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A comparative study of the photodissociation of physisorbed O₂ on Pt(111) and graphite

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Abstract. A comparative study of photodesorption from physisorbed oxygen layers on (highly oriented pyrolytic) graphite and Pt(111) surfaces has been carried out using continuously tuneable synchrotron radiation in the energy range 13–35 eV. The photodesorption of both O⁺ and O[−] species is detected. Through monitoring the ion yields as a function of the photon energy and coverage we have proposed a new mechanism for photodesorption of O[−] ions induced by inelastic scattering and attachment of photoelectrons originating from the adsorbate layer in the photon energy region between 25 and 30 eV.

1. Introduction

Photon-induced reactions within adsorbed layers provide routes for the modification of surfaces and surface processes involving adsorbed species which are inaccessible using purely thermal reactions [1–4]. The fundamental processes which may take place include photon-driven desorption, dissociation and surface reaction, and important applications arise in such diverse fields as photocatalysis, epitaxial growth, lithography, photon-induced etching and the direct laser writing of thin films [4].

Although thermal reactions arise as a result of the heating which takes place during intense irradiation of the surface, true photochemical processes can dominate at lower photon fluxes and these are normally classified as being either ‘direct’ or ‘indirect’ [1–3]. The former involve the direct photoexcitation of the adsorbate to higher electronic states as happens in the gas phase; the characteristics of the process may however differ from those observed in the gas phase because of the interaction of the ground and excited electronic states of the adsorbate with the underlying substrate and neighbouring molecules. In contrast, indirect mechanisms arise from initial photon absorption in the underlying substrate. Excitation of the adsorbate can then take place by subsequent electronic energy transfer, or by collision with ‘hot’ electrons, which are photoejected from the substrate into the adsorbed film at sufficiently high photon energies.

The surface photochemistry of physisorbed O₂ as a model system has been the subject of many studies, at both multilayer [5–7] and monolayer coverage [8]. The surface photochemistry of O₂ physisorbed on argon spacer layers on the graphite surface [9]

has recently been investigated to obtain further information on the relative importance of direct and indirect channels. This still does not provide unambiguous identification of the mechanisms since different physical processes can arise in the same photon energy range. Indirect processes should depend sensitively on the electronic structure of the substrate, whereas direct processes reflect the electronic properties of the adsorbate. The purpose of this work is therefore to concentrate on the new information (compared with previous studies) which can be obtained by comparing the photoexcitation characteristics of a given adsorbate on different substrate surfaces. In this paper we thus make a comparative investigation of the photodissociation of physisorbed O₂ on Pt(111) and highly oriented pyrolytic graphite (HOPG).

2. Experimental details

The reported experiments were conducted at beamline 3.1 of the Daresbury Synchrotron Radiation Source using monochromatized light in the energy range 13–35 eV from a Seya–Namioka monochromator. The light intensity was measured as a function of photon energy using a photomultiplier tube. The measured photon intensity was then used to normalize subsequent ion yields with respect to the photon flux. In all experiments the light was incident on the surface at approximately 40° to the surface normal. The desorbed ions were collected by a pulse counting quadrupole mass spectrometer (Hiden Analytical) perpendicular to the surface. The photon energy resolution was about 0.3 eV.

The experiments were performed in a vacuum chamber maintained at pressures below 2×10^{-10} mbar. The samples could be heated by electron bombardment and cooled to ~31 or ~29 K for graphite or Pt, respectively, using a liquid helium cryostat. The HOPG sample was cleaved in air prior to insertion in the vacuum system and was cleaned *in situ* by heating to 900 K. The Pt(111) sample was degreased in air and then cleaned in vacuum using Ar⁺ ion sputtering and annealing cycles; small traces of surface C which remained after this procedure were removed via (their) reaction with oxygen in adsorption–desorption cycles, with final heating to 1000 K in order to remove residual atomic oxygen.

In the case of negative-ion detection the photoelectron background was determined by measuring the signals for masses 14 and 15 for graphite and Pt(111), respectively, and assuming that these arose entirely from photoelectrons. This signal could then be subtracted from the signals obtained for the negative ions to obtain the true ion flux. The detected ion signals were optimized by varying the voltages on the front lens elements of the mass spectrometer. Experiments were performed in two modes; in the first mode the photon-induced ion yield was determined as a function of photon energy after particular exposures of the cold surface to O₂ gas; in the second mode the photon energy was fixed and the ion yield was measured as a function of time in a standing oxygen pressure of $\sim 2 \times 10^{-8}$ mbar.

3. Results and discussion

In order to make a reliable comparison of the photodesorption yields from the different substrates the determination of the number of the adsorbed layers is a crucial factor. In figure 1 we plot the coverage dependence of the O⁺ ion yield from oxygen adsorbed on Pt(111), together with the photoelectron drain current, at a photon energy of 25 eV and $T \sim 29$ K. The O⁺ signal starts to appear at a coverage of 4 L, where the photoemitted drain current reaches its minimum (denoted by A). The drain current is the electron current from ground to the sample to replace the photoemitted electrons (i.e. it is directly proportional

to the photoemitted current). To first order [10], the relative changes in the photoemission current are determined by the relative changes in $(h\nu - \phi)^2$, where ϕ is the work function of the substrate. So it is expected that changes in the work function can be detected by measuring the drain current. The molecular chemisorption of O₂ on Pt(111) leads to a peroxy-like state (O₂⁻²) [11,12], which means that the surface dipole layer is enhanced, leading to an increase in the work function of the O₂/Pt(111) system in comparison to the clean Pt(111) surface. The observed drop in drain current at low coverage is correspondingly assigned to the drop in work function due to molecular adsorption. At an exposure of ~ 5 L the drain current changes slope and the appearance of the ion signal is noted. We interpret this as the start of the build-up of the first physisorbed layer (i.e. on top of a saturated chemisorbed layer). In this way an exposure of ~ 5 L is associated with approximately one monolayer (ML) and this provides a useful coverage calibration for the O₂/Pt(111) system. In the case of O₂ physisorbed on graphite we have shown that a new photoexcitation channel leads to production of O⁻ at 15 eV peaks at about 1 ML coverage [8]. In this case the data are calibrated with respect to this coverage (i.e. given in terms of the number of monolayers).

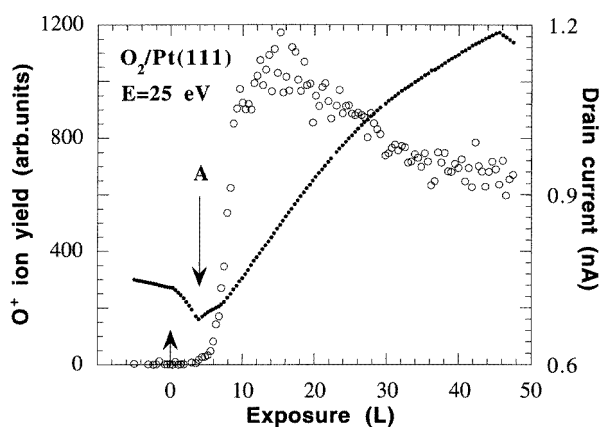


Figure 1. The coverage dependence of the O⁺ ion yield and drain current (empty and full circles, respectively) at a photon energy of 25 eV of O₂ adsorbed on the Pt(111) surface, at 29 K. The arrow A represents the monolayer coverage (see discussion in the text).

Figures 2(a)–(c) shows the yield of O⁺ ions as a function of photon energy for the gas phase, for 3 ML physisorbed O₂ on top of the chemisorbed layer of O₂ on the Pt(111) surface and ~ 3 ML O₂ physisorbed on graphite, respectively. The spectra show similar features for photon energies up to 30 eV. These include a threshold at 19 eV, followed by a shoulder at ~ 22 eV and a resonance feature at ~ 24 eV. The most prominent difference compared to the gas phase is the threshold behaviour at 31 eV. Such behaviour has been observed previously for solid O₂ and has been attributed to photoelectron-induced dipolar dissociation [5]. The exposure dependence can also give an insight into the photodissociation process. In figure 3(a) and (b) we plot the O⁺ ion yield and photoemitted current as functions of O₂ coverage on graphite (at 29 K) for incident photon energies of 24 and 28 eV, respectively. We see that the O⁺ ion yield in both spectra peaks at ~ 53 ML, as does the photoemitted current. We have recently monitored the photoemitted current as a function of time, at a photon energy of 33 eV, for an Si(100) surface held at 30 K and precovered with various amounts of O₂. The photoemitted current was found to be steady with time at coverages up to ~ 25 ML, but at coverages of 60 ML (120 ML) strong attenuation of the photoemitted

current within 60 (40) s was observed, attributed to a charging of the O₂ film. Charging of thick, insulating films of O₂ can be expected to occur on any substrate. Hence, due to the additional electric field of the positive ions, the probability of escape of O⁺ ions decreases. This can also account for the decrease of the O⁺ ion yield shown in figure 3. This interpretation is different to that in our previously published work [6, 7], where the attenuation of the positive-ion signal with coverage led us to assign it to a substrate-mediated process (photoelectron-driven dipolar dissociation). Moreover, the O⁺ ion yield at ~24 eV cannot be due to interband transitions within graphite (as previously assigned) because the same peak in the O⁺ ion yield is observed for 3 ML O₂ on one layer of molecularly chemisorbed O₂ on Pt(111) (figure 2(b)). It is highly unlikely that the same energy difference between occupied and unoccupied states would occur for two very different substrates. The similarity of the O⁺ ion yield from graphite and Pt(111) surfaces implies that the main process of dissociation is a direct one.

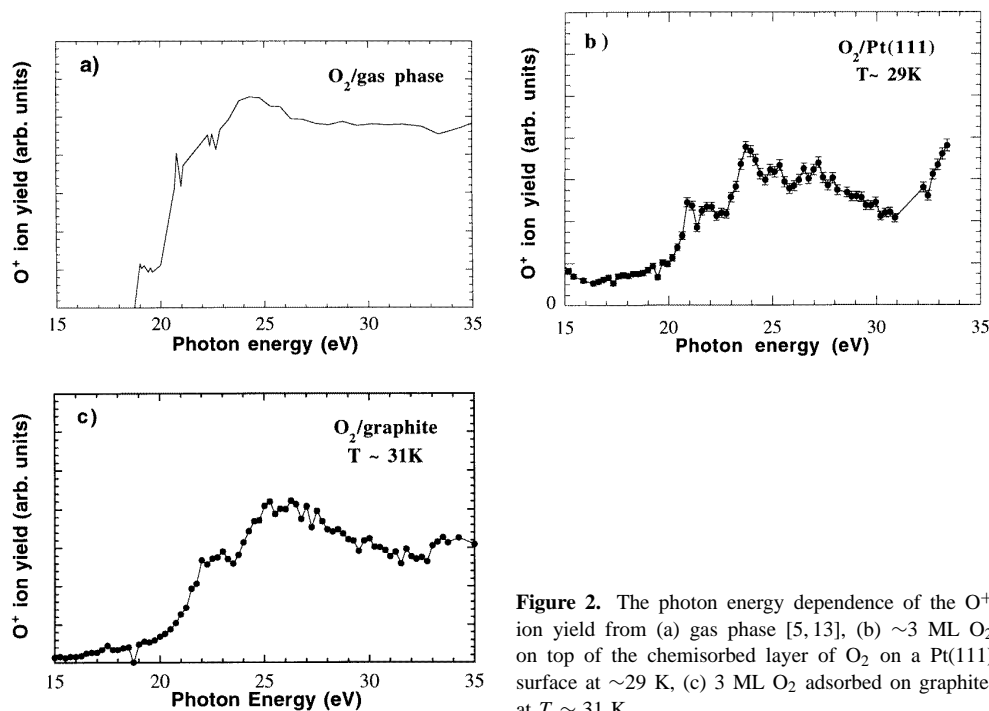


Figure 2. The photon energy dependence of the O⁺ ion yield from (a) gas phase [5, 13], (b) ~3 ML O₂ on top of the chemisorbed layer of O₂ on a Pt(111) surface at ~29 K, (c) 3 ML O₂ adsorbed on graphite, at $T \sim 31$ K.

In figure 4(a)–(c) we plot the yield of O[−] ions as a function of photon energy for the gas phase, for 3 ML physisorbed O₂ on top of the chemisorbed layer of O₂ on a Pt(111) surface and ~3 ML O₂ physisorbed on graphite, respectively. There exists a similarity between the features of all three spectra: a peak at ~17 eV, a common threshold at ~19 eV, followed by a peak at ~22 eV. In gas phase photoionization experiments, the onset at 18 eV, together with peak structures up to 23 eV, have been attributed to direct dipolar dissociation; the peaks have been assigned to the predissociation of the 3dσ Rydberg states which converge to the c⁴Σ_u[−] ion state [13]. The 4dσ Rydberg series, which converges to the same c⁴Σ_u[−] ion state, is believed to contribute to the O[−] and O⁺ ion yields for energies above ~23 eV [13]. From the clear similarities between the negative-ion signals emerging from the condensed oxygen layers on different substrates, graphite and Pt(111), the main process of excitation of O₂ is direct photodissociation in the photon energy range up to ~25 eV.

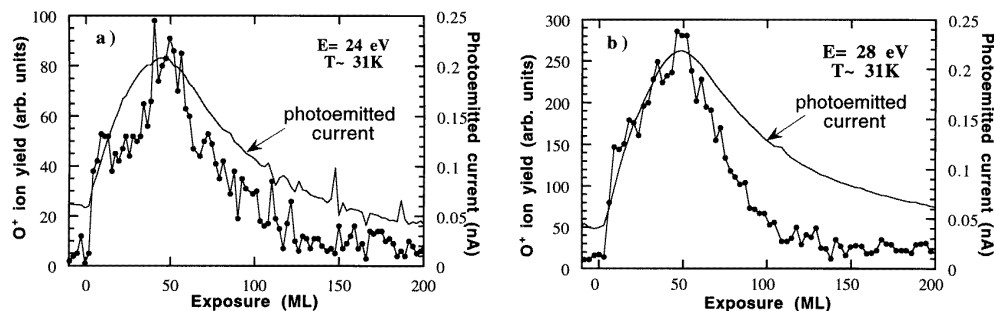


Figure 3. The coverage dependence of the O⁺ ion yield and photoemitted current (empty circles and solid line, respectively) at the photon energies of (a) 24 eV and (b) 28 eV of O₂ adsorbed on graphite, at ~31 K.

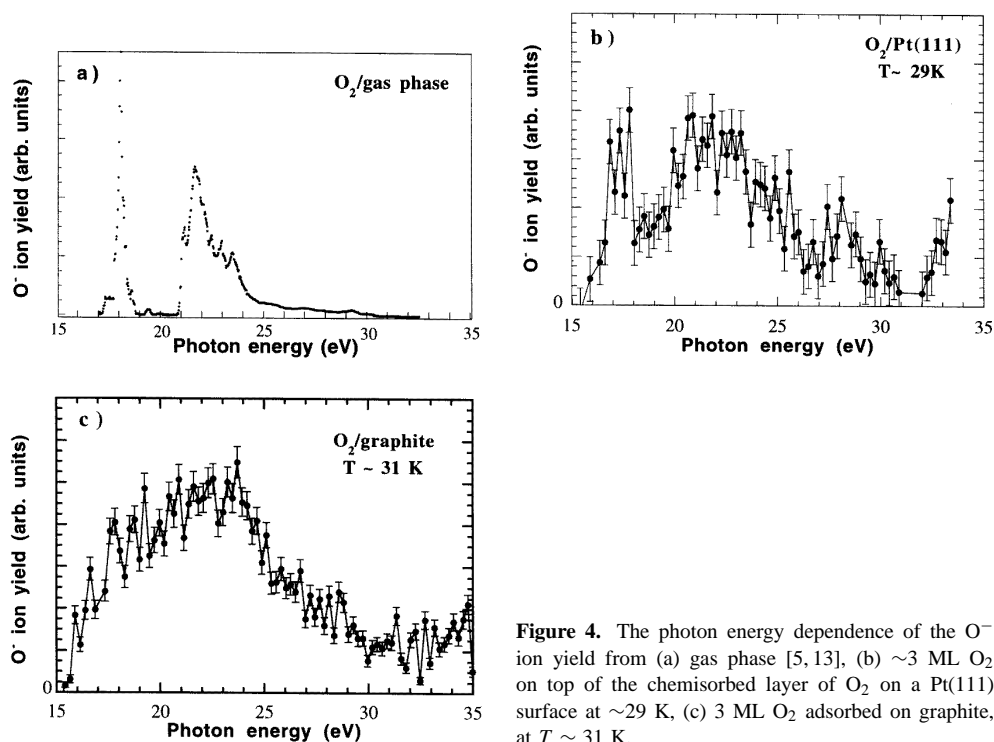


Figure 4. The photon energy dependence of the O⁻ ion yield from (a) gas phase [5,13], (b) ~3 ML O₂ on top of the chemisorbed layer of O₂ on a Pt(111) surface at ~29 K, (c) 3 ML O₂ adsorbed on graphite, at T ~ 31 K.

The most prominent difference in figure 4(b) and (c) compared with the gas phase (figure 4(a)) is the presence of an ion signal in the photon energy range of 25–30 eV. Despite the previous observation of this behaviour [5,9], no detail mechanism has yet been proposed. In order to investigate this behaviour further we plot in figure 5 the coverage dependence of the O⁻ ion yield as a function of O₂ thickness for three different photon energies, 22, 24 and 28 eV. First we note an almost perfectly linear increase of the O⁻ ion yield at 28 eV photon energy. The ion yield for the other two energies, 22 and 24 eV, exhibits a strong change of slope at ~7–8 ML. It is known that below a thickness of ~7 ML of rare gas (RG) adsorbed on a metal substrate the O⁻ negative-ion yield from O₂ adsorbed

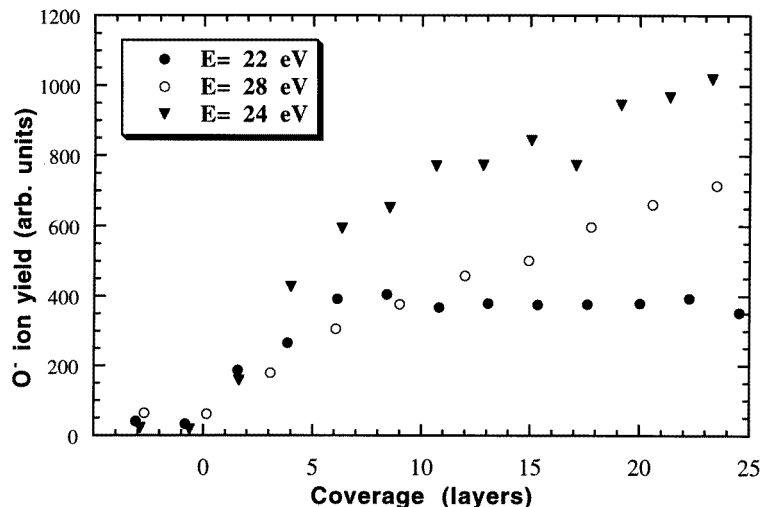


Figure 5. The coverage dependence of the O⁻ ion yield at photon energies of 22 eV (full circles), 24 eV (triangles) and 28 eV (empty circles) of O₂ adsorbed on graphite, at ~31 K.

on top of the RG grows and saturates with coverage because of neutralization and image-charge effects [14, 15]. This we believe explains the change of the slope at ~7 ML.

However, the coverage dependence at 28 eV suggests that another mechanism is more dominant at this energy. Since the gas phase data for O⁻ production by direct photodissociation in the same photon energy region does not show any substantial ion yield one must assume that *photoelectrons* may be responsible for such an effect. Negative-ion yield in this photon energy region is observed for *both* substrates (i.e. graphite and one physisorbed molecular oxygen layer on top of chemisorbed O₂/Pt(111)) and correspondingly we conclude that the photoelectrons from the underlying substrate are *not* a major cause of the effect since the electronic structures of graphite and chemisorbed O₂ on Pt(111) are quite different. Another source of photoelectrons is the adsorbate layer. Indeed, since the negative-ion signal at 28 eV photon energy rises linearly as a function of thickness and the same behaviour is observed for the drain current (proportional to the photoelectron emission). It is reasonable to assume that the photoelectrons come from the adsorbate layer. In order to estimate the maximum electron kinetic energy we note that in the gas phase the photoionization threshold from the $(1\pi_g)^{-1} X^2\Pi_g$ state is at 12.7 eV (see [16], [17] and references therein). This state has the highest branching ratio (relative photoelectron yield) in the photon energy range above 25 eV (40%) while the second-highest branching ratio in the same energy region, from the $a^2\Pi_u$ and $A^4\Pi_u$ states, reaches only about 20% [18–20]. In solid O₂ the threshold is shifted down by ~1.5 eV (from 12 to 10.5 eV) due to the dielectric polarization around a photoexcited hole [21, 22]. By assuming that the gas phase branching ratio in the physisorbed phase does not change significantly, because of the weak van der Waals interaction, at the photon energy of $\sim 28 \pm 0.5$ eV (where the peak in the O⁻ yield from Pt(111) appears in figure 4(b)) the photoelectrons from the adsorbate will have a maximum kinetic energy of ~17.5 eV.

Here we must note that in the electron-stimulated desorption (ESD) experiments with O₂ deposited on RG layers [14] and with solid O₂ [23] the O⁻ ion signal exhibits a peak at ~18 eV electron energy. It is believed that the observed feature arises predominantly from inelastic indirect processes [14, 24]. Electron energy loss (EEL) measurements from solid

O₂ have shown that around 50% of incident electrons with energies above 15 eV experience loss events and 70% of these will lose energy to the Schumann–Runge continuum of O₂ i.e. the broad resonant feature at ~9 eV electron loss (width of about ~3 eV) [24]. So there is a high probability that the photoelectrons with a kinetic energy of 17.5 eV will lose ~9 eV and hence end up with an energy of ~8.5 eV. The ESD results from solid O₂ have shown that dissociative electron attachment to the ²Π_u resonant state (at ~8 eV) has a maximum (note that the estimated residual kinetic energy in our case, 8.5 eV, is within the experimental resolution, ±0.5 eV) ([24] and references therein). So, it seems likely that photodissociation of physisorbed O₂ in the energy range 25–30 eV leading to desorption of O⁻ ions is primarily due to dissociative attachment of photoelectrons generated in the adsorbate layer, which are inelastically scattered in the film.

Finally we note that Huels *et al* [25] have also measured the kinetic energy distributions of O⁻ ions desorbed from solid O₂ at 8 and 17 eV by ESD. In both cases, the maximum of O⁻ kinetic energy peaks at ~1.5 eV and is relatively sharp (1.5–2 eV) compared with that at other incident electron energies (i.e. 10–14 eV). We suggest that the ESD results are also consistent with the inelastic scattering of 17 eV electrons by excitation of the Schumann–Runge continuum as we proposed in the PSD experiments. The main difference between the ESD results at 17 and 8 eV is the high-kinetic-energy tail, that Huels *et al* observed [25] at 17 eV incident beam energy, which perhaps can be explained as a contribution from direct DD processes which become accessible at this electron energy. Ideally, we would like to check our proposed mechanism by measuring the kinetic energy of the ions in PSD experiments. However, we were unable to perform this experiment due to the low photon flux in the VUV photon energy range produced at the synchrotron.

4. Conclusion

By monitoring the ion yield as a function of both photon energy and coverage of physisorbed O₂ on two different substrates (graphite and Pt) we have proposed a new mechanism for the photodesorption of O⁻ ions induced via the inelastic scattering and attachment of photoelectrons generated in the adsorbate in the photon energy range of 25–30 eV. We have also demonstrated that comparative investigations involving two different substrates provide valuable information which enables us to distinguish between the direct and indirect processes as well between the influence of adsorbate and substrate photoelectrons.

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