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Direct observation of size dependent activation of NO on gold clusters†

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Vibrational spectra of NO ligands adsorbed on cationic gold clusters are obtained using IR multiphoton dissociation spectroscopy. We observe a strong oscillation of the NO stretching frequency with increasing cluster size that reveals a clear odd–even dependence in the strength of the NO bond. For the corresponding CO complexes, no oscillation is found. This behaviour can be understood on the basis of the character and occupation of the frontier orbitals of the complexes.

Small transition metal clusters or nanoparticles often show fascinating catalytic properties. This is true not only for “traditional” catalyst metals, such as rhodium or platinum, but also for gold that is usually thought of as being inert because of its bulk state properties. A striking example for this activity is the catalysis of the oxidation of carbon monoxide by molecular oxygen by Au₈ supported on MgO.¹ More generally there is a significant interest in understanding the mechanism of catalytic reactions and specifically in oxidation reactions on late transition metals. Technologically important examples are the catalytic treatment of motor vehicle exhaust gas using a Pt–Pd–Rh catalyst² or the selective epoxidation of ethylene on silver catalysts.³

Most of the mechanisms for metal activated oxidation reactions occurring on the surfaces of metals or on clusters in the gas phase are based on the initial activation of the oxidant molecule, *e.g.* O₂ or NO, by donation of electrons into its antibonding orbitals.⁴ The activity of an oxidation catalyst is therefore related to the electron density on the metal particle. This electron transfer formally leads to superoxide (O₂[−]) or peroxide (O₂^{2−}) intermediate species in the case of O₂ and to NO[−] for NO. For instance, in the case of small deposited gold clusters it has been found that the available partial charge on the cluster plays a significant role in determining catalytic activity.¹

Recently, some information on the nature of adsorbed oxygen species on gold clusters has been obtained by vibrationally resolved UV photoelectron spectroscopy of the anionic complexes Au_{*n*}O₂[−].⁵ For sizes of *n* = 2, 4, and 6 vibrational modes at ~1440, 1230, and 1450 cm^{−1}, respectively, have been found—frequencies that lie between typical values for the O–O stretch vibration of superoxides (~1150 cm^{−1}) and for free molecular oxygen (1555 cm^{−1}). However, because of the low reactivity of anionic gold clusters with an odd number of Au

atoms towards O₂, only the cluster complexes Au_{*n*}O₂[−] with even *n* have been characterized.

Here, we make a direct measurement of the degree of activation of NO adsorbed on small gold cluster cations in the gas phase as a function of cluster size by measuring the NO stretching frequency, $\nu(\text{NO})$. This frequency is directly related to the force constant of the N–O bond and hence to its strength. We find a pronounced alternating dependence of $\nu(\text{NO})$ on the number of gold atoms in the cluster, *n*, with the even *n* complexes having a lower $\nu(\text{NO})$ and hence a weaker N–O bond. This alternation is reproduced by density functional theory, DFT, and a resulting molecular orbital analysis shows that the low $\nu(\text{NO})$ on the even *n* clusters correlates with double occupancy of the NO 2 π^* orbital, whereas the higher $\nu(\text{NO})$ on odd *n* clusters correlates with single occupancy. In comparison, the stretching frequency of CO, $\nu(\text{CO})$, adsorbed on the same cationic gold clusters shows no odd–even dependence on *n*, reflecting the metal centred nature of the HOMO in Au_{*n*}CO⁺ complexes.

We obtain the vibrational spectra of gas phase gold cluster complexes by infrared (IR) multiphoton dissociation spectroscopy. The experimental methods are similar to those used earlier in our investigations of transition metal cluster carbonyls.^{6,7} The cluster cations are produced in a laser ablation source and reacted with NO or CO prior to expansion to form a molecular beam. They are detected downstream using time-of-flight mass spectrometry. Prior to detection they are subjected to intense IR laser radiation that causes dissociation of the ligand when resonant with an IR active mode. Mass spectra are collected as a function of laser frequency and IR absorption by a specific complex is registered by depletion of its peak in the mass spectrum. The reagent gas pressure is adjusted so that there is no interference in the resulting IR spectra from complexes with more than one ligand attached. The experiments make use of the Free Electron Laser for Infrared eXperiments (FELIX)⁸ at the FOM Institute for Plasma-physics “Rijnhuizen” in Nieuwegein, the Netherlands.

Fig. 1 shows the IR depletion spectra of small gold cluster cations with a single NO molecule adsorbed. The IR absorption band, that ranges between 1780 and 1860 cm^{−1}, is identified as NO atop bound in a nitrosyl complex by comparison with known coordination compounds.⁹ The odd–even oscillation in $\nu(\text{NO})$ that is immediately apparent continues out to at least *n* = 20, the extent of our measurements, as shown in Fig. 2(a). Fig. 2(a) also shows $\nu(\text{CO})$ for some monocarbonyl Au_{*n*}CO⁺ complexes measured in the same way. These species show no odd–even oscillation. A related odd–even oscillation has been reported in the relative binding energy of O₂ with anionic gold clusters as estimated from

† Electronic supplementary information (ESI) available: Details of the structures, energetics and vibrational frequencies of the Au_{*n*}NO⁺ and Au_{*n*}CO⁺ complexes from DFT calculations. See DOI: 10.1039/b511710k

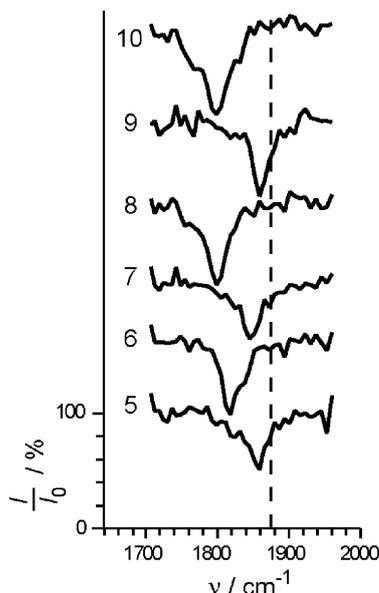


Fig. 1 IR multiphoton dissociation spectra of the NO complexes of cationic gold clusters Au_nNO^+ ($n = 5-10$). The dashed line indicates the frequency of the stretching vibration of free NO.

reaction studies made under equilibrium control.^{4e} Through correlation with the Au_n^- electron affinities, it was argued effectively that the biradical O_2 acts as an one-electron acceptor and that the stronger bonding of O_2 to odd-electron clusters results from pairing of electrons.

In coordination chemistry, the formalism that the NO ligand can bind as either NO^+ or as NO^- is used to understand the

existence of the two main classes of nitrosyl compound that were initially distinguished by the degree of bending in the M–N–O coordinate.⁹ In other words, NO can act either as an electron acceptor or an electron donor. Under this formalism, weakening of the NO bond, as indicated by lowering of $\nu(\text{NO})$, is indicative of the ligand binding as NO^- , due to the electron transfer increasing the occupancy of the π^* antibonding HOMO of NO. The odd–even oscillation in $\nu(\text{NO})$ is then simply understood through NO acting as an electron acceptor, with this interaction being significantly stronger for odd-electron Au clusters due to energy gains from electron pairing.

Au_2NO^+ is a special case. Although it contains an even number of gold atoms, it breaks the odd–even pattern with $\nu(\text{NO})$ even higher than in free NO (1876 cm^{-1}). Indeed, the fact that we observe Au_2NO^+ at all is also indicative of a different binding mechanism. Doubly charged Au_2^{2+} is calculated to be unbound leading to the expectation that the reaction with NO acting as an electron acceptor would lead to dissociation of the Au–Au bond. We propose that the strengthening of the NO bond in Au_2NO^+ , as indicated by $\nu(\text{NO})$, is indicative of the ligand binding as NO^+ , *i.e.* the binding of NO to Au_2^+ involves transfer of an electron from the π^* orbital of the NO to formally fill the hole in the HOMO of Au_2^+ . The electron transfer is feasible since the IP of Au_2 ($\sim 9.5 \text{ eV}$) is higher than that of NO, whereas all larger clusters have clearly lower IPs than NO.¹¹

To support our vibrational assignments and to develop a more complete frontier orbital picture of NO binding, we have carried out DFT calculations on the properties of the complexes of the gold cluster cations Au_n^+ up to $n = 8$ with NO and, for comparison, CO. Calculations on Au_nNO^+ have been reported before, however the observed oscillations in $\nu(\text{NO})$ are not reproduced.¹² The calculations on Au_nCO^+ agree mostly with earlier calculations.¹³ The planar geometries of the bare metal clusters are well established from ion mobility measurements¹⁴ and CO saturation studies.¹⁵ Moreover, the saturation studies show that the clusters retain their overall structure under the addition of successive CO molecules up to saturation. This means that the addition of a single CO or NO is not expected to cause isomerization of the cluster and extensive searches for structures with substantially rearranged cluster cores are not necessary. The structures of a comprehensive range of complexes with NO or CO initially adsorbed on different sites of the clusters, including atop (μ^1) bridging (μ^2) and three-fold (μ^3) arrangements, have been fully optimized, including the Au atom coordinates, using the TURBO-MOLE V5-7 DFT program package of Ahlrichs and coworkers¹⁶ using the included TZVP basis sets, the B3LYP functional and a relativistic effective core potential¹⁷ for the gold atoms.

We find that NO and CO bind exclusively in an atop arrangement and tend to favour low coordinated gold atoms. The lowest energy geometries are shown in Fig. 2(c). The only other stable structures found are also atop complexes, but with the ligand μ^1 bound to alternative edge Au atoms. The CO occupies the same sites as NO in most of the corresponding CO complexes, however it is always linearly bound. Details of the structures, energetics and vibrational frequencies of all calculated complexes are available as supplementary information.† The calculated ligand binding energies for the low lying complex structures are between -0.8 and -1.9 eV for Au_nCO^+ and -0.5 and -1.4 eV for Au_nNO^+ . The calculations started in μ^2 and μ^3 arrangements always converged to atop structures except in the case of the $\mu^2 \text{ Au}_3^+$ complexes. These converged to a transition state between two atop structures lying close in energy to the separate reactants.

The calculated $\nu(\text{NO})$ and $\nu(\text{CO})$ values are shown in Fig. 2(b). These stretching frequencies are scaled by a constant factor derived from the ratios of the experimental and calculated vibrational frequencies of the free ligand molecules

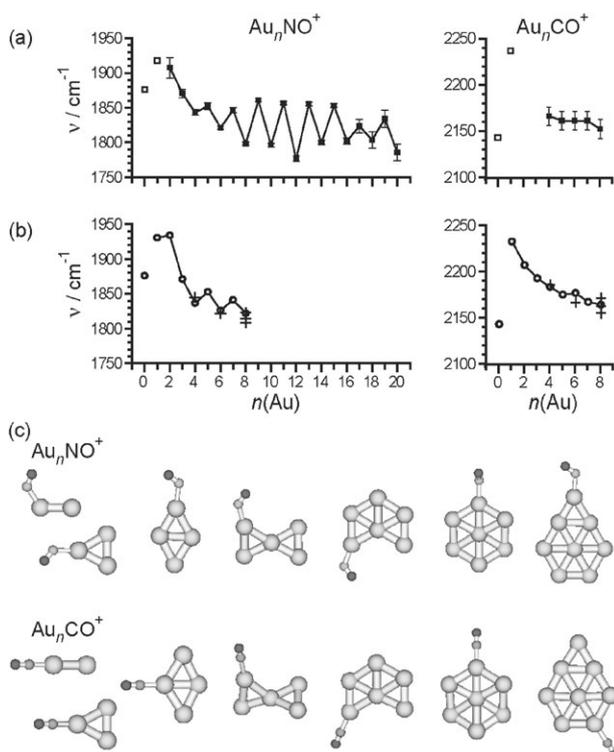


Fig. 2 Properties of Au_nNO^+ and Au_nCO^+ complexes. (a) Plots of the experimentally determined frequencies for the internal ligand stretches. Empty squares indicate the values for the free ligands and atomic gold complexes measured in rare gas matrices.¹⁰ The calculated frequencies of the ligand stretch vibrations of the complexes are shown in (b). The frequencies of the lowest energy structures are shown as circles. The crosses mark the frequencies of low-lying structures with the ligand bound in alternative atop positions. The calculated structures of the lowest energy complex are depicted in (c).

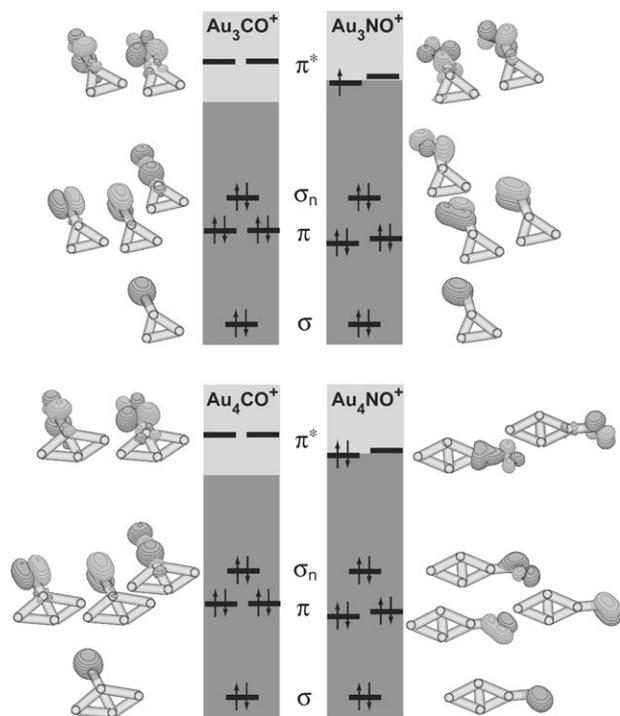


Fig. 3 Molecular orbital schemes for the NO and CO complexes of Au_3^+ and Au_4^+ . The density plots for the ligand localized orbitals and energy level ordering are from DFT calculations, although the relative energies are only indicated qualitatively. The energy ranges of the occupied metal centred orbitals are indicated by dark grey shading (dark blue in html).

(0.9506 for NO, 0.9671 for CO). There is good agreement with the experimental values of the internal stretching frequencies, confirming the spectroscopic assignment of $\nu(\text{NO})$ and $\nu(\text{CO})$ to atop bound ligands by comparison with known coordination compounds. In particular, the oscillations of $\nu(\text{NO})$ for the complexes of odd and even numbered gold clusters are reproduced, whereas for the CO complexes no oscillation is found. This conclusion holds even if we consider the frequencies for the other low lying atop isomers, as $\nu(\text{NO})$ and $\nu(\text{CO})$ are not markedly sensitive to the particular atop site occupied.

The bonding situation in the NO and CO complexes is illustrated using molecular orbital schemes in Fig. 3. We only depict those orbitals that have a strongly ligand centred character and that can be related to the corresponding orbitals of the free ligands. The relative energies and occupation numbers prove to be very similar for the energetically low lying σ , π and σ_n orbitals of NO and CO, however, there are pronounced differences for the π^* orbitals. In case of the NO complexes one π^* orbital forms the HOMO, whereas for the CO complexes both the HOMO and the LUMO are metal centred orbitals. For the CO ligands the π^* orbitals are significantly higher in energy (6.0 and 4.4 eV above the HOMO for $Au_3\text{CO}^+$ and $Au_4\text{CO}^+$, respectively). Due to these high energies the π^* orbitals of the CO ligands barely interact with filled metal centred orbitals of the gold cluster. As a consequence, the back-donation from the metal into the π^* orbitals is much less important for the binding of the CO ligands than it is in most other transition metal carbonyls. For the NO complexes the π^* orbital forming the HOMO is singly occupied for gold clusters Au_n^+ with an odd number of atoms and doubly occupied for even n . Therefore, the formal bond order of the NO is oscillating between 2.5 and 2. This oscillation in the bond strength is associated with an oscillation in the stretching force constant that is observed in the vibrational spectra.

In the case of $Au_2\text{NO}^+$ the HOMO has less pronounced π^* character and is mainly centred at the Au atom not binding to

the NO, as expected when NO acts as an electron donor. As a result, the binding situation in $Au_2\text{NO}^+$ is more similar to that in the carbonyls, with the vacated π^* orbitals forming the LUMO and LUMO + 1 orbitals. The different binding behaviour also affects other molecular properties. The NO bond length in $Au_2\text{NO}^+$ is calculated to be 1.11 Å, clearly shorter than in the larger complexes where it is calculated to be in the range of 1.13–1.14 Å. The NO is also much stronger bound with a binding energy of ~ 1.4 eV, whereas that value is within 0.5–0.8 eV for the larger cluster nitrosyls. Interestingly, the calculations predict for the Au–N–O angle in $Au_2\text{NO}^+$ a value of 127° that is within the range covered by the larger complexes of 123 – 129° (only $Au\text{NO}^+$ is linear^{10a}). This is not too surprising considering the recognized limitations of the formal assignment of the NO complexes to NO^+ vs. NO^- species on the basis of the M–N–O bending angle.⁹

The spectroscopically proven oscillation of the NO bond order implies a size dependence in the ability of NO to oxidize molecules such as CO on the surface of small gold clusters. So far we have not observed reactions between co-adsorbed CO and NO molecules on cationic gold clusters at room temperature. Nevertheless, the interaction of NO with gold clusters forms a model for more reactive transition metals, e.g. rhodium, where the catalytic oxidation of CO by NO is of great interest.³ In preliminary experiments we find that rhodium clusters are too reactive at room temperature to capture the molecular NO complex. Related to this, dissociative chemisorption of NO on Rh_6^+ has recently been deduced from ion trap experiments.¹⁸ On gold at elevated temperatures one may expect also to induce dissociation of NO that could be probed by a disappearance of the $\nu(\text{NO})$ band. Thus we propose the cationic gold clusters as a model system to study the size and temperature dependent reactivity of NO or similar oxidants.

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