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LETTER TO THE EDITOR

Electron stimulated desorption from selected phases of physisorbed CO/graphite: evidence for structure sensitive desorption dynamics

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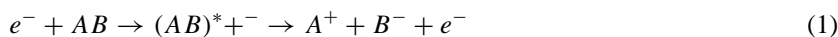
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Abstract. We have investigated electron stimulated desorption of O⁻, C⁻, O⁺ and C⁺ ions from selected surface phases of oriented CO molecules physisorbed on graphite using electron energies in the range 0–70 eV. In the case of the negative ions we observe, at high coverage, several dissociative attachment resonances below an electron energy of 18 eV, which are absent from the low-coverage (1–3 ML) regime. By contrast, a previously unobserved resonance at 19.5 eV in the O⁻ yield is apparent only in the monolayer. We also find that the onset of positive ion desorption varies between the different monolayer phases selected and we attribute this behaviour to the different orientation of the physisorbed molecules in the selected phases. These results indicate that structural effects influence the desorption process in a subtle, but measurable way.

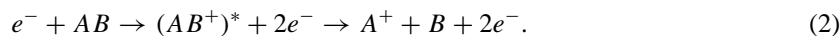
The stimulated desorption of ions and neutrals from molecular layers condensed on solid surfaces by electron and photon beams is of considerable interest in surface physics and chemistry [1–4]. With the possibility of selectively breaking molecular bonds via electron and photon impact, an understanding of the mechanisms and the dynamics of these non-thermal processes is important not only from a fundamental point of view, but also for many applications in areas such as surface modification and nanolithography [5].

In this letter we report the energy dependence of the electron stimulated desorption of O⁻, C⁻, O⁺ and C⁺ ions from selected surface phases or oriented CO molecules physisorbed on graphite. These surface phases distinguish themselves in the orientation of the adsorbed molecules, allowing us to explore the dependence of the desorption dynamics on the structure of the adsorbate film. The CO/graphite adsorption system was chosen in particular because the structure and phase diagram of the adsorbate/overlayer are well known [6–8]. Moreover, the dissociation cross section of the CO molecule in the gas phase has been extensively studied [9–14]. Electron stimulated desorption from CO films condensed on polycrystalline Pt has also been reported [15, 16]. In a recent paper, we compared results of photon stimulated desorption experiments from CO/graphite with preliminary ESD results in the monolayer regime [17]. Here we investigate ESD from ordered CO films on graphite in the monolayer and multilayer regimes with particular reference to the orientation of the adsorbed molecules.

Three different mechanisms have been identified for ion production by electron impact on diatomic molecules in the gas phase. The first mechanism, dipolar dissociation (DD), proceeds via an excited AB* state and results in the formation of an ion pair



(in our case $A, B = C, O$). In the gas phase the thresholds for the formation of O^-/C^+ and O^+/C^- ion pairs are 20.91 V and 23.5 eV, respectively [9,10]. A second mechanism, dissociative ionization (DI), leads only to the formation of positive ions and can be schematically represented by



The lowest dissociation limits for the two channels $C^+ + O$ and $O^+ + C$ are 22.4 eV and 24.8 eV, respectively [11]. In the energy region up to 35 eV three excitation channels, namely the $C^2\Sigma$ (22.5 eV), $F^2\Sigma$ (28 eV) and $G^2\Sigma$ (32 eV) states, have been identified for DI [14]. Dissociative attachment (DA), the third mechanism, involves the formation of an intermediate negative ion state. This intermediate negative ion state then dissociates into charged and neutral fragments according to the scheme



The thermodynamic thresholds [12] for the production of O^- and C^- via DA are 9.6 eV and 9.8 eV, respectively, if all fragments are produced in their ground states. If one or both of the fragments are generated in excited states the energetic thresholds are correspondingly higher. In an ESD experiment a DA process will be evident as a peak in the energy dependence of the ion yield [15,18]. In contrast, DD and DI processes involve the transition of the molecule to an excited state and will therefore be observed in the ion yield spectrum as a rising ion signal above the corresponding excitation threshold.

Our experiments were performed under UHV conditions with a residual gas pressure of 5×10^{-11} mbar. The low-energy electron beam was produced by the monochromator of an electron energy loss spectrometer (EELS). The electron beam impinged onto the sample at an incident angle of 60° with respect to the surface normal; the current was ~ 5 nA. Desorbing positive and negative ions were detected by a Hiden pulse counting quadrupole mass spectrometer at an angle of 30° to the surface normal. A correction for the background due to scattered electrons while measuring negative ions was obtained by subtracting the measured signal at a nominal mass of 14. The sample, highly oriented pyrolytic graphite, was mounted on a rotatable liquid helium cryostat and cooled to about 25 K. The sample temperature was monitored by a four-wire rhodium-iron resistance thermometer, located at the base of the cryostat near the sample. The sample was cleaved in air before mounting and cleaned regularly by electron-bombardment heating to 900 K in UHV. Surface cleanliness was monitored by EELS and low-energy electron diffraction (LEED).

The physisorbed CO films were prepared by filling the UHV chamber to a pressure of 5×10^{-8} mbar of CO. By using different dosages two different monolayer phases as well as a multilayer phase were prepared, which were characterized using low-current LEED. The LEED patterns obtained for the monolayer phases closely resembled those reported by Jensen and Palmer [8]. The low-density commensurate monolayer phase, formed at low coverages, consists of a $(2\sqrt{3} \times \sqrt{3})R30^\circ$ layer of two-dimensional rotors where the CO molecules are aligned parallel to the graphite surface in a herringbone structure [6]. At the sample temperature used throughout this experiment (25 K) this structure is believed to be partially rotationally melted [6]. Increasing the CO coverage resulted in the formation of the high-density incommensurate ('pinwheel') monolayer phase, while at even higher coverage the multilayer phase was formed [6]. The structure of both the high-density monolayer and the multilayer phases is thought to be very similar to the (111) face of bulk α -CO [6]. Here one in four molecules, the 'pin' molecule, is aligned perpendicular to the surface plane, while the other three molecules (the 'wheel' molecules) are tilted about 20° out of plane. From the experimental data available on the high-density monolayer it has not been possible

to deduce the precise tilt angles of the individual molecules [6]. Theoretical calculations indicate that the wheel molecules are nearly parallel to the substrate plane, with tilt angles ranging from 3.4 to 4° , while the pin molecule is oriented only about 1.8° off the surface normal [19]. It should also be noted that experiments indicate end-to-end orientational disorder both in bulk solid CO and in the low-density commensurate herringbone phase, so there is no evidence for a systematic arrangement of the inequivalent C and O ends of the molecules [6, 7, 19]. While the extent of end-to-end disorder is not known for the pinwheel phase, it is expected that this type of disorder also exists in this case [19].

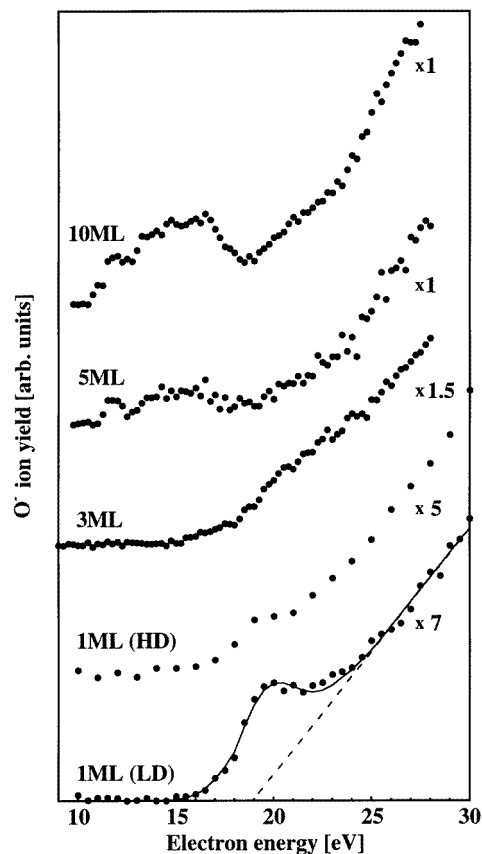


Figure 1. The electron energy dependence of the electron stimulated O^- desorption yield from CO physisorbed on graphite at five different coverages. Note that the counting times varied considerably between the spectra taken from the monolayer and the multilayer. The straight line shown in the case of the data from the low-density monolayer represents a fit (sum of a Lorentzian and a straight line) to the data. The dashed line indicates the extrapolation of the straight-line fit to the energy axis.

The dependence of the O^- ion current from CO films physisorbed on graphite on the electron impact energy is shown in figure 1 for five different coverages. The first result of particular interest is that in the monolayer regime, i.e. for both the low-density commensurate and the high-density incommensurate monolayer phases, desorption of O^- is only observed above an electron energy of 15 eV; no O^- ion signal was measured below this energy. For both monolayer phases the spectrum consists of a superposition of a resonant feature at an

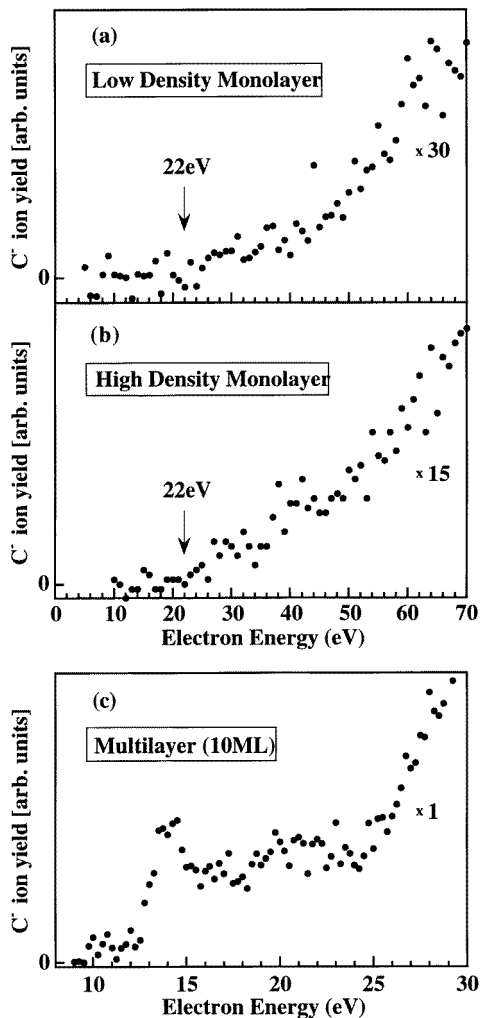


Figure 2. The electron energy dependence of the electron stimulated desorption yield of C^- ions from (a) the low-density monolayer phase, (b) the high-density monolayer phase and (c) a 10 ML thick multilayer of CO physisorbed on graphite.

energy of ~ 19.5 eV and a rising ion signal above a threshold of ~ 19 eV (see the fit to the data from the low-density monolayer phase in figure 1). The latter signal is attributed to the production of O^- via DD. A similar spectrum is also found for a CO coverage of 3 ML, although the resonance is less apparent. In contrast, when the coverage is increased to 5 ML we now observe additional structure in the energy region between 10 and 18 eV. O^- desorption from this 5 ML thick film sets in at ~ 11 eV. There is a maximum near 12 eV and a very broad peak at ~ 15 eV, which seems to contain contributions from more than a single resonant CO^- state. This observation is supported by the desorption spectrum from the 10 ML film where the broad peak around 15 eV appears to be composed of two or three individual contributions.

In the case of C^- ions (figure 2) differences between the electron energy dependence of

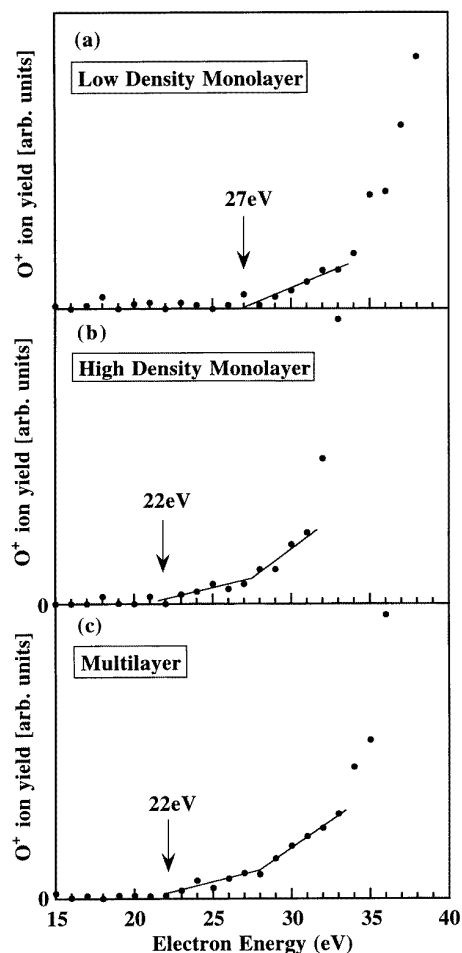


Figure 3. The electron energy dependence of the electron stimulated desorption yield of O⁺ ions from (a) the low-density monolayer, (b) the high-density monolayer and (c) a 10 ML thick multilayer of CO physisorbed on graphite.

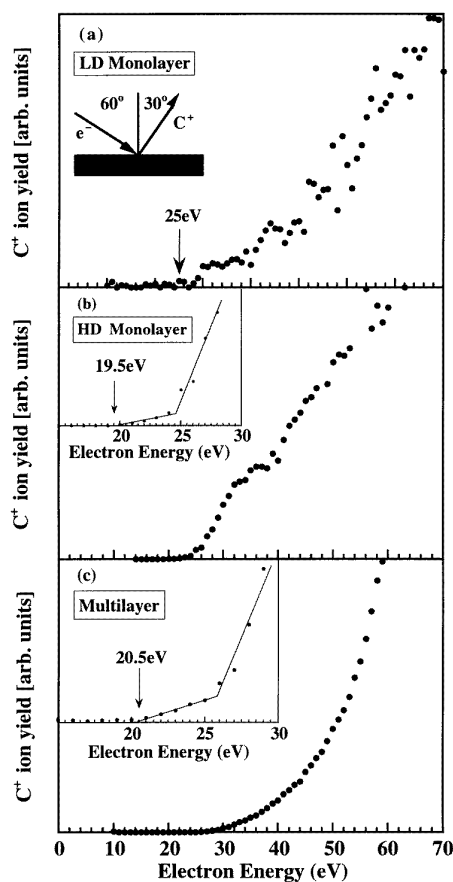


Figure 4. The electron energy dependence of the electron stimulated desorption yield of C⁺ ions from (a) the low-density monolayer, (b) the high-density monolayer and (c) a 10 ML thick multilayer of CO physisorbed on graphite.

the ion yield from the low-coverage and high-coverage regimes are also observed. In the monolayer (low-density monolayer phase, figure 2(a), and high-density monolayer phase figure 2(b)) the spectrum is dominated by DD. A threshold of ~ 22 eV is observed for C⁻ production and the ion signal increases with energy thereafter. In contrast to the monolayer phases, the energy dependence of C⁻ desorption from the 10 ML film shows additional rich structure in the energy region between 10 and 24 eV. The onset of C⁻ desorption at ~ 10 eV is followed by a resonance at ~ 14 eV.

For both negative ions, O⁻ and C⁻, we therefore observe several DA resonances below 18 eV in the high-coverage regime (≥ 5 ML), which are absent at low coverages (≤ 3 ML). In addition, it should be noted that in the gas phase O⁻ production is dominated by a DA resonance at 9.8 eV [12] and that the C⁻ yield shows four peaks at 10.3, 10.5, 10.8 and 11.0 eV [13]. All these features are not observed in any of the phases investigated.

We believe that the principal cause of this apparent suppression of the DA resonance below ~ 18 eV can be found in the kinetic energy distribution of the ions created. In order to be detected, the ions have to escape from the image/polarization potential of the substrate and neighbouring molecules, which has a value of ~ 1.5 eV in the monolayer on graphite [20]. In the case of a thicker film, where the outermost layer of molecules is further away from the surface, the value of the polarization potential is reduced to ~ 0.6 eV [21], allowing ions of lower kinetic energy to escape. In particular, O^- ions produced via the DA resonance at 9.8 eV observed in the gas phase possess only negligible kinetic energy (given the thermodynamical threshold of 9.6 eV, fragments produced by this reaction can only possess a kinetic energy of 0.1 eV or less), which explains the absence of this resonance from the desorption spectra from the monolayer and multilayer phases. Furthermore, Azria *et al* have shown that the kinetic energy of O^- ions desorbing from a physisorbed multilayer of CO is further lowered by the post-dissociation interaction via reactive scattering between the desorbing O^- ions and neighbouring CO molecules [16].

The broad peak at ~ 15 eV in the O^- yield for coverages greater than 5 ML has also been observed in previous studies [15, 16]. This peak has been assigned to O^- production via symmetry forbidden Σ^- states [16], although the idea of symmetry breaking of negative ion resonance states is presently the subject of debate [22, 23].

The second feature of particular interest in the negative ion yields is the appearance of a DA resonance at ~ 19.5 eV in the O^- desorption yield from both monolayer phases (figure 1), which has not been previously observed. This resonance does not appear explicitly at higher coverages, but seems to be responsible for the intensity found between ~ 18 eV and ~ 23 eV in these spectra.

This behaviour raises the following question: is this particular DA resonance enhanced in the monolayer regime or is it buried by the increased ion signal due to the appearance of other resonances in the multilayer? We find that the signal levels at higher coverage are greatly enhanced when compared to the monolayer, because of the appearance of the DA resonances below 18 eV and an increased DD signal (for example, at an electron energy of 25 eV typical ion signals from the multilayer are a factor of seven larger than those from the low-density monolayer phase). We therefore believe that the observation of the 19.5 eV DA resonance in the O^- yield is largely due to the suppression of other desorption channels in the monolayer. The energy of this particular resonance is well above the energetic threshold of 9.6 eV for the production of O^- ions via DA so ions created via this process should possess enough kinetic energy to escape from the substrate even in the monolayer regime†. A possible candidate for the 19.5 eV resonance is the $^2\Sigma$ negative ion resonance state. Recently, Jensen and Palmer found a broad peak, assigned to this particular negative ion resonant state, at an energy of ~ 18 eV in their EELS study of CO physisorbed on graphite [7].

We turn now to the production of positive ions; ESD results from the low-density monolayer phase, the high-density monolayer phase and a 10 ML thick multilayer are presented in figures 3 and 4. We observe the onset of O^+ ion desorption from the low-density monolayer phase at an electron impact energy of ~ 27 eV; no ion signal is detected above the noise level at lower electron impact energies (figure 3(a)). In contrast, the desorption of O^+ from the high-density monolayer (figure 3(b)) starts at an electron impact energy of ~ 22 eV. Thereafter the ion yield appears to increase linearly until a second threshold is reached at ~ 28 eV, a value similar to the onset observed in the case of the low-density

† This is confirmed by measurements of the kinetic energy distribution of O^- ions produced at an electron impact energy of 19 eV from CO films physisorbed on graphite at submonolayer coverage [24].

monolayer. In the case of desorption from the multilayer film (figure 3(c)) we find very similar behaviour to that of the high-density monolayer, at least below 30 eV. We estimate the accuracy of the measured thresholds (for both O^+ and C^+) to be of the order of ± 2 eV.

In broad terms, the desorption behaviour of C^+ ions (figure 4) is very similar to that obtained for O^+ . In the low-density monolayer phase (figure 4(a)), ion desorption starts at ~ 25 eV; no signal is detected above the noise level below this electron impact energy. As in the case of O^+ , the yield of C^+ exhibits a lower onset for ion production in both the high-density monolayer (figure 4(b)) and the multilayer (figure 4(c)); a threshold at ~ 20 eV is evident in both sets of data. In both these phases we find also evidence for a second threshold at ~ 25 eV, similar to the onset observed in the low-density monolayer.

In line with our previous study we attribute the higher thresholds observed at ~ 28 eV in the case of O^+ and at ~ 25 eV for C^+ to the onset of ion production via DI [17]. For O^+ we also find evidence for a further threshold at a higher electron energy in the desorption spectra (figure 3), which might be associated with a DI process via an energetically higher-lying excited state [17].

The principal result of interest in figures 3 and 4 is thus the observed difference in the onset of positive ion desorption for both O^+ and C^+ between the two structurally different monolayer phases. The onset of cation production for both O^+ (~ 22 eV) and C^+ (~ 20 eV) in the high-density monolayer and the multilayer appears to correspond well to the observed threshold for the production (via DD) of the corresponding negative ion (~ 22 eV for C^- and ~ 19 eV for O^- ; see figures 1 and 2)†. However, the delayed onsets observed in positive ion desorption from the low-density monolayer phase (when compared to the high-density monolayer, the multilayer and the gas phase) are unexpected. Moreover, desorption of the corresponding negative ions produced via DD from the low-density monolayer phase occurs well below the onsets of O^+ desorption (~ 28 eV) and C^+ desorption (~ 25 eV) from this phase. This result indicates that *post-excitation effects* quench positive ion desorption rather than a perturbation of the molecular excitation process itself.

We attribute the quenching of positive ion desorption from the low-density monolayer phase, where the CO molecules are physisorbed parallel to the graphite surface, to the screening and neutralization of the positive ion by substrate electrons [15]. Note also that neutralization is expected to increase the kinetic energy of the detaching anion and thus effectively increases the probability of anion desorption from the surface [15]. This is consistent with the fact that the thresholds of negative ion desorption via DD are *not* delayed with respect to the gas phase.

In the high-density monolayer one in four molecules, the pin molecule, is aligned perpendicular to the surface. Further, theoretical calculations [19] suggest that the centre of mass of the pin molecule is elevated by about 0.4 Å above the centre of the wheel molecules. We envisage that, when these upright molecules fragment as a result of electron impact, cations produced from the end of the molecule pointing away from the surface will be less likely to be screened and neutralized by substrate electrons. Furthermore, these fragments will be projected away from the surface, again decreasing the probability of neutralization and also of trapping by the image potential. In addition, ions created from the end of the molecule pointing up will experience a smaller image potential than the ions created closer to the surface [25]. Together these effects will increase the probability of desorption from this phase. We therefore suggest that the difference between the onsets of cation desorption

† The lowering of the observed thresholds for positive and negative ion production, compared to the gas phase values, might be attributed to image potential effects [4] and, in the case of negative ions, additionally to energy released when reactions (e.g. neutralization) of the corresponding positive ion with neighbouring molecules and/or substrate occur.

from these two monolayer phases directly reflects the different structural arrangements of the molecules in these phases. Similar behaviour may be anticipated in other adsorption systems.

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