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Mechanistic studies of the photodissociation of physisorbed O₂/graphite

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Abstract. We have investigated the vacuum ultra-violet photodissociation of molecular O₂ physisorbed on graphite using synchrotron radiation with photon energies in the range 13–35 eV. The yield of desorbed O⁺ ions shows a threshold at ~19.5 eV and resonances at 24.5 eV and 28.5 eV, contrasting strongly with the gas phase photodissociation cross section. The principal mechanism of O⁺ production appears to be dipolar dissociation driven by photoelectrons generated in the substrate. An enhancement in the detection efficiency of low-energy ions, compared with previous measurements, has identified an additional dissociation mechanism leading to the desorption of O⁻ ions. Specifically, the results support a channel for low-energy O⁻ desorption, attributed to the dissociative attachment of photoelectrons, again generated in the graphite substrate, to the physisorbed O₂ molecules.

1. Introduction

Photochemical processes operating in the gas phase are modified when a molecule is adsorbed on a surface, opening new channels for molecular dissociation and desorption. For example, excitation of the adsorbate may occur either through direct absorption of a photon or via the production of photoelectrons in the substrate, which in turn interact with the adsorbed molecule [1, 2]. Central to the elucidation of the dissociation/desorption mechanisms in these systems is the measurement of the photon energy dependence of the relevant cross section [3]. To date, most studies of surface photochemistry have been confined to the visible and near-UV regions of the spectrum. Here we employ synchrotron radiation from the Daresbury synchrotron radiation source to explore photochemical processes occurring in the vacuum UV.

The measurements presented here form an extension to a previous report of the photodissociation of O₂ physisorbed on graphite [4]. In that study the yield of O⁻ ions desorbed from the surface was recorded with a mass spectrometer via an ion energy filter that rejected low- (less than approximately 1 eV) energy ions. In the present experiment these measurements have been extended by also recording the low-energy O⁻ ion contribution to the signal. In addition, the yield of desorbed O⁺ ions as a function of photon energy is reported for the first time. The findings presented here indicate a major role for photogenerated carriers in the dissociation/desorption process. In particular, the production of O⁻ ions is dominated by the dissociative attachment of electrons photoemitted from

the graphite substrate to the adsorbed O_2 molecules. The O^+ ion signal, on the other hand, appears to be dominated by electron–molecule scattering processes that emphasize the importance of final state effects in the (substrate) photoabsorption process leading (ultimately) to desorption.

2. Experimental details

The data were recorded using synchrotron radiation from beamline 3.1 at the Daresbury synchrotron radiation source, incident at an angle of 40° to the surface normal. Synchrotron light was monochromated with a 1 m Seya-Namioka monochromator fitted with a 2400 l mm^{-1} ruled grating, blazed to give a maximum output at $\sim 24\text{ eV}$. The monochromator supplied a usable photon flux in the energy range 13–35 eV with a bandpass of 10 \AA . The variation of the photon intensity with energy was determined by monitoring the fluorescence signal from a sodium salicylate coated window, using a photomultiplier tube (Bialkali photocathode). This calibration was used to normalize the ion yield spectra to the photon flux. Desorbed positive and negative ions were detected with a Hiden pulse counting quadrupole mass spectrometer switching between the two ion detection modes. In this experiment a Bessel box energy filter, used previously [4], was removed from the mass spectrometer. Separate electron stimulated desorption (ESD) experiments [5] have shown that the effect of this modification is to enhance the detection efficiency of ions with kinetic energy below approximately 1 eV. The first element of the entrance lens to the mass spectrometer was located approximately 1 cm from the sample. Correction for the electron background, present when counting negative ions with the mass spectrometer, was made by subtracting the signal detected at mass 15, which was assumed to arise entirely from the photoelectron background. The front electrode of the quadrupole mass spectrometer was raised to a potential of +2 V to aid negative ion collection, while the same electrode was set to a potential of -12 V to enhance the collection of the less intense positive ion signal.

As in the previous experiment, the highly oriented pyrolytic graphite (HOPG) sample was mounted on a liquid helium cooled cryostat maintained at approximately 20 K. Experiments were conducted in ultra-high vacuum and following sample cleaning by electron bombardment heating.

The yields of both positive and negative atomic oxygen ions produced from about two monolayers of O_2 physisorbed on graphite substrate have been recorded as a function of photon energy in the range 13–35 eV. The dependence of the ion yields on O_2 exposure at a number of fixed photon energies has also been measured, in order to gauge the role of the photon–substrate interaction in the desorption process.

3. Results

3.1. O^+ yield

Figure 1 shows the O^+ ion signal as a function of photon energy obtained when the graphite sample was exposed to $\sim 4\text{ L}$ of O_2 . The ion yield shows no appreciable intensity before an initial threshold at 19.5 eV, after which the signal rises sharply, showing a shoulder at 22 eV and reaching a maximum at 24.5 eV. A second and broader peak follows, centred at 28.5 eV. Significantly, this behaviour shows little similarity with the energy dependence of the gas phase photodissociation cross section [6]. Since the electronic structure of physisorbed O_2 graphite corresponds closely with the electronic structure of the free molecule [7], the

results imply an indirect, i.e. substrate mediated, mechanism for molecular excitation [4, 8]. The assignment of a substrate mediated mechanism is again supported by the measured coverage dependence of the O^+ signal, which was recorded at a photon energy of 22 eV and is presented in figure 2. The appearance of a maximum in the coverage dependence (at relatively low O_2 exposure), followed by a decrease in the O^+ signal, is characteristic of a mechanism involving the photoproduction of electrons in the substrate [4, 8]. Furthermore, the location of the maximum in the coverage dependence of the ion yield allows some quantification of the film thickness. Recent ESD studies of O_2 /graphite [5] indicate that in the submonolayer regime the ion desorption yields are low, rising sharply during the formation of the second and third layers. The location of the maximum in the ion yield as a function of exposure (at ~ 4 L) is therefore expected to correspond to a coverage of two to three monolayers of physisorbed O_2 . The decrease of the ion yield after the low exposure maximum in the photon stimulated desorption experiments is then attributed to the attenuation of the photoemitted substrate electron during their transport to the outermost layer of the O_2 film from which the ion desorption can occur [4, 8].

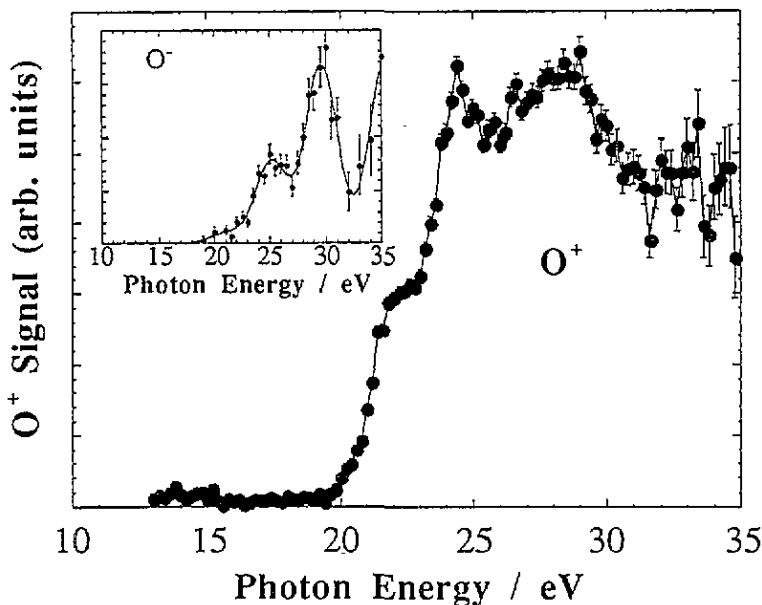


Figure 1. Desorbed O^+ signal from 4 L of O_2 physisorbed on graphite at 20 K as a function of photon energy. Inset: yield of O^- ions with greater than approximately 1 eV kinetic energy (see text) [4]. Both spectra have been corrected for the variation in photon flux with photon energy.

Another possible interpretation of the decay in the observed ion signal as a function of coverage merits some attention: the notion that this behaviour is a consequence of purely optical effects. One might imagine that the interference between the incident and reflected electric field vectors could result in a standing wave pattern, such that the magnitude of the electric field intensity decreased with increasing distance from the substrate-overlayer interface, assuming negligible absorption within the oxygen film [9]. This, in turn, would result in a reduction of the ion signal originating from direct molecular photoexcitation as a

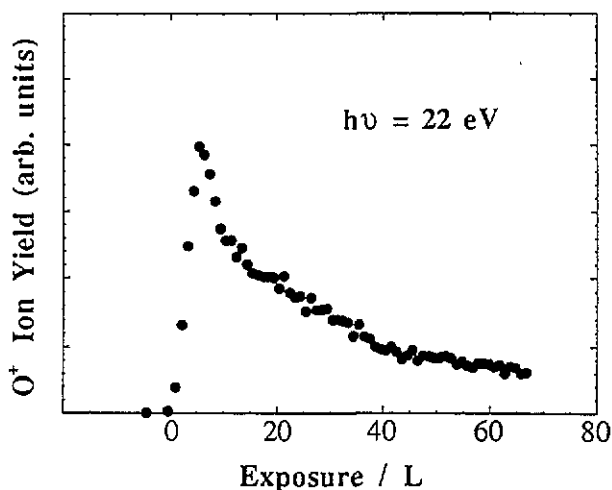


Figure 2. Coverage dependence of O^+ yield from O_2 /graphite with an incident photon energy of 22 eV.

function of film thickness, over a length scale given by the wavelength of the incident light, $\sim 56 \text{ \AA}$ at 22 eV. However, the electric field intensity variation as a function of distance from the substrate has been shown to follow a phase shifted cosine form [9], and so should be distinguishable from the roughly exponential response expected to accompany a substrate mediated mechanism—a result of the finite photoelectron mean free path in the overlayer. On this basis the approximately exponential decay of the ion signal recorded, e.g., at 22 eV (figure 2) suggests that optical effects are not a significant contribution to the coverage dependence, at least at this photon energy.

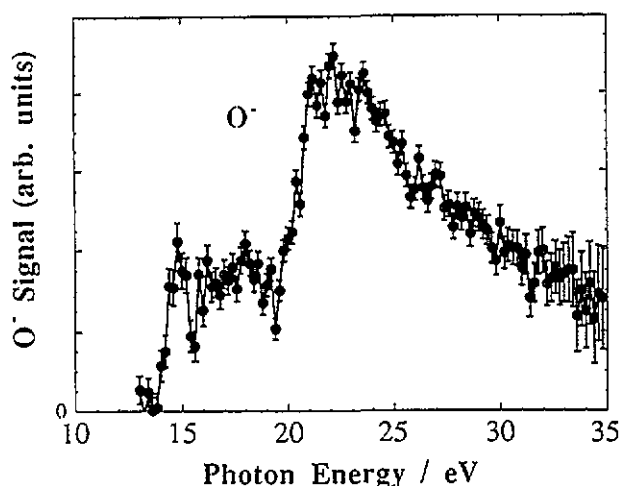


Figure 3. Desorbed O^- signal from 4 L of O_2 physisorbed on graphite at 20 K as a function of photon energy. The spectrum has been corrected for the variation in photon flux with photon energy.

We return now to the details of the ion yield as a function of photon energy (figure 1), the principal features of which are the threshold at 19.5 eV, the shoulder at 22 eV, and the peaks (resonances) observed at 24.5 eV and 28.5 eV. The requirement for O^+ production via (substrate driven) electron-molecule impact is that the photoemitted electron has a kinetic energy that exceeds the threshold for the dipolar dissociation (DD) mechanism given below.



In the gas phase the energetic threshold is 17.25 eV [6, 10]. With the O_2 as an adsorbate the energetic threshold of this process will obviously be lowered by the image charge potential of any ion fragment remaining on the surface [11]. In this case the energetic restrictions would no longer apply, but the appearance threshold will be limited by Franck-Condon considerations. However as the maximum in the ion pair absorption occurs at ~ 17 eV and as one would not expect the repulsive limb of the ion pair potential to be affected by image charge arguments, the appearance threshold should not be greatly lowered.

The work function of graphite is 4.5 eV, so the expected threshold for this process occurs at a photon energy of approximately 21.5 eV. However, figure 1 clearly shows that O^+ desorption is observed from a lower threshold at 19.5 eV, which compares with a major onset for O^+ production at around 19 eV in gas phase measurements [6], together with a maximum in intensity at 22 eV. These considerations indicate the likely contribution of a direct photoexcitation process at the lowest photon energies where O^+ is observed, leading to the shoulder observed in figure 1 at 22 eV. On the other hand, the coverage dependence of the ion signal at 22 eV (figure 2) indicates that the substrate mediated mechanism is already making an important contribution to the ion signal at this photon energy, consistent with the expected onset for this process at about 21.5 eV. It is worth remarking that this threshold is calculated on the assumption that the electron that collides with the physisorbed O_2 molecule, and has to lose a minimum of 17.25 eV in energy (or slightly less if one of the ion products remains on the surface) in order to give rise to dipolar dissociation, terminates at the vacuum level as in gas phase electron-molecule scattering. However, when we consider electron-molecule scattering in the O_2 film on the surface, we may expect that this threshold is shifted down in energy by the value of the image/polarization potential experienced by the scattered electron in the film. The image/polarization potential has a value of ~ 0.6 eV in the O_2 multilayer, which would lower the photoelectron driven dipolar dissociation threshold to about 21 eV. In summary, we propose that the O^+ yield in the photon energy range from 19 eV to ~ 24 eV may be resolved into two components, the first arising from direct molecular photoabsorption with a threshold of about 19 eV and which accounts for the appearance of the shoulder at around 22 eV in figure 1, and the second due to photoelectron driven dipolar dissociation, rising from a threshold at ~ 21 eV and which is already predominant at 22 eV, as judged from the coverage dependence (figure 2).

The other principal features in the observed ion yield are the resonances at 24.5 eV and 28.5 eV (figure 1). Since the cross-section for dipolar dissociation in electron-molecule scattering rises smoothly above threshold [10, 12], the existence of resonance structures is of particular interest, and has been addressed in connection with our previous study of O^- production from condensed O_2 /graphite [4]. The inset to figure 1 shows the measured O^- yield, which was obtained previously [4] with the ion energy filter in place (under these conditions O^- production is also dominated by dipolar dissociation—see below). The resonances observed in the main figure (O^+ signal) can be correlated with similar resonances in the inset (O^- signal), and suggest the importance of final state effects in the primary

photoexcitation event leading to photoelectron emission from the substrate. In our previous study, we identified the resonance in the O^- yield at ~ 25 eV with an expected optical interband transition (vertical in k -space) at the edge of the graphite Brillouin zone, from an initial state 2.5 eV below the Fermi level to an unoccupied state some 22.5 eV above the Fermi level. Note that the initial state gives rise to a maximum in the occupied density of states. We expect such a transition to give a maximum in the photoemission probability, and hence in the photoelectron driven dipolar dissociation cross section, at ~ 25 eV, which corresponds nicely with the first resonance in the O^+ yield (figure 1). We imagine that the second resonance observed in the O^+ yield at 28.5 eV, may have similar origin, though it would certainly be of interest in the future to correlate these photodesorption studies with photoemission experiments using the same range of photon energies.

3.2. O^- yield

Figure 3 shows the measured yield of O^- ions recorded concurrently with the O^+ signal. The results obtained are quite different from those for O^+ (figure 1). In contrast to the previous findings restricted to the detection of higher-energy O^- ions [4], significant signal intensity is observed for photon energies as low as 14 eV. Furthermore, the resonant structures identified in the earlier study at 25 eV and 30 eV are here replaced by a maximum at 22 eV followed by a slow decrease up to the maximum photon energy of 35 eV. The O^- count rates observed with the present experimental arrangement were typically >100 s^{-1} , significantly greater than the ~ 1 s^{-1} obtained previously. These results suggest that the ion signal in the present experiments is dominated by O^- ions of low kinetic energy, less than approximately 1 eV. In interpreting this contrasting behaviour for low-energy ions, we consider the mechanisms available for desorption over the photon energy range in question. In addition to the generation of O^- ions through a direct photon-molecule interaction (as observed in the gas phase, but with signal levels approximately 40 times smaller than the corresponding O^+ signals [6]), electron stimulated ion production may follow from photoelectron production in the graphite substrate (or the oxygen overlayer). In an electron-molecule impact event two processes are possible that result in the production of O^- ions. The first is dipolar dissociation, the scheme for which was given previously (reactions (1) and (2)). This has a threshold at ~ 17 eV, and a cross-section that rises monotonically as the electron energy is increased above this value up to at least 40 eV [10, 13]. In addition to the process of dipolar dissociation, bond fission to form a negative atomic ion, O^- , may also occur through dissociative electron attachment (DEA) to the molecule [14–16]. Capture of an incident electron with a specific incident energy can form a negative molecular ion state, which is unstable with respect to decay into the negative atomic ion and a neutral atom:



In ESD studies of condensed O_2 resonances in the negative ion yield have been observed in the range 6–15 eV [5, 16, 17]. Recent ESD studies of O_2 /graphite have demonstrated the predominance, for coverages of two monolayers or more, of a resonance centred at 8 eV [5], and which has been associated with a temporary negative ion state.

The cross section for negative ion production via this resonance is at least 100 times larger than that found off resonance [5]. This channel, however, leads to low ion kinetic energy, such that the resonance is completely suppressed when a retarding potential of

2 V is applied to the desorbed O^- ions [5]. The predicted threshold for DEA driven by photoelectrons generated in the substrate occurs at $8 \text{ eV} + 4.5 \text{ eV} = 12.5 \text{ eV}$, where 4.5 eV is the work function of graphite. However, the density of occupied states in graphite peaks sharply at about 2.5 eV below the Fermi level, or some 7 eV below the vacuum level [18], so in practice a threshold nearer to an incident photon energy of $\sim 7 \text{ eV} + 8 \text{ eV} = 15 \text{ eV}$ is not unexpected. For photon energies in excess of 14 eV, photoelectron attachment to the 8 eV resonance can take place either by the photoemission of electrons from occupied states further below the Fermi level or by inelastic scattering of higher-energy photoelectrons, which therefore lose energy before they reach the outer surface of the O_2 film from which ion desorption can occur.

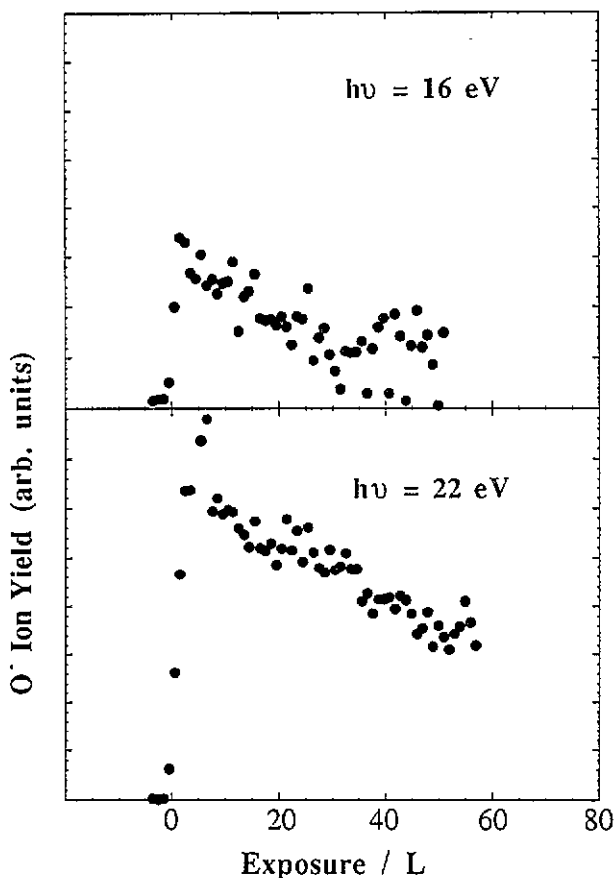


Figure 4. Coverage dependence of O^- yield from O_2 /graphite with incident photon energies of 16 eV and 22 eV. The data sets have not been normalized to account for the differences in light intensity at the two different photon energies.

The existence of an indirect, substrate mediated, photodissociation mechanism is reinforced by the results of figure 4, which shows the coverage dependence of the O^- signal obtained with a photon energy of 16 eV. Although the relatively low count rate achieved under these conditions results in a large degree of scatter in the data, a sharp initial rise in the ion signal followed by a slow decay is readily apparent. This is consistent

with the attenuation of the flux of photoelectrons produced in the graphite substrate as they propagate through the O₂ film towards the outer surface.

A similar decay in the desorbed O⁻ signal as a function of coverage is shown in the same figure for an incident photon energy of 22 eV corresponding to the peak ion yield in figure 3, i.e., above the step in the O⁻ signal at ~20 eV. This behaviour once more suggests that a substrate mediated mechanism operates at 22 eV, even though the gas phase O⁻ signal also shows a peak at 22 eV above a threshold at 20.6 eV [6]. The gas phase resonance corresponds to direct photoexcitation of the ion pair states responsible for dipolar dissociation. A second, more intense peak also occurs in the gas phase, very soon after the first threshold at 17.25 eV. This peak is assigned to Rydberg series mixing with ion pair states and is expected to be strongly quenched in the condensed phase [19]. Certainly, at the coverage represented in figure 3 (two to three monolayers) this process does not appear to have significant intensity. Although the probability of a small gas phase contribution to the O⁺ yield has been discussed in the previous section, the gas phase cross section for positive ion production is approximately 40 times larger than that for O⁻ [6]. Since the direct photoabsorption mechanism cannot account for the decay in the O⁻ signal with coverage (figure 4), we conclude that the appearance of the peak in the wavelength dependence of adsorbed O₂ at 22 eV is merely a coincidence.

How then do we account for the peak in the O⁻ yield at ~22 eV? As discussed earlier in connection with the O⁺ results, this energy lies above the threshold for photoelectron driven dipolar dissociation, ~21 eV. However, if this process were dominant at higher energies we would expect the O⁻ yield to track the yield of O⁺ ions, at least approximately, and to show resonances at the same energies as those seen in figure 1. More likely is that the O⁻ signal over the whole photon energy range is dominated by dissociative electron attachment, since, as indicated above, the cross-section for this process in ESD experiments is at least two orders of magnitude larger than that for dipolar dissociation when the O₂ coverage reaches a few monolayers [6]. In this case, we have to look to the density of occupied states in the graphite substrate in order to prompt an explanation for the 22 eV resonance feature—not final states because these are constrained by the location of the DEA resonance at ~8 eV above the vacuum level. Calculations by Fretigny *et al* [18] show a sharp maximum in the density of occupied graphite states at ~8 eV below the Fermi level, i.e. ~12.5 eV below the vacuum level. Population of the DEA resonance at 8 eV would therefore require a photon energy of 20.5 eV, which may account for the resonance observed at 22 eV, especially if inelastic electron scattering (which would shift the peak to higher photon energy) were taken into account. This interpretation must be taken as speculative for the present and calls for further experimental studies.

Finally, we note that the same DEA resonance at 8 eV could be populated by electrons produced by photoionization of the condensed O₂ film. In this event the step in the O⁻ yield at 20 eV would arise from the first ionization potential of O₂ (12 eV [20]) and the requirement, as before, to produce an electron with a kinetic energy of 8 eV. The O⁻ signal at higher photon energies (figure 3) would then be derived from the ionization of increasingly deep oxygen valence levels (lying 16 eV, 17 eV, 18 eV and 20 eV below E_{VAC}) [20]—the inherent photoemission peak widths would be convoluted with the DEA excitation profile. While this interpretation is attractive, it does not seem to concur with the observed feature of coverage dependence of ion yield at 22 eV, since electron generation within the adsorbed layer would not be expected to result in a decrease in yield with increasing oxygen coverage.

Of the above possible mechanisms, we consider that dissociative electron attachment to the physisorbed O₂ molecules is the most likely source of the O⁻ ions produced above (as

well as below) 20 eV. The coverage dependence indicates that the graphite substrate is the most probable source of the required photoelectrons. Further studies of these effects would clearly be useful, especially in conjunction with measurements of the photoelectron current as a function of photon energy and film thickness.

4. Conclusions

In summary, we have reported new studies of the mechanisms of photodissociation in a model physisorption system O₂/graphite, using synchrotron radiation in the energy range 13–35 eV. In comparison with our earlier study [4], we have identified new photon stimulated ion desorption channels in addition to those giving rise to high-energy positive and negative atomic ions through the process of photoelectron driven dipolar dissociation. In particular, the desorption of O⁻ ions has been detected below the energetic threshold for dipolar dissociation, and attributed to the capture, into a temporary negative ion resonance state, of electrons photoemitted from the graphite substrate, i.e., to dissociative attachment of substrate photoelectrons. The process of dipolar dissociation induced by photoelectrons generated in the substrate, generating the O⁻ ions of higher kinetic energy detected in our previous work [4], is believed to account for only a small proportion of the energy integrated O⁻ ion flux. On the other hand, this mechanism seems to be the main source of desorbed O⁺ ions, although a comparatively weak direct photoabsorption channel has also been identified in this case.

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