Optical absorption by magnesia-supported gold clusters and nanocatalysts: effects from the support, cluster and adsorbants

Michael Walter and Hannu Häkkinen

Department of Physics, Nanoscience Center, FIN-40014 University of Jyväskylä, Finland

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Abstract

Polarization-resolved optical spectra of magnesia-supported gold clusters Au$_N$/MgO ($N=1,2,4,8$), bound at a surface color center $F_s$ of the MgO(100) face, are calculated from the time-dependent density functional theory. The optical lines for $N=1,2$ are dominated by transitions that involve strong hybridization between gold and $F_s$ states whereas for $N=4,8$ intracluster transitions dominate. The theoretical optical spectra are sensitive to cluster structure and adsorbants (here CO and O$_2$ molecules on Au$_8$/F$_s$@MgO) which suggests polarization-resolved optical spectroscopy as a powerful tool to investigate structures and functions of chemically active, supported clusters.

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I. INTRODUCTION

Investigations of the physical and chemical properties of metal clusters are currently largely motivated by the question how their various remarkably size-dependent properties could be best utilized while the clusters are interacting with the environment, e.g., bound on or implanted in a support, or stabilized and surface-passivated by molecules. Understanding factors that dictate the stability, structure and function has relevance regarding atomic-scale design of components that could be of potential use in future nanotechnologies. To this end, spectroscopic tools and density functional theory (DFT) calculations can provide valuable insights.

Gold clusters and nanoparticles have attracted much attention recently due to their remarkable chemical and optical properties (for recent reviews, see e.g., 2,3). Gold clusters with a size of just a few atoms, supported by thin MgO films, have turned out to be paradigms to provide insight into the importance of quantum finite size effects in nanoscale chemistry – it has been demonstrated that by changing the size or elemental composition of the supported cluster even atom by atom one can quite dramatically affect the catalytic properties of the cluster4,5. Earlier DFT calculations have shown that the finite-size effects in the electronic spectrum of the nanocatalyst play a key role in CO oxidation reaction through binding and activating the oxygen molecule via a charge-transfer mechanism. Theoretical predictions4,5 of charging of the catalytically active Au$_8$ cluster, bound at the surface color center $F_s$ of the MgO film, were confirmed very recently by FTIR spectroscopy6.

Spectroscopic data on structure of supported metal clusters and ultrafine nanoparticles are still relatively scarce, with some notable exceptions from STM and STS spectroscopy7,8. Optical spectroscopy is currently a largely unexplored area, although it has long been used to study metal clusters in gas phase9. Here we present a systematic theoretical investigation of the optical properties of MgO-supported gold clusters, Au$_N$/MgO with $N \leq 8$, by analyzing the optical spectra calculated from the linear response time-dependent DFT (TDDFT). We discuss (i) the effects from the support, particularly from the $F_s$ states, dominating the spectra of $N = 1, 2$, (ii) the sensitivity of the spectra to the atomic structure of the cluster with examples for $N = 4, 8$, and finally (iii) the sensitivity of the spectra to adsorbants, by taking the example of CO and O$_2$ adsorption on the smallest CO-oxidizing cluster Au$_8$/MgO. It is shown that for all these cases, polarization-resolved spectra contain rich information.
on the nature of the dominant optical transitions and their connection to the structure and shape of the adsorbed cluster.

II. GROUND-STATE DFT CALCULATIONS

The atomic and electronic structure of the supported AuN/MgO system (comprising the vicinity of the color center of the MgO(100) surface, the adsorbed AuN cluster, and O2 and CO molecules) were calculated within the DFT in combination with Born-Oppenheimer (BO) Molecular Dynamics (MD)\textsuperscript{10} including self-consistent gradient corrections via the so-called PBE-GGA functional\textsuperscript{11}. Au(5d\textsuperscript{10}6s\textsuperscript{1}), Mg(3s\textsuperscript{2}), C(2s\textsuperscript{2}2p\textsuperscript{2}), and O(2s\textsuperscript{2}2p\textsuperscript{4}) electrons were included in the valence, and the interaction to the ion cores was described by scalar-relativistic non-local norm conserving pseudopotentials devised by Troullier and Martins\textsuperscript{12,13}.

The MgO surface is modelled by a two-layer ab initio cluster Mg\textsubscript{m}O\textsubscript{m} or F\textsubscript{s}@Mg\textsubscript{m}O\textsubscript{m-1}, embedded in an extended point-charge lattice to include effects of the long-range Madelung potential\textsuperscript{14}. For the embedding lattice, around 2100 alternating charges of +2 and -2 representing Mg and O ions, respectively, were used. In addition, those positive point charges that would be nearest neighbors to the peripheral O atoms of the central ab initio Mg\textsubscript{m}O\textsubscript{n} cluster have been replaced by "empty" Mg pseudopotentials (MgPP) in order to prevent unphysical polarization effects to O ions (see visualization of Au/Mg\textsubscript{13}O\textsubscript{13} in Fig. 1a)\textsuperscript{14}. The lattice parameter of the embedding part is fixed to the experimental lattice constant (4.21 Å) of bulk MgO. The cluster, molecules and nearest-neighbor Mg ions to the F\textsubscript{s} are treated dynamically in structural optimizations that included both steepest-descent and quenched molecular dynamics runs\textsuperscript{5,15}.

III. LINEAR-RESPONSE TDDFT CALCULATIONS

We follow the formulation of the linear response time dependent DFT given by Casida\textsuperscript{16} as implemented in ref.\textsuperscript{17}. Briefly, in order to get the weights \(F_I\) and energies \(\hbar\omega_I\) of optical transitions \(\{I\}\), one solves an eigenvalue problem \(\Omega F_I = \omega_I^2 F_I\) where the \(\Omega\) matrix elements are given by

\[
\Omega_{ij,kl} = \delta_{ik}\delta_{jl}\varepsilon_{ij}^2 + 2\sqrt{n_{ij}\varepsilon_{ij}n_{kl}\varepsilon_{kl}}K_{ij,kl}.
\]
Here \( \varepsilon_{ij} = \varepsilon_j - \varepsilon_i \) and \( n_{ij} = n_i - n_j \) are the difference of the KS particle-hole eigenvalues and occupation numbers, respectively. \( K_{ij,kl} \) is a coupling matrix that describes the linear response of the electron density \( \rho \) to the single-particle – single-hole excitations in the basis spanned by the ground state KS orbitals \( |i\rangle \). The transition matrix element in polarisation direction \( \hat{\epsilon}_\nu \) is

\[
(M_I)_\nu = \sum_{ij} \sqrt{\varepsilon_{ij}n_{ij}} \langle j | r_\nu | i \rangle (F_{ij})_{ij} \tag{2}
\]

and the corresponding polarization-dependent and polarization-averaged oscillator strengths are \( (f_I)_\nu = 2|(M_I)_\nu|^2 \) and \( \bar{f}_I = (1/3) \sum_{\nu=1}^{3} (f_I)_\nu \), respectively. The convergence of the spectra (oscillator strengths and energies of the major peaks) depends basically on three factors: (i) extent of the KS particle-hole basis, (ii) size of the plane-wave grid, and (iii) size of the ab initio \( \text{Mg}_m\text{O}_n \) cluster. Factors (i) and (ii) determine the quality of discretization of the continuum virtual states while factor (iii) dictates the overall behavior in the optical response of the MgO support - specifically the width of the band gap. We have carefully tested the convergence behavior of the calculated spectra in case of the smallest supported clusters \( (N=1,2) \) by using \( \text{Mg}_m\text{O}_{m-1} \) clusters extending up to \( m = 49 \). The converged theoretical optical band gap of the support is about 4 eV, which is in a fair agreement with the apparent gap of 6 eV measured for a few-layer thick MgO film\(^{18}\), taking into account the general tendency of DFT to underestimate band gaps of wide-gap insulators. However, the important transitions induced by the supported cluster fall into the band gap. These transitions can be calculated within 0.1 eV accuracy even with significantly smaller cluster sizes \( (m = 13, 25) \).

**IV. RESULTS AND DISCUSSION**

Application of the TDLDA method to an isolated gold atom leads to the optical spectrum shown in the inset to Fig. 1b (for comparison, we show also the optical spectrum based on KS-only transitions, i.e., by setting \( K_{ij,kl} = 0 \) in Eq. (1)). This spectrum was calculated by considering the \((5d^{10}6s^16p^07s^07p^0)\) KS states in the particle-hole basis. The KS spectrum consists of two strong transitions corresponding to single-particle excitations of \( 6s \to 6p \) (5 eV) and \( 5d \to 6p \) (6.1 eV). The lowest TDLDA optical line is found at 5.23 eV and it is an incoherent (destructive) superposition of the KS transitions \( 6s \to 6p \) and \( 5d \to 6p \) (the destructive interference is manifested by the reduced oscillator strength of the 5.23
FIG. 1: (color online) The supported Au atom: a) The ab initio cluster Au/Mg\textsubscript{13}O\textsubscript{13} with the peripheral “empty” MgPP sites, b) the polarization averaged spectrum (the inset shows the spectrum of a gas phase Au atom), c) the polarization resolved spectrum. d) and e) are polarization averaged and resolved spectra for the atom on F\textsubscript{s}. All spectra here and in subsequent figures are plotted by using a Lorenzian folding of 0.08 eV of individual optical lines. Note, that the spectra in d,e have been calculated for Au/F\textsubscript{s}@Mg\textsubscript{25}O\textsubscript{24}.

eV TDLDA line compared to the neighboring KS lines). Our result of 5.23 eV is in a fair agreement with the lowest experimental spin-orbit (SO) split transitions at 4.63 eV ($^{2}S_{1/2} \rightarrow ^{2}P_{1/2}$, final single-particle state assigned as (5$d^{10}6p^{1}$)) and 5.11 eV ($^{2}S_{1/2} \rightarrow ^{2}P_{3/2}$ (5$d^{10}6p^{1}$))\textsuperscript{19} taking into account the fact that the SO effect is not included in our calculations. Similarly, the next strong TDLDA transition at 7.3 eV corresponds to the experimental SO doublet 7.44 eV and 7.53 eV, assigned to transitions to the $^{2}P_{1/2}$, $^{2}P_{3/2}$ states with a (5$d^{10}7p^{1}$) single-particle configuration\textsuperscript{19}. We also note here, that another recent TDDFT calculation\textsuperscript{20} finds the first optical transition of an isolated Au atom at 5.23 eV, in full agreement with our result\textsuperscript{21}.

For the combined Au/MgO system, we find the lowest strong transitions at 3.38 eV and 3.61 eV, i.e, in the near-UV region (see Fig. 1b). The nature of these lines is revealed
FIG. 2: (color online) a) Two configurations for Au$_2$ bound to $F_s$, b) polarization averaged and c,d) resolved spectra. $d$(Au-Au)=2.61 Å and 2.62 Å for "up" and "tilted" geometries, respectively, compared to the gas-phase value of 2.55 Å.

by the the polarization-resolved spectra (Fig. 1c) which shows basically three peaks that have degenerate ($f_I$)$_v$ values, two of which (x,y polarization) at 3.38 eV and the z-polarized transition (i.e., excitable for z-polarized light) at 3.61 eV. The identical oscillator strengths in the x,y,z directions and the degeneracy pattern strongly suggest that these transitions mainly originate from the Au atom, perturbed and shifted by the support. (Note that neither the ideal MgO surface nor the gas phase atom have transitions anywhere near 3.5 eV). One can also locate a set of weak transitions in the region 1.7 eV – 1.9 eV that consists of three weak lines, of which two are z-polarized and one xy-polarized. In general, these lines are due to incoherent mixing of several KS transitions, but we note that they have a component of the atomic 5$d$→ 6$s$ character, which is dipole-forbidden in the gas phase atom but becomes partially "visible" via mixing with the substrate states.

The situation is dramatically changed when the $F_s$ defect is introduced (Fig. 1d,e). Several strong lines are now seen in the range 1.8 eV – 3.5 eV. Fig. 1e reveals strikingly that basically all of the transitions are polarized only in the z-direction, i.e., perpendicular to the surface. A stronger coupling to the $F_s$ states also enhances the oscillator strength of the bands around 2 eV which have the contribution from the gas-phase forbidden 5$d$→ 6$s$ transition.

For Au$_2$, bound at $F_s$, we have found two almost isoenergetic geometries (Fig. 2a); the
FIG. 3: (color online) The configuration a) and polarization resolved spectrum b) of Au₄ bound to Fₛ.

"tilted" geometry with the Au-Au axis 33° from the surface normal is 0.1 eV more stable than the dimer standing "up". This slight difference in the adsorption geometry shows up drastically in the TDLDA spectrum (Figs. 2b-d): the "up" geometry has transitions only in the z-direction whereas the spectrum of the "tilted" cluster has a clear y-component at 3.1 eV (y is the direction to which the dimer is tilted). Based on the clear difference between the TDLDA spectra in Figs. 2b-d we predict that in this simplest non-trivial case of adsorption of a gold cluster on the defect site of MgO surface, experimental optical spectra could yield a definitive answer on the binding geometry.

Au₄, whose optimum binding geometry has previously been found to be that of a tilted rhombus-like structure⁵ (Fig. 3a), has a very strong transition close to 2.5 eV (Fig. 3b). This transition is solely in the direction of the long axis of the cluster. The tetramer is thus the smallest cluster which "screens out" the transitions involving major (z-)components from the color center, which had been found to be dominant for the monomer and dimer.

We now turn to discussion of the optical properties of the "smallest MgO-supported nanocatalyst" for CO oxidation, namely Au₈⁴,⁵,⁶ Two isomeric structures were discussed in Ref.⁵, where the open structure A is more stable than the compact structure B by 0.3 eV (see Fig. 4a, note that similar geometric motifs yield locally stable isomers also for neutral gas-phase gold octamers where open structures are favored due to relativistic bonding effects²²,²³). Fig. 4b shows that these two isomers yield very different, characteristic spectra: while the more stable open structure A has a series of intense transitions covering most of the optical range and yielding characteristic line shapes, the spectrum of structure B has less oscillator strength below 2.7 eV. Fig. 4c gives more insight into the strong absorption bands at 2.1 eV, 2.4 eV, and 2.65 eV of structure A: they are mostly transitions involving the long axis (∼y-direction) of the cluster. Bands after 3 eV start to have major contributions also from transitions in the other two polarization directions. Again, Figs. 4b-c suggests that in
FIG. 4: (color online) Au$_8$ on $F_s$: a) Two configurations and b) their polarization averaged spectra. c) The polarisation resolved spectra of structure A.

FIG. 5: (color online) Au$_8$ and absorbed molecules on $F_s$: a) The configurations of the adsorbed molecules and the spectra of b) structure A with and without O$_2$ and c) structure B with and without CO/O$_2$.

principle it should be possible to distinguish different isomers of adsorbed gold octamers via high-resolution optical data.

Finally, we show examples about modification of the optical spectra by adsorbant molecules in Fig. 5, here CO and O$_2$. Fig. 5b shows that adsorption of the O$_2$ molecule
TABLE I: Local charges on the constituents of the structures shown in Figs. 4a) and 5a). Support includes the MgO surface with the color center.

| Structure | Au$_8$ | CO | O$_2$ | support |
|-----------|--------|----|-------|---------|
| A         | -0.37  |    | +0.37 |         |
| A+O$_2$   | +0.73  | -1.26 | +0.53 |         |
| B         | -0.20  |    | +0.20 |         |
| B+O$_2$   | +0.60  | -1.11 | +0.51 |         |
| B+CO      | +0.38  | -0.51 | +0.13 |         |

to the structure A of the gold octamer strongly suppresses the absorption bands at 2.1 eV, 2.4 eV, and 2.65 eV, furthermore, a new clear absorption band appears now at 1.5 – 1.7 eV. Analysis of the polarization-resolved spectra (not displayed) shows disappearance of the bands connected to excitations along the long axis of structure A. On the other hand, adsorption of CO or O$_2$ to the structure B of Au$_8$ does not significantly modify the absorption spectrum below 3 eV (Fig. 5c). This finding can be correlated to charge transfer from Au$_8$ to O$_2$ (see Table 1): local charge on the MgO-supported gold octamer (structure A) changes from $-0.37e$ to $+0.73e$ upon oxygen adsorption, and O$_2$ gains a charge of $-1.26e$ that goes to the originally empty $2\pi^*$ antibonding orbitals, i.e., the adsorbed dioxygen is activated to a peroxo-like state. This charge-transfer-induced activation was shown to be the key to the catalytic activity. In the TDDFT framework, the significant change of the oxidation state of the gold octamer A upon dioxygen adsorption ($1.1e$ in total) obviously depletes those single-particle KS states from the TDDFT basis, that have a major contribution to the strong excitations of the bare cluster in the energy range shown. O$_2$ and CO adsorption on structure B are accompanied by a smaller change of the oxidation state of gold ($0.8e$ and $0.58e$ in total, respectively).

We have shown that polarization-resolved optical spectra of magnesia-supported gold clusters contain rich information about the binding mode and structure of the cluster and possible adsorbant molecules. Specifically, optical spectra contain complementary information about the adsorption of CO and O$_2$ molecules on the catalytically active center Au$_8$/F$_s$@MgO and the related charge transfer. Emerging applications of surface-sensitive optical spectroscopic tools to this and other chemically active supported metal clusters are...
likely to help significantly in gaining detailed understanding of structures and functions of reaction centers of nanocatalysts.

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* Electronic address: hannu.hakkinen@phys.jyu.fi

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13. We use the core radii (in \(a_0\), "tilde" denotes the local component) of: Au: \(\tilde{s}(2.5), \tilde{p}(3.0), \tilde{d}(2.0)\);
O: \(s(1.45), \tilde{p}(1.45)\); C: \(s(1.50), \tilde{p}(1.54)\); Mg: \(s(2.5), \tilde{p}(2.75)\). We expand the KS states in a plane wave basis with 62 Ry cutoff.
The structures for Au$_N$/F$_4$@MgO with $N = 1, 4, 8$ have been reported previously in ref. 5, in addition, here we optimized the structures for $N = 2$. See Refs. 4 and 14 for a general discussion on the suitability of embedded-cluster DFT models for description of oxide-supported metal clusters.

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It is clear that the absolute values of local charges depend somewhat on the method of analysis as there is no unambiguous way to assigning volume to a given atom. We use here a simple scheme where the charge at a given point on the real-space electron density grid is always assigned to the nearest atom (analogous to defining a Wigner-Seitz primitive cell in solids). Furthermore, details of surface relaxation and xc-functionals can introduce variations of the order of 0.1 e. Relative changes of the local charge, e.g., upon adsorption of a molecule to a cluster, are more meaningful than the absolute values.