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Analysis of resonancelike peaks in angle-resolved ultraviolet photoemission spectroscopy from adsorbed atoms

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The physical origin of resonancelike peaks in the emission spectra of angle-resolved ultraviolet photoemission is analyzed. Emission from the $3d$ core level of Ni(001)–$c(2\times2)$ Se is studied. Evidence is found that the emission peaks exhibit strong dependence to the adsorbate-substrate geometry. Contrary to the gas-phase explanation in terms of the formation of a temporary "excited atom," we suggest that emission peaks from adsorbed species are due to constructive interference of the final-state electron wave between overlayer and substrate layers. Because of this strong dependence to the adsorbate-substrate spacing, it is recognized that the resonancelike peak can be used to determine surface bonding geometry.

I. INTRODUCTION

In the study of angle-resolved ultraviolet photoemission spectroscopy (ARUPS) from adsorbed molecules and atoms on transition-metal surfaces, one very interesting result is the detection of "reasonancelike" peaks in the emission spectra as a function of incident photon energy. Such peaks have been experimentally observed for adsorbed molecules such as CO on Ni(001),[1,3] Ni(111),[2] Pt(111),[2] Ir(111), and Ir (100),[4,5] as well as adsorbed atoms such as $c(2\times2)$ and $p(2\times2)$ S on Ni(001).[6,7] Although the emission peaks from adsorbed species have somewhat broader half-widths, typically 3–9 eV,[3,6,7] nevertheless, comparison has been made between these peaks and resonance-enhancement peaks that were observed in the photoionization cross section of gas-phase molecules. In the gas phase, the photoionization cross section from an initial state is sometimes enhanced at a particular photon energy. The commonly accepted explanation is the formation of a temporary excited (and autoionizable) atom or resonance.[8] At the gas-phase resonance, the outgoing electron is trapped by a penetrable barrier of the host molecular potential.

In this paper, we present evidence that for some adsorbed atoms on a metal substrate, the energy of the resonancelike peaks exhibits strong dependence to the adsorbate-substrate spacing. This suggests that the physical origin of the peaks for adsorbed species may not be entirely similar to that of a resonance in the gas-phase molecule. The concept of a gas-molecule resonance is primarily a property of the emitting species alone. In the lowest approximation, the resonance energy should be independent of the adsorbate-substrate distance.

Because of the strong dependence of the resonancelike peak energy to adsorbate-substrate spacing, we suggest that the resonance peaks from adsorbed species are due to constructive interference of the final-state electron wave between the adsorbate layer and the first few layers of the substrate. This strong dependence of the peak position to adsorbate-substrate distance indicates that resonancelike features can be used to study bonding geometries of the adsorbed species.

Our calculations indicate that resonancelike peaks are present in many adsorbate-substrate systems: in this paper, we present results of emission peaks from the $3d$ level of Se in the system Ni(001)–$c(2\times2)$ Se. However, we also found emission peaks from valence states of CO, O, S, and Se on Ni(001). Those results are presented elsewhere.[9] Moreover, for a given initial level, not one, but a number of emission peaks are present at final-state electron energies spanning over a wide range. The presence of multiple peaks, whose energy depends sensitively on the adsorbate-substrate spacing, is further evidence that the peaks are products of wave interference and not due to the formation of an excited atom. The strong dependence of peak energies to *interlayer* distance also suggests that the peaks are not due to emergence conditions of propagating beams related to a single layer lattice.

We present in Sec. II the emission spectra as a function of photon energy. In Sec. III, results of azimuthal dependence at fixed photon energy are presented. A summary is given in Sec. IV.

II. EMISSION FROM A CORE STATE: THE Se $3d$ LEVEL ON Ni(001)

We study emission spectra from the $3d$ core level of Se from the chemisorption system Ni(001)–$c(2\times2)$ Se. The ionization energy of this level is

57 eV below the Fermi level. The Se 3d wave function is calculated from the self-consistent $X\alpha$ scattered-wave method for a Ni_5Se cluster. The photoemission excitation matrix elements and final-state electron scattering are solved according to our earlier model.[10,11] The refractive index of the nickel substrate as a function of incident photon energy is taken from the work of Wehenkel and Gauthe.[12] Emissions from this level for final electron kinetic energies $E_k = 22$–152 eV are calculated at 2.5-eV intervals for the following geometry: incident $\theta_{ph} = 60°$, ϕ_{ph} along the [100] direction and electron exit angle $\theta_e = 0°$. Emissions from s and p polarized light are calculated separately. Multiple scatterings of the final-state electron between the Se and Ni layers are properly calculated, i.e., a low-energy electron diffraction (LEED) problem for the final-state electron is solved.[11,13,14] The Se overlayer is first placed at a four-fold site at three different Se-Ni spacings: $d_\perp^s = 1.55$, 1.945, and 2.339 Å. The value $d_\perp^s = 1.55$ Å corresponds to the structure determined earlier by LEED analysis.[15,16] The emission spectra are shown in Fig. 1 for p-polarized light. In the energy range $E_k = 22$–152 eV, four major peaks exist for $d_\perp^s = 1.55$ Å. These peaks are marked 1–4 in Fig. 1. The peaks are rather broad, with full width at half maximum Γ ranging from 10 to 14 eV. This means that the spatial extent of the final-state electron wave function is quite narrow in the direction normal to the surface.[8]

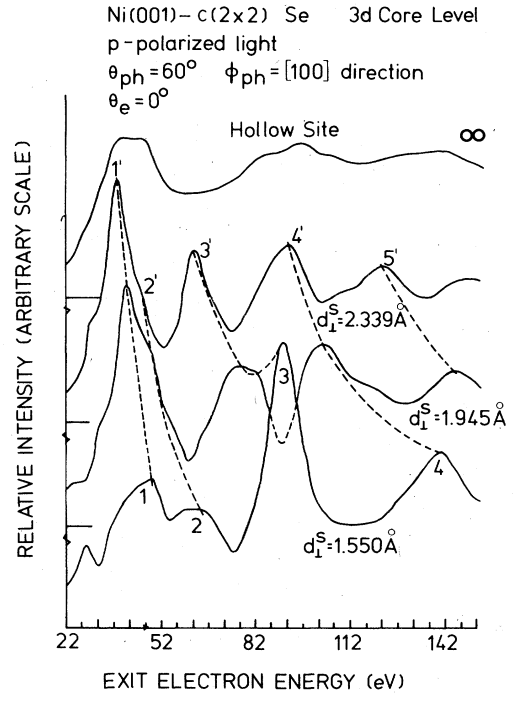

FIG. 1. Sensitivity of photon resonance curves to changes in Se-Ni interlaying spacing $d_\perp^s$ for $c(2\times2)$ Se–Ni(001). The Se atom is at the hollow site (four-fold site); p-polarized light is used. The azimuthal direction of the photon is $\phi_{ph} = [100]$.

In Fig. 1, we note that the peaks move systematically to lower energies as $d_\perp^s$ is increased, indicating the inverse dependence of wave vector to interlayer spacing in an interference phenomenon.[17] The emission from a single Se layer with a $c(2\times2)$ lattice is also shown in Fig. 1 (curve marked ∞). It corresponds to the case where the Se overlayer is separated by a large distance from the Ni substrate, i.e., the case where multiple scatterings from the Ni substrate is not important. There is a very broad peak at low energy, and two more broad structures at higher energies. The half-widths of these peaks are of the order 25–30 eV. These very broad peaks could be due to emergence conditions of new diffraction beams related to the single $c(2\times2)$ Se lattice. As $d_\perp^s$ is decreased, *interlayer* scattering between the overlayer and substrate causes new peaks to be formed and peak widths to become narrower ($\Gamma \approx 12$–15 eV). The existence of the four peaks is recently confirmed by the experiments of Kevan *et al.*[18]

As the Se-Ni interlayer spacing $d_\perp^s$ is varied, the peaks marked 1–4 in Fig. 1 move substantially in energy. However, at the $d_\perp^s = 2.339$-Å spacing, peaks 3′ and 4′ at $d_\perp^s = 2.339$ Å move to almost line up with peaks 2 and 3 at $d_\perp^s = 1.550$ Å. A new peak at $d_\perp^s = 2.339$ Å (peak 5′, not shown at $d_\perp^s = 1.550$ Å) moves to near the energy position of peak 4 of $d_\perp^s = 1.550$ Å. The end result is that it is more difficult to distinguish between geometries $d_\perp^s = 1.550$ and 2.339 Å than between, say, 1.550 and 1.945 Å. Since $d_\perp^s = 2.339$ Å corresponds to the Se-Ni spacing for top-bonded Se atoms, this "accidental" coincidence in peak positions makes it more difficult to distinguish between the two bonding sites. Such a "double coincidence" in peak positions has also been found in some cases in LEED structural analysis. However, one should be able to resolve this double coincidence by measuring at other electron exit angles.

The Se atoms are then placed at the top-bonded site. The same initial wave function for the 3d core level is used. The final state has to be recalculated, since the scattering conditions are clearly changed as a result of the new geometry.[19] The emission spectra for p-polarized light at $d_\perp^s = 1.550$, 1.945, and 2.339 Å are shown in Fig. 2. Again, we note substantial movements of peak

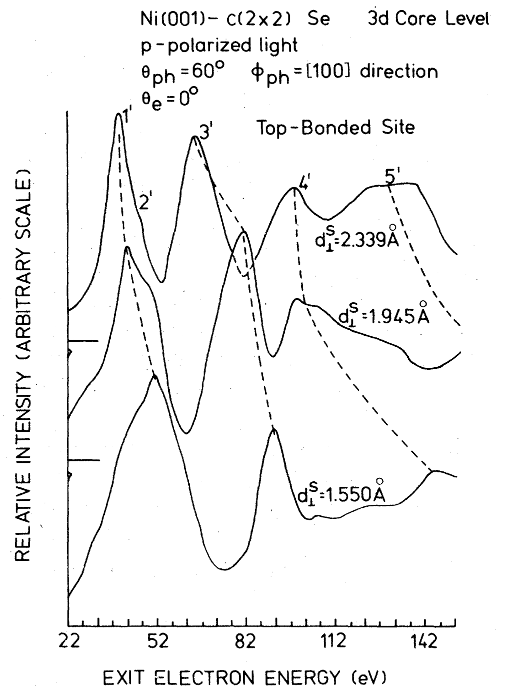

FIG. 2. Sensitivity of photon resonance curves to changes in Se-Ni interlaying spacing $d_\perp^s$ for $c(2\times2)$ Se–Ni(001). The Se atom is at the top-bonded site; p-polarized light is used.

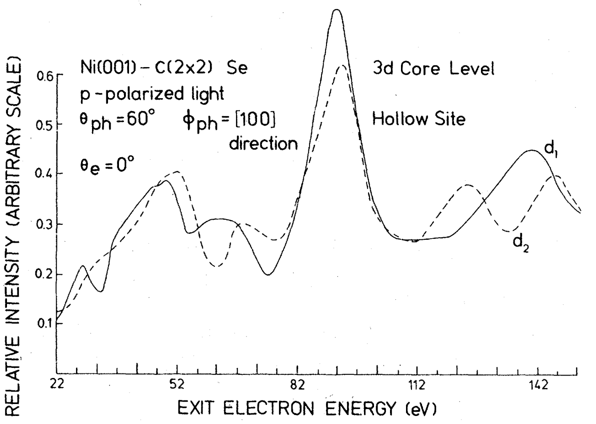

FIG. 4. Sensitivity of photon resonance curves to changes in substrate Ni-Ni interlayer spacing for $c(2\times2)$ Se–Ni(001). The Se atom is put at the hollow site and the Se-Ni interlayer spacing is fixed at $d_\perp^s=1.550$ Å. Solid line, substrate Ni-Ni interlayer spacing at $d_1=1.76$ Å; broken line, substrate Ni-Ni interlayer spacing at $d_2=2.50$ Å.

positions as $d_\perp^s$ is varied. It is interesting to note that for $d_\perp^s=2.339$ Å, the spectra for peak-bonded and fourfold bonded Se are rather similar. This relative insensitivity to the registry shift at *constant* $d_\perp^s$ may be the result of $\theta_e=0^\circ$, i.e., normal electron emission. At off-normal emission angles, there may be higher sensitivity to registry shifts at constant $d_\perp^s$.

The emission spectra for s-polarized light are also calculated. In Fig. 3, we present the results for fourfold bonded Se at $d_\perp^s=1.550$ Å (solid line) compared with top-bonded Se at $d_\perp^s=2.339$ Å (broken line). Again, the double coincidence is in evidence: peaks 3′, 4′, and 5′ move to near the energy position of peaks 2, 3, and 4. Thus it is necessary to rely on peak shifts of 5–10 eV to distinguish between the two spacings, 1.550 and 2.339 Å. By comparison, peak positions shifted by 8–20 eV as the spacing is changed from 1.550 to 1.945 Å.

We also note that for the same adsorption geometry of the Se atom, the peak positions for p- and s-polarized light are very similar. At normal electron exit, i.e., $\theta_e=0^\circ$, the p-polarized light (with $\vec{A}_p$ in the yz plane) couples to the d_{z^2} and d_{yz} initial states, while the s-polarized light (with $\vec{A}_s$ along the x axis) couples to the d_{xz} state. The apparent insensitivity to matrix-element effects supports the argument that the emission peaks are products of final-state scattering processes.

We proceed to investigate whether more than one Ni layer are involved in the diffraction process that gives rise to the emission peaks. To do this, we put the Se overlayer at the fourfold site and keep the Se-Ni spacing fixed at $d_\perp^s=1.550$ Å. We then change the substrate Ni-Ni interlayer spacing

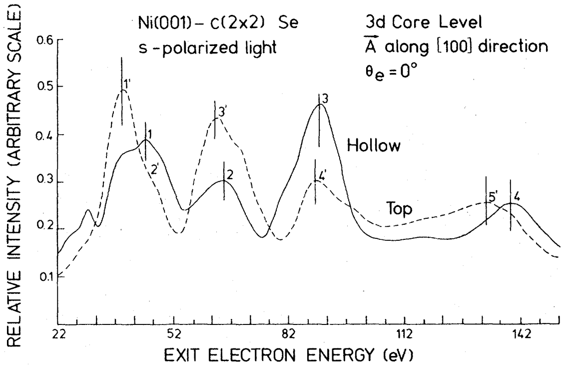

FIG. 3. Comparison of photon resonance curves for $c(2\times2)$ Se–Ni(001). s-polarized light is used. Solid line, hollow site Se at $d_\perp^s=1.550$ Å; broken line, top-bonded Se at $d_\perp^s=2.339$ Å.

from $d_1 = 1.76$ Å (the correct value) to $d_2 = 2.50$ Å. The two emission spectra for p-polarized light are shown in Fig. 4. We note that the position of emission peaks is rather sensitive to the substrate Ni-Ni interlayer spacing. This result indicates that *at least* two layers of Ni atoms participate in the diffraction process that determines the position of emission peaks. This evidence again argues against the explanation of the emission peaks in terms of excited-state resonances involving the adsorbate alone. It seems that the real physical process involves interference and diffraction of the final-state electron off a number of substrate layers.

III. AZIMUTHAL SPECTRA AT CONSTANT PHOTON ENERGY

We have also studied the azimuthal emission profiles at fixed incident photon energy. To preserve the highest symmetry in the azimuthal profiles, we choose the photon incidence $\theta_{ph} = 0°$ using unpolarized light, and the detector is rotated relative to the crystal. With such an arrangement, the azimuthal profile is expected to show the C_{4v} symmetry of the Ni(001)-$c(2\times2)$ Se system. Three photon energies are used such that the exit electron has kinetic energies $E_k = 17$, 37, and 57 eV. In Fig. 5, we show the azimuthal profiles from the 3d Se level for three geometric arrangements: (i) The emission from an $c(2\times2)$ plane of Se atoms without the Ni substrate, (ii) the emission from Ni(001)-$c(2\times2)$ Se with the Se atoms placed at fourfold sites at a spacing of $d_\perp^s = 1.550$ Å, and (iii) same as in case (ii), except that the Se atoms are placed at top-bonded sites at $d_\perp^s = 2.339$ Å.

For emission from a core level with unpolarized light at $\theta_{ph} = 0°$, the azimuthal profile is a circle if there is no final-state scattering from neighboring atoms. We note that the azimuthal profiles from the plane of Se atoms alone [Fig. 5a] are not circularly symmetric. This means that final-state scattering is important within the $c(2\times2)$ Se overlayer lattice. This is especially true at higher kinetic energies. Comparing these profiles with those of top-bonded Ni(001)-$c(2\times2)$ Se [Fig. 5(c)], many close similarities are evident. At a smaller $d_\perp^s$ distance, i.e., the fourfold bonded case where $d_\perp^s = 1.550$ Å [Fig. 5(b)], the azimuthal profiles differ more from those of the $c(2\times2)$ Se plane. This is reasonable, since the effect of the Ni substrate is expected to be larger at the smaller $d_\perp^s$ binding distance.

Perhaps the most striking finding here is that for this system, the major azimuthal structure comes from multiple scattering within the plane of $c(2\times2)$ overlayer. This could be a *general* feature for core level emissions; however, more systems with core level emission should be studied before this generalization can be made. By studying Figs. 5(b) and 5(c), one can use quantitative differences to distinguish between fourfold and top-bonded sites (both have C_{4v} symmetry). However, by comparison, the intensity-energy profiles at fixed photon incident angle are more sensitive indicators of adsorption spacing.

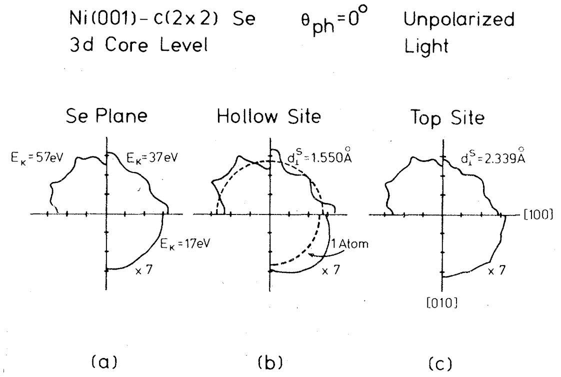

FIG. 5. Azimuthal profiles for $c(2\times2)$ Se–Ni(001). The detector is rotated relative to the crystal. Normal incident unpolarized light is used. Electron emission angles are $\theta_e = 40°$ for E_k at 17 eV, $\theta_e = 35°$ for E_k at 37 eV, and $\theta_e = 33°$ for E_k at 57 eV. (a) Emission from an $c(2\times2)$ plane of Se atom without the Ni substrate. (b) Emission from hollow site Se at $d_\perp^s = 1.550$ Å; the arcs (broken lines) are the profiles if there is no final-state scattering from neighboring atoms. (c) Emission from top-bonded Se at $d_\perp^s = 2.339$ Å.

IV. CONCLUSION

We can summarize the behavior of emission peaks (Figs. 1–4) from the 3d core level of Se by the following observations.

(i) The "resonancelike" peaks in the intensity-energy spectra seem to be common features in many adsorbate-substrate systems. They occur at different energies for different adsorbate-substrate systems, so experimentally one has to know where to look. Moreover, usually a number of sharp peaks exist in an extended energy range, say, 150 eV.

(ii) The emission peaks seem to result from interference processes involving the final state and the adsorbate and top substrate layers. This can explain the multiple number of peaks in an extended energy range and the movement of each peak to lower energy as the surface interlayer spacing is increased. The exact interference dependence is probably complicated; a number of propagating beams with wave vectors $\vec{k}(\vec{g})$ compete to form peaks.[20] Here, $\vec{g}$ is a reciprocal-lattice vector of a surface layer. The very strong dependence of peak position to adsorbate-substrate geometry seems to argue against explanation in terms of single layer beam emergence thresholds or the formation of temporary excited states involving the adsorbates alone.

(iii) The peak positions exhibit high sensitivity to the adsorbate-substrate geometry. This sensitivity can be utilized to study the chemisorption position of adsorbates. At normal emission angle, there is a lesser sensitivity to the adsorbate-substrate registry at constant $d_\perp^s$. Also, for the $3d$ core emission of Se on Ni(001), there is a double coincidence between the fourfold spacing of 1.550 Å and top-bonded spacing of 2.339 Å. The two sets of peaks move into energy positions with differences of 10 eV or less. However, we expect that this accidential coincidence will be lifted at off-normal exit angles.

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[1] R. J. Smith, J. Anderson, and G. J. Lapeyre, Phys. Rev. Lett. 37, 1081 (1976); J. Vac. Sci. Technol. 14, 384 (1977).

[2] G. Apai, P. S. Wehner, R. S. Williams, J. Stohr, and D. A. Shirley, Phys. Rev. Lett. 37, 1497 (1976).

[3] C. L. Allyn, T. Gustafsson, and E. W. Plummer, Chem. Phys. Lett. 47, 127 (1977).

[4] G. Broden and T. N. Rhodin, Solid State Commun. 18, 105 (1976).

[5] T. N. Rhodin and C. Brucker, Proceedings of the Seventh International Vacuum Congress and Third International Conference on Solid Surface, Vienna, 1977 (unpublished).

[6] E. W. Plummer, T. Gustafsson, and S. P. Weeks (unpublished).

[7] C. H. Li and S. Y. Tong, Phys. Rev. Lett. 40, 46 (1978).

[8] G. J. Schulz, Rev. Mod. Phys. 45, 423 (1973). Schulz mainly discusses the temporary negative ion, but the physical process involved there is very similar to that of the electron in an autoionizable "excited" state, except for the difference of one-electron charge in the host potential.

[9] S. Y. Tong and C. H. Li (unpublished); Bull. Am. Phys. Soc. 23, 417 (1978).

[10] S. Y. Tong, C. H. Li, and A. R. Lubinsky, Phys. Rev. Lett. 39, 498 (1977).

[11] C. H. Li, A. R. Lubinsky, and S. Y. Tong, Phys. Rev. B 17, 3128 (1978).

[12] C. Wehenkel and B. Gauth, Phys. Status Solidi B 64, 515 (1974).

[13] A. Liebsch, Phys. Rev. B 13, 544 (1976); Phys. Rev. Lett. 38, 248 (1977).

[14] A. Liebsch, *Electron and Ion Spectroscopy of Solids* (Plenum, London, 1978).

[15] J. E. Demuth, D. W. Jepsen, and P. M. Marcus, Phys. Rev. Lett. 31, 540 (1973).

[16] M. A. Van Hove and S. Y. Tong, J. Vac. Sci. Technol. 12, 230 (1975).

[17] S. Y. Tong, *Progress in Surface Science*, edited by S. G. Davison (Pergamon, Oxford, 1975), Vol. 7, No. 1.

[18] S. D. Kevan, D. Rosenblatt, D. Denley, B-C. Lu, and D. A. Shirley, Phys. Rev. Lett. 41, 1565 (1978).

[19] S. Y. Tong and M. A. Van Hove, Solid State Commun. 19, 543 (1976).

[20] S. Y. Tong and N. Stoner, J. Phys. C 11, 3511 (1978).