Competing Routes for Charge Transfer in Co-Adsorption of K and O_2 on Graphite

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We have investigated a model co-adsorption system using electron energy loss spectroscopy. When the dispersed phase of K/graphite is exposed to O_2 at 25 K, the charge donated by the alkali is depleted, as evidenced by a reduction of the surface plasmon energy from ~ 320 to ~ 130 meV. The co-adsorbed O_2 species is molecular, with a vibrational frequency consistent with the $^2\Pi_g$ ground state of O_2^-. The results demonstrate local transfer of charge from alkali to co-adsorbate, consistent with a simple electrostatic model. By contrast, CO perturbs the K-graphite interaction only weakly.

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The adsorption of alkali metals on surfaces is the focus of considerable current interest [1-7]. One important motive for these studies is the prototypical role played by the alkali metals in our understanding of both the geometric [2,3] and electronic [4-7] structure of surface systems. Important discoveries have recently been made in respect of the adsorption site [2], charge state [4], and elementary excitations [5,6] of the adsorbed alkali metals. Another important motivation for the widespread interest in alkali adsorption is the role of alkali metals as promoters in catalytic reactions. As a consequence, the co-adsorption of alkali metals and small molecules on solid surfaces is also the subject of intensive investigation [8,9]. From the fundamental point of view, the competing routes for charge transfer (or redistribution) from the electropositive alkali metal to (a) the surface and (b) the co-adsorbed molecule represent a key and as yet incompletely understood element in the problem. In this Letter, we address the co-adsorption problem via a study of the interaction of an alkali metal (potassium) with a co-adsorbed molecule (O_2) on a substrate (graphite) which is chosen because it presents an easily recognized signature (the surface plasmon frequency) of the amount of charge donated to the substrate [6]. Moreover, O_2 physisorbs on the naked graphite surface such that the geometrical and electronic structure resulting from the molecule-surface interaction in the absence of the promoter is extremely well characterized [10-12].

Recent investigations of the submonolayer adsorption of K on graphite using electron energy loss spectroscopy (EELS) have revealed unique features in the excitation spectrum of this system [6,13]. In particular, a surface plasmon mode [14] of especially low frequency, about 40 meV, has been observed in the case of clean graphite [15], which is shifted upwards in energy to about 320 meV as the coverage of potassium on the surface increases [6,13]. This result indicates a redistribution of charge from the potassium atom towards the graphite substrate, as confirmed by recent model [16] and first principles [17] calculations. The structural phase diagram of K/graphite has also been well characterized and exhibits, in particular, a first order phase transition from a well-ordered dispersed phase featuring large K-K separation to a close-packed phase at a coverage of ~ 0.1 monolayers (ML) [6,13,18]. This allows us to prepare a well-defined alkali metal structural phase whose electronic interaction with the substrate is uniquely defined by the corresponding excitation spectrum.

The adsorption of molecular O_2 on graphite has also been the target of extensive work in the recent past, because the physisorbed films which can be prepared on graphite provide a key testing ground for our understanding of critical phenomena in low dimensions [12,19]. At low temperatures ($T < 47$ K) O_2 physisorbs on graphite, manifesting a rich variety of structural phases which have been characterized by a range of techniques [10-12,20, 21]. At a temperature of 25 K the physisorbed layer exhibits an orientational phase transition from the lying down (δ) phase to the standing up (ζ) phase in the submonolayer regime. Detailed studies of the vibrational states and electronic structure [11,20] of physisorbed O_2/graphite indicate that the perturbation of the gas phase properties by the surface is minimal.

The experiments were performed using an electron energy loss spectrometer which doubles as a high resolution low energy electron diffractometer as previously described [22]. The highly oriented pyrolitic graphite sample was mounted on a liquid-helium cold finger [23]. The sample was cleaved in air and cleaned in ultrahigh vacuum (base pressure $< 3\times10^{-10}$ Torr) by resistive heating to ~ 1100 K prior to exposure to O_2 gas and/or to deposition of K from a getter source.

Figure 1 shows the EELS spectra obtained when the open 7×7 phase of K on graphite (K-K separation ~ 14 Å) is exposed to O_2. The O_2 exposure is given in langmuirs (1 L $=1\times10^{-6}$ Torr sec). Two sets of spectra are shown, collected with two different scattering geometries, inset (electron beam energy 9 eV in each case). The panels on the left of Fig. 1 show the EELS spectra obtained in the specular direction where the dipole scattering mechanism dominates and the low frequency graphite surface plasmon mode [6,13] is visible on top of the in-

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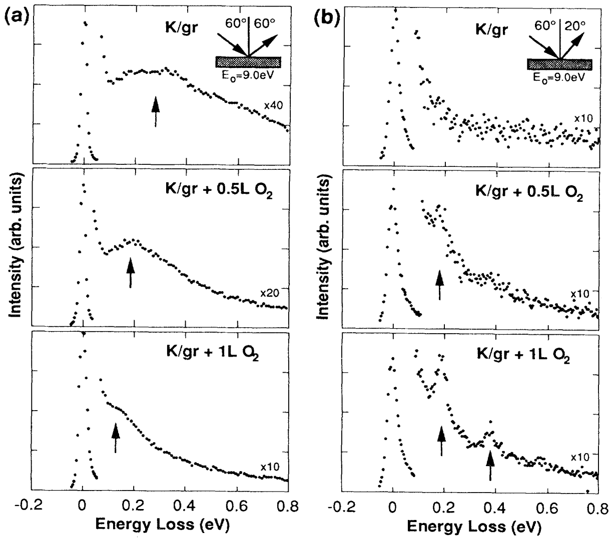

FIG. 1. Electron energy loss spectra from co-adsorbed K and O_2 on graphite as a function of increasing O_2 exposure. Two series of spectra are shown: (a) specular scattering geometry (inset), showing the K/graphite surface plasmon, which decreases in energy as more O_2 is co-adsorbed; (b) off specular scattering geometry (inset), showing the vibrational energy loss peaks characteristic of physisorbed O_2. The incident electron energy is 9 eV in both cases, and the sample temperature is < 30 K.

tense continuum of low energy electron-hole pair excitations characteristic of the semimetallic graphite substrate [24]. It is seen that the frequency of the plasmon mode shifts from the value, ~320 meV, characteristic of the dispersed K phase down to ~130 meV when 1 L O_2 is added. Calibration of the O_2 exposure using high resolution LEED indicates that 6 L are needed to produce the monolayer δ phase of O_2/graphite. The panels on the right of Fig. 1 show the EELS spectra recorded 40° from the specular direction (20° from the normal to the surface). With this geometry (and an electron beam energy of 9 eV), the vibrational transitions of physisorbed O_2 (O-O stretch frequency 192 meV) are visible via the resonance scattering mechanism [11,25] and grow in intensity with increasing O_2 coverage. In addition, high resolution LEED studies show diffraction peaks at 1.6 and 2.1 Å^{-1} characteristic of the submonolayer δ phase of physisorbed O_2 observed on the clean graphite surface [10], while the diffraction peak associated with the 7×7 K dispersed phase [6,13] disappears following exposure to O_2.

Two principal conclusions can immediately be drawn from the data presented in Fig. 1. First, the reduction of the graphite plasma frequency when O_2 is added to the dispersed phase of K on graphite indicates that the *electronic charge donated to the substrate by the alkali is withdrawn on co-adsorption of* O_2 . This also explains the removal of the 7×7 diffraction peak, since this phase is stabilized by a repulsive K-K interaction mediated by charge transfer to the surface [16]. Second, physisorbed O_2 is already observed on the graphite surface while the reduction in the surface plasma frequency is continuing. However, what is not clear is where the charge withdrawn from the substrate goes.

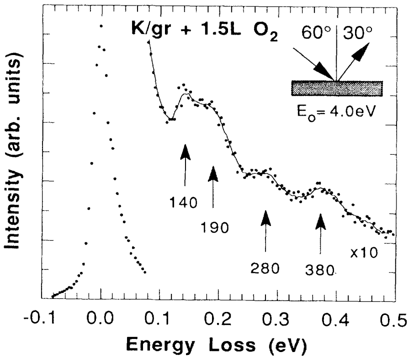

FIG. 2. Electron energy loss spectrum from co-adsorbed K and O_2 (1 L) on graphite at $T < 30$ K. The incident electron energy is 4.0 eV and the off specular scattering geometry is shown (inset). Vibrational energy loss features associated with the $v=0\rightarrow1$ and $v=0\rightarrow2$ modes of physisorbed O_2 are observed at ~190 and ~380 meV, respectively. The vibrational mode of a different molecular O_2 species is seen at ~140 meV, together with an overtone at ~280 meV. The solid line is a multipoint smoothed curve generated from the experimental data and is shown with the experimental data points as a guide to the eye.

Figure 2 presents an EELS spectrum obtained with a lower electron beam energy ($E_0=4$ eV) than Fig. 1 following exposure of the 7×7 dispersed phase of K to 1.5 L of O_2. The scattering geometry (inset) is again chosen to access the resonance scattering mechanism [25]. In this case, a new loss feature is clearly seen at $\sim140\pm5$ meV (with an overtone at $\sim280\pm5$ meV) in addition to the physisorbed O_2 vibrational transitions at $\sim190\pm5$ meV ($v=0$-1) and $\sim380\pm5$ meV ($v=0$-2). This new loss feature, which is absent from the EELS spectrum of physisorbed O_2 on graphite [11], has a frequency close to the vibrational frequency of the $^2\Pi_g$ ground state of the gas phase O_2^- negative ion, 133 meV [26]. The appearance of this feature strongly suggests that the electronic charge, withdrawn from the substrate following exposure of K/graphite to O_2, is donated instead to co-adsorbed O_2 molecules, creating a species akin to O_2^- with which further, physisorbed O_2 molecules coexist on the surface. Moreover, the coexistence of physisorbed O_2 in the submonolayer coverage regime proves that this charge transfer is the result of a *local* interaction between coadsorbed alkali atoms and O_2 molecules. If the charge were transferred from the alkali-doped substrate to the adsorbed O_2 molecules, physisorbed O_2 could not be observed before the depletion of the substrate charge was complete, i.e., before the plasma frequency had stopped falling.

We have also investigated the resonance scattering cross section corresponding to the 140 meV feature in the energy loss spectrum of Fig. 2. The intensity of this mode as a function of electron beam energy is shown in

Fig. 3 (scattering geometry inset), together with the cross section for the $v=0$–1 excitation of physisorbed O_2 (i.e., the 190 meV feature of Fig. 2). In the case of the physisorbed O_2, a well-defined resonance is observed with a peak at ~ 8 eV; this resonance is assigned to the ${}^4\Sigma_u{}^-$ negative ion shape resonance (the "σ resonance") of the O_2 molecule, as previously observed [11,25]. In the case of the 140 meV feature, a resonance is again observed, although this time the resonance energy is shifted down to ~ 4 eV. This behavior compares with the recently reported shift in the σ resonance energy between the physisorbed and molecularly chemisorbed superoxide state in EELS of O_2/Pt(111) [27]. In the case of chemisorbed O_2/Pt(111), the resonance energy is lowered to 3.75 eV, close to the value found here, and the increased intramolecular bond length of the chemisorbed molecule has been identified as an important factor in this energy shift (as previously established in near-edge x-ray absorption fine structure studies of the σ resonance observed in small molecules [28]). The resonance results are therefore also consistent with the creation of a perturbed molecular O_2 species by charge transfer from the K adatoms on the graphite surface.

In order to address the fundamental question of why the valence electronic charge of K is donated to co-adsorbed O_2 rather than to the graphite substrate, we estimate the total energy of the present system based on a simplified ionic model. If one electron is donated by K to the graphite substrate, the change in total energy is given by

$$E_g = I_K - \Phi_g - 1/4d_K\,, \tag{1}$$

where I_K is the ionization energy of potassium, Φ_g the work function of graphite, and d_K denotes the distance between the K adatom and the surface. The last term in Eq. (1) represents the attractive interaction between the K^+ ion and its image in the substrate. On the other hand, if one electron is donated by K to O_2, and the complex $K^+[O_2]^-$ is formed on the surface, the resulting change in total energy is given by

$$E_{O_2} = I_E - A_{O_2} - \frac{1}{4d_K} - \frac{1}{4d_{O_2}} + \frac{1}{\sqrt{(d_K+d_{O_2})^2+r^2}} - \frac{1}{\sqrt{(d_K-d_{O_2})^2+r^2}}\,, \tag{2}$$

where A_{O_2} is the electron affinity of O_2, d_{O_2} is the distance between the O_2 molecule and the graphite surface, and r is the lateral separation between K and O_2. The third (fourth) term of Eq. (2) represents the interaction between K^+ ($O_2{}^-$) and its image charge. The second to last term is the sum of the Coulomb repulsion energy between K^+ and the image of $O_2{}^-$ and that between $O_2{}^-$ and the image of K^+. The last term of Eq. (2) is the direct Coulomb attraction energy between K^+ and $O_2{}^-$. Assuming $d_K \sim 5$ bohrs, the C-K layer spacing in bulk C_8K [29], together with $I_K = 4.3$ eV [30] and $\Phi_g = 4.5$ eV, we obtain $E_g = -1.56$ eV. Based on a tight-binding model, Janiak *et al.* [31] suggested recently that O_2 adsorbs on top of the K atom (i.e., $d_{O_2} > d_K$ and $r=0$). With $d_{O_2} - d_K = 5$ bohrs, as used by these authors, and $A_{O_2} = 0.44$ eV [32], we have $E_{O_2} = -1.81$ eV. If, on the other hand, $K^+[O_2]^-$ lies down on the graphite substrate, assuming $r=5$ bohrs and $d_K = d_{O_2} = 5$ bohrs, we have $E_{O_2} = -1.87$ eV. This choice of d_{O_2} may be reasonable, since the resulting image potential ($-1/4d_{O_2} = -1.36$ eV) is in accord with the observed image potential shift of the $O_2{}^-$ negative ion resonance, 1–1.5 eV [11]. The above values of E_{O_2}, which are slightly lower than E_g, suggest therefore that the K charge is more likely to be donated towards O_2 than to the substrate, which is in agreement with the experimental observation. Given the rather small energy difference between E_{O_2} and E_g, it may be expected that the charge transfer route may be sensitive to the physical parameters of the co-adsorbed molecule. For example, in the case of CO, assuming the same parameters as those for O_2 except for the electron affinity. $A_{CO} = -1.5$ eV [32], we have $E_{CO} = 0.13$ eV (0.07 eV) for formation of the standing (lying down) $K^+[CO]^-$, which is much higher than E_g. Therefore it may be expected that the K electronic charge is not removed from the graphite substrate upon CO adsorption, primarily because of the negative electron affinity of the CO molecule.

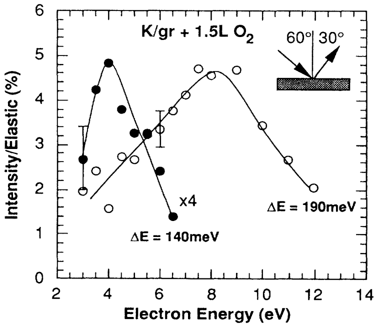

FIG. 3. Resonance energy profiles for O_2 (1.5 L) co-adsorbed with potassium (~ 0.1 ML) on graphite at $T < 30$ K. The intensities of the 140 and 190 meV loss features, normalized to the diffuse elastic intensity, are plotted as a function of incident electron energy. The angle of incidence is 60° and the emission angle is 30° throughout.

A striking confirmation of this prediction is provided by the experimental results obtained when the 7×7 phase of K/graphite is exposed to 1 L of CO (corresponding to a coverage of ~ 0.2 ML). In stark contrast to the case of O_2 co-adsorption, Fig. 1, the addition of CO *does not change the frequency of the alkali-doped graphite plasmon.* In this case, the valence electron density of the alkali metal is donated to the substrate in preference to the co-adsorbed CO, as predicted by the electrostatic model.

In summary, we have exploited the different scattering mechanisms available in electron energy loss spectroscopy to expose the nature of the charge redistribution in a model co-adsorption system, using the surface plasma frequency of semimetallic graphite as a signature of charge transfer to the substrate, and the vibrational frequency (and negative ion resonance characteristics) of co-adsorbed O_2 (and CO) as a signature of charge transfer to the co-adsorbed molecule. From these studies an appealing picture emerges of direct, local charge transfer from the alkali to the co-adsorbed molecule, rather than the substrate (depending on the electron affinity of the molecule in question). Similar studies of alkali-molecule co-adsorption on other semimetallic or narrow-band-gap substrates, which are also expected to present a signature of charge transfer from the alkali [33], will help to establish the generality of the local alkali-molecule interaction exposed by this work.

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