Selective Structural Sensitivity and Simplified Computations of Angle-Resolved Ultraviolet Photoemission Spectroscopy

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The intensity modulations in a constant initial-state spectrum are found to possess selective sensitivity to layer spacings just below the emitting atom. This can be used to successively determine unknown spacings in a complex surface structure. A simple computation method is found to work accurately at electron energies above 60 eV.

Although much work has focused on the use of angle-resolved ultraviolet photoemission spectroscopy (ARUPS) to study surfaces, it remains to be established whether this technique can become a convenient and practical tool for determining surface structures. Part of the problem is in the computation procedure. The multiple-scattering theory of ARUPS contains the dynamical low-energy electron-diffraction (LEED) wave function as an ingredient.[1-2] This means calculations of ARUPS are necessarily more lengthy than a dynamical LEED calculation of the same system. The utility of a technique is limited if the accompanying theoretical analysis is very cumbersome. Thus, could one simplify ARUPS calculations without sacrificing the accuracy in the analysis? And does the ARUPS technique possess special structural sensitivities that make it particularly useful for determining certain surface spacings?

In this Letter, we present results that show the following: (i) The intensity modulations in a constant-initial-state spectrum (CISS)[3-5] do possess *selective* sensitivities to certain surface spacings. The evidence found indicates that the CISS modulations are useful in determining spacings of complex adsorbed molecules. (ii) At moderately high kinetic energies (e.g., $E_{\text{kin}} \geq 60$ eV), a simple approximation scheme, called the quasidynamical method,[6] produced very accurate intensity results when compared with those of the full dynamical calculation. This means that calculations are economical and simple if experimental data above $E_{\text{kin}} = 60$ eV are used.

We first show the selective sensitivity of CISS intensity modulations. We use as an example the Ni(001)$c(2\times2)$-CO system. Suppose CO adsorbs on Ni(001) with the C end down, then an unknown surface distance is the Ni-C interlayer spacing. Knowledge of this spacing in many cases also fixes the adsorption site: E.g., for top, bridge, and (fourfold) hollow sites, the Ni-C spacings are, respectively, 1.83 ± 0.05, 1.30 ± 0.05, and 1.06 ± 0.05 Å. Variations due to different "number of bonds" at the different sites are of the order 0.05 Å only. Another unknown distance is the O-C spacing. Knowledge of this spacing determines the angle of tilt, if any, of the CO axis from the surface normal.[7,8] In a typical LEED analysis of this system, the intensity-voltage (*IV*) curves contain interferences of the LEED electron with both of the unknown spacings. This means the two unknowns must be solved *simultaneously* from the same set of LEED data.

In ARUPS, we found a selective sensitivity which conveniently *resolves* the two unknowns. It works in the following way: If the C end of CO is down, then the CISS spectra from a C atom (e.g., the C 1*s* orbital) may be used to determine the Ni-C spacing. We found that the C 1*s* intensity spectra are sensitive to the Ni-C spacing. But more importantly, the C emission is insensitive to the CO spacing. This fact can be seen from Fig. 1. The C 1*s* spectrum contains two main peaks in the energy range shown. The positions of the two peaks are sensitive to the Ni-C spacing: E.g., the peak at $E_{\text{kin}} = 86$ eV moves down by more than 23 eV when we vary $d_\perp^{\text{Ni-C}}$ from 1.6 to 2.0 Å (upper panel). For this peak, $\Delta E/\Delta d_\perp^{\text{Ni-C}} = (5.75\ \text{eV}/(0.1\ \text{Å})$. On the other hand, these peaks are only slightly shifted when the CO spacing is varied. For example, looking at the peak near 70 eV (Fig. 1, middle panel), its position changes by only 3 eV as $d_\perp^{\text{CO}}$ is varied from 1.13 to 1.53 Å. The value of $\Delta E/\Delta d_\perp^{\text{CO}}$ is (0.75 eV)/(0.1 Å). This insensitivity is because, to first order in backscattering, the phase differences which produce peaks in the C 1*s* spectrum are independent of $d_\perp^{\text{CO}}$.

Since emissions from C are not sensitive to the CO spacing, we can use them to determine the Ni-C spacing. After the Ni-C spacing is found, we use the emission from O (e.g., the O 1*s* level) to determine the CO spacing (Fig. 1, bottom panel). Here, the peaks in the O 1*s* spec-

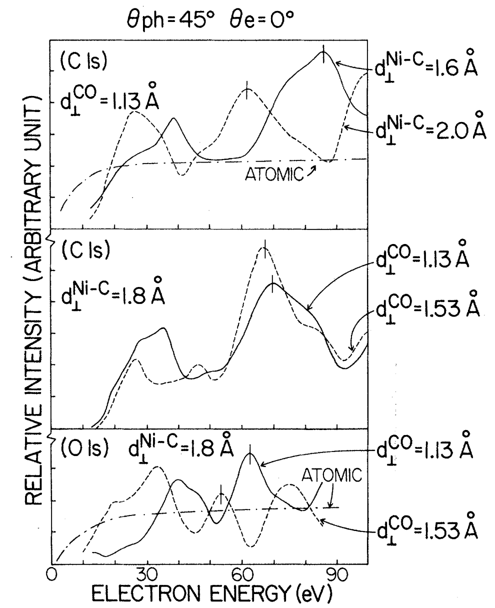

FIG. 1. Intensity spectra for Ni(001)$c(2\times 2)$-CO, p-polarized light along [100], CO bonded at top site.

trum are again sensitive to variations in the CO spacing. For example, $\Delta E/\Delta d_{\perp}{}^{\rm CO} = (2.38\ {\rm eV})/(0.1\ {\rm \AA})$ for the peak at 62.5 eV in Fig. 1, bottom panel.

Thus, the rule seems to be that CISS intensity peaks from core levels of an atom in a given layer are most sensitive to the spacing between that layer and the layer below it. The CISS peaks are insensitive to layer spacings *above* the emission layer. This selectivity can be very useful because there are systems where one may start with the layer just above the deepest unknown spacing and work up, determining in turn different unknown spacings in a molecular adsorption system.

If CO were to adsorb with the O end down (a highly unlikely case), one may use the O emission to determine the Ni-O spacing, then the C emission to determine the O-C spacing. We have used the 1s core levels of C and O as examples, but the same conclusions should spply to other core levels.

We now turn to the question of simplifying calculations of CISS intensity spectra. The CISS spectrum in ARUPS, an IV curve in LEED, and modulations in surface extended x-ray-absorption fine structure (SEXAFS) all have a common origin, i.e., the elastic scattering of an electron with energy $E_{\rm kin}$ among different atomic centers.

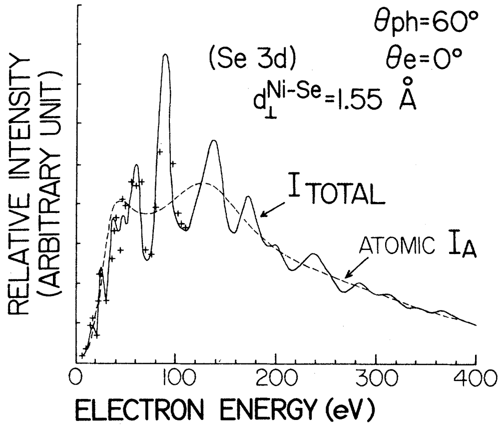

FIG. 2. Intensity spectra for Ni(001)$p(2\times 2)$-Se; Se bonded at hollow site. QD calculation below 100 eV (crosses), p-polarized light along [100].

In LEED, the IV curve is measured for fixed incident $\vec{k}_i$ and fixed final $\vec{k}_f$ directions. In ARUPS, the incident direction is not fixed. The emission at final direction $\vec{k}_f$ may be expressed as the square of a sum over a set of beam directions with parallel momenta $\vec{k}_{f\parallel} + \vec{g}$. In SEXAFS, the final direction $\vec{k}_f$ is further 4π integrated. The results are that, in most materials, LEED IV curves in the range $E_{\rm kin} = 10-400$ eV require a full dynamical theory. SEXAFS, because of the spherical average, requires only a kinematical theory. We found that ARUPS intensity spectra lie somewhere in between. We illustrate this by an example: Ni(001)$p(2\times 2)$-Se.[3,5] In Fig. 2, we show the calculated spectra in the energy range 10 to 400 eV, using a full dynamical theory. The

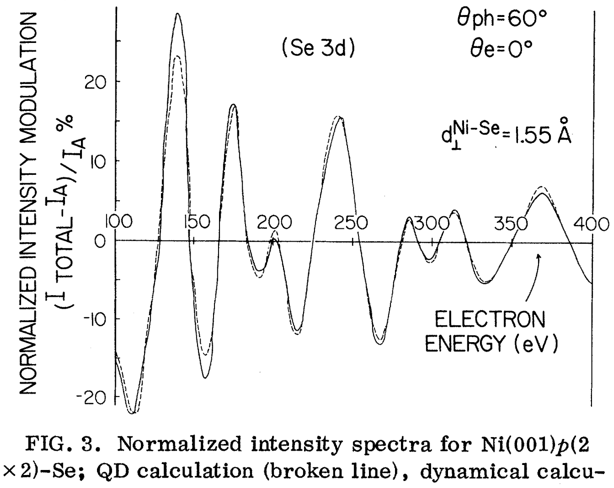

FIG. 3. Normalized intensity spectra for Ni(001)$p(2\times 2)$-Se; QD calculation (broken line), dynamical calculation (solid line). Other conditions same as in Fig. 2.

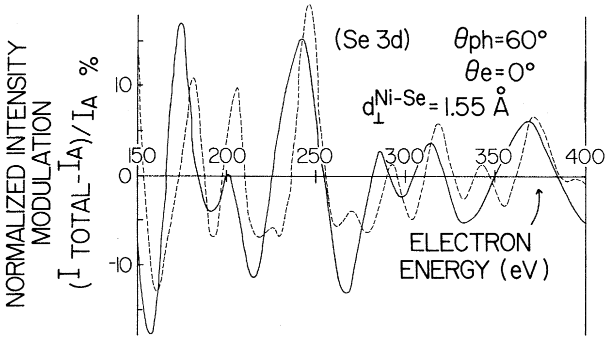

FIG. 4. Normalized intensity spectra for Ni(001)$p(2\times2)$-Se; kinematical calulation (broken line), dynamical calculation (solid line). Other conditions same as in Fig. 2.

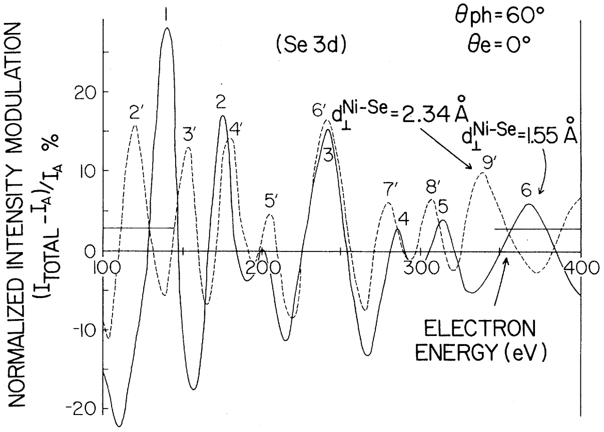

FIG. 5. Normalized intensity spectra for Ni(001)$p(2\times2)$-Se; $d_\perp^{\text{Ni-Se}} = 2.34$ Å (broken line), $d_\perp^{\text{Ni-Se}} = 1.55$ Å (solid line). Zero of broken line: horizontal bars. Other conditions same as in Fig. 2.

atomic emission from ad adsorbed Se (i.e., final-state scatterings from neighboring atoms are excluded) is also shown: I_A in Fig. 2. Kevan *et al.*[3] have experimentally measured the emission below 150 eV and the measured data are in good agreement with the calculated results shown here.[5] In Figs. 2 and 3, results of a first-order quasi-dynamical (QD) calculation[6] are compared to those of the full dynamical theory. We note that at energies below 60 eV (Fig. 2), there are important differences between the two calculations. Above 60 eV, peak positions agree very well and above 100 eV, the first-order QD results are almost as accurate as the full dynamical results (Fig. 3). The first-order QD method contains the following final-state scattering events: (i) *all* forward scatterings; (ii) one backscattering from each layer; (iii) within a layer, one scattering from each atom. In our calculations, the final state is not a plane wave, and effects of the core hole at the emission site are included through the use of transition-state potential and radial wave function R_{nl}. The intensities at above 100 eV are normalized as $(I_{\text{total}}-I_A)/I_A$, similar to plots in SEXAFS. We also tested whether the very popular kinematical method (i.e., one scattering from each atom) would work in this energy range. The results for $E_{\text{kin}} = 150-400$ eV are shown in Fig. 4. We note that up to $E_{\text{kin}} = 400$ eV, the kinematical method still produces serious errors. We conclude that more than one forward-scattering must be included, at least for E_{kin} up to 400 eV.

It remains to show that peaks in the high-energy range are sensitive to the Ni-Se spacing. We use the dynamical method and calculate CISS intensity spectra for a number of $d_\perp^{\text{Ni-Se}}$ distances. The results for $d_\perp^{\text{Ni-Se}} = 1.55$ and 2.34 Å are shown in Fig. 5. We note large movements in peak positions. We number corresponding peaks to indicate these movements. For example, peak 6 at 368 eV moves down to 6′ at 242 eV, a shift of 126 eV. For $d_\perp^{\text{Ni-Se}} = 2.34$ Å, three additional peaks, 7′, 8′, and 9′, move into the range above 250 eV. Even between peaks 6 and 9′, the shift in peak energy is 30 eV $[\Delta E/\Delta d_\perp^{\text{Ni-Se}} = (3.8\text{ eV})/(0.1\text{ Å})]$. It is obvious that with such high sensitivity, binding sites may be determined from energy positions of such peaks.

In conclusion, we have shown that core-level emissions of ARUPS have selective sensitivity to layer spacings below the emitting atoms. This can be used to successively determine surface spacings in complex structures. Furthermore, if it is experimentally feasible, one should measure intensity spectra above $E_{\text{kin}} = 60$ eV. This would greatly simplify the computational effort, making the theoretical task comparable to those in SEXAFS. Also, at $E_{\text{kin}} > 60$ eV, we are above energies where some atomic emissions have sharp resonance peaks (from initial radial orbitals with nodes).[9] The atomic emissions I_A are smooth curves at $E_{\text{kin}} > 60$ eV. There may be a mild modulation (e.g., see Fig. 2), but this modulation has a very large period. In practice, instead of the calculated I_A, one may even use a smooth average of the measured $I_{\text{total}}^{\text{expt}}$.

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Diffusion in a Two-Dimensional System

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The velcotiy autocorrelation in a two-dimensional Lennard-Jones system is obtained by the molecular-dynamics method. At moderate densities the autocorrelation function decays slowly, proportional to the inverse time whereas it decays rapidly at high density. The model is compared with monolayers of methane adsorbed on the basal plane of graphite. The influence of the substrate on the diffusion is small and the calculated and experimentally obtained diffusion constants agree at high density.

Molecular-dynamics calculations of the velocity autocorrelation function (v.a.c.) in a two-dimensional system of hard disks[1] show that the v.a.c. decays inversely proportional to the time at least at intermediate densities. This "non-Langevin" behavior can lead to a logarithmic divergence in the expression for the diffusion coefficient for the two-dimensional system.[2] Recently there has been published[3] some experimental data for diffusion in monolayers of methane on the basal plane of graphite. The diffusion constants were obtained from quasielastic scattering of neutrons on the monolayers and assuming Brownian movements of the interacting methane molecules. The conclusion from the experiments was that the monolayers behaved "two dimensionally" and in accordance with other experimental data of monolayers of simple molecules adsorbed on solid surfaces.[4] This film can be described by a two-dimensional Lennard-Jones system[5,6] and the purpose of the present calculations is to analyze the decay in this system of the v.a.c. and to compare the resulting diffusion with the experimental data from Ref. 3.

The molecular-dynamics calculations are performed for two basic systems of $N = 256$ and $N = 576$ Lennard-Jones particles, respectively, and with periodic boundaries. The program is written in double precision and the calculations are carried out using the Verlet algorithm[7] with a reduced-time step $\Delta t^* = (\Delta t)(\epsilon_{gg}/m)^{1/2}2^{-1/6}\sigma_{gg}^{-1} = 0.005$, where ϵ_{gg} and σ_{gg} are the potential parameters in the Lennard-Jones potential for the pair interaction between the particles in the two-dimensional system and m is the mass of the particles. We have compared the calculations with the experimental data for methane and used the values[8] $\sigma_{gg} = 3.783$ Å and $\epsilon_{gg}/k = 148.9$ K. With these values of the energy parameters the reduced-time step corresponds to 7.6×10^{-15} s, which is found to be sufficient.

The present calculations are performed with and without an external potential, $u_1(\vec{r})$, which simulates the underlying solid substrate. Steele[9] has derived an expression for $u_1(\vec{r})$ as a Fourier series in multiple of the reciprocal-lattice vectors $\vec{b}_1$ and $\vec{b}_2$. To second order in the expansion he finds that

$$u_1(\vec{r}) = -2a_1\{\cos(2\pi\vec{b}_1\cdot\vec{r}) + \cos(2\pi\vec{b}_2\cdot\vec{r}) + \cos[2\pi(\vec{b}_1+\vec{b}_2)\cdot\vec{r}]\} + 4a_2\{\cos[2\pi(\vec{b}_1+2\vec{b}_2)\cdot\vec{r}] + \cos[2\pi(2\vec{b}_1+\vec{b}_2)\cdot\vec{r}] + \cos[2\pi(\vec{b}_1-\vec{b}_2)\cdot\vec{r}]\}, \qquad (1)$$