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One-dimensional model of normal photoelectron diffraction

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A simple one-dimensional electron-scattering model is used to interpret recent observations of normal photoelectron diffraction for Se($3d$), S($2p$), and O($1s$) on Ni(001). The method shows promise as a quick and simple approach to determining the adsorbate structural parameter $d_\perp$ from photoelectron-intensity—versus—energy curves.

Recently, a new experimental surface-structure technique called normal photoelectron diffraction (NPD) has been applied to several adsorbate-surface systems.[1,2] In NPD one measures the adsorbate photoemission current normal to the surface as a function of electron kinetic energy. The analysis of the data requires a full dynamical multiple scattering theory in order to determine the principal structural parameter $d_\perp$. Such calculations are quite complicated and could severely limit an otherwise attractive experimental method for adsorbate structure determination. Here we will present a simplified model of normal electron-surface scattering which hopefully will ameliorate this problem. The method is applied to the systems Se($3d$), S($2p$), and O($1s$) on Ni(001) over the full energy range reported in Refs. 1 and 2.

Figure 1 shows the geometry of the one-dimensional NPD model to be described in the following. In our coordinate system $d=d_\perp+\frac{1}{2}a$ because in the real systems studied by NPD the distance from the adsorbate to the first substrate atom is $d_\perp+a$, i.e., the adsorbate occupies the fourfold hollow site. An electron photoemitted from the adsorbate A is represented by a unit wave incident from the left and a wave reflected back from the substrate S with amplitude C. The wave wave function for the region $-d<z<0$ therefore is

$$\psi(z)=\exp(ik_Az)+C(k_A,k_S)\exp(-ik_Az)\;, \tag{1}$$

where $k^2=2(E-V)$ in a.u. and C is the reflection coefficient for one-dimensional (1D) low-energy-electron diffraction (LEED).[3] In NPD, however, C must also contain a phase factor $\exp(i\phi)$ that allows for an approximate satisfaction of the relative symmetry of direct and backscattered electrons. This is elaborated in the discussion of Fig. 4. The inner potential V_s is usually known from LEED calculations on the pure substrate or else both V_A and V_s become empirical parameters. The NPD current is proportional to $(k_A/k_0)\,|\psi(z)|^2$ at the detector and thus by the joining conditions also proportional to $(k_A/k_0)\,|\psi(-d)|^2$. We therefore obtain

$$I_{\rm NPD}(E)=I_0(E)\,|\psi(-d)|^2\;, \tag{2}$$

where $I_0(E)$ is a smooth envelope function the main energy dependence of which is determined by the photoionization probability. Inserting Eq. (1) into Eq. (2) we have

$$I_{\rm NPD}(E)=I_0(E)\sum_{\pm k_A}|1+C(k_A,k_S)\exp(2ik_Ad)|^2\;, \tag{3}$$

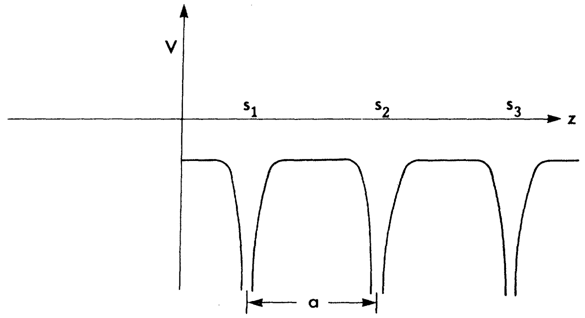
where we have included a summation over $\pm k_A$ because the left-right choice of the coordinate system is immaterial. That is, the final result, which is symmetric in k_A, is given by

$$I_{\rm NPD}(E)=I_0(E)[1+|C|^2+2({\rm Re}C)\cos2k_Ad]\;, \tag{4}$$

${\rm Re}C(k_A,k_S)$ is symmetric in k_S and k_A. The simplicity of Eq. (4) will become even more apparent in conjunction with the figures.

In Figs. 2—8 and the following discussion we summarize our results using Eq. (4). These results are of course preliminary since we have made no attempt to optimize parameters.[4] In particular, $I_0(E)$ has been replaced by a

(a) Pure Substrate



(b) Adsorbate Substrate

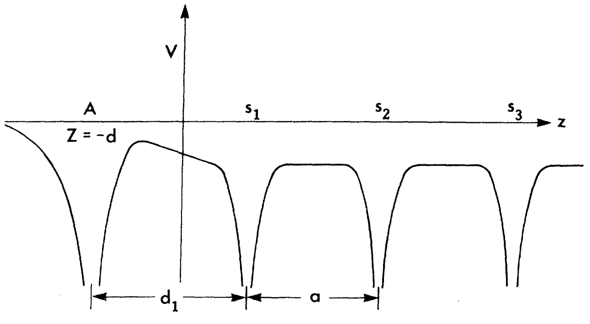


FIG. 1. 1D scattering model of NPD.

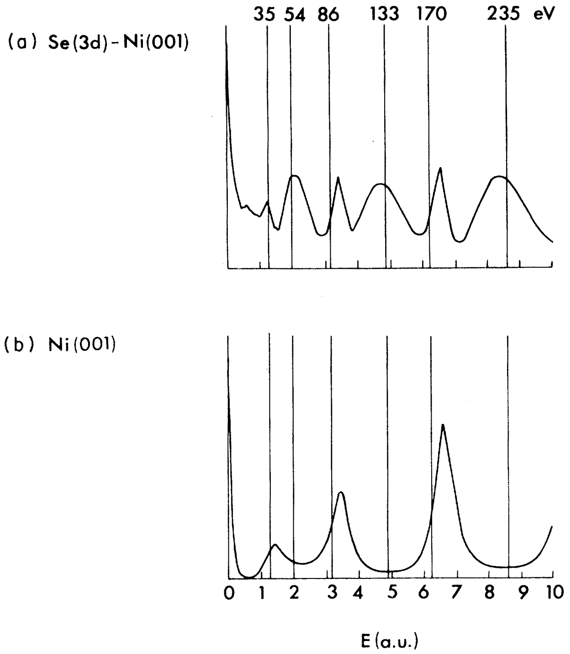


FIG. 2. 1D intensity calculations. (a) NPD Se($3d$)—Ni(001). (b) LEED Ni(001). Inner potentials: $\mathrm{Re}V_s=-14$, $\mathrm{Im}V_s=8.1$ eV; $\mathrm{Re}V_A=0$. Structure parameters: $a=1.76$, $d_\perp=1.55$ Å. Vertical lines denote experimental and/or exact diffraction peaks.

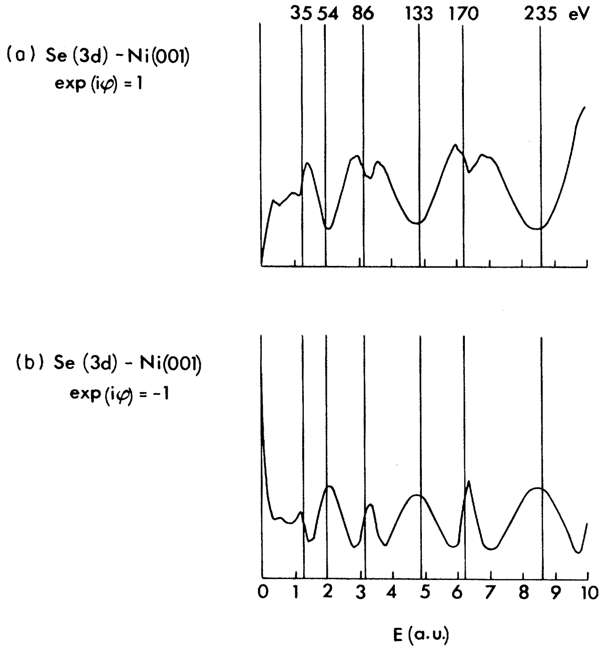


FIG. 4. 1D NPD for Se($3d$)—Ni(001). (a) Phase factor of the reflected wave equals + 1; (b) phase factor of the reflected wave equals − 1. All other parameters are the same as in Fig. 3.

constant since it is a slowly varying function of E and hence has little effect on the NPD peak positions.

In Fig. 2 the results for Se($3d$)—Ni(001) are displayed for the geometry that gives the best agreement between the experimental NPD and the full dynamical electron-scattering calculations, i.e., $d_\perp=1.55$ Å and the Ni lattice constant, $a=1.76$ Å. The real part of the inner potential V is also taken from Ref. 2 and is −14 eV. The imaginary part of V is chosen in order to obtain the best possible agreement between the exact and the kinematic 1D results for the pure substrate. Although not necessary, this can always be approximately accomplished as shown in Ref. 3 and makes the subsequent calculations very easy to carry out. The 1D scattering from the pure substrate is also shown in order to note an interesting comparison. That is, the substrate gives rise to every other diffraction

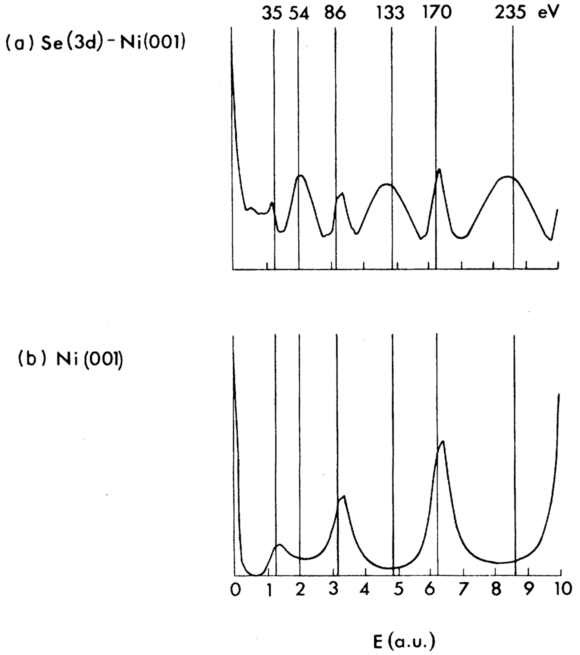


FIG. 3. Same as Fig. 2 except that the structure parameters are $a=1.80$, $d_\perp=1.53$ Å.

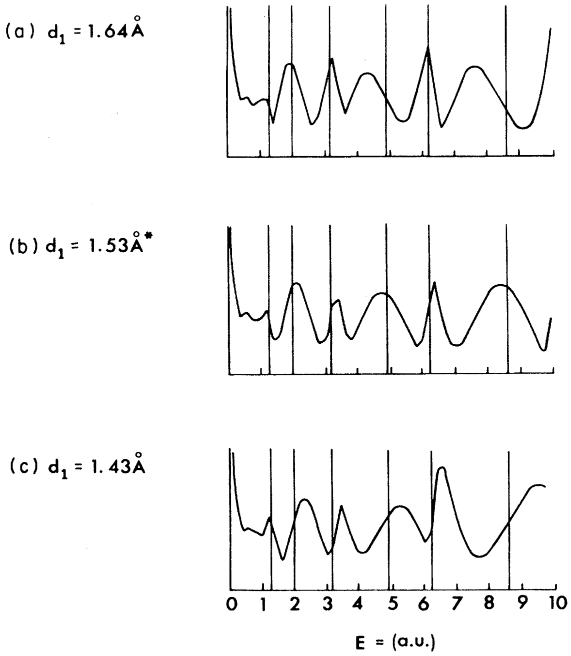


FIG. 5. Effect of varying $d_\perp$ in increments of 0.2 a.u. All other parameters are the same as in Fig. 3.

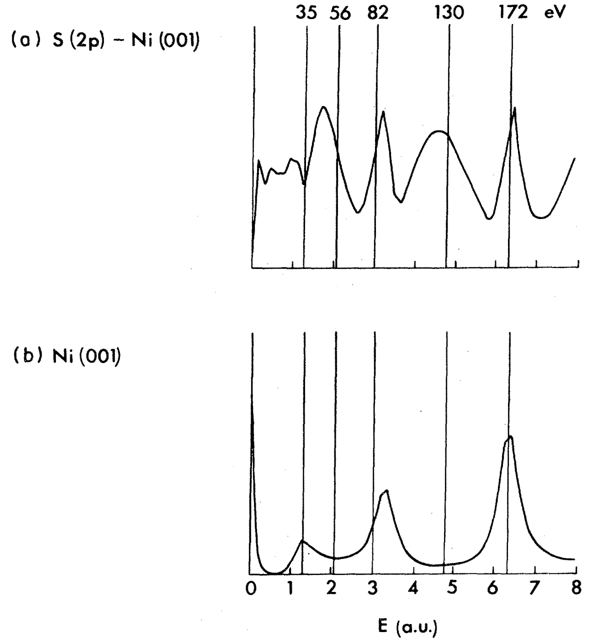


FIG. 6. 1D intensity calculations. (a) NPD S(2p)—Ni(001) (b) LEED Ni(001). Inner potentials: $\mathrm{Re}V_s=-14$, $\mathrm{Im}V_s=8.1$ eV; $\mathrm{Re}V_A=\mathrm{Im}V_A=0$. Structure parameters: $a=1.76$, $d_\perp=1.30$ Å. Vertical lines denote experimental diffraction peaks.

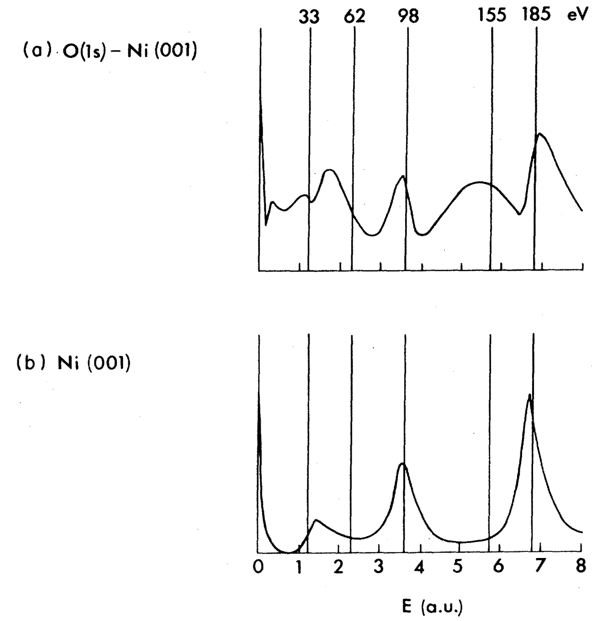


FIG. 8. 1D intensity calculations. (a) NPD O(1s)—Ni(001). (b) LEED Ni(001). Inner potentials: $\mathrm{Re}V_s=-11$, $\mathrm{Im}V_s=-8.1$ eV; $\mathrm{Re}V_A=\mathrm{Im}V_A=0$. Structure parameters: $a=1.76$, $d_\perp=0.9$ Å. Vertical lines denote positions of experimental diffraction peaks.

peak—a result seen in all of our calculations. The vertical lines mark the positions of experimental and/or full dynamical diffraction peaks. Even with this simple unoptimized model we see moderately good agreement between the 1D theory and the correct results.

In Fig. 3 the same comparison is made for slightly modified values of the structural parameters, $d_\perp=1.53$ and $a=1.80$ Å. It is seen that improved agreement with experiment and full dynamical theory is obtained. However, until the 1D method is fully optimized the physics that can be drawn from this result would be premature. The main purpose of this figure is to give an example of a simple trial-and-error attainment of "best" agreement. Also in this comparison of graphs one more clearly sees the interesting fact alluded to above that when an adsorbate is added to the substrate every other peak is filled in, i.e., the substrate itself gives rise to every other peak in the NPD spectrum.

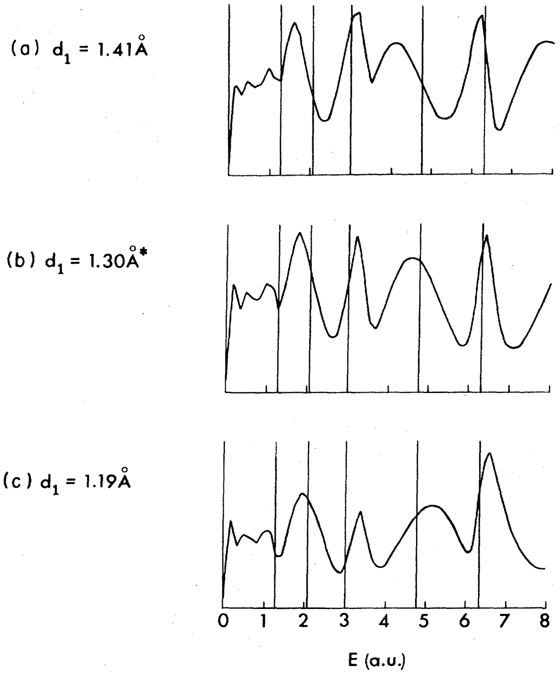


FIG. 7. Effect of varying $d_\perp$ in increments of 0.2 a.u. All other parameters are the same as in Fig. 6.

In Fig. 4 the phase relationship between the initial and final states is clearly shown. If the initial state of the electron emanating from the adsorbate has a given parity with respect to the z direction, then the final state must exhibit the opposite parity by virtue of the photoionization selection rule. This can be incorporated in the phase factor $\exp(i\phi)$ of the reflection coefficient C. Thus if the initial state has angular momentum L then $\phi=(L+1)\pi$ will properly account for this symmetry. Thus for Se(3d) $L=2$ and $\exp(i\phi)=-1$. The NPD curve for this case is shown in Fig. 4(b). For comparison the choice $\exp(i\phi)=1$ is shown in Fig. 4(a). The maxima and minima are essentially interchanged which is in agreement with the effect found in full dynamical calculations.[5]

Figure 5 is a collection of graphs designed to show the sensitivity of 1D NPD to the important structural parameter $d_\perp$. Of the three graphs displayed the middle one with the asterisk for $d_\perp=1.53$ Å clearly displays the best overall agreement. The variation of 0.1 Å causes large deviations of the peak positions from the experimental values, again denoted by vertical lines.[6] This is an example of the kind of analysis that could be useful in determining a preliminary set of structure parameters from which a more detailed refinement might proceed.[7]

In Fig. 6 we show results for S(2p)—Ni(001) with $d_\perp = 1.30$ Å. They are analogous to those in Figs. 2 and 3 for Se(3d). The results are quite similar, although at this level of parameter optimization the agreement with experiment is not as good. In this system the same phase relationships are displayed as were discussed previously except that now $L=1$ for the initial state and thus $\exp(i\phi)=1$ since $\phi=\pi(L+1)$.

Figure 7 shows the same type of sensitivity to $d_\perp$ as displayed for Se(3d). The asterisk again denotes the graph that agrees best with the experimental NPD for S(2p). In this case all of the vertical lines mark experimental peak positions.

Finally in Fig. 8 we show our preliminary results for the O(1s)—Ni(001) system. Here the distance $d_\perp = 0.9$ Å is quite a bit smaller than in either of the previous cases. Thus if the adsorbate is located at the vacuum level only the highest energy peaks are in reasonable agreement with experiment. Here again we defer a discussion of possible reasons for this until complete parameter optimization is attained.[8]

The 1D theory reported here can be shown to be essentially a modified version of renormalized forward scattering theory.[3] However, the principal contribution is now taken to be in the precise forward and backward direction and a further perturbation theory based on the model is then developed. This work is currently in progress and it should be noted that it has more far reaching consequence than just NPD. Its applications to LEED are also being studied.[9]

In conclusion it appears that the theory of 1D electron scattering of NPD may be sufficiently good to provide a method for adsorbate-surface $d_\perp$ determination that is sufficiently fast and simple to serve as a preliminary to full dynamical calculations.[10]

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[1] S. D. Kevan, D. H. Rosenblatt, D. R. Denley, B. C. Lu, and D. A. Shirley, Phys. Rev. B 20, 4133 (1979).

[2] D. H. Rosenblatt, J. G. Tobin, M. G. Mason, R. F. Davis, S. D. Kevan, D. A. Shirley, C. H. Li, and S. Y. Tong, Phys. Rev. B 23, 3828 (1981).

[3] J. B. Pendry, *Low Energy Electron Diffraction* (Academic, New York, 1974), p. 84.

[4] A work now in progress is a least-squares technique for optimizing parameters that is being developed. This is in the spirit of R-factor analysis popular in LEED. Also our Eq. (4) can be Fourier transformed rather easily for comparison to the work in Ref. 2 and more recent work of the Lawrence Berkeley Laboratory group [J.J. Barton *et al.* (unpublished)].

[5] S. D. Kevan (private communication).

[6] Note also that the peaks shift to lower energy as $d_\perp$ is increased, in agreement with an observation in Ref. 2. There the analogy with extended x-ray absorption fine structure is also alluded to and this comes into our model through the term $\cos(2k_A d)$ seen in Eq. (4).

[7] All the calculations reported here were done with an HP-85 desk top minicomputer. On the order of 1.5 min were required for each of the full NPD graphs.

[8] A calculation for $d_\perp = 0$ gave very poor agreement with experiment adding one small additional piece of information to the O-Ni(001) structure puzzle. See, for example, J. Stöhr, R. Jayer, and T. Kendelewicz, Phys. Rev. Lett. 49, 142 (1982).

[9] J. L. Carr, M.S. thesis, Georgetown University, 1983; J. L. Carr and W. L. Clinton (unpublished).

[10] Work similar to ours has been reported by S. Y. Tong and J. C. Tang, Phys. Rev. B 25, 6526 (1982); S. Y. Tong, W. M. Kang, D. H. Rosenblatt, J. G. Tobin, and D. A. Shirley, *ibid.* 27, 4732 (1983).