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COVERAGE DEPENDENCE OF ADSORBATE-SUBSTRATE BOND LENGTHS; CHLORINE AND CAESIUM ADSORBED ON SILVER SINGLE CRYSTALS

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Abstract

SEXAFS has been employed to investigate several submonolayer phases of Cl and Cs adsorbed on various single crystal silver planes. For chlorine adsorption, the nearest-neighbour bond distance is found to be invariant with coverage. In complete contrast, a dramatic increase in the substrate-adsorbate bond length is observed with increase in coverage of Cs. This different behaviour of Cl and Cs adsorbates is discussed in terms of the electron transfer processes between electronegative and electropositive adsorbates and the substrate.

INTRODUCTION

The aim of the surface EXAFS work presented here was to investigate various submonolayer phases of both a strongly electronegative species, chlorine, and a strongly electropositive species, caesium, adsorbed on silver. Evidence for a fundamental difference in the electronic behaviour of the two species is given by the way in which they modify the substrate work function; with increase in coverage of the alkali, the substrate work function initially exhibits a rapid non-linear decrease. This reaches a minimum at less than a monolayer, then increases slightly (to a plateau) beyond a monolayer. Adsorption of chlorine, on the other hand, merely causes a linear increase in the substrate work function.

From a macroscopic point of view, the systems investigated are of particular interest with regard to the commercial oxidation of ethylene to ethylene oxide. Silver is a very effective catalyst in this reaction, whilst adsorbed chlorine is used as a modifier, increasing the selectivity of the catalyst to the epoxidation route. Addition of small amounts of alkali, however, causes a vast increase in the total activity of the catalyst. Thus, due to the difference in nature of the two species (Cs is a 'donor' atom whilst Cl is an 'acceptor' species), the way in which the surface properties are modified is by very different mechanisms.

EXPERIMENT AND ANALYSIS

The SEXAFS measurements were made on station 3, beamline 6 at the Daresbury Synchrotron Radiation Source (SRS). The beamline and monochromator are described in detail by MacDowell et al. [1].

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The experiments were carried out in a conventional, stainless steel ultra-high-vacuum chamber, with a base pressure of $5 \times 10^{-11}$ mbar. The crystals were cleaned by argon ion bombardment and anneal cycles until no contaminants were evident in the Auger spectra and sharp (1x1) Low Energy Electron Diffraction (LEED) patterns were observed. The crystal was dosed with chlorine using an electrolytic source, and with caesium using a getter source.

The measurements were made by collecting the total secondary electron yield by monitoring the drain current leaving a tungsten mesh, placed at a distance of 3 cm from the sample. The bulk data used to obtain correct phase shifts were obtained by mounting a series of model compounds in the same vacuum system, and measuring the bulk EXAFS by the same method. The series of model compounds included: AgCl, AgBr, CsCl, CsI, CsBr, and Ag$_2$S. All data were taken at 110 K, where deviation from the simple harmonic approximation is negligible [2].

The data were analysed using the Daresbury-based EXCURVE [3] program, which uses the 'curved wave' scattering description [4].

RESULTS

Chlorine adsorbed on Ag(111)

SEXAFS data were taken from Cl adsorbed on Ag(111) at coverages of 0.4 and 0.7 monolayers (where a monolayer is defined as the same surface concentration as a close-packed Ag(111) plane). A complete structural determination for the higher

Fig. 1 (a) The full line shows the k$^3$ weighted, back transformed experimental frequency spectrum (to include real space components up to 5.0 Å) together with the theoretical multishell fit (broken line), of the phase observed at a coverage of 0.7 monolayers of Cl/Ag(111).

(b) Experimental and theoretical Fourier transforms of (a).
coverage phase is published elsewhere [5]. A LEED I(V) analysis is not a viable technique for either of these phases, since no long-range order exists for the low coverage phase, whilst there is only weak order [7,8] at the higher coverage.

The data for the high and low coverages are presented in figs. 1 and 2, respectively, where the $k^3$ weighted, experimental frequency spectra (Fourier filtered to include components out to 5.00 Å) and the corresponding radial distribution functions, are compared to the theoretical fits. The nearest neighbour adsorbate-substrate bond distance determination, in both cases, was 2.70 ± 0.01 Å.

Fig. 2. (a) The full line shows the $k^3$ weighted, back transformed experimental frequency spectrum (to include real space components up to 5.0 Å) together with the theoretical multishell fit (broken line), of the phase observed at a coverage of 0.4 monolayers of Cl/Ag{111}. (b) Experimental and theoretical Fourier transforms of (a).

Chlorine adsorbed on Ag{110}

The measurements were made at two different chlorine coverages: 0.5 monolayers and 0.75 monolayers. Long-range order is observed for both of these phases [6,8]. At a coverage of 0.5 monolayers a simple p(2×2) LEED pattern exists, whilst at the higher coverage an incommensurate structure is observed. A model for the latter phase is presented elsewhere [9].

The experimental and theoretical frequency spectra and radial distribution functions are shown in figs. 3 and 4 for the high and low coverages, respectively. The nearest-neighbour distance was determined to be 2.59 ± 0.04 Å for both phases, thus, the invariance with coverage of the adsorbate-substrate distance is verified for the chlorine species. A large error bar is associated with these measurements, compared to those from Cl/Ag{111}, due to a glitch occurring in the raw spectra.
Fig. 3. (a) The full line shows the $k^3$ weighted, back transformed experimental frequency spectrum (to include real space components up to 6.0 Å) together with the theoretical multishell fit (broken line), of the phase observed at a coverage of 0.75 monolayers of Cl/Ag{110}. (b) Experimental and theoretical Fourier transforms of (a).

Fig. 4. (a) The full line shows the $k^3$ weighted, back transformed experimental frequency spectrum (to include real space components up to 6.0 Å) together with the theoretical multishell fit (broken line), of the phase observed at a coverage of 0.5 monolayers, of Cl/Ag{110}. (b) Experimental and theoretical Fourier transforms of (a).
Caesium adsorbed on Ag\{111\}

Cs on Ag\{111\} was investigated at coverages of 0.15 and 0.30 monolayers. The latter corresponds to an almost close-packed layer of Cs atoms and the raw data from this are shown in fig. 5.

![Fig. 5. A normalised raw surface EXAFS spectrum, of the caesium L\(_3\) edge, from the 0.3 monolayer phase on Ag\{111\}.](image)

The first nearest-neighbour distance for the higher coverage phase is determined to be 3.50 ± 0.03 Å, whilst that for the lower coverage phase is found to be 3.20 ± 0.3 Å. The variation in bond distance is interpreted as the transition from an 'ionic' to a 'covalent' nature of the adsorbate-substrate bond with increase in coverage. Fig. 6 provides a visual appreciation, in frequency terms, of the observed

![Fig. 6. Superimposition of the first shell contributions from both the high coverage (covalent) and low coverage (ionic) phases of Cs/Ag\{111\}. The obvious difference in frequency provides a visual demonstration of the change in bond distance with increasing coverage.](image)
bond distance increase. It shows the superimposition of the first shell contributions from both the high and low coverage phases. The overlayed frequency curves are extracted from the theoretical spectra (a back-transform of the first peak in the experimental Fourier transform would also include the interfering back-scattering resonance from the second shell [10]).

It should be emphasised that a variation in the substrate-adsorbate bond distance, as a function of coverage, has never been treated in either classical or quantum mechanical approaches. This work indicates that there is, indeed, a change in this parameter and that future theoretical calculations should include this as a variable in a quantitative way.

DISCUSSION AND CONCLUSIONS

Results for Cl and Cs adsorbed on Ag[111] demonstrate the unique capacity of SEXAFS to elucidate surface structures without long-range order. In particular, the sensitivity of the technique is illustrated by the detection of the bond distance variation (of 0.30 Å) when Cs is adsorbed on Ag[111].

Most importantly, the studies here reveal a fundamental difference in behaviour of the electropositive and electronegative species; the adsorbate-substrate distance is independent of coverage for Cl on both Ag[111] and Ag[110], whilst there is a marked dependence with adsorption of Cs.

Lang and Williams [12,13] have studied the adsorption of a strongly electropositive, a strongly electronegative and a covalent species (Li, Cl and Si, respectively) adsorbed on a jellium substrate. The calculated local density of states for the three systems are shown in fig. 7. For lithium, the adsorbate resonance is initially mostly unoccupied, since it lies mainly above the Fermi level; whereas the chlorine resonance is totally filled as it lies completely below the Fermi level. The silicon resonance lies almost exactly halfway across the Fermi level, exhibiting covalent character, with equal amounts of bonding and anti-bonding character.

Considering the alkali metal case, as the coverage increases the resonance moves down over the Fermi level and the occupation of its resonance increases; i.e., the electron transfer is back to the adsorbate atom. The alkali-substrate bond then becomes more covalent, resembling that illustrated for Si in fig. 7. However, the occupation of the chlorine resonance cannot vary with increased coverage as it is fully occupied from the initial stages of adsorption. Since the occupation of the Cs resonance is varying with coverage, the equilibrium distance (for minimum energy

![Fig. 7](image_url) The local density of states at the adsorption site for an electronegative, electropositive and covalent species (from ref. [12]).
of the adsorbate) will also vary. However, since the occupation of the Cl resonance is invariant with coverage, nothing is to be gained (in terms of energy) by altering its distance from the surface.

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REFERENCES

   A.A. MacDowell, D. Norman and J.B. West, to be published.


