



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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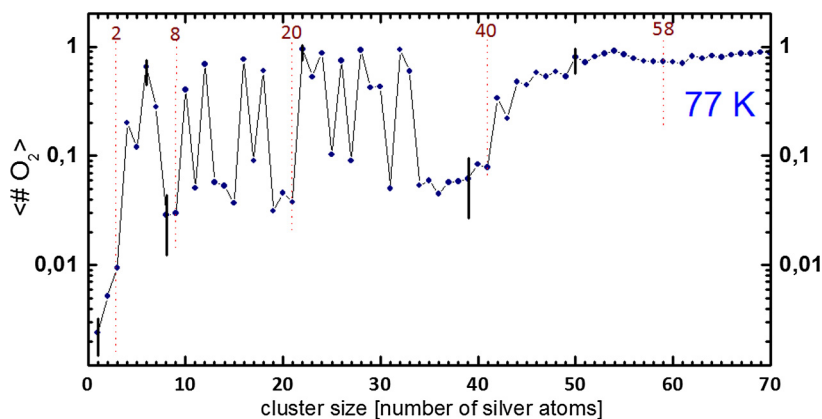
### R É S U M É

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

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