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Condensed matter physics in the 21st century: The legacy of Jacques Friedel

Silver and oxygen: Transition from clusters to nanoparticles

*Argent et oxygène : des agrégats aux nanoparticules*

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ABSTRACT

By varying the sizes of isolated and charged silver particles, we may observe a wide range of reactions from weak molecular-oxygen physisorption to strong oxygen chemisorption. The global electron configuration dominates the stability of the silver–oxygen complexes. Our experimental studies at 77 K show a cluster regime below 40 free valence electrons in the system. Here each atom of silver added to the complex cause strong alternations of the oxygen binding by quantum effects. Bigger silver–oxygen complexes show smoother size dependence. As is rather typical for nanoparticles, the quantum effects are here less important, while the system size still matters. The electrostatic interaction between the charge state of the nanoparticle and the charge transfer of the reaction accounts for the general trends observed at silver, as it is in related oxygen–metal complexes.

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R É S U M É

Quand on fait varier la taille de particules d'argent isolées et chargées, on peut observer une grande variété de réactions, depuis la faible physisorption de l'oxygène moléculaire jusqu'à la forte chimisorption de cet élément. C'est la configuration électronique globale qui domine la stabilité des complexes argent–oxygène. Nos travaux expérimentaux à 77 K mettent en évidence un régime d'agrégats tant que le nombre total d'électrons de valence reste inférieur à 40. Chaque atome d'argent supplémentaire provoque alors, par des effets quantiques, de fortes alternances de la liaison de l'oxygène. Quand ils sont plus gros, les complexes argent–oxygène ont une dépendance en taille moins accidentée. Comme c'est généralement le cas dans les nanoparticules, les effets quantiques sont alors moins spectaculaires, mais la taille du système a encore son importance. L'interaction électrostatique entre l'état de charge de la nanoparticule et le transfert de charge de la réaction explique les tendances générales observées pour l'argent, comme dans les complexes oxygène–métal analogues.

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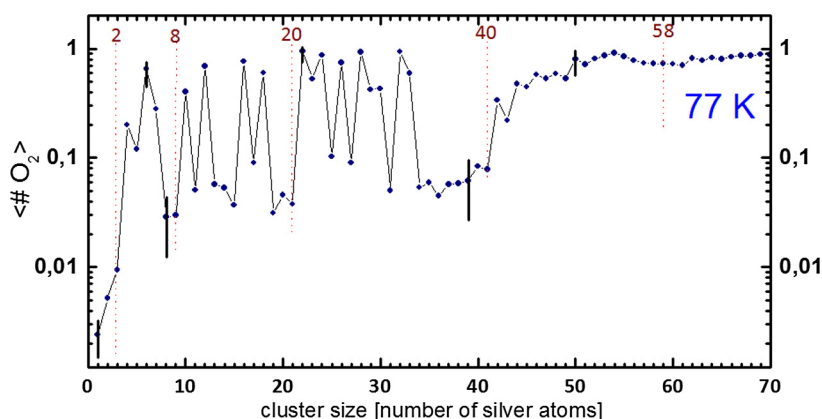


Fig. 1. A silver cluster passes through a reaction chamber in a flow of a helium with a partial oxygen pressure of $6 \cdot 10^{-3}$ mbar. The time of interaction between gas and clusters is long enough to reach an equilibrium between adsorption and evaporation. Differential pumping separates the clusters from the gas and a time-of-flight mass spectrometer detects the mean number of adsorbed O_2 per cluster. We use this number $\langle \#O_2 \rangle$ as a measure of adsorption. We detect a general increase with cluster size, to which strong variations due to quantum effects are superposed. The positive charge on the cluster hinders the electron transfer to O_2 for the chemisorption, but the surface-charge density decreases with increasing cluster size and damps the effect. The electronic shell closings of the pure Ag_n^+ system within the 3D-Jellium model are marked by the red dotted lines. Clusters slightly above these sizes have delocalized extra-electrons, which support reactions with oxygen. Clusters slightly below prefer to accept electrons and are consequently less reactive toward oxygen. The amplitude of the odd-even alternation in the reactivity toward oxygen decreases with size, but persists within the whole size range investigated. At the 40-electron shell closing, we locate the cluster-to-nanoparticle transition.

A part of Jacques Friedel's original contributions to various branches of solid-state physics dealt with structure and surface dislocations and their influence on the electronic structure in metallic clusters [1]. The physical properties of such clusters are known to deviate strongly from the bulk [2]. Many size-dependent effects with strong local variations in small metallic clusters are due to the quantum configuration of delocalized electrons caged in the finite volume of the cluster. In spite of their strong simplifications, Jellium models [3] often provide the main features of the observation [4], as it is the case for silver clusters in interaction with oxygen [5]. Other observations, like the physisorption of rare gases on the clusters [5b], however, are dominated by the geometry of volume and surface of the clusters. With increasing cluster size, the importance of the global electronic structure decreases, while local geometric effects persist and finally dominate [6]. Within this transition, the coupling between volume distortion, surfaces dislocations and electronic structure, as studied by Jacques Friedel, could provide specific effects [7]. Their understanding could have some impact on applications in catalysis or superconductivity.

The interaction between oxygen and silver clusters has been the subject of several experiments within the last 20 years [5,8]. In a recent article on the interaction of gas phases of silver clusters with selected gases [9], we discuss the size dependence of physisorption and chemisorption in relation to the bulk limit. The studies cover an extended size range up to 70 silver atoms and include a cluster-to-nanoparticle transition, on which we will focus in this article.

In our experiments, silver cluster cations in a helium atmosphere are exposed to molecular oxygen under variable partial pressures, temperatures, and durations. At 77 K, the temperature is too high for the condensation of multilayers of oxygen to occur around the clusters. On the other hand, the oxygen partial pressure ($6 \cdot 10^{-3}$ mbar), the interaction time (0.9 ms) and thus the number of collisions between O_2 and clusters are sufficiently high for a dynamic equilibrium between oxygen condensation and oxygen evaporation. After separation of clusters and gas by differential pumping, high-resolution time-of-flight mass spectrometry detects the intensities of pure silver clusters and those with different amounts of adsorbed molecules. We calculate the mean number of adsorbed O_2 -molecules per cluster $\langle \#O_2 \rangle$ as shown in Fig. 1.

A glow discharge in the growing area ionizes the silver clusters. The resulting mass spectra of pure cluster ions are smooth, indicating that the ionization is not at the origin of local intensity variations [5b]. Since the dependence on the particle size of the collision probability is also smooth, the adsorption pattern reflects the stability of the complex [8a,9]. We thus take $\langle \#O_2 \rangle$ as a measure of oxygen adsorption, or more precisely of the strength of the oxygen adsorption relative to neighboring cluster sizes (Fig. 1). $\langle \#O_2 \rangle$ shows pronounced local variations at small clusters, while the mean adsorption increases with cluster size (Fig. 1). This is in contrast to the nitrogen physisorption, where the adsorption steeply decreases for electrostatic reasons [5b,9].

For small clusters, quantum effects are strongly superimposed on the general trend. In contrast to the bulk, metal clusters confine a small number of electrons that tend towards pairing and configurations with closed shells, which leads to pronounced variations of the oxygen adsorption. Silver clusters with an unpaired valence electron are typically more reactive than their neighbors are. This leads to an odd-even alternation. The stability pattern of silver particles with one oxygen molecule is shifted by one silver atom or one free electron compared to the bare silver particle [8a]. This indicates that the reaction binds one electron. The oxidation state of each oxygen atom is thus $-1/2$, corresponding to a superoxide. This observation is in agreement with earlier experiments on molecular chemisorption on clusters of "coinage" metals at

low temperatures [5a,8a,8c,10]. The odd–even alternation is decreasing with size, but persists up to $n = 70$ (Fig. 1) [9] and indicates that superoxo-like molecular chemisorptions dominate at 77 K, as expected based on the bulk limit [11].

The character of the bond between cluster and O_2 is polar covalent [9]. There is a partial charge transfer from the cluster to the molecule, which enhances the global positive charge on the metallic part of the cluster [8e,9]. This promotes the physisorption of rare gases or of nitrogen [8e], whereas it hinders the coadsorption of multiple oxygen molecules [9].

Pronounced gaps in the reactivity are below clusters with 2, 8, 20 and the 40 delocalized valence electrons, which correspond to closed electronic shells within the Jellium model [3]. In the superatom analogy [12], those shell closings can be seen as “rare gases”. The observed reactivity gaps at Ag_8^+ , Ag_{19-20}^+ and especially at Ag_{34-40}^+ are due to the tendency of those clusters to accept electrons in order to complete the almost filled shells. In a manner similar to halogens, those clusters prefer reactions with electron donors instead of oxygen. Related gaps in the reactivity between copper clusters and oxygen were noted even up to the 92 electron-shell closing [10a]. On the other hand, the “alkaline” and even the “alkaline–earth metals” $Ag_{5,11,23,43}^+$ are reactive with oxygen. They chemisorb O_2 in spite of their paired electron configuration in order to approach the shell closing downwards. For chemisorptions on gold clusters, the odd–even effects are similarly pronounced, but shell closings and reaction gaps are more complex, and the super atom analogy is less obvious than in the case of silver [5a,10f,13] or copper [10a]. This can be addressed to the stronger influence of d-electrons [1,14].

The positive trend in the size dependence of oxygen chemisorption is related to the positive charge on the metallic particles: charging shifts the ionization potentials and the electron affinities and so influences the reactivity to oxygen [15]. The chemisorption of electron donors is supported by positive charge on the clusters [16], electron acceptors by negative charge [17]. Since the growing surface dilutes the surface charge density on the particles, both effects are damped by increasing cluster size [5b,13b,16a]. In our case, the positive charge hinders oxygen chemisorption on small silver clusters. Positively charged gold clusters with CO [13] and D_2 [18] show opposite trends in the size dependence, respectively.

Fig. 1 shows a transition at 42 silver atoms. Here a smooth size-dependent development replaces the strong local variations of the small clusters. As discussed above, those variations at small sizes are quantum effects. They correspond well to a Jellium description of delocalized electrons caged in the finite volume of the cluster. Consequently, each silver atom contributes one free s electron and can switch the adsorption and potentially change the reactivity by more than an order of magnitude. Such non-scalable size dependence is typical for clusters. At 42 silver atoms, an electronic shell is closed. The ionization extracted one electron. Another one is localized by oxygen chemisorption. The complex at 42 silver atoms contains thus 40 delocalized electrons. This shell closing is marked by a sudden increase in the stability of the silver–oxygen complex. Above this size, however, we detected no further pronounced steps in the chemisorption probability. We observe from here on smooth size dependence, as is typical for nanoparticles by contrast to the atom-to-atom alternations of the cluster regime.

The reduction in the odd–even effect is not due to the influence of double oxygen chemisorption at those clusters with paired electrons. At higher oxygen pressure, double oxygen adsorptions are observable on clusters with more than 21 silver atoms [5b], but at the pressure of $6 \cdot 10^{-3}$ mbar, single oxygen adsorptions dominate for all clusters shown in Fig. 1. The cluster-nanoparticle transition might appear especially sudden, since a gradual reactivity decrease towards smaller clusters could be hidden by the large reactivity gap below the 40-electron closed shell.

Only a few studies on chemisorption of coinage metal clusters cover a sufficiently large size range to observe cluster-to-nanoparticle transitions. In all those observations, the transition occurs at relatively small particle sizes of some dozens of atoms. In neutral gold clusters with chemisorbed CO, the transition is less sudden, but at about the same size as in the oxygen–silver–cation-system [10e,10f]. The copper–oxygen system preserves the cluster regime with quantum effects up to bigger particles with at least 100 copper atoms [10a]. Calculations show, furthermore, that gold nanoparticles needed a size of several hundred of atoms for quantitative agreement with predictions based on a scaling by the surface-to-volume ratio [19].

Electronic effects cause the differences in oxygen chemisorption of small particles or in the bulk. In the cluster limit, there are quantum effects of the electrons that are caged by the surface of the metallic particle. In the nanoparticle regime, the electrostatic effect of the particle charging is responsible for the differences to the bulk surface limit. Geometric effects like special reaction sites on the surface of the particle are, for the case of silver, only secondary for the local adsorption variation [5b,8a]. Nevertheless the interaction between geometry and electronic configuration, as studied by Jacques Friedel, might be well involved in the fading global electronic shell effects and thus in the location of the cluster-to-nanoparticle transition in our system.

In summary, we reported the adsorption of oxygen at free silver–cluster cations. Up to 40 valence electrons, the stability of the oxygen–cluster complex follows a superatom behavior. Pronounced quantum effects with electron pairing and shell effects promote single complexes with well-defined stoichiometry. Variations in self-capacitance of the clusters hinder or promote the oxygen reaction and reveal the charge transfer of oxygen interaction.

At the closing of the 40-electron shell, we located a cluster-to-nanoparticle transition. Above, the quantum effects become less important than classical electrostatic trends. Positive charging on the silver nanoparticle hinders the charge transfer into the oxygen molecule. This effect decreases with increasing particle size and causes increasing oxygen adsorption.

Catalytic, biocidal or medical applications of nano silver require well-defined levels of oxygen activation. The broad variation in reactivity and thus in oxygen activation at small clusters implies that ensembles of silver particles are more likely to provide appropriate reaction conditions than the bulk limit.

However, optimizing the system in the cluster regime for a given application would imply the need to mass select a precise number of silver atoms, since each atom changes the conditions qualitatively. In the nanoparticle regime, by contrast, the variations are smoother and less excursive. Here, even rough mass selection to a certain size range could help to enhance the performance of the material. Our studies show that this nanoparticle regime already starts above about 40 silver atoms.

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