulk phase. Perhaps some of the most investigated systems are those of the gold nano particles which demonstrate a remarkable catalytic activity, notably towards low temperature oxidation reactions involving molecular oxygen as first observed by Haruta *et al.*^[1]

Unlike other transition metal oxidation catalysts, which typically perform oxidation *via* the Mars-van-Krevelen mechanism,^[2] formation of the key O²⁻ intermediate is thermodynamically prohibited on gold and the mechanism by which gold nano-particles activate O₂ remains unclear. Furthermore, depending on the system, rather different mechanisms may be relevant; for example the catalytic activity of small Au clusters deposited on MgO substrates towards CO oxidation has been found to depend on the ability of the system to transfer electrons into the Au clusters, rendering them negatively charged.^[3] Other findings suggest that the activation of O₂ on deposited Au particles occurs at the three-phase boundary between the Au cluster, the metal oxide, and the gas phase.^[4] One experimentally fruitful approach to model this multiphase system has been to exploit the well defined environments and experimentally and theoretically tractable sizes of small gas-phase clusters, which have themselves been observed to catalyze oxidation reactions with molecular O₂.^[5]

The naturally emerging questions are, how is the molecular O₂ activated and which species are involved in the oxidation mechanism? One currently accepted picture comes from the observation that only the even sized Au cluster anions react with O₂, and then only bind a single O₂ per cluster.^[6] This reactivity has been correlated to the alternating electron affinities^[7] of the gold clusters which arise from their alternating closed-open shell electronic structure. It is therefore assumed that the activation of O₂ is through single electron donation from the anionic cluster into the O₂ π* orbital, which is anti-bonding in nature, and thus the O–O bond is weakened forming a superoxo (O₂⁻) moiety upon complexation. This picture has also been confirmed by theoretical studies.^[8] Some of the Au_kO₂⁻ complexes (k≤7) have been further characterized by anion photoelectron spectroscopy (PES) and although vibrational substructures have been observed these only lead to insights into the final state of the detachment process, *i.e.* the neutral complex.^[9] The PES spectra reveal that on small odd-sized Au cluster anions O₂ is

essentially molecularly physisorbed.^[9c] Significant differences in the reactivities towards O₂ have been used to discriminate between different isomers of gold cluster anions up to Au₁₈⁻.^[10]

As the activation of the O₂ molecule upon complexation changes the bond order this process can be sensitively probed using vibrational spectroscopy. For instance free O₂ has a stretching frequency of 1556 cm⁻¹ while electron transfer into the π* orbital successively lowers this frequency to 1074 cm⁻¹ for a superoxo, O₂⁻, or 866 cm⁻¹ for a peroxo, O₂²⁻, species.^[11] Here we analyze the bonding of O₂ in the complexes formed with anionic gold clusters using infrared multiple photon dissociation (IR-MPD) spectroscopy. All the experiments reported were performed using a molecular beam apparatus housed at the Free Electron Laser for Infrared eXperiments (FELIX) facility^[12] in Nieuwegein, the Netherlands. Full details of the machine can be found elsewhere^[13] but in summary clusters are formed via laser ablation from a solid target rod of gold and reacted at ~173 K with molecular O₂ which is pulsed into the reaction channel attached to the cluster source block. The IR spectra of the complexes are measured mass selectively by recording the changes in their mass spectrometric intensity as a function of the IR excitation frequency *i.e.* via depletion spectroscopy. In these experiments we covered the range from 700 to 1400 cm⁻¹ to include the regions where activated O₂ (O₂⁻ and O₂²⁻) would be expected to absorb, however, for all complexes investigated bands are only observed between 1000 and 1100 cm⁻¹.

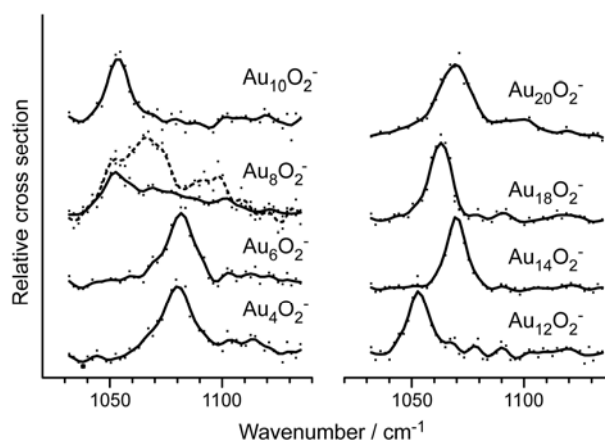


Figure 1: IR-MPD spectra of even sized gold cluster-oxygen complexes, Au_{2n}O₂⁻. The traces are a 5-point binomially weighted running average of the raw data points (black dots). For Au₈O₂⁻ two traces are shown, one continuous the other dashed and are intended to emphasize the different features observed in the spectra under different source conditions, see text.

Figure 1 shows the IR-MPD spectra recorded in each of the even sized anionic gold cluster-oxygen complex mass channels (Au_{2n}O₂⁻; n=2–7,9,10). The spectra are obtained from parent depletion spectra and then power normalized to yield a relative cross section. These were the only clusters in the size range investigated to show binding of O₂, in agreement with previous studies.^[6,7,9a,14] The non-

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observation of a Au_{16}^- cluster complex is also in agreement with previous studies and has been attributed to the spherical aromaticity of the cage-like Au_{16}^- which gives rise to an anomalously high electron affinity (EA) and therefore unfavorable electron donation.^[15] For all the $\text{Au}_{2n}\text{O}_2^-$ complexes the IR-MPD spectra show a band in a narrow range around 1060 cm^{-1} . This is a characteristic value for an O–O stretch of a superoxo moiety and can be assigned as such given that no other vibrational fundamentals are expected at this frequency.

With the exception of Au_8O_2^- all the spectra show only a single, relatively narrow ($\sim 15\text{ cm}^{-1}$ full width at half maximum) feature with a maximum depletion of $\sim 80\%$ of the initially observed signal intensity. The exact position of this band depends on the cluster size and varies by around $\pm 20\text{ cm}^{-1}$, although there doesn't appear to be a smooth monotonic trend with size, as for instance seen in the stretching frequency of CO bound to charged transition metal clusters.^[16] The general trend with growing cluster size is for $\nu(\text{O}-\text{O})$ to decrease until a minimum around $\text{Au}_{10}\text{O}_2^-$ and $\text{Au}_{12}\text{O}_2^-$ before $\nu(\text{O}-\text{O})$ increases again until $\text{Au}_{20}\text{O}_2^-$ which represents the largest size studied (Fig. 2a).

Au_8O_2^- is somehow special; a broader feature is seen which appears to be composed out of multiple, apparently three, not well resolved bands. The detailed shape of the band envelope sensitively depends on the cluster source and reaction conditions. As examples, two spectra are shown for Au_8O_2^- with the first one (continuous line) highlighting the most red-shifted peak centered at 1043 cm^{-1} and the second (dashed line) emphasizing the two features to the blue of this first one at 1059 cm^{-1} and 1102 cm^{-1} respectively. The sum of the depletions for all 3 features is greater than 100% , indicating interconversion between the isomers on the μs timescale of the experiment. The two different spectra correspond to slightly different O_2 and He carrier gas backing pressures which appear to sensitively influence the identity of the reacting gold clusters, the structure of the formed complexes with O_2 , or perhaps even both.

In order to obtain a more detailed insight into the O_2 binding geometries and to resolve the origin of the different features in the Au_8O_2^- spectra a series of density functional theory (DFT) calculations were performed on the smallest cluster sizes ($\text{Au}_{2n}\text{O}_2^-$; $n=2-5$), the results of which are summarized in Figure 2. The calculations were performed using the TURBOMOLE v6.2 package^[17] employing the TPSSH^[18] functional with the def2-TZVP^[19] basis set and a scalar relativistic potential for the core electrons of the Au atoms. Many starting geometries were tried using the ground and low-lying isomer structures from previous studies^[10b,c,20,21] as a basis for generating the oxygen complexes. The resulting putative ground state structures are given in Figure 2b and reveal two different binding motifs for O_2 : bridging (μ^2) and non-bridging (μ^1). The smaller clusters ($n=2,3$) favor μ^1 whilst the larger clusters ($n=4,5$) prefer μ^2 . Figure 2a compares the calculated $\nu(\text{O}-\text{O})$ frequencies with the experimental ones. Qualitatively the agreement is good with an almost uniform offset of $\sim 80-90\text{ cm}^{-1}$ between theory and experiment, lending weight to the validity of the calculations. Additional information, including higher energy isomers, can be found in the Supporting Information.

The structure of Au_4O_2^- is similar to the one reported before^[9b] with the O_2 binding to a two-coordinated Au apex atom. In Au_6O_2^- a similar binding is found. Au_8O_2^- is discussed in more detail below. For the pure Au_{10}^- metal cluster several isomers have been identified before via anion PES in combination with O_2 titration resulting in the conclusion that the most stable Au_{10}^- isomer (D_{3h}) is not reactive towards O_2 ^[10c,21]. We observe this in our mass spectrum as Au_{10}^- shows significantly less conversion into the oxygen complex and

thus the spectra reported herein are dominated by the (small) fraction of reactive Au_{10}^- isomers. The lowest energy structure of $\text{Au}_{10}\text{O}_2^-$ we identify corresponds to a cluster isomer which is not amongst the ones reported by Huang and Wang^[10c,21]. It is, however, formed upon attachment of O_2 to several of the energetically low-lying isomers reported by them and further relaxation. Whilst the O_2 complexes of the other planar Au_{10}^- structures are local minima, their O–O stretch typically appears at significantly higher frequencies than our assigned structure (e-I) although other only slightly higher lying isomers (d-I and d-III in the Supporting Information) cannot be ruled out. As there are no other features in the IR-MPD spectrum of $\text{Au}_{10}\text{O}_2^-$ this suggests that all these complexes relax into a single structure. $\text{Au}_{12}\text{O}_2^-$ shows a band very close to that of $\text{Au}_{10}\text{O}_2^-$ and it may be assumed that there is a similar O_2 binding geometry, involving a 7-Au atom hexagonal motif, which is known to be present for the planar isomer of Au_{12}^- ^[22] and a complex very similar to the ones seen for $\text{Au}_{10}\text{O}_2^-$ or Au_8O_2^- b-I can be formed from this species. For this size and the larger clusters, however, we have refrained from additional calculations. For the larger sizes the O–O stretching frequency increases. Neither Au_{14}^- nor Au_{20}^- are expected to possess the hexagonal motif observed in the Au_8^- – Au_{12}^- clusters and thus are expected to prefer an apex-binding mode, similar to that observed for Au_4O_2^- and Au_6O_2^- , as predicted by Molina and Hammer for $\text{Au}_{20}\text{O}_2^-$.^[23]

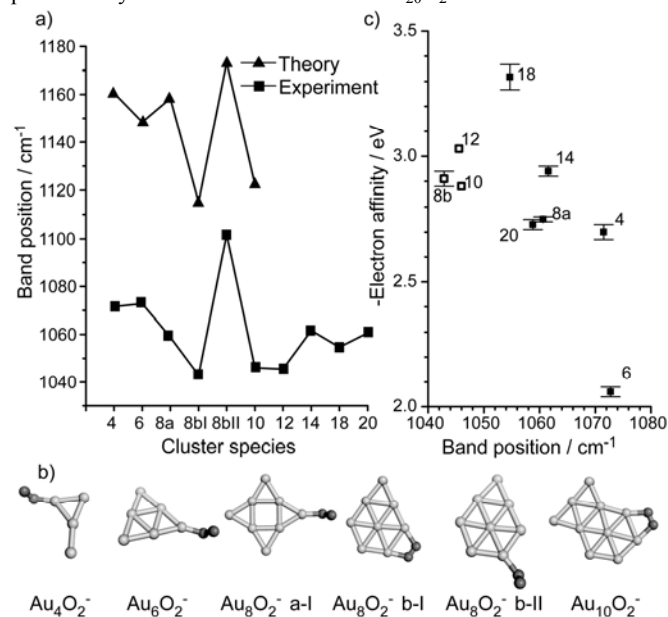


Figure 2: a) Comparison of the theoretically predicted and the experimentally observed O–O stretching frequencies. The connecting lines are given as a guide for the eye. The experimental error of the frequencies is estimated to be on the order of $\pm 3\text{ cm}^{-1}$. b) The structures corresponding to the putative global minima and two additional isomers for Au_8O_2^- . c) Correlation between electron affinities of the gold clusters and the experimentally determined $\nu(\text{O}-\text{O})$ values. 8b-II is not included as it is assumed to be an intermediate structure. For Au_{10}^- we have used an estimated EA based on the DFT calculations, see Supporting Information. The labels indicate which cluster (and isomer) the data refer to. Open squares are μ^2 type binding, closed μ^1 .

For Au_8O_2^- we experimentally observe a more complicated band structure, suggesting the presence of multiple isomers. From anion PES two isomers have been identified before, a planar star-shaped D_{4h} symmetric one (8a) and an edge-capped hexagon of C_{2v} symmetry (8b). The C_{2v} isomer has been reported to be more

reactive towards O₂.^[10b] This is in agreement with our finding of a μ^2 complex of 8b (isomer 8b-I) being the overall lowest energy configuration for Au₈O₂⁻, with the 8a-I complex predicted to lie 0.11 eV higher in energy and 8b-II 0.30 eV higher than that. Of all the structures calculated these three isomers also show the highest O₂ binding energy, ranging from 0.98 eV for the 8b-I isomer to 0.57 eV for 8b-II. The calculated frequency for 8b-I is rather low and can be related to the most red-shifted peak in the Au₈O₂⁻ spectrum. Isomer 8b-II, which can be viewed as a precursor to the formation of the more stable b-I isomer, but with a μ^1 bound O₂ has a $\nu(\text{O-O})$ about ~ 60 cm⁻¹ higher in frequency, which agrees with the width of the experimentally observed band pattern. For the second Au₈⁻ isomer the most stable O₂ complex (8a-I) shows a μ^1 O₂ bound to the two-coordinate apex atom, similar to the smaller Au_{2n}O₂⁻ complexes. Such a structure is predicted to give a $\nu(\text{O-O})$ which lies between those of the two 8b complexes and is only slightly too high for the experimentally observed middle feature.

One could wonder whether the variations in $\nu(\text{O-O})$ are, at least in part, determined by the electronic structure of the bare gold clusters. Electron affinities (EAs) are an easily accessible measure of this and Figure 2c shows a plot of the experimentally observed EAs (taken from references [10,21,24]) as a function of the observed $\nu(\text{O-O})$ frequency. For Au₁₀⁻ we instead use a calculated vertical detachment energy (VDE) for the Au₁₀⁻ parent isomer corresponding to the minimum energy structure of Au₁₀O₂⁻ as an experimental EA is not known (for details see the Supporting Information). For the non-bridging complexes (μ^1) we find an approximate anti-correlation between the EA and $\nu(\text{O-O})$, i.e. those clusters with a low EA show a stronger O-O bond and thus a high $\nu(\text{O-O})$. Such an observation is perhaps counter-intuitive as one would expect those gold clusters with a lower EA to be more likely to donate this electron density into the O₂ π^* -orbital, and give a weaker O-O bond and a lower $\nu(\text{O-O})$. According to Koopmans' theorem the EA of a species is a measure of the energy of its HOMO, ϵ_{HOMO} . A low EA corresponds to a higher lying HOMO, and thus a larger energy separation between it and the energetically much lower O₂ π^* -orbital (as $\text{IE}(\text{O}_2) \gg \text{EA}(\text{Au}_n)$), i.e. larger $|\epsilon_{\text{HOMO}} - \epsilon_{\pi^*}|$. When $|\epsilon_{\text{HOMO}} - \epsilon_{\pi^*}|$ is large the extent of overlap between the gold cluster HOMOs and the O₂ π^* is reduced, and thus less electron density is transferred into the O₂ π^* , resulting in the observed stronger O-O bond, and a higher $\nu(\text{O-O})$. Such a picture corresponds to a molecular variant of the Newns-Anderson binding model which has been used to rationalize the reactivities of noble metal surfaces with a variety of small ligands.^[25] Indeed it has also been shown by Hoffmann^[26] that such DOS pictures are intimately related to the frontier orbital ones, and thus applicable to the present discussion. Under this model, as the energy separation between the metallic d-bands and the adsorbate orbitals increases the resultant states, which are of cluster-O₂ anti-bonding character, begin to rise above the Fermi level. This has two effects, firstly, the aforementioned reduction in electron donation into the O₂ π^* and concomitant strengthening of the O-O bond, secondly the cluster-O₂ interaction is expected to strengthen, in agreement with previously reported reactivities^[7] in which Au₄⁻ and Au₆⁻ are the most reactive towards O₂ binding, despite in the present work showing the smallest activation.

In summary we have presented IR-MPD spectra of the anionic gold cluster O₂ complexes and show direct experimental evidence for the formation of a superoxo moiety upon complexation. The frequency of the $\nu(\text{O-O})$ vibration, and thus the extent of activation, can be approximately anti-correlated with the EA of the gold cluster. This is in contrast with the direct correlation previously established for the reactivities of the gold anions with O₂ and results in a picture

of the more reactive species leading to a weaker activation of O₂ which may have some bearing in future understanding of nano-sized gold catalysis.

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