A photoelectron diffraction investigation of vanadyl phthalocyanine on Au(111)

D.A. Duncan[1], W. Unterberger[2], K. A. Hogan[3], T. J. Lerotholi[1], C. L. A. Lamont[3], D.P. Woodruff[1]*

[1] *Physics Department, University of Warwick, Coventry CV4 7AL, UK*

[2] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

[3] *Dept. of Chemical & Biological Sciences, University of Huddersfield, Queensgate, Huddersfield HD1 3DH, UK*

Abstract

Scanned-energy mode photoelectron diffraction using the O 1s and V 2p emission perpendicular to the surface has been used to investigate the orientation and internal conformation of vanadyl phthalocyanine (VOPc) adsorbed on Au(111). The results confirm earlier indications from scanning tunnelling microscopy that the V=O vanadyl bond points out of, and not into, the surface. The V=O bondlength is 1.60±0.04 Å, not significantly different from its value in bulk crystalline VOPc. However, the V atom in the adsorbed molecule is almost coplanar with the surrounding N atoms and is thus pulled down into the approximately planar region defined by the N and C atoms by 0.52 (+0.14/-0.10) Å, relative to its location in crystalline VOPc. This change must be attributed to the bonding interaction between the molecule and the underlying metal surface.

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* corresponding author, email: d.p.woodruff@warwick.ac.uk

1. Introduction

The metallophthalocyanines, MPc, have attracted considerable interest in recent years, as an important class of organic semiconductors with a range of valuable electronic and optical properties and resultant potential applications [1, 2]. For example, vanadyl phthalocyanine (VOPc), investigated here, possesses a large third-order nonlinear optical susceptibility, ultra-fast optical response, and good stability against visible light irradiation.(e.g. [3, 4, 5, 6]). Most associated structural investigations are concerned with the properties of deposited thin films of these materials (e.g. [7, 8]), but there have also been a number of investigations of the earliest stages of such growth and the properties of the first molecular layer and its interaction with the substrate. Typically, MPcs are near-planar molecules that appear to 'lie flat' on the surface at the substrate interface, although there are very few detailed structural studies of these adsorbed layers. Most MPcs contain a single metal atom at the centre of the molecule, but in VOPc the V-O axis lies perpendicular to the plane of the molecule, leading the vanadyl oxygen atom to 'stick out' of the overall molecular plane. A model of the structure of this molecule, as determined in its crystalline form [9], is shown in Fig. 1; note that while the O atom lies 1.58 Å above the V atom in this structure, the V atoms also lies some 0.56 Å above the nearest neighbour N atoms, and even higher relative to the C atoms that are not strictly planar in configuration.

A scanning tunnelling microscopy (STM) study of VOPc deposited onto Au(111) yielded images that show ordering and symmetry consistent with an overall flat-lying orientation of the molecular plane, but raised the interesting question of whether the V=O bond is directed into or out of the surface [10]. Based on considerations of the electronic structure of the adsorbed molecule and its impact on the appearance of the STM images, it was concluded that the V=O points out of the surface, as might have been anticipated to be more physically reasonable. However, a simple structural study, such as that presented here, offers a far more direct route to establishing this molecular orientation. In this context, we may also note the results of a structural study of SnPc on Ag(111) [11] by normal incidence X-ray standing waves (NIXSW) [12]. In SnPc the Sn atom lies

significantly out of the plane defined by the surrounding atoms, and the Sn atom is found to lie closest to the Ag surface in most adsorption phases; i.e. in this system the central atom points down to the substrate. However, this study also finds that in one structural phase both orientations of SnPc (Sn up and Sn down) coexist. The question of the molecular orientation is therefore not trivial, although the situations of a central metal atom and a central V=O species are clearly different. Here, we present the results of an investigation of the Au(111)/VOPc system using scanned-energy mode photoelectron diffraction (PhD), a method that offers a means to obtain element-specific local structural information on adsorbed molecules [13, 14]. Our study allows us to clearly establish that the V=O bond of VOPc does, indeed, point outwards from the surface in a monolayer film on Au(111), but also provides some quantitative information on the internal structure of the adsorbed molecule.

While the structure of VOPc on Au(111) is of intrinsic interest, our study was also motivated by a rather different issue related to the chemical properties of surface vanadyl species at vanadium oxide surfaces. Our particular interest has been in the (0001) face of vanadium sesquioxide, V_2O_3, with a bulk structure comprising alternate buckled V_2 layers and planar O_3 layers, $-O_3VV'O_3VV'-$ etc. It is generally believed that when this surface is prepared in a low partial pressure of oxygen in an ultra-high vacuum system, it has a 'half-metal' termination but with additional oxygen atoms bonded atop these surface metal atoms to form local vanadyl species (i.e. to produce a termination, $-O_3VV'O_3V=O$). Moreover, it has generally been assumed that hydroxylation of this surface would lead to H attachment to these vanadyl O atoms (i.e. - $-O_3VV'O_3V-OH$) which would retain their V-atop sites. Our structural study of these surfaces using the PhD technique, however, failed to provide clear support for these ideas and, in particular, seems to show rather clearly that the hydroxyl O atoms are *not* in these atop sites [15, 16; specifically, the rather clear 'spectral signature' that we would expect to see in PhD from a hydroxyated vanadyl species was not observed.

Photoelectron diffraction exploits the coherent interference between the directly-emitted component of a photoelectron wavefield emitted from a core level of an atom, and the

components of the same wavefield elastically scattered by the surrounding atoms. This interference provides information on the relative position of the emitter and scatterer atoms. In the scanned-energy mode, one commonly finds that a measurement in a direction that corresponds to 180° backscattering from a near-neighbour of the emitter atom leads to particularly strong long-period modulations in the measured intensity as a function of photoelectron wavevector (and thus energy), due to this single backscattering event switching between constructive and destructive interference. Thus, for a vanadyl V=O species pointing out of a surface, one expects to see this type of clear modulation behaviour in the O 1s photoemission signal detected normal to the surface. This was not observed, in particular, for the $V_2O_3(0001)$–OH surface in which the emission from the O atoms in the hydroxyl species can be distinguished from that from the substrate oxide O atoms by their difference in O 1s photoelectron binding energy. VOPc on Au(111) would appear to provide a simple test of this expectation, the V=O species being orientated in space by its location in the phthalocyanine molecule that is adsorbed on the planar Au surface. This does, indeed, prove to be the case. The O 1s PhD data does show the expected modulation behaviour described above, providing a clear measurement of the V=O bondlength within the adsorbed molecule as well as identifying the molecular orientation. A more complete analysis of both O 1s and V 2p PhD measurements in normal emission, however, also yields some information on the adsorption-induced modification of the molecular conformation..

2. Experimental Details

The experiments were conducted in a conventional ultra-high vacuum surface science end-station equipped with the usual facilities for sample cleaning, heating and cooling. This instrument was installed on the UE56/2-PGM-1 beamline of BESSY II which comprises a 56 mm period undulator followed by a plane grating monochromator [17]. Sample characterisation *in situ* was achieved by LEED and by soft-X-ray photoelectron spectroscopy (SXPS) using the incident synchrotron radiation. These wide-scan SXPS spectra, and the narrow-scan O 1s and V 2p spectra used in the PhD measurements, were obtained using an Omicron EA-125HR 125 mm mean radius hemispherical electrostatic

analyser, equipped with seven-channeltron parallel detection, which was mounted at a fixed angle of 60° to the incident X-radiation in the same horizontal plane as that of the polarisation vector of the radiation. As the present study was focussed on characterising the scattering within the vanadyl species of the adsorbed VOPc molecules that is believed to be aligned perpendicular to the Au(111) surface, all PhD measurements were made in a single geometry detecting photoelectrons in normal emission and thus along the vanadyl V=O axis.

The Au(111) crystal was cleaned *in situ* by several cycles of 500 eV Ar ion bombardment followed by brief annealing to ~600 ℃; typically the LEED showed a nominal (1x1) pattern, but with the weak splitting of the integral order beams characteristic of the herring-bone reconstruction of the clean surface. SXPS showed no evidence of surface contamination. The VOPc, obtained from Alfa Aesar, was evaporated from an indirectly-heated horizontal glass tube with line-of sight of the sample. The source temperature during deposition, as measured by a thermocouple in contact with the outside of this tube, was 300-350 ℃, while the sample temperature during deposition was generally ~150 ℃. The SXPS signals of first the N and C 1s emission peaks, and then the lower coverage O 1s and V 2p peaks, were used to determine the conditions required for reasonable dosing rates. An estimate of the coverage was obtained by comparing the intensity of the N 1 s and C 1s signals with that of the Au 4d emission at a photon energy of 900 eV, using the relative photoionisation cross-sections calculated by Yeh and Lindau [18] and the attenuation length of the Au 4d photoelectrons given by the NIST database [19]. This led to an estimated coverage of 0.015 ML. For comparison, we note that the published STM images of the ordered layer of VOPc formed on Au(111) [10] indicate that the area occupied by each VOPc molecule is approximately 200 Å^2, implying a molecular coverage for this single complete molecular layer of ~0.035 ML. Our coverage is thus ~50% of the saturation coverage of this first molecular layer.

Three separate sets of scanned-energy photoelectron diffraction data were recorded at normal emission from the O 1s signal from different surface preparations, by recording a sequence of photoelectron energy distribution curves (EDCs) around this photoemission

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peak at equal steps in photon energy in the photoelectron kinetic energy range of ~ 60-300 eV at normal emission. In addition, two such sets of V 2p emission PhD data were collected in a similar manner in the kinetic energy range from ~60-250 eV. These data were processed following our general PhD methodology (e.g. [13, 14]) in which each of the individual EDCs is fitted by the sum of a Gaussian peak, a step and a template background. The integrated peak areas were then plotted as a function of photoelectron energy and each final PhD modulation spectrum was obtained by subtraction of, and normalisation by, a smooth spline function representing the non-diffractive intensity and instrumental factors.

3. Results and data modelling

Figs. 2 shows the normal emission O 1s and V 2p PhD modulation spectra extracted in this way for several different measurements. Clearly the main modulation features are reproducible despite the relatively high noise level to be expected in view of the very low adsorbate coverage; with only one V and one O atom per adsorbed molecule, the coverage of these emitter atoms is at least an order of magnitude less than that associated with most PhD structural studies of small molecules at saturation coverage on surfaces [13, 14]. In view of the consistency of the repeated measurements, the structural analysis that follows was conducted using averages of these multiple measurements (also shown in fig. 2) in order to achieve some reduction of the noise. The O 1s PhD spectra show a single dominant modulation that appears to be approximately periodic in photoelectron wavevector (proportional to the square root of the energy); this would be consistent with there being a single dominant backscattering pathway. The V 2p PhD spectra, on the other hand, seem to show only a single significant valley and peak at low energy. This behaviour is qualitatively in agreement with our expectation that the molecule lies flat on the surface with the V=O bond pointing outwards along the surface normal; we may then expect 180° backscattering from the V atom to dominate the PhD modulations for the O 1s spectra at normal emission, while the V 2p PhD spectrum should show no similar periodic modulations due to backscattering.

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To test this interpretation properly, however, requires quantitative modelling of the elastic scattering, and this was performed with multiple scattering computer codes developed by Fritzsche [20, 21, 22] that are based on the expansion of the final state wave-function into a sum over all scattering pathways that the electron can take from the emitter atom to the detector outside the sample. The quality of agreement between theory and experiment was judged not only by eye, but also by the value of an objective reliability- or *R*-factor, defined as a normalised summation of the squares of the differences between the experimental and theoretical modulation amplitudes at each point in the spectra [13, 14]. In general these calculations are performed using a large cluster of several hundred scatterer atoms, most notably including the higher atomic number metallic substrate atoms. In the present case, however, we have focussed on modelling only the intramolecular scattering.

The rationale for omitting the role of Au substrate scattering is that there are good reasons for believing that this will not make a large contribution to the PhD modulations. Three factors determine the importance of this Au scattering contribution, namely the atomic scattering cross-section, the distance of the scatterer atoms from the emitter atoms, and the emitter-substrate lateral registry. While in general, atoms of higher atomic number have higher scattering cross-sections, Au (like other 5d metals such as Pt) is actually a weak backscatterer in the electron energy range ~100-200 eV in which there is a deep minimum in the backscattering cross-section (e.g. [23, 24]). For example, at an energy of ~150 eV, the backscattering amplitude from an Au atom is a factor of ~10 less than that of Cu and, indeed, is smaller than that of C. Secondly, the distance of the nearest-neighbour Au atoms to the O and V emitter atoms can be expected to be no less than ~5 Å and ~3 Å respectively (assuming the lowest-lying atoms in the molecule are ~2.5-3.0 Å above the Au surface plane), with most Au atoms at substantially greater distances. The propagation of the electrons between emitter and scatterer, and from the scatterer to the detector, is attenuated in amplitude by a 1/r factor due to the spherical wave nature of the propagation, and longer scattering paths incur increased inelastic scattering, so the role of more distant scatterers is strongly attenuated. Of course, some of the O-C intramolecular distances also exceed 3 Å and we show below that scattering

from the C atoms closest to the O and V emitters does contribute to the observed PhD modulations, but the fact that there are several C atoms in symmetrically-equivalent positions relative to the normal-emission detection direction significantly enhances their role. Thirdly, we note that the VOPc molecule does not appear to form a commensurate structure with respect to the underlying Au(111) substrate. Strictly, we only know, from the published STM images [10], that the VOPc layer has a periodicity that is large (~5x) compared to that of the substrate, and that the overlayer has a different symmetry (near-square rather than hexagonal). Moreover, one STM image of this publication (fig. 8) actually appears to show that the 'herring-bone' reconstruction of the Au(111) persists under the VoPc layer, indicating that the molecule has little influence on the Au surface structure and that an incommensurate overlayer structure is most probable. The dominance of intermolecular interactions over the corrugation of the substrate potential in determining the molecular ordering, implied by this incommensuration, has been observed explicitly for at least one other large molecule on this same surface [25]. Clearly, the VOPc molecules cannot all adopt identical lateral adsorption sites on the Au(111) substrate. The Au backscattering effect therefore comprises an incoherent average of the PhD modulations over many different local adsorption sites, each at a potentially different height above the surface. Indeed, if the overlayer is truly incommensurate, there are an infinite number of inequivalent sites. This leads to a very strong attenuation of the resulting PhD modulations. Some estimate of this effect can be gained from PhD studies of atomic O on Cu(100) [26] and Cu(111) [27] in, respectively, ordered and disordered phases; the resulting modulations were found (in experiment and simulations) to be reduced by more than a factor of 2 as a result of the disorder (simulated by many different adsorption sites). In this system, however, the O-Cu distance is essentially constant even in the disordered state on Cu(111), whereas this will not be true for the V and O atoms in VOPc in different sites on Au(111), so the attenuation of the associated PhD modulations can be expected to be substantially greater.

We should also note, as remarked earlier, that PhD measurements made in a direction corresponding to 180º backscattering from a nearest-neighbour atom are commonly

dominated by the interference arising from this single scattering pathway, so for the O 1s PhD at normal emission we may expect, if the V=O bond points out of the surface, that intramolecular scattering from the nearest-neighbour V atom will dominate in this way. This does, indeed, prove to be largely correct, although intramolecular scattering contributions do prove to be significant.

Of course, despite our good reasons for believing that Au scattering will contribute little to the measured PhD spectra, it would be preferable to explore this effect in detail with quantitative multiple scattering simulations. In practice, though, the huge associated parameter space (multiple low-symmetry lateral registry sites, each at different absorbate-substrate interlayer spacings) is far too large to be optimised by just two normal emission experimental PhD spectra. However, some indication of the true importance of these omitted scattering paths may be obtained from our attempts to fit the experimental data by intramolecular scattering alone. If the Au scattering contribution is very significant, we can expect only poor fits for physically reasonable structures with these restricted calculations. As we show below, this proves not to be the case.

As remarked above, the O 1s PhD spectrum appears, on inspection, to be consistent with an adsorption geometry in which the V=O bonds points outwards from the surface, and in this case it is this modulation spectrum that is expected to provide the most information on the internal conformation of the adsorbed VOPc molecule as the O 1s emitter atom is ideally located for backscattering from the V atoms and its near-neighbour N and C atoms. However, if the orientation of the adsorbed molecule is inverted, with the V=O bond pointing down towards the substrate, it is the V 2p PhD spectrum that may be expected to provide more structural information, at least of the V=O bondlength through 180° backscattering from the O atom. After performing some preliminary calculations we have therefore conducted the structure determination by adopting a consistent procedure in which we have optimised the fits to both of these spectra simultaneously for both of the possible molecular orientations.

We first consider the influence of photoelectron scattering within the vanadyl species

alone. Fig. 3 shows a comparison of the averaged experimental O 1s PhD spectrum (Fig. 2), with the results of a multiple scattering calculation that included only the O emitter atom and the nearest-neighbour V atom. The molecule is assumed to lie flat on the Au(111) surface with the V=O bond perpendicular to the surface and pointing outwards. Fig. 3 also shows a similar comparison for the averaged V 2p PhD spectrum using the same structural model containing only the V (emitter) and O atoms. The V-O distance has been adjusted to optimise the fit to the O 1s PhD spectrum, and has a value of 1.62 Å. This compares with a value in the crystalline phase of VOPc of 1.580±0.003 Å [9]. The agreement between theory and experiment is not perfect, but this simple calculation clearly reproduces the main modulation features of the O 1s PhD experiment data, although the lowest energy modulation peak is significantly displaced in energy. The fit to the V 2p modulation spectrum is poor. Of course, with the V=O bond pointing outwards along the surface normal we have already remarked that there is no contribution to the V 2p PhD from intramolecular backscattering close to the favoured 180° scattering angle, and as this calculation only includes the O atom (located at 0°) as a source of single scattering, the poor fit to the V 2p PhD is to be expected. In fact in this calculation the only modulation present in the V 2p PhD spectrum comes from double scattering involving backscattering from both the O atom and the V emitter.

Fig. 4 shows the results of a similar calculation for the best-fit structure (as determined by the combined *R*-factor for both the O 1s and V 2p PhD spectra) in which scattering from all the N and C atoms, as well as the V and O atoms, have been included. In view of the small data set, the large number of (weakly-scattering) N and C atoms, and indeed the neglect of Au scattering effects, it is clearly unrealistic to expect to obtain meaningful and precise optimised positions of all the scattering atoms in an unconstrained fashion. In order to achieve this optimised fit to the experimental data we have therefore first conducted a series of calculations on unconstrained models including scattering from only sub-sets of the N and C atoms within the molecule in order to explore the importance of their different scattering contributions. These calculations showed that the most important scattering contributions (beyond those from the V and O atoms) arise from the ring of four N atoms that are closest to the V atom, while a significant influence

is also seen from the eight C atoms that are closest to the V atom. This is not particularly surprising; this relative ordering of importance corresponds to the most important contributions arising from the shortest scattering paths from the two emitter atoms and, for the O emitter, from the atoms closest to the favoured 180° backscattering geometry. The fact that the innermost N atoms, in particular, but also the next shell of C atoms, do have a significant influence on the PhD spectra, means that their location relative to the O and V emitter atoms can be optimised to achieve the lowest R-factor. Nevertheless, the variation of the R-factor with the structural parameters determining the position of these atoms shows multiple minima, so to locate the physically meaningful solutions constraints were applied to the local interatomic bondlengths. Specifically, the V-N and N-C nearest-neighbour distances were initially constrained to lie within 0.1 Å of their values in crystalline VOPc [9]) while the C-C bonds were fixed to within ~0.03 Å or these crystalline values. In addition the outer phenyl rings were assumed to have only a minimum tilt relative to the molecular plane, consistent with the optimised positions of the inner N and C atoms found with the smaller clusters.

Comparison of Figs. 3 and 4 shows clearly that including the additional intramolecular scattering leads to a very significant improvement in the agreement with the experimental data, the combined R-factor value for the two spectra falling from 0.46 to 0.24. The influence of the additional scattering contributions is mainly seen at lower energies, consistent with the fact that the scattering cross-sections of the low-mass N and C atoms fall off steeply with increasing energy. Of course, this is also true for the O atom as a scatterer, and accounts for the fact that the V 2p PhD spectrum shows almost no modulation above ~150 eV. The improvement in the fit to the V 2p spectrum is particularly noticeable; unlike the O emitter, the V atom has no dominating backscatterer atom so including the nearby N and C atoms has a particularly pronounced effect in this low-energy region. The most pronounced effect on the O 1s PhD spectrum is a significant shape change of the lowest-energy peak, bringing the energy of this feature into significantly better agreement with experiment. The length of the V=O bond in this calculation is 1.60 Å, within 0.02 Å of the value in crystalline VOPc. Fig. 5 shows a side view of the VOPc molecule, comparing its conformation in its bulk crystalline solid with

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that determined here when adsorbed on Au(111). Adsorption appears to make the molecule significantly more nearly planar; the near-neighbour N and C atoms have almost the same height above the surface and are significantly more nearly coplanar with the V atom. The location of the C atoms in the outer phenyl rings cannot be determined with any meaningful precision from the PhD simulations, but the planarity of the inner atoms suggests this must also be the case for these outer atoms if reasonable constraints are applied to all the relevant bondlengths.

A key question that needs to be answered to validate this discussion concerns the precision with which these atomic positions can be determined relative to the O and V emitter atoms. Our standard procedure to provide an objective measurement of the precision is to define a variance of the minimum R-factor, $\mathrm{var}R_{min}$, based on the size of the experimental data set, and establish how large a variation of the different structural parameters is required in order for the R-factor value to exceed the sum $R_{min} + \mathrm{var}R_{min}$. In the present study the small data set leads to a relatively large value of $\mathrm{var}R_{min}$ of 0.08. On this basis the V-O distance is 1.60±0.04 Å, clearly consistent with the value in bulk crystalline VOPc of 1.580±0.003 Å [9]; the relatively low precision of our value reflects the small data set. The precision in locating the innermost N and C atoms is, of course, significantly worse. The PhD technique determines the location of scatterer atoms relative to the emitter, and typically shows significantly greater sensitivity to the emitter-scatterer distance than to the angle of this emitter-scatterer vector. Bearing in mind that we have constrained the V-N distances within a limited range, and that the V 2p PhD is sensitive primarily to the V-N and V-C (and V-O) distances (but not the bond angles) it is evident that it is the O 1s PhD that provides the main information on the relative heights of the N and C atoms, and thus on the degree of planarity of the molecule. The distance of the O atom to the inner shell of four nearest-neighbour N atoms, O-N_{nn} is found to be 2.50(+0.14/-0.07) Å, to be compared with a value of 2.90 Å in crystalline VOPc. Similarly, the distance from the O atom to the inner shell nearest-neighbour C atoms, O-C_{nn} is 3.49(+0.24/-0.12) Å, compared with 3.72 Å in crystalline VOPc. These comparisons do indicate that the enhanced molecular planarity reflected in the best-fit structure, relative to that in crystalline VOPc, as shown in Fig. 5, is, indeed, significant.

Indeed, calculations of the values and precision of the $V-N_{nn}$ and $V-C_{nn}$ distances projected along the V-O direction are -0.05(+0.14/-0.10) Å   and -0.25(+0.28/-0.14) Å. The negative values indicate the N and C atoms are below the V atom and closer to the substrate, and may be compared with values of -0.57 Å and -0.65 Å, respectively, in the crystalline solid. The key difference induced by the adsorption appears to be that the vanadyl species is pulled down into the molecular plane defined by the nearest-neighbour N atoms by 0.52(+0.14/-0.10) Å, such that it is only the O atom that is very significantly out of the approximately planar location of the remaining atoms. Notice that the change in the interlayer spacing of the nearest neighbour N and C atoms given by these figures, 0.12(+0.31/-0.17) Å, is clearly not formally significant.

This analysis assumes that the molecule is oriented with the V=O bond pointing outwards from the surface. Could it be that the molecule inverted, with the V=O pointing inwards towards the Au bulk? To investigate this possibility we have investigated a similar structural optimisation of such a model through comparisons of the results of the multiple scattering simulations with the experimental PhD spectra. The structural search failed to identify any structural model with the molecule in this orientation that gave a reasonable fit to both the V 2p and O 1s PhD spectra; the lowest R-factor found for such structures was 0.79. A moderate fit to the V 2p spectrum was possible, but this gave a very poor description of the O 1s spectrum. The only structure identified that provided a reasonable fit to the O 1s spectrum was found to be entirely unphysical, with the V and adjacent N atoms almost coincident in space. To illustrate the problem we show in Fig. 6 the results of a calculation for a model in which the best-fit structure of Fig. 4 was simply inverted. Clearly the simulated O 1s spectrum is quite unlike that of the experiment, as reflected in an overall R-factor of 0.86. We conclude, therefore, that the PhD data clearly excludes this possible orientation of the adsorbed molecule.

4. General discussion and conclusions

Scanned-energy mode photoelectron diffraction using the O 1s and V 2p emission perpendicular to the surface has been used to investigate the orientation and internal

conformation of vanadyl phthalocyanine (VOPc) adsorbed on Au(111). The O 1s PhD spectrum shows a reasonably strong long-period modulation characteristic of backscattering from the V atoms directly below, as to be expected if the V=O vanadyl bond points out of the surface, along the surface normal. The observation of this clear (predicted) modulation function reinforces the conclusions of an earlier PhD study of the surface regarding the influence of surface vanadyl species on the $(0001)V_2O_3$ [15, 16]. This observation also indicates that the VOPc molecule adsorbs onto the Au(111) surface with the V=O pointing out of, rather than into, the underlying substrate.

A fully quantitative evaluation of the PhD data using multiple scattering simulations confirms this molecular orientation and shows that the V=O bondlength is 1.60±0.04 Å, not significantly different from its value in bulk crystalline VOPc. However, the calculations indicate that the V atom in the adsorbed molecule is almost coplanar with the surrounding N atoms and is thus pulled down into the approximately planar region, defined by the N and C atoms, by 0.52(+0.14/-0.10) Å, relative to its location in the molecule in crystalline VOPc. This change must be attributed to the bonding interaction between the molecule and the underlying metal surface.

In general the PhD technique provides rather reliable quantitative structural information, but in the present case we have used a small data set and made a number of simplifications in the data analysis. Could these influence the precision of the conclusions? One constraint we have applied is to limit the range of variation of the intramolecular bondlengths. With so many potential structural parameters, and a limited data set, such a constraint is necessary to identify a meaningful solution. The more distant C atoms (relative to the O and V emitters) contribute little to the scattering, while interatomic bondlengths are unlikely to change in a molecule of this type by more than a few hundredths of an Ångström unit, so this constraint seems unlikely to influence the results. Potentially more significant is the neglect of Au scattering. For the V=O orientation and bondlength it is clear that the conclusions are very stable; even allowing only scattering from the V and O atoms provides a closely similar value for the V=O bondlength. It is more difficult to conclusively exclude the possibility that the Au

scattering has no influence the V-N interlayer spacing because a significant change in the PhD spectra below 100 eV, where the Au scattering cross-section is large, could influence the structural optimisation, particularly for the V emitter that is closest to the substrate. On the other hand, the fit to the O 1s PhD spectrum is the one that is most sensitive to this modification to the molecular conformation, and the O atom is (even with the V=O pulled down into the molecular plane) more than 2 Å above the underlying C atoms and so likely to be almost 5Å above the outermost Au layer. It is unlikely, therefore, that Au scattering has a significant influence on our numerical conclusions.

There are very few previous structural studies of adsorbed planar or near-planar molecules with which to compare this result. The most relevant is probably the NIXSW study of SnPc on Ag(111) [11] discussed in the Introduction. In addition, NIXSW has also been used to study fully fluorinated copper phthalocyanine, $F_{16}CuPc$, on Cu(111) and Ag(111) [28]. This investigation showed that adsorption on these two surfaces (with the phthalocyanine plane parallel to the surface) led to different changes in the relative heights of the C and F atoms, but the height of the central Cu metal atom above the surface was not determined. NIXSW has also been used to investigate the adsorption of PTCDA (1,4,5,8-perylene-tetracarboxylicacid-dianhydride) [29] on Ag(111) and was able to show that inequivalent O atoms on the periphery of the nominally planar molecule (four carboxylic O atoms at the corners and two intermediate anhydride O atoms) occupy different heights above the surface, clearly an effect of the nature of the molecule-substrate bonding. Both of these previous studies clearly support the notion that bonding of large near-planar molecules to metal surfaces can lead to some modification of the internal conformation of the molecule . In the present case, the rather large shift of the V atom down into the near-planar region defined by the C and N atoms would appear to indicate that the V atom itself does have a significant interaction with the underlying Au surface.

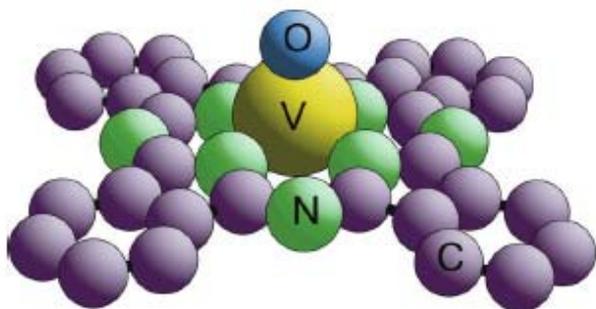**Acknowledgements**

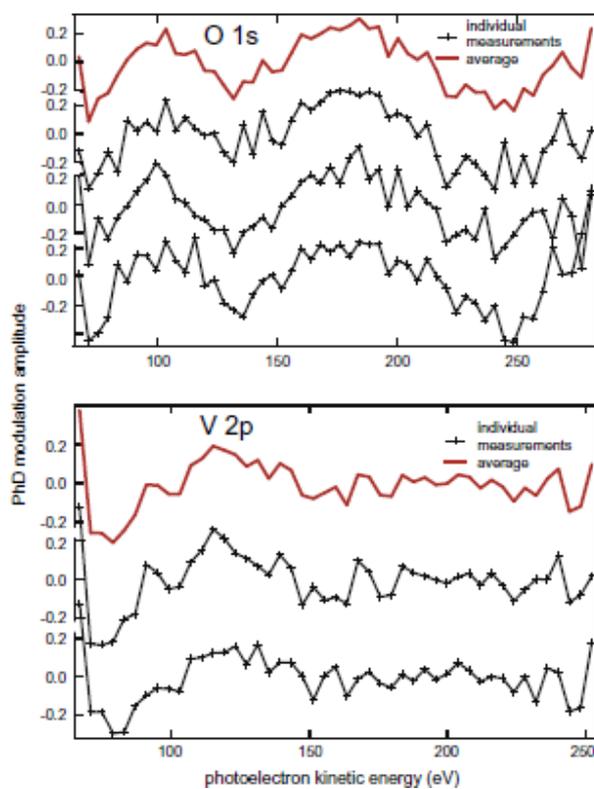**Figure Captions**

Fig. 1 Model of the VOPc molecule

Fig. 2 Comparison of the three separate experimental measurements of the O 1s PhD spectra and two separate measurements of the V 2p PhD spectra from VOPc on Au(111) at normal emission. Also shown are the average spectra, used in the structure determination, that are obtained from these individual measurements.
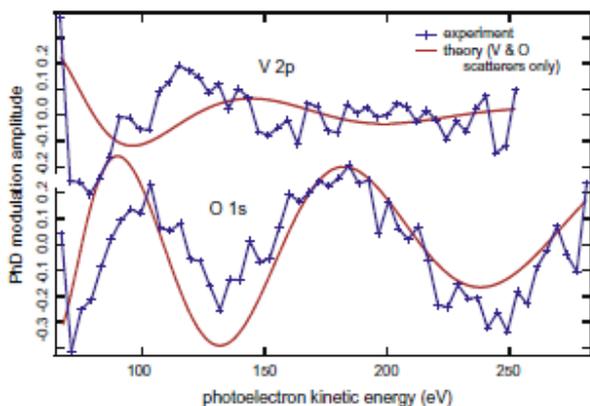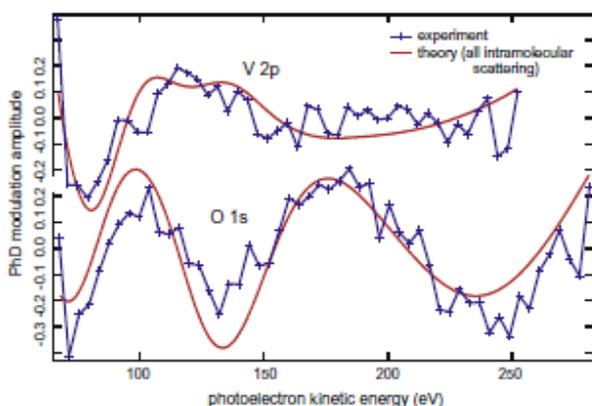
Fig. 3 Comparison of the averaged experimental O 1s PhD and V 2p spectra from VOPc on Au(111) (fig. 2) with the results of multiple-scattering simulations of a structurally-optimised model (with the V=O bond pointing out from the surface) assuming scattering only from the V and O atoms. The overall *R*-factor is 0.46.

Fig. 4 Comparison of the averaged experimental O 1s PhD and V 2p spectra from VOPc on Au(111) (fig. 2) with the results of multiple-scattering simulations for the structurally-optimised model (with the V=O bond pointing out from the surface) including scattering from all atoms within the molecule. The overall *R*-factor is 0.29.
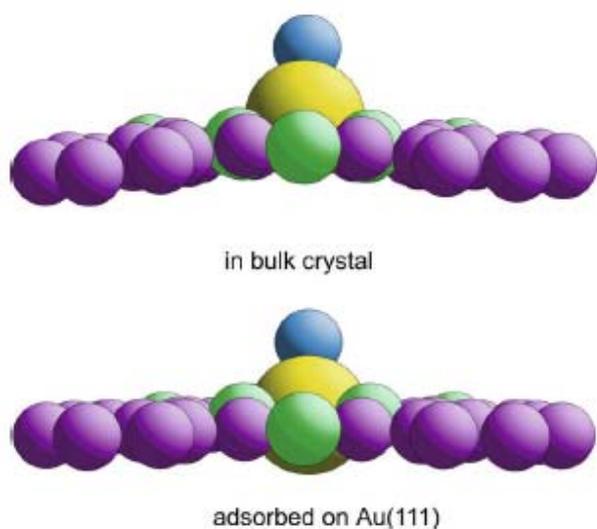
in bulk crystal

adsorbed on Au(111)

Fig. 5 Side view of the VOPc molecule in the bulk crystalline solid [9] and as found in this study for the molecule adsorbed on Au(111).
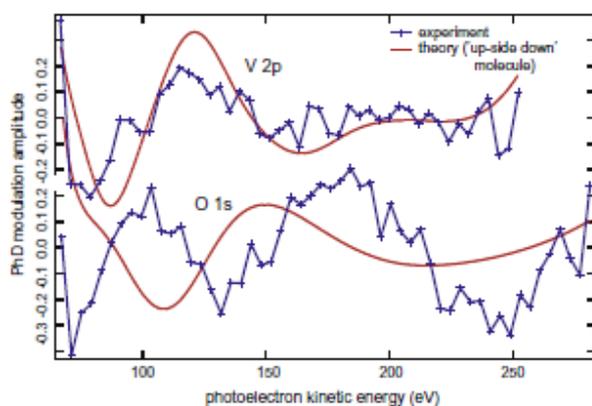

Fig. 6 Comparison of the averaged experimental O 1s and V 2p PhD spectrum from VOPc on Au(111) (fig. 2) with the results of multiple-scattering simulations for a structural model in which the molecule is inverted such that the V=O bond points into the Au(111) substrate. The overall R-factor is 0.86.

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