Extraction of Surface Structural Information from Angle-Resolved Ultraviolet Photoemission Spectroscopy

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(Received 19 September 1977)

The dependences of photoionization cross section on incident photon energy and electron emission on polar exit angle are used to determine the location of chemisorption sites. Calculations are made for the $c(2\times2)$ S-Ni(001) and CO-Ni(001) systems. Comparing with experiment, it is found that angle-resolved ultraviolet photoelectron spectroscopy data are very sensitive to the coordination number of the adsorption site and less sensitive to the overlayer-substrate interlayer spacing.

Recent rapid advances in the understanding of angle-resolved ultraviolet photoemission spectroscopy (ARUPS) data[1-15] revealed much potential of this technique for the characterization of clean and chemisorbed surface layers. In terms of the theoretical interpretation, it is apparent that calculations based on the multiple-scattering approach for both initial- and final-state wave functions produce reasonable agreements with the experimental data.[4,6,14] One very interesting question concerning ARUPS is whether its emission spectra can lead to successful determinations of surface structures of adsorbed species. In this Letter, we present direct evidence of ARUPS for the determination and discrimination of chemisorption sites. We demonstrate this sensitivity of ARUPS to surface geometry via examples of photoionization resonance curves and electron polar emission plots. Two overlayer systems are considered: $c(2\times2)$ S-Ni(001) and Co-Ni(001). Furthermore, examples are given to illustrate which types of geometric information that are most readily analyzed by ARUPS measurements.

The chalcogen sulphur forms an ordered $c(2\times2)$ overlayer on Ni(001). The important geometric information in such a system are the following: (i) the coordination number of the adsorption site, and (ii) the vertical d spacing between adsorbate-substrate layers. From these two numbers, the S-Ni bond length and bond angle can be deduced. We first show the sensitivity of photon energy resonance curves to binding geometry. It is widely known that emissions from 4σ and $5\sigma(1\pi)$ levels of CO exhibit resonance peaks at various photon energies.[1,3-6,10] Such a resonance peak is also present in the $c(2\times2)$ S-Ni(001) system. In Fig. 1, we show the emission from the S $3p$-derived level for p-polarized light at $\theta_{\text{ph}} = 45°$. The experimental curve of Plummer, Gustaffson, and Weeks[16] clearly shows a sharp peak at $\hbar\omega = 17$ eV. The calculated emission is for the S atom placed at a fourfold-coordination site at interlayer distance 1.3 Å, i.e., the structural configuration determined by LEED (low-energy electron diffraction) analysis.[17,18] In the calculation, an initial-state wave function generated from a self-consistent $X\alpha$ scattered-wave method and a multiple-scattering final state from the dynamical LEED formalism are used.[14] Without adjusting any dynamical inputs from previous calculations,[19] the calculated emission curve

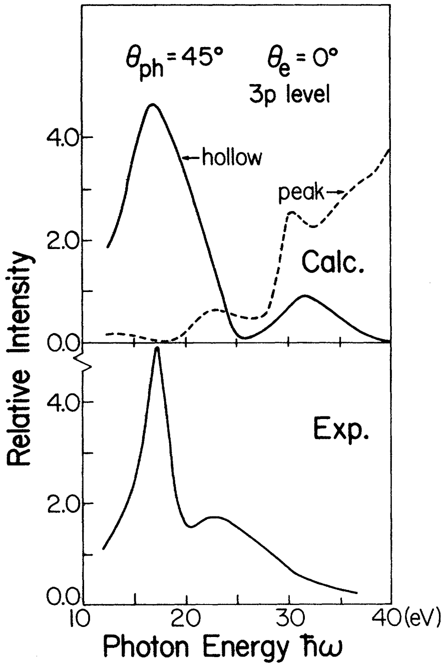

FIG. 1. Comparison between theory and experiment for photon resonance curves for $c(2\times2)$ S-Ni(001). Calculations: solid line, S at fourfold site; broken line, S at peak site.

(solid line) reproduces the resonance peak at exactly $\hbar\omega = 17$ eV. The calculated peak is somewhat wider than the data. Since the resonance peak depends on final-state scatterings from S and surrounding nickel atoms, it is reasonable to expect that the resonance profile depends sensitively on the coordination number of the binding site. Putting the S atoms directly above the next layer nickel atoms, the emission dependence on photon energy changes drastically (broken line). There is no longer a resonance peak at $\hbar\omega = 17$ eV.

Figure 2 shows the sensitivity of ARUPS polar emission plots on site coordination number. Emission from the S $3p$-derived level is shown. The calculated curve (solid line)[19] for which the S atom sits at the fourfold site shows reasonable agreement with the data (open circles).[16] The calculated emission from peak bonded S on Ni (broken line) is in poor agreement with experiment. Similar clear differences between calculated curves for fourfold and peak sites are observed using s-polarized light.[6]

We now examine the sensitivity of ARUPS polar emission profiles to the adsorbate-substrate interlayer d spacing. Putting S at a fourfold site and varying the d spacing from 1.30 Å (solid lines) to 1.43 Å (broken lines), the calculated emission plots are shown in Fig. 3 for p- and s-polarized light. Except for the fact that the emission from the larger d spacing is slightly weaker, the angular dependence of the two interlayer spacings are very similar. We can perhaps understand this result by comparing ARUPS with LEED analysis. Angle-resolved UPS and LEED probe at different surface factors: ARUPS primarily at local directions and symmetries of surface bonds; LEED, on the other hand, at the long-range scattering order of surface atoms. Structural changes that preserve bond symmetries and directions (e.g., variance in d spacing) are less sensitive to probes of ARUPS. LEED analyses are sensitive to bond-length changes of less than 0.1 Å. On the other hand, LEED analysis relies on differences in the scattering factors of components of an adsorbed molecule to determine the orientation of that surface molecule. It would have difficulties in molecules where the components have similar scattering powers, take, e.g., the NO molecule. The adsorption orientation of such a molecule should be more readily determined by ARUPS.

The 4σ level of CO-Ni(001) exhibit a well-known resonance peak at $\hbar\omega = 35$ eV.[5] Davenport used this resonance feature to establish that CO adsorbs on Ni(001) with the C atom down.[4] Because

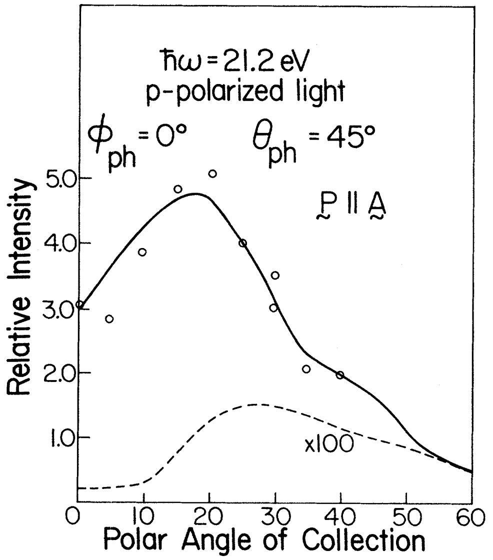

FIG. 2. Comparison for polar intensity plots for $c(2\times 2)$ S-Ni(001). Solid line, S at fourfold site; broken line, S at peak site; circles, experiment. The nomenclature of the photon azimuthal angle is the same as in Ref. 19. The notation $\vec{P}\parallel\vec{A}$ indicates electron-emission plane containing the photon $\vec{A}$ vector.

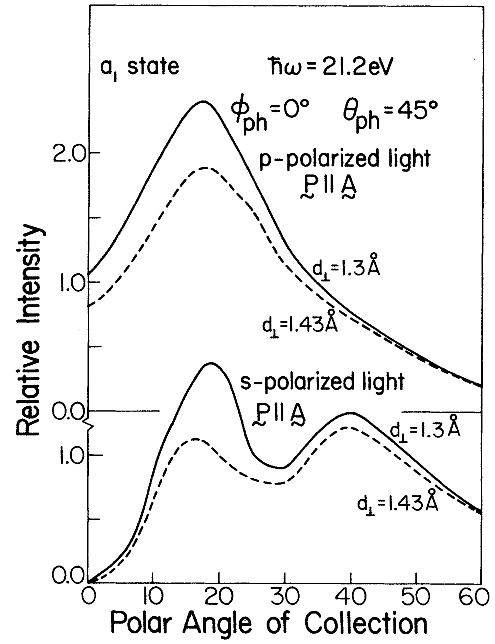

FIG. 3. Sensitivity of polar intensity plots to changes in S-Ni interlayer spacing $d_\perp$ [for $c(2\times 2)$ S-Ni(001)]. (The S atom is at the fourfold site.)

his calculation is for an oriented CO molecule without any substrate atoms, it is impossible to tell there how many Ni atoms the CO molecule is bonded to. Here, we investigate CO bonded at two different registries: (i) CO bonded on top of one Ni atom (peak bonded), and (ii) CO bonded at the hollow of four Ni atoms. The emission spectra for both bonding configurations show a C_{4v} symmetry. Other bonding sites, e.g., bridge-bonded CO, are not considered here because their emission spectra would exhibit symmetries different from C_{4v}. These other bonding sites are more easily studied by azimuthal emission plots than photon resonance curves. In Fig. 4, the calculated emission dependence on photon energy is shown for CO bond to one Ni atom (solid line). Again, using the same dynamical inputs for the final-state scattering as in LEED calculations, a sharp resonance peak is obtained for peak-bonded CO. The shape and peak width compare very well with experiment (open circles). The calculation uses an inner potential $V_0 = 11.2$ eV and the resonance peak energy is low compared to the data. Since the inner potential in the final-state scattering is an adjustable parameter used to fit peak positions between theory and experiment (as in LEED), we find the best fit in the resonance peak position is for a zero inner potential. Judging from the fact that, at the peak-bonded site, the 4σ level of CO juts out far away from the nickel surface, the zero-inner-potential value is not entirely unreasonable. But we emphasize that the position of the calculated peak is adjustable via the inner-potential value. Although the 4σ level is believed to be only mildly perturbed by the chemisorption process, however, the resonance peak depends on the final state, which scatters strongly off neighboring nickel atoms. Putting CO at a fourfold-bonded site, with $V_0 = 11.2$ eV, we find that instead of a sharp peak at $\hbar\omega = 36$ eV, the calculated curve shows a broad plateau which rises at $\hbar\omega \approx 30$ eV (broken line). Since we have used V_0 as an adjustable parameter, we redid the calculations using a zero inner potential. For peak-bonded CO, except for the aforementioned shift in the peak energy, the shape and half-width of the resonance peak remain essentially the same. The emission from fourfold-bonded CO, with a zero inner potential, shows indications of a broad peak (dash-dotted line). However, the half-width of this broad peak is 19 eV, compared to 13 eV in both the data and calculation for peak-bonded CO. It is interesting to note that the resonance behavior of S and CO are exactly opposite: The S system exhibits a sharp resonance peak at the fourfold binding site whereas the CO system shows a sharp resonance at the peak-bonded site. Also, since the experimental data is for a saturated CO coverage on Ni(001),[5] our result would indicate that few or no CO are bound to the fourfold-coordination site at the coverage of the experiment.

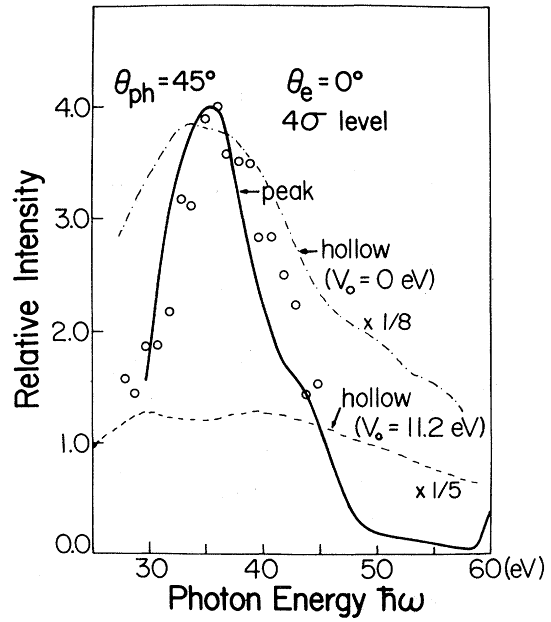

FIG. 4. Comparison of photon resonance curves for $c(2\times 2)$ CO-Ni(001). Solid line, peak-bonded CO; broken line, fourfold-bonded CO, $V_0 = 11.2$ eV; dash-dotted line, fourfold-bonded CO, $V_0 = 0$ eV; open circles, experiment.

We are grateful to Dr. H. L. Yu for supplying us with a scattering potential for CO at the fourfold site based on his self-consistent $X\alpha$ scattered-wave calculations. This work was supported in part by a National Science Foundation Grant No. DMR 73-02614.

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Variational Cellular Model of the Molecular and Crystal Electronic Structure

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(Received 30 June 1977)

A variational version of the cellular method is developed to calculate the electronic structure of molecules and crystals. Because of the simplicity of the secular equation, the method is easily implemented. Preliminary calculations on the hydrogen molecular ion suggest that it is also accurate and of fast convergence.

The multiple-scattering method has been applied successfully to a wide range of solids, molecules, and molecular clusters.[1,2] However, there are some molecular geometries where the muffin-tin potential has to be improved considerably if one wants to obtain an electronic structure with a reasonable degree of physical realism.[3] The unsatisfactory features of the muffin-tin approximation applied to open structures are already known from previous calculations of electronic structure of solids.[4] For open structures, the muffin-tin approximation is poor because of the large volume where the potential is constant. To circumvent this limitation, it is becoming common practice to overlap the spheres circumscribing the atoms,[5] thus minimizing the bad effects of a constant potential in a much extended region. This procedure improves the results considerably, as examplified by the case of the ion H_2^+ to be discussed below. The extension of the multiple-scattering method to non-muffin-tin potentials, that has been tried by some authors, is difficult and costly to implement.[6] In preference to the methods which deal with muffin-tin potentials, we suggest in this Letter a new approach to the problem of finding the one-electron solutions of the Schrödinger equation for molecules and crystals. Our starting point goes back to the Wigner-Seitz-Slater cellular method,[7] where the solution of the boundary condition problem is reformulated by us as a variational principle. A critical test of the model is made by carring out preliminary calculations of the hydrogen molecular ion H_2^+. As will be shortly seen, one important asset of the present method is the elimination of the constant-potential region of the multiple-scattering method. In this respect, the good features of the overlapping-spheres model can be also expected in the present case.

The present method has a resemblance to the one proposed by Antoci and Nardelli.[8] Their method and ours have a common starting point, which is a variational expression for the energy eigenvalue.[9] While Antoci and Nardelli use spherical cells centered at the nuclei, our cells can have any shape, which is an asset for open structures. On the other hand, in the interatomic region, Antoci and Nardelli expand the wave function in terms of functions which are regular at the origin and at infinity. Thus, in the interatomic region, the wave function is not an exact solution of the Schrödinger equation for the energy eigenvalue. In this respect, the method of Antoci and Nardelli is an extension for molecules of the augmented-plane-wave method for crystals, and one cannot expect rapidly converging wave functions. The method we present below is differently motivated: We attempt to formulate the cellular method in a variational way. Thus we add to the flexibility of the cellular method a much fast-