Adsorbate Resonant States: Resonance Energy Shifts Due to Elastic Multiple Electron Scattering

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We show that the energy of adsorbate resonant states observed in a number of electron spectroscopies is profoundly affected by the multiple scattering of the incident and/or emitted electrons participating in the resonance. High-resolution electron-energy-loss spectroscopy is used to investigate the $X\,{}^3\Sigma_g^- \rightarrow a\,{}^1\Delta_g$ electronic excitation of O_2 physisorbed in two different monolayer phases on graphite. The observed 2-eV shift in the resonance energy between the $\zeta\,2$ and δ phases is shown to be produced by elastic multiple scattering within the molecular overlayers. This phenomenon, in other electron spectroscopies, will lead to disagreement in the resonance energies located by different experimental techniques.

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The observation of resonant states is an important application of a number of electron spectroscopies. Photoemission,[1] inverse photoemission,[2] and near-edge x-ray-absorption fine structure[3] (NEXAFS) are examples and recently there has been a series of observations of negative-ion resonances in both physisorbed and chemisorbed molecules using high-resolution electron-energy-loss spectroscopy (HREELS).[4-9] Measurement of the resonance energy is relevant to chemical bonding schemes and can be used to determine important structural information such as bond lengths.[3] Yet there exist several unresolved discrepancies between the resonance positions as measured by different techniques[10] —even variations of the same experiment. In this paper we expose a crucial factor in resolving this issue, by demonstrating that multiple scattering of the incident or detected electron shifts the observed resonance energy. This energy shift is a function of the structure of the surface within which the molecule sits and is not an intrinsic molecular shift. Moreover, since the extent of this shift is dependent upon the scattering geometry we propose that these discrepancies depend sensitively upon the mode of observation.

While many molecular resonance energies in the gas phase have been determined,[11,12] the influence of the surface upon the measured resonance energy of an adsorbed molecule has received little quantitative attention. In this paper we investigate the changes which occur to the observed resonance energy when a molecule is adsorbed on a crystal surface. To quantify our arguments we have chosen to concentrate upon a particular example; the negative-ion resonance observed in HREELS. Here negative-ion resonances are observed by measuring the dependence on electron energy of the cross section for molecular excitation.[4-9] Enhancements are seen at specific energies due to the formation of a temporary negative ion of the target molecule: The probe electron can be trapped in a quasibound molecular orbital which decays (with a characteristic lifetime) by inelastic electron re-emission, leaving the molecule in a vibrationally or electronically excited state. However, the primary purpose of this paper is to demonstrate a quite general phenomenon; when a molecule is adsorbed onto a surface the elastic multiple scattering of the incident and emitted electron among the surface atoms and molecules can profoundly affect the resonance energy observed in spectroscopies involving electron emission or capture.

In gas-phase HREELS the only scattering event encountered by the inelastically scattered electron on route from the electron gun to the detector is the formation of the negative ion itself. In such a dilute system the observed variation of the scattered intensity as a function of the incident electron energy is the intrinsic resonance profile of an isolated molecule.

When a molecule is adsorbed onto a surface this resonance profile can be altered by a number of factors. The most straightforward of these is the lowering of the observed resonance energy by the image potential.[13] However, in addition, a more important and more unpredictable effect occurs as a consequence of the large elastic scattering cross section of atoms and molecules within the energy range for which resonances are commonly observed.[8,14] This implies that a substantial proportion of the detected electrons arriving at or emitted from the resonant molecule undergo elastic multiple scattering by other adsorbed molecules and the substrate producing strong modulations of the observed resonance profile as a function of the incident electron energy. The extent of this modulation depends sensitively upon the adsorption geometry and both the energy and the symmetry of the resonance itself, and also profoundly affects the angular distribution of loss electrons.[7,8]

In order to obtain a quantitative estimate of the magnitude and consequences of this elastic multiple scattering let us consider an experiment in which a beam of incident electrons of wave vector k impinges on a molecule. The electron energy E is chosen to be close to the energy of a negative-ion resonance of the molecule. Inelastically scattered electrons are detected with wave vector k' and energy $E-\alpha\delta E$ ($\alpha=1,2,\ldots$), δE being the fundamental energy loss associated with the excitation of the molecule.

The intensity of detected electrons can be written as a matrix element:[8]

$$I^{0\alpha}(E,k,k')=|\langle k',E-\alpha\delta E\,|f^{0\alpha}|\,k,E\rangle|^2, \qquad (1)$$

where $f^{0\alpha}(E)$ is the energy-dependent transition operator for the capture, excitation, and emission from a negative-ion resonance which occurs through the electron states $|k\rangle$ and $|k'\rangle$. The energy variation of the transition operator f is entirely responsible for the resonance profile of a molecule in the gas phase since in free space $\langle k,E\,|\,r\rangle$ is a plane wave and Eq. (1) becomes

$$I^{0\alpha}_{\text{gas phase}}(E,k,k')=|f^{0\alpha}(E)|^2. \qquad (2)$$

However, when a molecule is adsorbed on a surface the electron states $\langle k',E-\alpha\delta E\,|\,r\rangle$ and $\langle r\,|\,k,E\rangle$ are no longer plane waves but contain contributions from a variety of multiple-scattering paths linking the surface atoms and molecules. In general, we know little about the form of these states without resorting to a full multiple-scattering calculation of the propagation of electrons within the surface.[8] To proceed further we rewrite Eq. (2) in an angular momentum basis:

$$I^{0\alpha}_{\text{adsorbed}}(E,k,k')\propto\left|\sum_{lm}\sum_{l'm'}\langle k',E-\alpha\delta E\,|\,lm\rangle\langle lm\,|f^{0\alpha}|\,l'm'\rangle\langle l'm'\,|\,k,E\rangle\right|^2, \qquad (3)$$

where $\langle r\,|\,lm\rangle$ denotes a spherical partial wave centered upon the molecule which traps the electron to form a negative-ion resonance. We now assume that each electron which undergoes resonant scattering is captured from and emitted into a single partial wave (l,m) (Ref. 14) in which case Eq. (3) simplifies to

$$I^{0\alpha}_{\text{adsorbed}}(E,k,k')\propto|f^{0\alpha}_{lm,lm}|^2\sigma_{lm}(E), \qquad (4)$$

$$\sigma_{lm}(E)=|\langle k,E\,|\,lm\rangle|^2\,|\langle k',E-\alpha\delta E\,|\,lm\rangle|^2. \qquad (5)$$

In the case of an adsorbate system the intensity of detected electrons factorizes into two terms; the resonance profile of the molecule in the gas phase $|f^{0\alpha}_{lm,lm}|^2$ and $\sigma_{lm}(E)$, which describes the energy dependence of the multiple scattering of electrons propagating to and from the molecule. $\sigma_{lm}(E)$ modulates the resonance profile of the molecule in the gas phase and is determined by the electron wave functions of the incident and emitted electron in the vicinity of the resonant molecule.

In order to estimate the magnitude and influence of a multiple scattering upon the observed resonance profile we have constructed a calculational scheme to evaluate $\sigma_{lm}(E)$. Our method is explained in detail elsewhere[8] but includes a full dynamical treatment of the multiple scattering of electrons prior to and after participation in the resonance. We use conventional LEED theory[15] to evaluate the electron wave functions $\langle k,E\,|\,r\rangle$ which are then coupled to the molecular resonance through a single partial wave. This allows us to evaluate the energy dependence of $\sigma_{lm}(E)$ directly.

As a first application we have measured the energy dependence of the cross section for the $X\,^3\Sigma_g^-\rightarrow a\,^1\Delta_g$ *electronic* excitation of molecular O_2 physisorbed in two structurally different monolayer phases (the ζ 2 and δ phases) on graphite at low temperature. These profiles, shown in Fig. 1, were obtained by monitoring the intensity of the 977-meV loss peak due to the excitation as a function of the incident electron energy in a fixed scat-

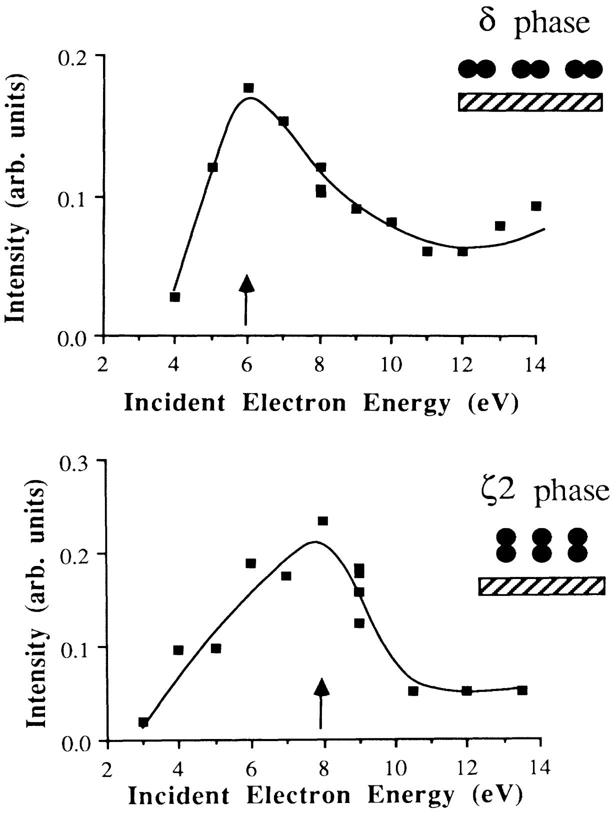

FIG. 1. Resonance energy profiles obtained by a HREELS study of the monolayer ζ 2 and δ phases of O_2 on graphite. Shown is the experimentally observed intensity of electrons inelastically scattered by exciting the $X\,^3\Sigma_g^-\rightarrow a\,^1\Delta_g$ O_2 electronic excitation at 977-meV energy loss plotted as a function of the incident electron energy. The angle of incidence is 60°; the emission angle is 40°. The solid lines are guides to the eye through the experimental data points.

tering geometry. We assign the resonance structure seen in both phases to the formation of the $^2\Pi_u$ temporary negative ion observed in the gas phase.[16] Electron capture and emission from this resonance occurs predominantly via the $d\pi$ partial wave.[17]

The two overlayer phases investigated represent two distinct overlayer geometries. In the δ phase the molecules lie parallel to the surface within a rectangular lattice.[18] In the ζ 2 phase the molecules occupy a hexagonal lattice and stand almost normal to the surface.[19] The effect of this difference in overlayer structure upon the resonance energy profile of the $^1\Delta_g$ negative ion is shown in Fig. 1. We see a marked 2-eV shift in the resonance peak which lies close to 8 eV in the ζ 2 phase and at 6 eV in the δ phase.

The origin of this shift can be determined by considering Fig. 2(a) in which we display $\sigma_{lm}(E)$ calculated for the O_2 on graphite system assuming capture and emission via the relevant $d\pi$ partial wave and also the $p\sigma$ and $p\pi$ partial waves for comparison. For this calculation we employed the adsorption geometry and optimized nonstructural parameters determined from an independent study of the angular distribution of inelastically scattered electrons[20] for the two overlayer phases. The strong energy variation of $\sigma_{lm}(E)$ is clearly apparent and changes substantially as the overlayer structure is altered. The influence of multiple scattering also depends upon the resonance symmetry. This is because the partial wave which matches onto the molecular resonance depends upon the symmetry of the resonance, and the proportion of electrons arriving in each partial wave is a different function of energy for each partial wave.

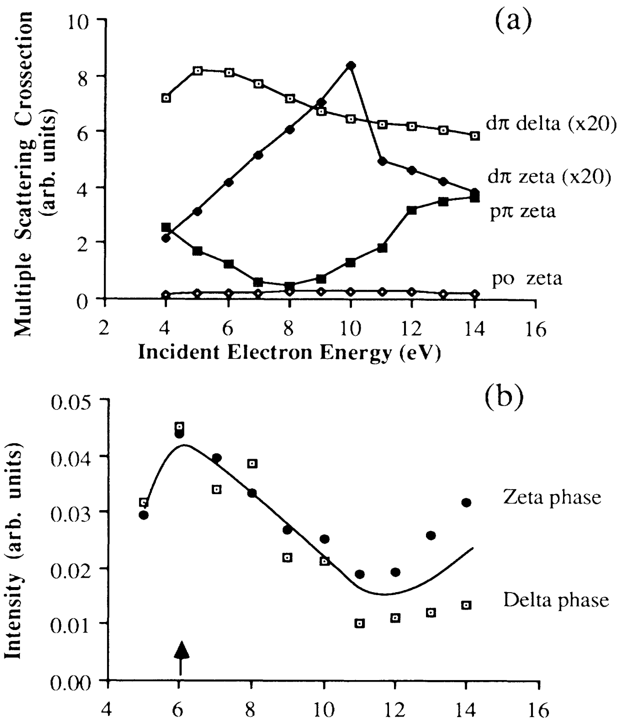

FIG. 2. (a) Calculated effective multiple-scattering cross sections $\sigma_{lm}(E)$ [see Eq. (5)] for the monolayer ζ 2 and δ phases of O_2 on graphite for capture and emission via the $d\pi$ partial wave assuming molecules tilt at angles of 25° and 75° from the surface normal in the ζ 2 and δ phases, respectively (Ref. 20). Cross sections for the $p\sigma$ and $p\pi$ partial waves are shown for comparison. The angle of incidence is 60°; the emission angle is 40°. (b) The intrinsic O_2 molecular resonance profile obtained by removing the energy variation of multiple scattering from the measured resonance profiles of Fig. 1. We assume that emission and capture occurs through the $d\pi$ partial wave. The angle of incidence is 60°, and the detection angle is 40° from normal.

In order to see how this modulation due to multiple scattering affects the observed resonance profiles we invert Eq. (4),

$$I_{\mathrm{molecular}}(E) = I_{\mathrm{observed}}(E)/\sigma_{lm}(E)\,. \qquad (6)$$

This allows us to remove the modulation of the observed intensity caused by multiple scattering to recover the intrinsic molecluar resonance profile $I_{\mathrm{molecular}}(E)$. Figure 2(b) shows the result of applying this procedure to the resonance profiles of Fig. 1. We see that a *single* molecular resonance at 6 eV produces *both* the measured resonance peak at 6 eV in the δ phase and the 8-eV peak for the ζ 2 phase. The effect of multiple scattering is to shift the observed resonance energy upwards by ~2 eV in the ζ 2 phase.[21]

In Fig. 3 we display $\sigma_{lm}(E)$ calculated for a different set of experimental conditions, where the detected intensity is integrated over the entire backscattering hemisphere. Under these conditions it is clear that the energy and structural dependence of the angle-averaged $\sigma_{lm}(E)$

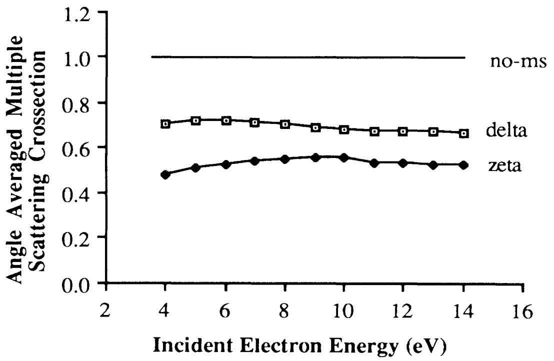

FIG. 3. Angle-averaged multiple-scattering cross sections for $d\pi$ capture and emission in the ζ 2 and δ phases of O_2 on graphite. These quantities were obtained by averaging over all polar angles of detection. For comparison the energy-independent constant cross section ($\equiv 1$) obtained in the absence of any multiple scattering is shown.

is smoothed relative to that obtained at a single emission angle (Fig. 2) and is close to the constant value (=1) expected in the absence of multiple scattering. For this experiment we conclude that the intrinsic molecular resonance profile would not be significantly shifted by multiple scattering, the effect of the averaging being to suppress the modulation due to dynamical effects. The overall reduction of the resonance cross section by approximately 30% to 50% reflects the damping of the electrons as they propagate through the surface.

Figure 3 has two important implications. Firstly, the extent of the shift in the observed resonance profile depends critically upon the scattering geometry and thus the mode of observation. Secondly, we predict that angle integration suppresses dynamical modulations and gives a more accurate picture of the accurate resonance profiles.

Finally, we wish to emphasize that the origin of the energy shifts described in this paper is a quite general phenomenon which will be present in other electron spectroscopies[1-3] which probe adsorbate resonant states.[22] Indeed we believe that we have identified a major factor for shifting the relative location of resonance energies observed with different experimental techniques. Clearly, considerable care is needed when interpreting the results of such experiments since the identification of the resonance symmetry on energy grounds alone can lead to erroneous assignments. In the case of negative-ion resonances observed in HREELS we have shown that a proper treatment of multiple scattering together with an investigation of the angular emission profiles provides sufficient information to both identify the resonance and determine the adsorption geometry.

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[21] This *relative* shift cannot be accounted for by the image potential which would be expected to produce the *same* small downward shift (~ 1 eV) relative to the gas-phase resonance energy for O_2 molecules in either the ζ 2 or δ overlayer. The energy of the molecular resonance we uncover (~ 6 eV) is shifted down by $\sim 1-2$ eV relative to the gas-phase value. *This* shift is probably primarily due to the image interaction. Note that there is an uncertainty of up to 1 eV in the *absolute* value of the experimental beam energies.

[22] The energy shifts described in this paper will not occur for resonances with widths smaller than V_{0i}, the imaginary part of the electron energy in the surface (Ref. 12), which is typically -0.5 eV for resonance energies below 10 eV. This is because variations of $\sigma_{lm}(E)$ occur on a scale greater than $2V_{0i}$.