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 (O22−) 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 Au8O4−.2 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 (1535 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 Au8O4− with n = 6 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, ν(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 ν(NO) on the number of gold atoms in the cluster, n, with the even n complexes having a lower ν(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 ν(NO) on the even n clusters correlates with double occupancy of the NO 2p* orbital, whereas the higher ν(NO) on odd n clusters correlates with single occupancy. In comparison, the stretching frequency of CO, ν(CO), adsorbed on the same cationic gold clusters shows no odd–even dependence on n, reflecting the metal centred nature of the HOMO in AunCO+ 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.4,5 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)6 at the FOM Institute for Plasmaphysics “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.7 The odd–even oscillation in ν(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 ν(CO) for some monocarbonyl Au5CO+ 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

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

reaction studies made under equilibrium control. Through correlation with the Auₙ⁺ electron affinities, it was argued effectively that the biradical O₂ acts as an one-electron acceptor and that the stronger binding of O₂ 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. 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 ϵ(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 ϵ(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.

Au₂NO⁺ is a special case. Although it contains an even number of gold atoms, it breaks the odd–even pattern with ϵ(NO) even higher than in free NO (1876 cm⁻¹). Indeed, the fact that we observe Au₂NO⁺ at all is also indicative of a different binding mechanism. Doubly charged Au₂⁺ 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 Au₂NO⁺, as indicated by ϵ(NO), is indicative of the ligand binding as NO⁺, i.e. the binding of NO to Au₂⁺ involves transfer of an electron from the π* orbital of the NO to formally fill the hole in the HOMO of Au₂⁺. The electron transfer is feasible since the IP of Au₂⁺ (≈ 9.5 eV) is higher than that of NO, whereas all larger clusters have clearly lower IPs than NO.

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 Auₙ⁺ up to n = 8 with NO and, for comparison, CO. Calculations on Au₂NO⁺ have been reported before, however the observed oscillations in ϵ(NO) are not reproduced. The calculations on Au₂⁺CO agree mostly with earlier calculations. The planar geometries of the bare metal clusters are well established from ion mobility measurements and CO saturation studies. 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 (μ¹) bridging (μ²) and three-fold (μ³) arrangements, have been fully optimized, including the Au atom coordinates, using the TURBOMOLE V5-7 DFT program package of Ahlrichs and coworkers using the included TZVP basis sets, the B3LYP functional and a relativistic effective core potential 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 μ¹ bound to alternative edge Au atoms. The CO occupies the same sites as NO in most of the corresponding NO 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 Au₂⁺CO³⁻ and 0.5 and 1.4 eV for Au₂NO⁺. The calculations started in μ² and μ³ arrangements always converged to atop structures except in the case of the μ² Au₃⁺ complexes. These converged to a transition state between two atop structures lying close in energy to the separate reactants.

The calculated ϵ(NO) and ϵ(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.
the NO, as expected when NO acts as an electron donor. As a result, the binding situation in Au$_2$NO$^-$ is more similar to that in the carbynols, 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$_2$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$_2$NO$^-$ a value of 127° that is within the range covered by the larger complexes of 123–129° (only AuNO$^+$ is linear$^{18}$). 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.$^{19}$ On gold at elevated temperatures one may expect also to induce dissociation of NO that could be probed by a disappearance of the ω(NO) band. Thus we propose that 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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