

Selection rules in resonance electron scattering from adsorbed molecules

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We demonstrate the existence of selection rules for resonance electron scattering from adsorbed molecules observed in high-resolution electron-energy-loss spectroscopy which give rise to nodes in the angular distribution of inelastically scattered electrons. These extinctions, which are expected to occur for isolated oriented molecules, survive adsorption—even when the presence of elastic multiple scattering strongly perturbs the angular emission profiles. These nodes occur at fixed angles to the surface normal and are characteristic of both the resonance symmetry and adsorption geometry. The prospects for using these selection rules to directly determine both the resonance symmetry and the molecular adsorption site are discussed.

Recently there have been several reports of the observation of negative-ion resonances in adsorbed molecules.¹⁻⁸ Such resonances, which are well known in the gas phase,^{9,10} appear to survive both physisorption and chemisorption on a variety of substrates. Recently we showed that the angular distribution of loss electrons emitted from such a resonance can be interpreted to determine both the resonance symmetry and the adsorption geometry.^{5,6} A crucial component of this analysis was a proper treatment of the multiple scattering of the incident and emitted electron wave field prior to and after the formation of the negative ion. Below 20 eV, the energy range within which most resonances are observed, the elastic scattering cross section of the surface atoms and molecules is approximately their physical dimension.¹¹ This gives rise to strong dynamical effects which radically perturb the angular emission profiles of the adsorbed molecule compared to those of an isolated oriented molecule. Consequently, only limited information can be gained by comparing the gas-phase angular profiles to those from an adsorbed molecule.

Although our multiple-scattering analysis can successfully determine both the complete adsorption geometry and resonance symmetry it would be appealing to gain some insight into these parameters without resorting to a full dynamical calculation of electron scattering in the surface. To this end we demonstrate the existence of selection rules for resonance scattering by adsorbed molecules which give rise to nodes in the angular distribution of loss electrons at fixed angles relative to the surface normal. In certain cases the presence or absence of such extinctions can be used to predict the adsorption site and resonance symmetry.

The excitation of resonant states is an application of many different electron spectroscopies. In the case of high-resolution electron-energy-loss spectroscopy, an incident electron of well-defined kinetic energy is captured within a localized electronic state of the target molecule to

form a temporary negative ion.¹⁻⁵ The localized nature of this state results in a greatly increased probability of the trapped electron undergoing an energy loss by exciting a molecular vibration. By detecting these loss electrons we select only those electrons which have participated in the formation of the negative ion.

A common feature of all negative-ion resonances is that the electrons decaying from the resonance are emitted into one or more partial waves which match onto the quasi-bound molecular orbital in which the electron was trapped.^{10,12} For an *isolated oriented* molecule this gives rise to a characteristic angular distribution of loss electrons which are ejected predominantly into the lobes of this localized molecular orbital. This emission profile is especially simple when a single partial wave dominates the emission process.¹² This situation is illustrated schematically in Fig. 1(a) which shows electrons being emitted into a $p\sigma$ partial wave as would be the case for the deexcitation of, for instance, a $^4\Sigma_u$ resonance in a homonuclear diatomic molecule. In this case electrons are emitted predominantly along the molecular axis. Conversely, and more importantly for the discussion contained within this paper, *no* electrons are emitted at emission angles corresponding to nodes of the molecular orbital. For an *isolated oriented* molecule this gives rise to extinctions in the angular emission profiles.

The mechanism by which an incident electron is captured to form the negative ion is simply a time reversal of the emission case since tunneling into the resonant state occurs through the same partial waves into which the decaying electrons are ejected. Thus, it is impossible to excite the resonance for incident electron angles for which electrons are injected into nodes of the molecular orbital as is illustrated in Fig. 1(b). Clearly if we know the resonance symmetry then we can predict the molecular orientation from the emission profiles and angles of incidence for which there is no observed excitation of the resonance. If, instead, we know the molecular orientation then we can

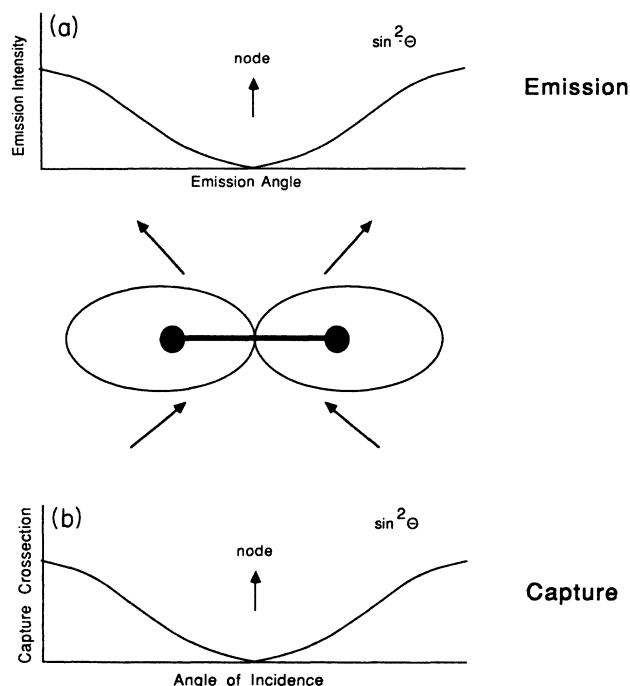


FIG. 1. (a) Schematic diagram of resonant emission into a $p\sigma$ partial wave by an *isolated oriented* homonuclear diatomic molecule showing the existence of a node in the angular distribution of loss electrons for normal emission. The angular distribution of loss electrons is the $\sin^2\theta$ profile expected for emission into a pure p wave. (b) Schematic diagram of the excitation of the resonant homonuclear diatomic molecule shown in (a). Electrons are captured through a $p\sigma$ partial wave producing a node in the differential capture cross section for normal incidence. The paths contributing to the capture cross section are the time reversal of those shown in the emission case (a) and therefore the excitation probability as a function of incident angle is the $\sin^2\theta$ profile expected for capture into a pure p wave.

determine the resonance symmetry. In the hypothetical case of an isolated oriented molecule, the existence of these nodes would provide useful information about the orientation and excitation of the molecule under investigation. The purpose of this paper is to show that these nodes exist in situations far removed from this idealized system because of selection rules which govern resonance electron scattering from adsorbed molecules.

The above discussion concerns an isolated, oriented molecule, a situation which, in practice, can never be realized. For molecules in the gas phase, although sufficiently dilute to be regarded as isolated, these nodes are "washed out" by the rotational averaging of the angular profiles. Although a molecule can be oriented by adsorbing it onto a crystal surface it then cannot be regarded as isolated. This is because the incident and emitted electron multiply scatter among the surface atoms and molecules prior to and after the formation of the resonance: a consequence of the large scattering cross section of atoms and molecules below 20 eV (Ref. 11). This multiple elastic scattering can dominate both the observed angular distribution of emitted electrons and the differential capture cross sec-

tion.⁶ However, we shall now demonstrate that these extinctions, in many cases, remain.

The argument is facilitated by the example adsorbed molecule shown in Fig. 2 which is a schematic diagram of a resonant homonuclear diatomic molecule which emits into a p_z partial wave. In the absence of the substrate there is a node of emitted intensity normal to the molecular axis: a consequence of the $\sin^2\theta$ dependence of the emitted wave field. Now let us consider adsorbing this molecule onto a surface. The emitted electrons can now make their way to the detector along a variety of multiple-scattering paths which involve scattering among the atoms within the substrate. These paths interfere to radically alter the angular distribution of detected intensity compared to the isolated molecule. However, in the presence of the substrate and provided that the center of symmetry of the adsorbed molecule lies in a mirror plane of the surface, the node still exists, *independent of the extent of the multiple scattering*.

This selection rule occurs when the partial wave into which the resonance decays lies across a mirror plane of

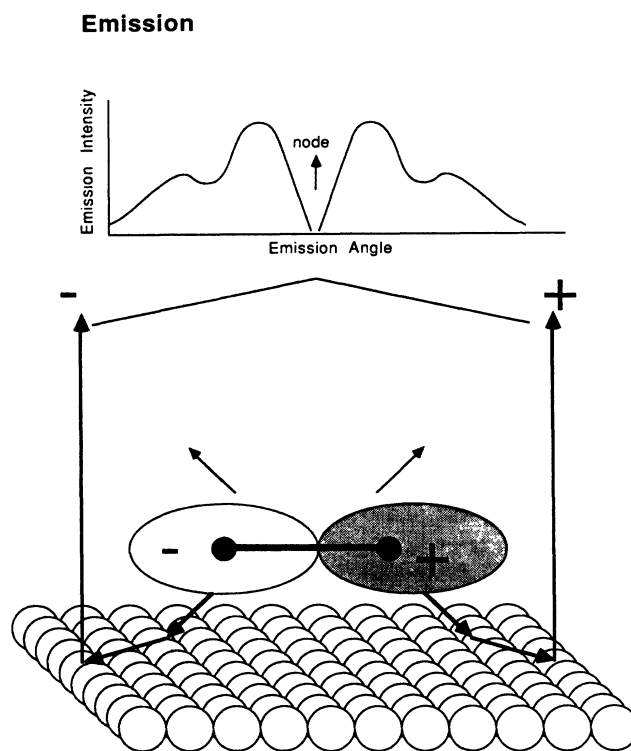


FIG. 2. Schematic diagram of resonant emission into a $p\sigma$ partial wave by a homonuclear diatomic molecule oriented by adsorption across a mirror plane of a single-crystal surface. Instead of traveling directly to the detector the emitted electrons undergo multiple elastic scattering by the substrate or adjacent molecules (not shown). Although, compared to the isolated molecule shown in Fig. 1, the emission profile is perturbed by interference between these paths the node for normal emission remains. This is because the molecule lies across a mirror plane of the surface and the electrons emitted with opposite phase into opposite lobes of the p -wave interfere destructively along the surface normal.

the surface which, in Fig. 2 occupies the zy plane. For p -wave emission electrons emitted into the half space $x > 0$ and $x < 0$ have opposite phase. Thus, for every electron path which starts with emission into the $x > 0$ half space and terminates with emission along the normal surface is an equivalent path which starts with emission into the $x < 0$ half space but with opposite phase. These pairs of scattering paths interfere destructively producing a node in the emitted intensity along the normal surface, shown schematically in the upper panel of Fig. 2. An identical argument holds for the differential capture cross section for which incident electrons follow time-reversed paths to those illustrated in Fig. 2: For normal incidence the resonance cannot be excited.

Although this discussion concerns a specific example, it is clear that the presence of these selection rules is a quite general phenomenon which will occur for other resonance symmetries and adsorption geometries. For example, in the presence of a substrate containing a 180° rotational axis passing through the molecular center of symmetry, a $^2\Pi_u$ resonance (for which $p\pi$ is the relevant partial wave) in an upright homonuclear diatomic molecule cannot be excited at normal incidence and always yields a node in the emitted intensity along the surface normal. In contrast, a $^4\Sigma_u$ resonance (for which $p\sigma$ is the relevant partial wave) can be excited for all angles of incidence and will produce intensity across the entire backscattering hemisphere.

In order to confirm the existence of such selection rules we show in Fig. 3 the calculated and measured angular emission profiles for the excitation of a $^4\Sigma_u$ shape resonance at 8.5 eV in a monolayer of O_2 on graphite. We consider the physisorbed δ phase.¹³ in which the oxygen molecules are thought to lie flat on the surface. The angle of incidence is 61° . The dominant decay channel for the $^4\Sigma_u$ resonance is the $p\sigma$ partial wave, i.e., a p -wave aligned along the molecular axis and parallel to the surface. In this case we expect a selection rule to produce a node in the emitted intensity along the surface normal.

Consider first the calculated angular distributions of Fig. 3. Let us compare the angular profile evaluated using a full dynamical treatment of the multiple scattering of the incident and emitted electron within the surface with that of the isolated oriented O_2 molecule; the $\sin^2\theta$ variation expected for emission into a pure $p\sigma$ partial wave. Although the emission profile is radically altered by multiple scattering, the extinction which occurs for normal emission is preserved. This clearly demonstrates the existence of a selection rule in the dynamical limit.

The measured angular distribution, also shown in Fig. 3, shows excellent agreement with the calculated profile. More importantly, for the discussion contained within this paper, there is a strong dip in intensity for normal emission; the manifestation of the expected selection rule. We attribute the absence of an *absolute* node to small angle ($\pm 10^\circ$) dynamical tilting of the molecules out of the sur-

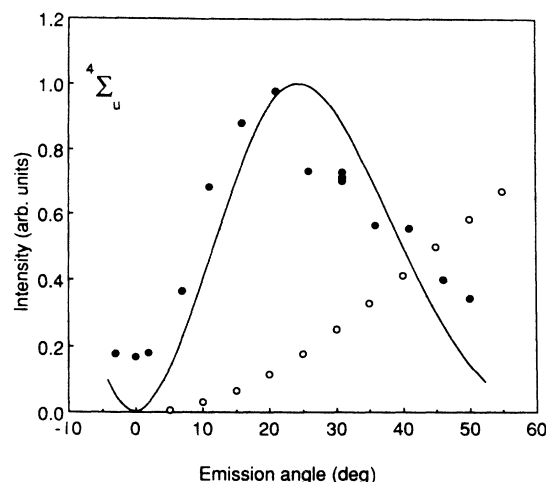


FIG. 3. The measured (solid circles) and calculated (solid line) intensity of the fundamental O-O stretching mode for the δ phase of physisorbed O_2 on highly oriented pyrolytic graphite as a function of the electron emission angle for excitation of a $^4\Sigma_u$ resonance at an incident electron energy of 8.5 eV. The angle of incidence is 61° off normal. The molecules are assumed to lie flat on the surface and the resonance decays into a $p\sigma$ partial wave. The selection rules described in this paper result in a node in the angular distribution of loss electrons for normal emission. For comparison the profile expected from this molecule in the absence of any multiple scattering is shown (open circles): this is simply the $\sin^2\theta$ angular distribution for pure p -wave emission.

face plane.¹⁴ Therefore this data represents an approximate realization of the selection rule which is weakly broken by the motion of the O_2 molecules in the overlayer.¹⁵

Finally, we note that the presence of such extinctions is *unique* to resonance scattering via negative ions. This is because the angular distribution of electrons decaying from the negative ions independent of the angular distribution of electrons captured by the molecule. In essence the emitted electron "forgets" its scattering history prior to capture, unlike elastic scattering which shows a strong forward-scattering peak along the direction of the incident beam. This last point serves to emphasize the utility of resonance electron scattering as a probe of surface structure and the electronic states of adsorbed molecules.

In this paper we have illustrated the presence of extinctions in the angular emission profiles from negative-ion resonances of adsorbed molecules. These nodes are a consequence of selection rules for resonance scattering which we have shown give considerable insight into the adsorption geometry and the resonance symmetry. Although both of these quantities can only be determined uniquely by a proper dynamical analysis of the emission profiles,^{5,6} we believe that the knowledge of such selection rules considerably enhances the prospects of resonance scattering as a new tool for surface analysis.

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Emission

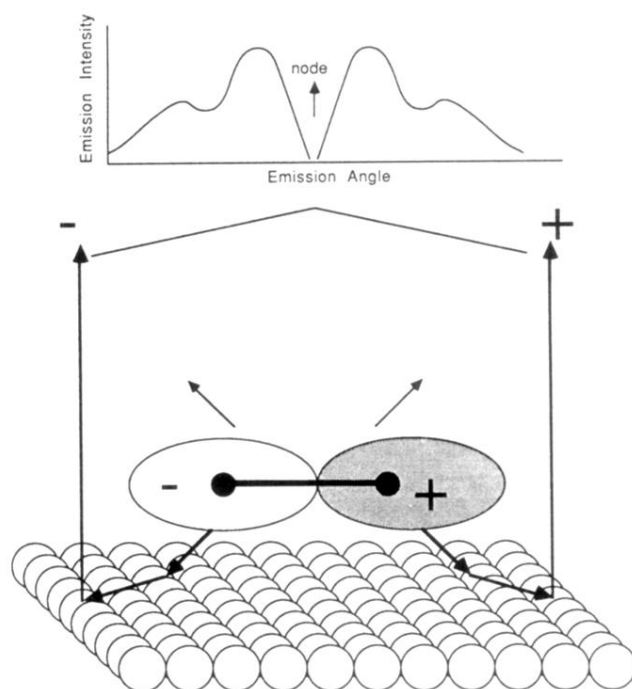


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