Selective Resonance Population in Electron Scattering by Adsorbed Molecules

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We have investigated vibrational excitation of physisorbed O_2 by electron impact in the 4–14-eV range, where a single broad resonance is observed in gas-phase studies. We show that by orienting the molecule in two different alignments on the surface of graphite it is possible to *selectively populate* two different negative-ion resonance states in this energy range, the $^4\Sigma_u$ state (at ~8.5 eV) and the $^2\Pi_u$ state (at ~6 eV), each of which leads to molecular vibrational excitation. Calculations show that this selective resonance population arises from the distinctive differential electron-capture cross sections of the two molecular states, into which electrons are "fed" by the surrounding surface structure.

The role of short-lived molecular resonances in a variety of surface processes is a topic of increasing attention. These transient species are now not only known to be of considerable significance in a whole set of surface spectroscopies [electron-energy-loss spectroscopy (EELS),[1-5] photoemission,[6] inverse photoemission,[7] x-ray absorption,[8] and surface enhanced Raman scattering (SERS)[9]], but they are also postulated to act as intermediates in a range of pathways in surface chemical dynamics (molecule-surface scattering,[10] adsorbate molecular dissociation,[11] electron- (Ref. 12) and photon- (Ref. 13) stimulated desorption, and electron-beam-stimulated reactions.[14] In this context the negative-ion resonances which are beginning to be observed in electron-impact studies of various adsorbates are of particular importance, since they elucidate details of the resonance lifetime[15] and symmetry[4,16] in addition to the resonance energy. Here the physisorbed O_2 molecule has been a key model system and the subject of intensive investigation, exposing a wide spectrum of new phenomena.[1,2,4,12,13,17]

Vibrational excitation of physisorbed O_2 via a resonance located somewhere between 5 and 10 eV has been a common feature of various EELS studies,[1,2,4] yet the identification of the resonance(s) remains elusive, and both the $^4\Sigma_u$ and $^2\Pi_u$ negative-ion states have been invoked. The situation is due, in part, to the uncertainty over the identity of the single broad resonance observed in gas-phase EELS experiments.[18] In this Letter we demonstrate that resonant vibrational excitation of O_2 can proceed via both the $^4\Sigma_u$ (at 9 eV) and $^2\Pi_u$ (at 7 eV) states. We show that these negative ions can be *preferentially selected* by orientating the O_2 molecule in two different alignments on the surface of graphite and exploiting the distinct differential electron-scattering cross sections of the two states.

The ground-state O_2 molecule has two electrons with parallel spins in the highest occupied $2p\pi_g^*$ molecular or-

bital, leading to the well-known paramagnetic moment of the molecule. An electron can be added to the system in various ways to create a negative ion, and potential-energy curves for the low-energy negative ions have been calculated.[19] On energy grounds, the resonance in the cross section for vibrational excitation of gas-phase O_2 (centered at 9.5 eV) observed by Wong, Boness, and Schulz[18] was attributed to the $^4\Sigma_u$ state (a single-particle shape resonance), though a contribution from the $^2\Pi_u$ state (a core-excited Feshbach resonance), which is also known to lead to dissociative attachment[12,20] (at 7 eV), could not be excluded. Various workers have subsequently observed a vibrational resonance at *approximately* the same energy in the physisorbed phase,[1,2,4] but the distribution in measured resonance energies over these studies (from 5 to 9 eV) is too broad to be attributed solely to experimental errors (typically ±0.5 eV). One possible interpretation[1] of these conflicting results is that there are indeed two resonances, one or other of which manifests itself more strongly in different contexts. This Letter explores that possibility.

Our experiments were performed on the O_2/graphite system. O_2 was dosed onto the graphite surface at low temperatures $(T \sim 25$ K) to create either the low-coverage submonolayer δ phase or the higher-coverage $\zeta 2$ phase. The established crystallographic structures of these phases were confirmed with low-current low-energy electron-diffraction (LEED) measurements.[21] The O_2 molecular axes lie approximately parallel to the surface in the δ phase,[22] and approximately perpendicular to the surface in the $\zeta 2$ phase.[23] EELS measurements were performed with a wide-angle spectrometer described previously.[4]

Figure 1 shows the observed resonance profiles for the two phases, obtained by measuring the intensity of the $v = 0$-1 fundamental vibrational excitation of O_2 as a
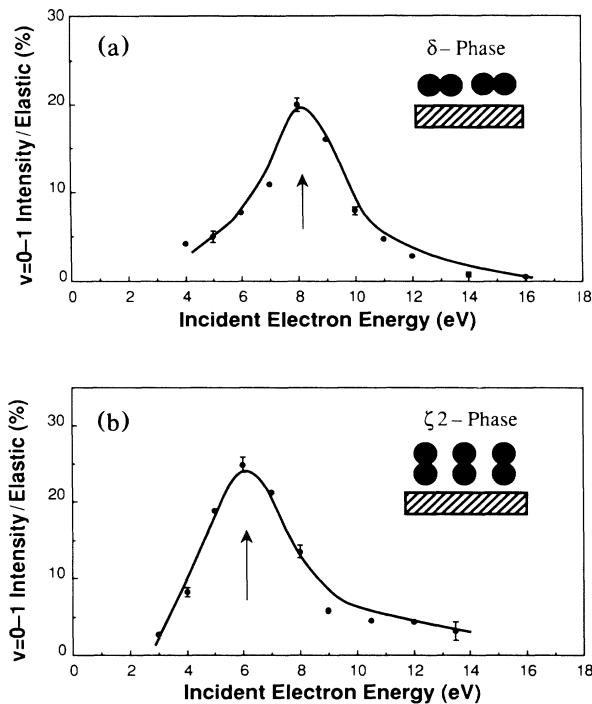
FIG. 1. Resonance energy profiles obtained from an EELS study of the monolayer δ and $\zeta 2$ phases of O_2/graphite at 23 K. The experimentally observed intensity of the $v = 0$-1 vibrational excitation of O_2 at 191-meV energy loss (normalized to the diffuse elastic intensity) is plotted as a function of the incident electron energy. The angle of incidence is 60° from the normal in each case, and the detection angle is (a) 20° and (b) 40°.
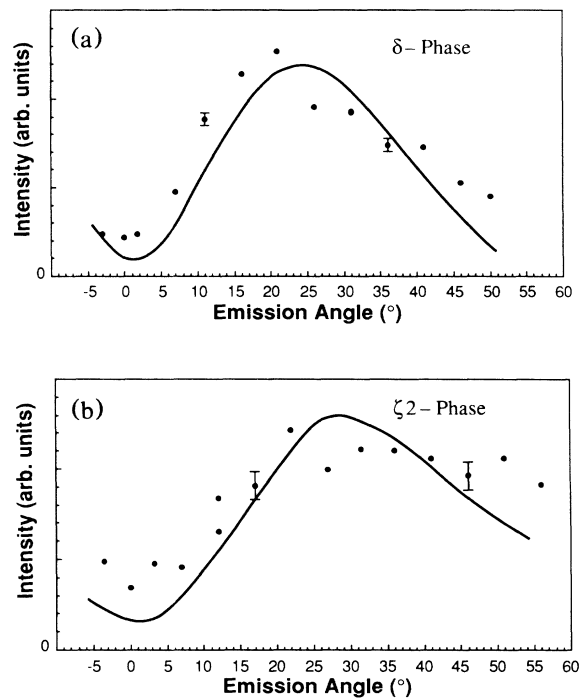

FIG. 2. Angular distributions of resonantly scattered electrons. Shown is the intensity of the $v = 0$-1 O_2 vibrational excitation as a function of detection angle (labeled with respect to the surface normal), for the δ phase (at 8.5 eV) and the $\zeta 2$ phase (at 6.5 eV). The electron-beam energies are chosen to be near the peaks in the resonance profiles of Fig. 1. The angle of incidence is 60° in each case. Note the dip in intensity along the normal to the surface in both cases. The solid lines are the angular distributions calculated for electron scattering via the $^4\Sigma_u$ resonance in the δ phase (assuming a molecular tilt of 15° from the surface) and the $^2\Pi_u$ resonance in the $\zeta 2$ phase (assuming a molecular tilt of 15° from the normal).

function of incident electron-beam energy. The loss intensities were normalized against the diffuse elastic intensity, though other normalization procedures were found not to shift the resonance peak energies significantly. In the δ phase, Fig. 1(a), a single peak is observed, centered at ~ 8.5 eV. This is ~ 1 eV below the center of the broad gas-phase peak, a result readily attributed to the attractive interaction between the negative ion and its image in the substrate.[24] In the $\zeta 2$ phase, Fig. 1(b), a resonance is again observed, but this time shifted down in energy to ~ 6 eV. This shift in resonance energy relative to the δ phase cannot be accounted for in terms of the image interaction, which is expected to be very similar for the δ and $\zeta 2$ phases, since both are monolayer structures.

There are two possible causes for the observed shift in energy of the resonance profile between the δ and $\zeta 2$ phases. Recently it was shown that multiple elastic scattering of electrons on route to and emerging from a resonance can lead to shifts in the measured resonance energy as a function of adsorbate structure.[17] However, explicit calculations of this effect in the present case predict a shift of < 0.5 eV between the δ and $\zeta 2$ phases, which clearly cannot account for the (reproducibly) observed 2.5-eV shift. This leaves us with the alternative

explanation of the energy shift, namely, that we are observing different resonances in the two phases.

In order to confirm this explanation we show in Fig. 2 the angular distributions of vibrationally inelastic electrons obtained near the center of the resonances in the δ and $\zeta 2$ phases. Such angular distributions depend upon the symmetry of the resonant state, as well as the orientation of the molecules on the surface.[4,16] At the qualitative level, the measured angular distributions look rather similar in the two phases: note, in particular, the minimum of intensity along the normal to the surface in both cases. We recently proposed a set of selection rules which give rise to nodes in the angular distribution of electrons emitted from negative-ion resonances under conditions of high structural symmetry. For example, the distribution of electrons emitted in a $p\sigma$ partial wave from a molecule lying down flat on a surface shows a node along the surface normal if there is a structural mirror plane running through the center of the molecule. Given that in the δ phase the O_2 molecules are approxi-

mately flat (and that the structure has, for zero molecular tilt, the requisite mirror plane), and that the $^4\Sigma_u$ resonance is expected to emit electrons in a $p\sigma$ wave,[16] we are led to the conclusion that in the δ phase the resonance observed is the $^4\Sigma_u$ state. The $^2\Pi_u$ state, emitting electrons in a $p\pi$ wave, would give substantial intensity (in fact, a maximum) along the surface normal in the "lying down" δ phase. When we come to the $\zeta2$ phase, the similar observed angular distribution demands that the resonance identification be reversed. Here a $p\pi$ (consistent with the $^2\Pi_u$ state) would give a minimum on the normal, while a $p\sigma$ wave (consistent with the $^4\Sigma_u$ state) would give substantial intensity in that direction. Thus it appears that the 6-eV resonance in the $\zeta2$ phase is predominantly due to the $^2\Pi_u$ state, not the $^4\Sigma_u$ state; i.e., the resonance observed has switched between the two phases.

The conclusion that the 8.5-eV resonance in the δ phase has $p\sigma$ symmetry ($^4\Sigma_u$), while the 6-eV resonance in the $\zeta2$ phase has $p\pi$ symmetry ($^2\Pi_u$), is confirmed by full calculations of the angular distributions in the two cases (solid curves in Fig. 2), performed using the LEED-type multiple-electron-scattering framework described previously.[25] For the δ phase, the best fit to the data is obtained with a $p\sigma$ partial wave (and a small molecular tilt of 15° from the horizontal), while in the $\zeta2$ phase, the best fit comes from a $p\pi$ wave (and again a small tilt, 15°, from the vertical[26]).

The question that remains is why we observe the different resonances in the two phases. On the face of it there are again two possibilities. (i) The $^2\Pi_u$ resonance is quenched by interaction with the surface in the δ phase, and similarly the $^4\Sigma_u$ resonance in the $\zeta2$ phase. (ii) The electron-scattering geometry chosen causes the $^4\Sigma_u$ state to be preferentially populated in the δ phase, and the $^2\Pi_u$ state in the $\zeta2$ phase. On the basis of studies of a number of different molecules physisorbed on graphite,[27] where we find that the reduction in resonance lifetime compared with the gas phase, judged by the relative overtone intensities,[15] is very small, we reject (i) as the major factor. (Though in the case of chemisorbed molecules where the interaction with the surface is stronger, and where resonances are also observed,[3,5] this type of effect appears more likely.) This leaves us with (ii). The point here is that the electron wave field approaching a given molecule has to "supply" a partial-wave component of the appropriate symmetry, to be captured by the molecule, in order to populate a particular resonant state.[16,17] To form a $^4\Sigma_u$ resonance a $p\sigma$ wave is needed; for the $^2\Pi_u$, a $p\pi$. The amplitude of a particular partial wave which impinges on the molecule in question will be a function of the angle of incidence of the electron beam and of the surface structure through which the incident electrons elastically scatter.[17] Similarly, in electron emission from the resonance, the efficiency with which a given emitted partial wave couples to the plane wave actually detected by the electron

analyzer is a function of the collection angle and the surface structure. What we need to know are the relative proportions of the $p\sigma$ and $p\pi$ partial waves which can couple the incident wave field to the detected plane wave via the negative-ion resonances in question ($^4\Sigma_u$ and $^2\Pi_u$, respectively), for the δ and $\zeta2$ phases, given the scattering geometry used in each case. Our calculations reveal that the proportions of these partial waves are highly sensitive to the orientation of the molecule relative to the incident and detected electron beams—a feature which is manifest (for given molecular orientation) in the structured angular distributions of Fig. 2. Further, we find that the ratio $p\sigma/p\pi$ is significantly larger in the δ phase than in the $\zeta2$ phase over the whole energy range we have investigated—by a factor of 5.5 at 6 eV and 4.7 at 8 eV, for example, values which are nicely consistent with the observed predominance of the $p\sigma$-symmetry $^4\Sigma_u$ resonance in the δ phase (and, conversely, of the $p\pi$-symmetry $^2\Pi_u$ state in the $\zeta2$ phase). It is this "selective resonance population" which enables us to resolve the two different resonances in the present case, and isolate both their energies and their symmetries.

Thus it appears we are able to account for the variety of O_2 resonance energies observed in different EELS studies of physisorbed O_2.[1,2,4] Depending on the adsorbate structure in any particular system, and on the scattering geometry utilized, either the $^4\Sigma_u$ or the $^2\Pi_u$ resonances (or both), with their different energies, may be substantially populated. The gas-phase results[17] are also explicable: the single broad resonance contains both $^4\Sigma_u$ and $^2\Pi_u$ contributions, with the $^4\Sigma_u$ dominant, presumably because it couples more strongly to vibrational excitation. In terms of the spectroscopies and chemical processes involving intermediate resonant states outlined at the start of this Letter, our results focus attention on the need to provide an electron wave field with the appropriate symmetry, and not just the requisite energy, if a resonance is to be efficiently populated.

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