Determination of Adsorbate Molecular Orientation from Resonance Electron-Scattering Angular Distributions

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(Received 8 April 1987)

We have measured the angular profile of electrons inelastically scattered from oriented molecular O_2, physisorbed on graphite at 20 K. Electrons ejected after vibrational energy loss from a temporary negative-ion resonance observed near 9 eV have an angular profile which peaks at $15° \pm 5°$ from the normal to the crystal surface, independent of the incident beam angle. From an analysis of these angular distributions we are able both to identify the O_2 negative-ion state (as $^2\Pi_u$) and to determine the orientation of the O_2 molecular axis (as $25° \pm 5°$ from the vertical) in what we believe to be the monolayer $\zeta 2$ phase.

Strong enhancement of the cross sections for vibrational excitation of homonuclear diatomic molecules through the formation of temporary negative-ion resonances was a well established phenomenon in gas-phase electron scattering by the early 1970's.[1] In the gas phase the molecules are, of course, orientationally disordered. In 1981 Sanche and Michaud[2] and Demuth, Schmeisser, and Avouris[3] independently made the first observations of resonant vibrational excitation of certain diatomic molecules, including O_2, physisorbed on polycrystalline metal films at liquid-helium temperatures, proving that the gas-phase negative-ion states survive physisorption.[4] In these experiments the angular distribution of scattered electrons could not be measured, and in any case one would expect the adsorbed films to be orientationally disordered given the nature of the substrate. This Letter presents a study of the angular distribution of electrons inelastically scattered from molecular O_2, physisorbed and orientated on the basal plane of graphite. The observed angular profiles are found to peak away from the specular direction at an angle to the crystal which is independent of the incident electron beam angle. These profiles depend upon the symmetry of the orbital which traps the incident electron to form the temporary negative-ion state and they provide a new way of determining the orientation of the molecule with respect to the surface.

Analysis of the differential cross sections for resonant electron scattering from an isolated diatomic molecule consists of matching the partial-wave expansion of the incoming and outgoing electron waves to the molecular negative-ion state formed when the electron is temporarily trapped.[5] When such a resonance is formed, the electron "forgets" its initial direction and is emitted into the partial wave of lowest l consistent with the symmetry of the relevant molecular orbital, which dominates the angular distribution of scattered electrons, at least for a homonuclear molecule with inversion symmetry.[1,5] Characteristic angular distributions are, in fact, observed

even in the orientationally disordered gas phase[1]; this arises because the electron-trapping probability also depends on the molecular orientation so that molecules in certain orientations contribute more strongly to the vibrationally inelastic cross sections than others. The peak positions are thus determined by the incident electron-beam direction. When the molecule is oriented, however, the peaks in the angular distribution are expected to occur at fixed angles referenced to the molecular axis, provided that just one partial wave dominates the cross section, whatever the incident beam angle may be.[5] This expectation also holds good for a physisorbed molecule, although in analyzing the angular distributions one has to take account of possible interference effects arising from elastic electron scattering by the substrate and the coadsorbed molecules, as we show later.

The experiments were performed with an electron-energy-loss spectrometer (EELS) consisting of a flange-mounted hemispherical monochromator and hemispherical analyzer mounted on a turntable in the UHV chamber. The analyzer can be rotated from the in-line position through 120° towards the monochromator. Crystals of highly ordered pyrolytic graphite[6] were cleaved with tape in air and mounted on a helium-coolable sample stage described in detail elsewhere,[7] which can be rotated through 360° independently of the analyzer. Note that the use of azimuthally disorientated highly ordered pyrolytic graphite means that the scattering plane samples an azimuthal average of adsorbate orientations. When the sample was placed in UHV, the EELS spectrum was marked by contaminant loss peaks, even after the bakeout, at around 150 and 350 meV. These were removed by our heating the crystal to 1300 K.

The phase diagram of O_2 on graphite exhibits a rich variety of molecular phases,[8] and provides a model system for the study of an oriented molecule. We chose a region of the phase diagram for EELS analysis where the ζ phase occurs. Previous diffraction studies of this

phase (neutron scattering,[9] LEED,[10] and x-ray scattering[11-13]) have determined the unit-cell parameters. The LEED study of Toney and Fain[10] distinguished two regions of the ζ phase ($\zeta 1$ and $\zeta 2$); at temperatures between 18 and 38 K they found a triangular, incommensurate phase ($\zeta 2$). The size of the O_2 molecule in relation to the O_2-layer lattice constants has led to the conclusion that the molecule stands upright on the surface in the ζ phase,[11,12] in contrast, for example, to the lower-coverage δ phase where the molecules are generally thought to lie flat.[11,12,14] It has been noted,[10] however, that there seems to be room for the molecules to tilt slightly towards the surface in the ζ phase (as a result of the substrate field).

In the absence of a diffractive probe, we prepared what we believe to be the monolayer ζ phase according to a prescription derived from the LEED/thermal desorption study of You and Fain.[15] With two layers of the ζ phase on the surface at 20 K, they found two thermal desorption peaks as the temperature was raised, at 32 K (the outer layer) and 47 K (the inner layer). Thus we condensed a multilayer of O_2 at 20 K, warmed slowly to 35 K, and held the temperature there until the pressure recovered (for, say, 5 min) and then cooled again to 19 or 20 K, where the EELS experiments were performed. These temperatures were chosen in order to obtain the $\zeta 2$ phase while allowing for a possible temperature drop of up to 6 K between the sample surface and the mounting block containing the thermometer (because no O_2 was seen in the EELS spectrum above a block temperature of 41 K).

Figure 1 is set out to demonstrate the observation of a negative-ion resonance near 9 eV in O_2. (The energy of the resonance is one reason for our choosing O_2 for this study, rather than other diatomic molecules which have resonances in the technically more difficult 0–3-eV range.[1,3]) Figure 1(a) shows the EELS spectrum obtained at beam energy 8.5 eV, taken 12° from specular towards the surface normal, with an incident angle of 37.5°. A sequence of vibrational overtones is seen, characteristic of the formation of a temporary negative ion,[1-4] in addition to the fundamental O-O stretch vibration. The fundamental frequency is 191 ± 3 meV, close to the gas-phase frequency (194 meV[16]) and thus signifying physisorption. In Fig. 1(b) the impact-energy dependence of the cross section for the fundamental is plotted,[17] and shows a broad resonance profile which peaks at a beam energy between 8.5 and 9 eV. The error in the beam energies shown is estimated to be ± 0.5 eV. A similar broad profile, with a peak close to 9.5 eV, was observed in the gas phase[18] and attributed predominantly to the $^4\Sigma_u$ shape resonance, although a contribution from the $^2\Pi_u$ Feshbach resonance, which gives rise to dissociative attachment with a peak near 7 eV in both gas phase[1] and condensed[19] O_2, cannot be ruled out.[20] We show below that the angular distributions of scat-
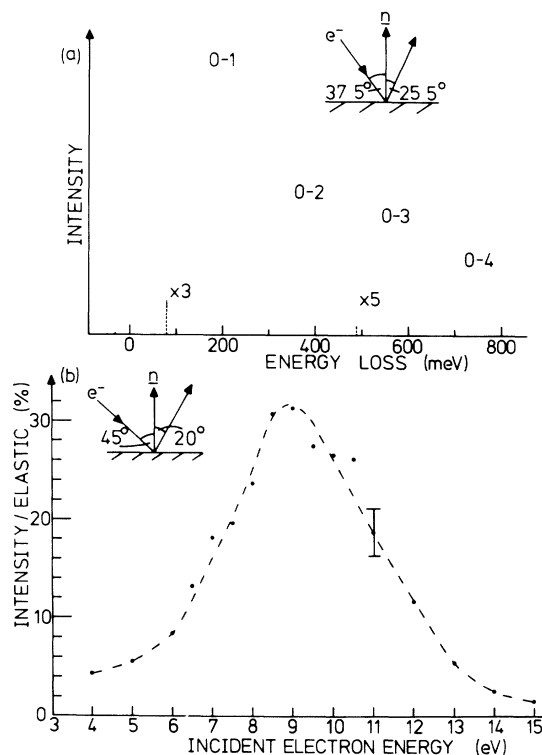

FIG. 1. (a) EELS spectrum of one monolayer of O_2 physisorbed on graphite at 20 K. Incident electron energy 8.5 eV, incident angle 37.5°, outgoing angle 25.5°. The vibrational transitions are labeled. (b) Intensity of the $v = 0-1$ vibrational mode, normalized to the elastic peak intensity, plotted against incident electron energy at fixed incident and outgoing angles (inset).

tered electrons which we observe for physisorbed O_2 on graphite indicate that the $^2\Pi_u$ state is dominant in this case.

Figure 2 shows the intensity of the $v = 0-1$ vibration observed in the EELS spectrum as a function of the electron analyzer position, for two different angles of incidence, 65° and 50°. The angle scale is given with respect to the normal to the surface in each case, because, as can be seen, each of the curves has a peak (to within experimental accuracy, $\pm 5°$) at the same angle from the normal, i.e., at $15° \pm 5°$. When the incident angle is changed by rotation of the crystal, the peak appears at a different angle from the specular direction, but at the same angle with respect to the surface. This result plainly accords with the behavior expected[5] of resonant electron scattering from an oriented molecule.[21]

The angular distributions of Fig. 2 allow us to determine both the symmetry of the resonance and the orientation of the O_2 molecule. Consider first an isolated O_2 molecule; an electron trapped to form a negative ion of $^4\Sigma_u$ ($^2\Pi_u$) symmetry would be ejected predominantly into a $p\sigma$ ($p\pi$) partial wave. However, in the case of a phys-
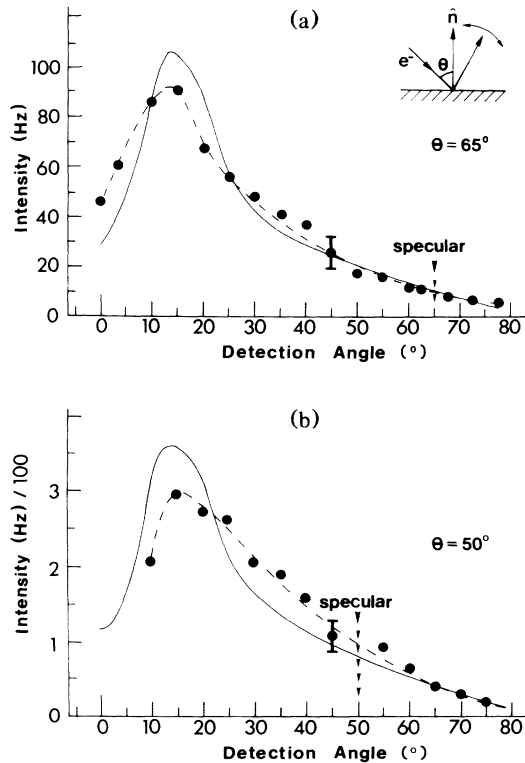
FIG. 2. Angular profile of electrons inelastically scattered after excitation of the $v = 0-1$ transition in one monolayer of O_2 on graphite for two different angles of incidence, (a) 65° and (b) 50°. Temperature 18 K in (a) and 19 K in (b). The incident electron energy is 8.5 eV in both cases. The detection angle is labeled with respect to the normal to the crystal. The dashed lines are guides for the eye through the experimental points. The solid curves are the profiles calculated for electron emission from the $^2\Pi_u$ resonance of an O_2 molecule in the $\zeta2$ phase with the molecular axis oriented at 25° from the normal to the surface. The intensity of each of the calculated profiles has been normalized by our equating the area under it with that under the corresponding experimental profile.

isorbed layer we must take into account interference effects arising from elastic scattering of the ejected electron by the coadsorbed O_2 molecules and the graphite substrate; indeed, the angular distributions measured themselves suggest this is necessary, in that the experimental profiles of Fig. 2 are not the $\cos^2\theta$ curves of a pure p wave. The solid curves in Fig. 2 are the results of a calculation of the angular distribution of detected electrons which includes a full treatment of multiple scattering within the overlayer.[22] The partial wave describing the initially emitted electron was coupled to a "time-reversed" LEED state, calculated by conventional LEED methods[23] modified to treat a molecular overlayer. The differential elastic cross section for O_2 was calculated by the multiple-scattering method of Dill and Dehmer.[24] Care was taken to average over the complete azimuthal range of domain directions found on the highly ordered

pyrolytic graphite surface. In order to determine both the symmetry of the resonance and the orientation of the molecule we performed extensive calculations[25] of the angular distributions for emission from both the $^4\Sigma_u$ and $^2\Pi_u$ states. The calculated profiles were compared with those measured for a wide range of molecular tilt angles in the $\zeta2$ phase. The calculated distributions shown in Fig. 2 are for emission from the $^2\Pi_u$ resonance, and a tilt of 25° from the vertical,[26] the conditions which give the best fit to the experiment. We consider the agreement in this case to be highly satisfactory. The profiles calculated for emission from the $^4\Sigma_u$ state did not resemble the measured angular distributions for any tilt angle. We conclude that the $^2\Pi_u$ negative-ion state makes the predominant contribution to the observed resonant scattering at 8.5 eV, and that the O_2 molecular axis stands at 25° from the normal to the surface (with an estimated error of $\pm 5°$) in what we believe to be the monolayer $\zeta2$ phase.

The tilt angle proposed is consistent with the lattice constants obtained from diffraction experiments.[9-13] Barrett and Meyer[27] found that the equilibrium distance between molecular centers in solid α-O_2 (3.20 Å) was obtained with good accuracy by the postulate that the calculated 0.002-a.u. charge-density contours,[28] which contain approximately 95% of the molecular electronic charge density, just touch (a nearest-neighbor distance of 3.18 Å is predicted on this basis). When this empirical rule is applied to the $\zeta2$ phase of O_2 on graphite, with the lattice constants taken from LEED,[10] we find that the contours touch when all the molecules tilt from the vertical by 15°–18°, depending on the direction of the tilt. This value is close to the experimentally determined tilt angle (25° $\pm 5°$) obtained from the angular profiles of scattered electrons.

We remark in conclusion that it may be possible to make a determination of adsorbate molecular orientation by the method presented here for many similar, weakly bound systems and even, perhaps, some chemisorbed systems where negative-ion resonances are beginning to be observed.[29]

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[22]We calculate the effective reflectivity of graphite seen by the overlayer at the experimental energy (8.5 eV) to be less than 1% and therefore expect the influence of the substrate upon the angular distributions to be negligible. In general, however, the reflectivity of the substrate cannot be ignored, particularly in this low-energy region (i.e., $\lesssim 20$ eV) where peaks in reflectivity of several percent can occur. The effect of high substrate reflectivity upon the resonant state is discussed by A. Gerber and A. Herzenberg, Phys. Rev. B **31**, 6219 (1985).

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