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An unusual adsorption site for methoxy on Al(111) surfaces

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Abstract. The adsorption site of the methoxy (CH_3O) species on Al(111) has been investigated using the technique of normal incidence standing x-ray wavefield absorption. By recording the x-ray absorption of the O atom of this species at both the (111) and $(\bar{1}\bar{1}\bar{1})$ -normal incidence Bragg scattering conditions (at normal and 70.5° incidence to the surface) the adsorption site was obtained by simple real-space triangulation. The species is adsorbed in a three-fold symmetry hollow site with an O–Al layer spacing of 0.70 ± 0.10 Å, (as found for chemisorbed oxygen), but the site occupied is the HCP hollow directly above an Al atom in the second layer, and not the FCC site (above an Al atom in the third layer) which is occupied by chemisorbed oxygen. This appears to be the first example of an adsorbate with a clear preference for this HCP hollow site on an otherwise clean FCC (111) surface.

1. Introduction

The determination of the structural parameters associated with adsorption on well-characterized single-crystal surfaces, notably the adsorbate–substrate registry, the nearest-neighbour bond length, and the extent of any adsorbate-induced reconstruction of the substrate, is a key step in understanding the adsorption and reactivity properties of solid surfaces. A particularly relevant, but difficult, subset of such problems is those associated with molecular adsorbates and those molecular species which only form as a result of a chemical interaction catalysed by the surface ('catalytic intermediates'); such species clearly have direct relevance to the underlying mechanisms of heterogeneous catalysis (including identification of 'active sites'), but these adsorbates are often sensitive to electron beam damage and do not form long-range ordered overlayers, thus excluding many of the common structural methods.

Here we report on a structural study of one such catalytic intermediate, methoxy (CH_3O -) formed by the catalytic deprotonation of methyl alcohol (CH_3OH), at an Al(111) surface. This species is known to form on a range of metal surfaces, but has been studied most extensively on Ag and Cu surfaces because of its interest as a probable intermediate in the industrial production of methanol (typically achieved over zinc oxide/copper catalysts [1]). Its formation on aluminium surfaces as a result of methanol decomposition has been inferred in several electron spectroscopy and desorption studies over polycrystalline surfaces [2–4], and has been specifically identified by vibrational spectroscopy on Al(110) [5] and Al(111) [6].

The technique we have used to investigate this problem is normal incidence standing x-ray wavefield absorption (NISXW). In this method, absorption at the adsorbate

atom, of the standing x-ray wavefield set up at a Bragg scattering condition, is measured as the incident photon energy is scanned through the Bragg condition. The location of the nodal planes of the standing wavefield shift in a systematic fashion as the Bragg condition is traversed [7], so that the absorption profile provides a characteristic 'signature' of the atomic location of the absorbers relative to the substrate scattering atoms. A novel feature of our NISXW method relative to the more generalized geometry is that, by working at normal incidence to the scatterer planes, the Bragg condition becomes rather insensitive to the exact angle of incidence, making the experiment tolerant to rather large substrate crystal mosaicity, and thus making studies of standard metal crystals straightforward [8-10]. A potential limitation of a single NISXW or SXW measurement, namely that one obtains only an adsorbate-substrate layer spacing in a particular direction, can be overcome by measuring two different Bragg scattering conditions using scatterer planes at different angles to the surface; this provides two different layer spacings which can be used to obtain the absolute adsorption site by simple real-space triangulation. In the present case this has been achieved using the (111) reflection at normal incidence and the ($\bar{1}11$) reflection at 70.5° incidence to the Al(111) surface.

One further aspect of the experimental method used here which deserves note is the application of the SXW method to investigate the structure associated with an adsorbate containing only light (first full row of the periodic table) elements. Elements of low atomic number have no very deep electronic core levels (the deepest, 1s, levels of O and C have binding energies of approximately 530 and 290 eV), whereas the lowest energies associated with a Bragg reflection in a metal crystal are much higher (typically at least 3 keV). This means that the photoabsorption of the standing x-ray wavefield by these light atoms is typically weak, leading to a poor signal-to-noise ratio for a SXW experiment. For this reason, the SXW method is not generally appropriate (indeed it may even prove impossible to use) for these low atomic number adsorption systems [11]. The system studied here, although falling into this class of problem, is rather more favourable. In particular, Al has a particularly large lattice parameter among FCC metals, so that (111) normal incidence Bragg condition is particularly low in energy (2660 eV); in addition, Al itself has rather few (widely spaced) core levels, so that the O 1s photoelectron emission peak at this Bragg energy occurs at a kinetic energy at which the background electron emission from Al is weak. These two factors lead to a larger signal, and a much better signal-to-background ratio than is typical for light atom adsorption systems. Clearly, there is a narrow range of such systems which would be amenable to study, but the NISXW method is unlikely to prove generally useful for problems such as those involving light adsorbates on transition metal substrates.

2. Experimental method and results

The experiments were performed at the Science and Engineering Research Council's (SERC's) Daresbury Laboratory, taking x-rays from the Synchrotron Radiation Source (SRS) on the SEXAFS beamline (line 6.3) which is equipped with a pre-focusing mirror and an ultra-high vacuum (UHV) two-crystal monochromator [12, 13] now fitted with water-cooled diffracting crystals. A conventional UHV surface science spectrometer chamber installed on the end of this beam line is equipped with the

usual sample manipulation, heating, cooling and cleaning facilities, with a double-pass cylindrical mirror analyser for synchrotron radiation photoemission and Auger electron spectroscopy, and with low-energy electron diffraction (LEED) optics.

The Al(111) sample was prepared by the usual combination of x-ray Laue alignment, spark machining, mechanical polishing and *in situ* argon ion bombardment and annealing until a well-ordered clean surface was obtained as judged by LEED and Auger electron spectroscopy. The surface methoxy species was prepared by exposing the clean Al(111) surface to 15 L of methanol at a substrate temperature of approximately 150 K. As this temperature was the lowest we could obtain with our cooling stage but lies rather close to the nominal temperature (143 K [6]) at which physisorbed methanol dissociates to adsorbed methoxy with the associated desorption of molecular hydrogen, two different measurement procedures were investigated. In one experiment the sample was maintained at this low temperature whilst the NISXW measurements were performed. In a second approach, the sample was allowed to warm to room temperature following the low-temperature exposure, and NISXW measurements were made at room temperature. Oxygen 1s photoemission data indicated no change in the coverage during this heating; this coverage was similar to that obtained by exposure of the clean surface to 10 L oxygen, a procedure leading to an estimated 20–30% of a monolayer [14]. Because the monochromator installed on the beam line does not permit photoemission or photoabsorption measurements below photon energies of about 2 keV, it was not possible to perform any *in situ* characterization of the molecular state of the adsorbate. It is clear from prior characterization by others [2–6], however, that the preparation procedure we have used results in only the methoxy species being present on the surface. As a check we also performed Auger electron spectroscopy *after* taking the NISXW measurements (to avoid the consequences of electron-induced dissociation), and these results clearly showed both O and C present on the surface at levels consistent with the stoichiometry of methoxy. As we shall see, the NISXW results also show that the O adsorption site geometry in this preparation is quite different from that found for chemisorbed oxygen (and also indicate that only one type of site is occupied by oxygen atoms).

The NISXW measurements were made, as in our previous applications of the method [8–10, 14], by recording, in four sequential photon energy scans through the appropriate Bragg peak, electron emission signals at kinetic energies characteristic of photoabsorption in the Al substrate and the O atoms of the methoxy adsorbate, and at kinetic energies some 50 eV higher than each absorption edge in order to provide signals representative of the background level. In the case of the Al substrate absorption, the signal monitored was the Al KLL Auger peak at 1390 eV kinetic energy. Photoabsorption in the O atoms was monitored by measuring the O 1s photoemission peak intensity; the high kinetic energy of this feature (about 2130 eV) at the (111) normal incidence Bragg condition (2660 eV) produced a much better signal-to-background ratio than was obtained for the O KLL Auger peak (510 eV) which lies on a substantial inelastically scattered electron background from the Al 1s photoemission peak. Note that the kinetic energy of the O 1s signal (> 2 keV) is sufficiently high that the role of photoelectron diffraction effects in backscattering can be very safely neglected in the NISXW measurements; in particular, at these energies we can extrapolate the results of photoelectron diffraction data [15] (rarely collected above 400 eV in the backscattering geometry) to conclude that the amplitude and energy width of such modulations should be of order 1% and 100 eV respectively. In each of these sequential measurements of the electron yield at specific kinetic

energies, concurrent measurements were made of the total electron yield. These total yield absorption profiles provided a check on any possible energy drift between measurements (due to storage beam movement or monochromator crystal temperature changes).

The resulting photoadsorption NISXW profiles for the O and Al absorbers at the (111) and $(\bar{1}11)$ -normal incidence conditions from the low-temperature sample preparation are shown in figure 1, together with smooth lines which represent theoretical fits for specific structural models. Our fitting procedure is also as described previously [8-10, 14]. Specifically, the Al substrate profiles were fitted assuming that the associated structure is known (Al atoms on ideal Al lattice sites) and optimizing the absolute energy, the instrumental Gaussian energy broadening, and the coherent fraction of the absorbers. The O absorption profiles were then fitted using the same values of the non-structural parameters, and adjusting only the O-Al substrate layer spacing, and the coherent fraction for the O atoms. All fits used a coherent fraction of 0.9, which provides some measure of the degree of disorder beyond that which can be accounted for by the Debye-Waller factor associated with the bulk Al substrate atoms (taking the bulk Debye temperature). The O-Al layer spacings used for the fits in figure 1 are 0.70 Å for the (111) reflection and 0.95 Å for the $(\bar{1}11)$. A second data set recorded from the sample at room temperature yielded best fit values 0.05 Å larger, a difference which falls within our estimated random error for fitting of ± 0.10 Å and which we do not regard as significant.

In order to obtain the adsorption site from these two layer spacings, we use the principle of triangulation illustrated in figure 2. In particular, if we take the measured (111) layer spacing, we can calculate the $(\bar{1}11)$ layer spacing we would expect for each of the possible high-symmetry adsorption sites. Notice that our observation of a high coherent fraction excludes the possibility of low-symmetry adsorption sites; the substrate has $3mm$ (C_{3v}) symmetry, and adsorption in any site having a lower symmetry than this (such as a bridge site) would necessarily lead to occupation of several different sites (probably in domains on the surface) each related by symmetry operations of the substrate $3mm$ point group. These different sites would be inequivalent relative to any specific $(\bar{1}11)$ -type plane, so that at least two significantly different $(\bar{1}11)$ layer spacings would be found. The NISXW profile resulting from this mixture could only be fitted by more than one layer spacing, or by some average layer spacing with a low coherent fraction (typically 0.5 or less).

There are three possible $3mm$ symmetry adsorption sites: atop, FCC hollow above an Al atom in the third substrate layer, and HCP hollow above an Al atom in the second layer. Taking the measured (111) layer spacings of 0.70 ± 0.10 Å (low temperature) and 0.75 ± 0.10 Å (room temperature) at these three sites leads to predicted $(\bar{1}11)$ spacings of 0.23 ± 0.04 Å (atop), 1.79 ± 0.04 Å (FCC hollow) and 1.01 ± 0.04 Å (see figure 2), to be compared with the experimental values of 0.90 ± 0.10 Å and 0.95 ± 0.10 Å. Clearly, the HCP hollow value fits well, and the other sites lie well outside the estimated experimental errors.

3. Discussion

One particularly interesting aspect of the structural conclusions drawn in the previous section is the similarity and the difference between the case of methoxy on Al(111) and chemisorbed oxygen on the same surface. The oxidation properties of aluminium

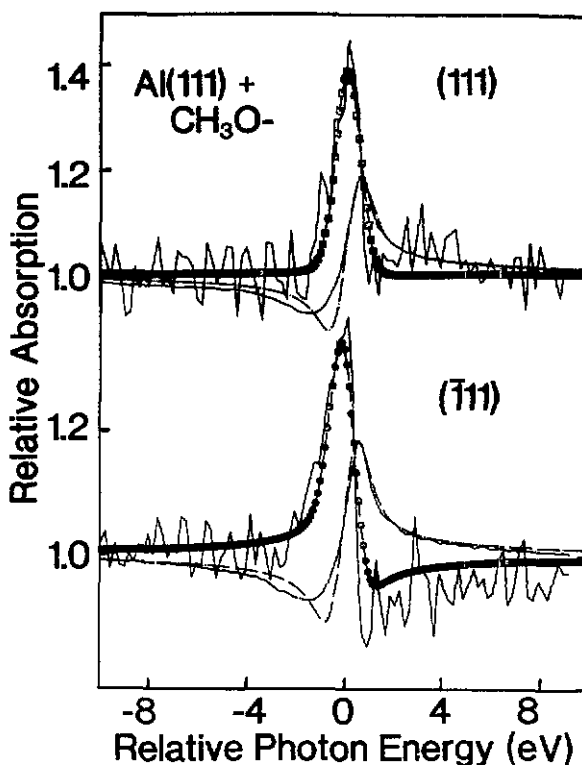


Figure 1. Experimental NISXW absorption profiles for both Al and O x-ray absorption at the (111) and $(\bar{1}11)$ -normal incidence Bragg conditions, for methoxy on Al(111), compared with best fit theoretical curves using the parameter values described in the text. The experimental data are shown as full lines joining the data points (the lower noise data being for Al absorption). The theoretical fits to the Al data are shown as dash-dot lines, whilst the fits to the O absorption data are shown by dashed lines joining theoretical data points plotted as squares ((111)) and circles ($(\bar{1}11)$).

surfaces have been studied extensively and a complete review of this field lies outside the scope of this paper (see [16] for an extensive review up to 1984, and [14] as a source of some more recent references). A key finding is that the (111) surface is the one face on which a clear chemisorbed phase has been identified, and there is now a consensus that LEED [17–19], SEXAFS [20–22] and NISXW [14] measurements are all consistent with a model in which oxygen atoms occupy FCC hollow sites at an O–Al top layer spacing of approximately 0.70 Å. Although this layer spacing is essentially identical to that found in the present study of methoxy on Al(111), the clear difference between the two adsorption systems is highlighted by comparison of the NISXW data for methoxy in figure 1 with figure 3 in which we reproduce the NISXW data for the Al(111)/O system [14]; the (111) data for the two systems are almost identical but the $(\bar{1}11)$ profiles are quite different, showing the change in site at constant layer spacing perpendicular to the surface.

If we assume that the atom locations in the Al substrate are undisturbed by the presence of the methoxy, the measured layer spacing and site imply an Al–O nearest-neighbour distance of 1.79 ± 0.04 Å, essentially identical to that for chemisorbed oxygen (for which direct SEXAFS measurements yield values of 1.79 Å [21] and 1.76 Å [22]). We should stress here that the SXW method determines the adsorption site

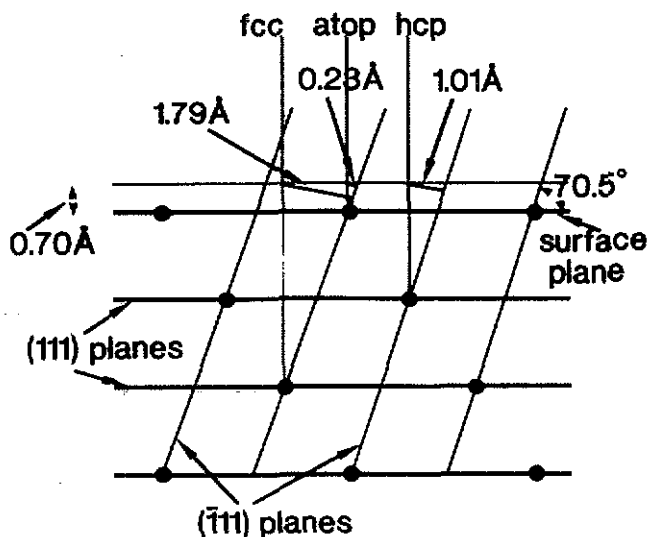


Figure 2. Schematic sectional diagram of Al(111) showing the principle of real-space triangulation of (111) and $(\bar{1}\bar{1}\bar{1})$ NSIXW profiles to determine the adsorption site of oxygen. The 0.70 Å (111) O-Al layer spacing is shown to be consistent with three different (111) spacings for the FCC hollow, atop, and HCP hollow sites, as described in the text.

relative to the continuation of the underlying bulk Al in which the standing wavefield is established; this means that any integrated contraction or expansion of the outmost Al layers will produce a systematic error of this value in the local spacing deduced by equating it to the SXW layer spacing. (By contrast SEXAFS measures the true local distance.) Nevertheless, the similarity of the LEED, SEXAFS and NISXW results for oxygen chemisorption, coupled with the fact that layer spacing variations at a surface are typically smallest for the closest-packed surfaces, suggests that the implied nearest-neighbour distances quoted above are unlikely to be seriously in error unless the methoxy produces major surface reconstruction (as has been found for the very strongly bonding S-containing analogue, methyl thiolate (CH_3S -bond) on Cu(111) [10, 23].

Any assessment of the significance of the bond length and adsorption site relative to other studies of methoxy is severely constrained by a dearth of data. The only other quantitative studies of surface methoxy species are for Cu(100) and Cu(111) substrates, principally based on the results of scanned energy mode photoelectron diffraction [24, 25]. On Cu(111) methoxy is found to occupy the FCC hollow site with a Cu-O nearest-neighbour distance of 1.88 ± 0.05 Å [24], whilst on Cu(100) the adsorption site is off-hollow (between the hollow and bridge sites but closer to the hollow) with a longer nearest-neighbour distance of 2.00 ± 0.05 Å from photoelectron diffraction [25] and 1.97 ± 0.05 Å from SEXAFS [26]. Note that in the photoelectron diffraction study on Cu(100), the fact that the adsorption site is of low symmetry causes some coupling of the Cu-O distance and off-hollow distortion parameters in the structure determination, a problem which could lead to the rather large Cu-O distance.

In view of the apparent equivalence of the Al-O distance for chemisorbed oxygen and methoxy on Al(111), it is interesting to compare these Cu-O nearest-neighbour distances for methoxy on copper with those found for copper oxides and

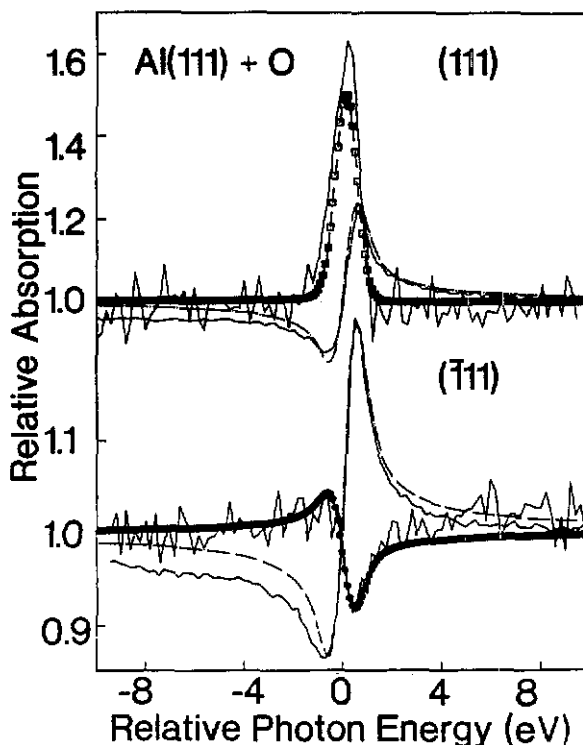


Figure 3. Experimental and theoretical NISXW profiles as in figure 1, but for the case of chemisorbed O on Al(111) (achieved by a 10 L exposure to oxygen gas). A more detailed discussion of these data is given in [14].

for chemisorbed oxygen on copper. The Cu-O spacing in bulk Cu_2O is 1.85 Å, whilst for the (2×1) -O chemisorption structure on Cu(110) the best SEXAFS value appears to be 1.82 ± 0.02 Å [27], and on Cu(100), Cu-O bond lengths found by SEXAFS have covered the range 1.94 Å [28] to 1.84 Å [29]. No simple ordered oxygen chemisorption structure is found on Cu(111), but SEXAFS results indicate a Cu-O nearest-neighbour distance of 1.83 ± 0.02 Å for this system [30]. Proper analysis of the chemisorption structures formed by oxygen on copper surfaces is complicated by the fact that adsorbate-induced substrate reconstructions occur, and evaluating the exact nearest-neighbour bond length from techniques which locate all atom positions rather than measuring this parameter directly (as in SEXAFS) must locate the displaced substrate atoms rather precisely. Nevertheless, it seems that on Cu(100) the ordered chemisorbed phase probably does involve Cu-O distances close to, or even shorter than, the 1.85 Å value of the bulk oxide (as on the (110) surface) [31, 32].

Although the Cu-O distances in the two methoxy systems appear to be longer than in these chemisorbed oxygen and oxide systems, the significance of the difference, in statistical terms, is marginal. Indeed, only the result for methoxy/Cu(100) lies outside the rather narrow range 1.85 ± 0.03 Å, and if the difference between the (100) and (111) surfaces is significant, it is presumably the (111) face with the three-fold coordinated hollow site occupation which provides the most appropriate comparison for our present purposes; for this case, the Cu-O distance for methoxy adsorption is approximately 0.04 ± 0.06 Å longer than for the oxygen chemisorption structures (that

is, it is the same within experimental uncertainties).

Of course, there is no general reason to expect free oxygen atoms to form closely similar metal substrate bond lengths to those of surface methoxides. The chemistry of atomic oxygen and of oxygen-bonding ligands is quite different. This is particularly clear in considering aluminium oxides in which a range of different bond lengths (typically 1.85–1.92 Å) associated with different oxygen coordinations is possible. The rather short Al–O distance for the chemisorbed Al(111)(1×1)-O phase has been rationalized [21] as resulting from the lower oxygen coordination number of the surface Al atoms relative to those of the bulk oxides. In the case of the chemisorbed oxygen system, this oxygen coordination of each surface Al atom is 3 (to be compared with 4–6 in bulk oxides); for methoxy our average coverage is certainly less than the complete monolayer coverage of the chemisorbed oxygen phase, but the local coverage may be higher if islanding occurs as in the chemisorbed oxygen system [33]. A further factor which may give some clue as to the likely surface bond length is the degree of charge transfer; unfortunately, there is an almost total absence of relevant data; a work function decrease has been noted for methoxy on polycrystalline Al [3], but the degree of charge transfer to be inferred from this is far from clear. We can therefore only remark that the rather short Al–O bond length which methoxy shares with chemisorbed oxygen on Al(111) is at least broadly consistent with the behaviour seen on copper surfaces, but the two situations are clearly far from equivalent.

Whilst the significance of the Al–O bond length is therefore not clear, the observation of the occupation of the HCP hollow site appears to be unique. The HCP and FCC hollows of an FCC elemental surface differ only in their third (and greater) nearest-neighbour distances, so one might expect the difference in the binding energies of adsorbates at these two sites to be very small. Indeed, at low coverages there are adsorption systems (such as I on Ag(111) [34, 35]) in which the adsorbates appear to occupy both sites on an equal basis. In an ordered overlayer structure in which a single site is occupied, however, the FCC site is invariably found to be the preferred site; in particular, O on Al(111), Ni(111) and Ir(111), S on Ni(111), Rh(111), Pd(111), Ir(111) and Pt(111), Au on Pd(111) and ethylidyne (C_2H_3) on Pt(111) [36] as well as methoxy on Cu(111) [24] all fit this pattern. Moreover, in the few cases which have been investigated by techniques which allow investigation of structures having no long-range order, if a single hollow site is occupied even at low coverage, it is invariably the FCC hollow. One particular system in which the HCP hollow site was found to be occupied is that of ethylidyne on Rh(111) [37] which contrasts with the system of ethylidyne on Pt(111) [38] in which the FCC hollow is occupied (in the same (2×2) ordered phase). In this case, however, ethylidyne on Rh(111), unlike the case on Pt(111), involves co-adsorbed atomic hydrogen, and it has been proposed that H occupation of the preferred FCC site (site blocking) may account for the HCP site occupation [37]. In the present case of methoxy/Al(111), the same explanation does not appear to be tenable. Whilst methanol is believed to decompose on Al(111) to produce co-adsorbed methoxy and atomic hydrogen, the thermal desorption spectra show that this hydrogen is desorbed as molecular hydrogen, predominantly at the decomposition temperature of 143 K [6]. Although some hydrogen desorbs at higher temperatures in a thermal desorption spectrum [6], it is clear that all such desorption occurs well below room temperature, so the fact that we observe the same structure at room temperature demonstrates that co-adsorbed hydrogen cannot account for our result.

One feature of the HCP site which could favour its occupation is the fact that

there is a substrate atom directly below in the second layer, so a higher effective coordination is available. However, the large (111) layer spacing is such that higher coordination is only possible if an adsorbed atom penetrates below the top layer (as in the formation of a surface oxide phase on Al(111) [14, 22]), and in the present case this is not the result that we obtain. In view of the fact, as we have noted, that the energetic distinction of the two hollow sites must be rather subtle, it seems that the key to this novel behaviour will only be revealed through the application of sophisticated theoretical calculations.

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