Determination of Adsorbate Geometries from Intramolecular Scattering in Deep-Core-Level X-Ray Photoemission: CO on Ni(001)

L.-G. Petersson, S. Kono, and N. F. T. Hall Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

and

C. S. Fadley^(a)

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université de Paris-Sud et Centre National de la Recherche Scientifique, 91405 Orsay, France

and

J. B. Pendry

Daresbury Laboratory, Science Research Council, Daresbury, Warrington WA4 4AD, United Kingdom (Received 29 January 1979)

In angle-resolved x-ray photoemission from the C 1s level of CO adsorbed on Ni(001), a peak in intensity with magnitude $I_{\text{max}}/I_{\text{back}} \approx 1.5$ and full width at half maximum $\approx 25^{\circ}$ is found to point along the surface normal. Single-scattering calculations for both a single CO molecule and a finite cluster verify that this peak is due to intramolecular scattering by O. The average orientation of CO is thus determined to be within 12° of normal, with an undetermined rms vibrational notion of $\leq 35^{\circ}$.

Azimuthal anisotropies in deep-core-level xray photoemission (XPS) from atoms adsorbed on single-crystal surfaces have recently been observed^{1, 2} and found to be well described by a single-scattering (kinematical) theoretical model. thereby providing a method for determining surface atomic geometries.² In particular, the extremely forward-peaked nature of electron-atom scattering at XPS energies of $\sim 10^3$ eV is expected to lead to several simplifications in analyses of such data.^{1, 2} In this study, a further aspect of this technique is explored: *polar* anisotropy in core-level emission from a molecular adsorbate, specifically CO on Ni(001). If C is bonded to Ni as expected,³⁻⁷ the effect of interest is *intra*molecular forward scattering of C 1s photoelectrons by O, which may produce a peak in intensity directly along the bond direction according to the simple diffraction mechanism indicated in Fig. 1(a). We here report the first observation of such scattering and compare the experimental data with the results of single-scattering calculations at various levels of exactness to deduce new information concerning the CO bonding geometry. A question of particular interest is whether the CO is oriented normal to the surface or at some angle with respect to it.^{3, 4, 6, 7}

The experimental system and procedure has been discussed elsewhere.^{1, 2} Monochromatized Al $K\alpha$ radiation was used to excite photoelectrons from a 2.0-L (1 L = 10⁻⁶ Torr · sec) exposure of CO on a Ni(001) surface. Core-peak angular-distribution measurements verified a high degree of surface order in the nickel substrate, initial surface cleanliness (only $\leq 3\%$ monolayer of contaminant C), the final presence of a 0.4–0.5 monolayer coverage of CO of nearly 1:1 stoichiometry that is consistent with the $c(2\times2)$ geometry expected⁷ and observed by *in situ* low-energy electron-diffraction (LEED) measurements, and the



FIG. 1. (a) Schematic of the dominant intramolecular scattering mechanism in C 1s emission from CO, showing the approximate intensity profile expected. Calculations of atomic scattering factors at XPS energies (e.g., Ref. 8) verify that the phase shift for forward scattering is very small ($\leq \pi/6$) as shown. (b) Experimental geometry, illustrating the two types of polar scans and the type of azimuthal averaging performed theoretically. (c) Cluster of five CO molecules and nine Ni atoms used for some calculations.

VOLUME 42, NUMBER 23

stability of the surface composition over the duration of the experiments. The C 1s and O 1s peaks associated with CO adsorption were furthermore narrow [full width at half maximum (FWHM) of 1.1 eV for C and 1.8 eV for O] and symmetric, suggesting the predominance of a single CO chemical state. The kinetic energies involved are C 1s, 1196 eV, and O1s, 950 eV. Polar-angle scans of C 1s and O 1s intensities were made for two different types of azimuthal directions, [100] and [110], as shown in Fig. 1(b). The electron polar angle θ is defined with respect to the surface and polar-angle rotations are about an axis perpendicular to the plane of x-ray incidence and electron emission, with a fixed angle of 72° between the latter two directions. Thus, the relevant atomiclike core-level photoelectric cross sections remained constant during all polar scans reported here. C 1s and O 1s scans as summed over the four symmetry-equivalent $\langle 100 \rangle$ azimuths are shown in Fig. 2. No statistically significant differences were found between these data and an analogous sum over $\langle 110 \rangle$ azimuths.

The O 1s intensity in Fig. 2 shows a smooth variation with θ , whereas C 1s exhibits a significant peak for normal emission. This behavior suggests that C is bonded to Ni in adsorption as expected, and that intramolecular scattering is a significant effect, as we verify more quantitatively below. As backscattering of O 1s electrons from either C or Ni should then be a very small effect at this high energy,^{1, 2} the principal cause of the monotonic variation of O 1s intensity with θ is a purely instrumental response function of a



FIG. 2. Polar-angle dependence of the absolute O 1s and C 1s intensities from Ni(001) + 2 L CO, expressed in arbitrary units with maximum = 1.0. O 1s intensities have been multipled by 2.8.



FIG. 3. (a) Comparison of theoretical polar scans calculated for a single CO molecule (dotted lines) and for the cluster of Fig. 1(c) (solid lines) at various tilt angles θ_t . Plane-wave scattering is assumed, and all curves have the same strength for the incident, unscattered wave. No noticeable differences are found between the curves for different θ_t 's of the single CO molecule for $\theta \leq 45^{\circ}$. (b) Comparison of the experimental ratio $(C \ 1s)/(O \ 1s)$ with cluster calculations using incident plane waves at different tilt angles θ_t . The anisotropies I_{\max}/I_{back} are most correctly measured relative to the low- θ background of unscattered intensity for both experiment and theory, but to facilitate comparing peak positions and shapes, intensities are plotted relative to the absolute minimum and normalized. (c) The same as (b), but for calculations with an isolated CO molecule and spherical incident waves. (d) The same as (c), but with vibrational averaging about an average orientation along the normal $(\overline{\theta}_t = 0)$ and various values of the rms vibrational amplitude θ_{rms}.

type discussed previously.⁹ This function should furthermore be essentially identical for both C 1s and O 1s,⁹ and so the intensity ratio (C 1s)/ (O 1s) will provide a normalized indicator of the effects of final-state scattering on the C 1s intensity, and this is presented in Fig. 3(b). The amplitude of the principal peak in anisotropy at 90° as measured relative to the background intensity is $I_{\text{max}}/I_{\text{back}}=1.49-1.54$ and its FWHM =24-27°. A less intense peak at $\theta \approx 40^{\circ}$ is also suggested, but its true intensity is uncertain.

As a first approximation for interpreting these effects theoretically, we will use a single-scattering model that has been successfully applied previously to XPS emission from the core levels of a Cu substrate with an O adsorbate.² As simplified slightly to apply to the present problem of C 1s emission, the model assumes photoemission matrix elements with a polarization dependence corresponding to a plane-wave final state,² purely atomic scattering factors⁸ as quadratically interpolated to the correct atomic number and kinetic energy, and plane waves incident on any scattering center, but neglects any effects due to inelastic scattering, vibrational motion, and the surface potential barrier. At most, only a finite cluster of scattering atoms around the C emitter is considered. The CO axis is tilted at various angles θ_t with respect to the surface normal, but the azimuthal orientation of any tilt is averaged over all possible directions to allow for a likely degree of freedom in bonding orientation, as shown in Fig. 1(b). A nine-point directional average is also taken over the electron-analyzer acceptance cone.⁹ In order to determine the potential importance of *extra* molecular effects such as Ni backscattering or scattering from other adsorbed molecules, calculations have been performed both for a single CO molecule with a C-O distance of 1.15 Å as found in Ni(CO)₄ (Ref. 7) and for a symmetric cluster consisting of one CO emitter, four nearest-neighbor CO scatterers, and nine Ni scatterers, with CO bonded in the expected head-on geometry, 5^{-7} [see Fig. 1(c)]. The Ni-C distance used was 1.8 Å, in agreement with both a LEED analysis for this system and the known structure of $Ni(CO)_4$.⁷ As shown in Fig. 3(a), the cluster and single-CO results for polar scans at various tilt angles between 0° and 20° agree to within $\pm 10\%$ of the overall anisotropy predicted, with only low-level fine structure or small shifts in subsidiary maxima or minima that would be very difficult to resolve experimentally being added by the extramolecular effects. Thus,

the dominant effect producing the peak at 90° is verified to be intramolecular forward scattering by O. {By contrast, the peaks in the cluster results at ~22° are found to be due to forward scattering by O in nearest-neighbor CO's along $\langle 100 \rangle$ directions [cf. Fig. 1(c)].}

The cluster results for various tilt angles are compared in Fig. 3(b) with the observed ratio (C 1s)/(O 1s), and there is generally very good agreement between experiment and theory as to the primary peak position and width for all tilt angles $\leq 10^{\circ}$, although for $\theta_t = 0^{\circ}$, the theoretical peak width is only about $\frac{2}{3}$ of that observed. For $\theta_{\star} \gtrsim 12^{\circ}$, it is found that the primary peak maximum moves away from normal and follows almost exactly the orientation of the molecular axis, mimicking the results expected for a single molecule tilted in the plane of the polar scan with no azimuthal averaging. For $\theta_t \gtrsim 10^\circ$, the presence of a weak first-order diffraction peak at $\theta \approx 40$ – 50° is also qualitatively consistent with the experimental results [cf. Fig. 1(a)], although some of the intensity in this region is found to be due also to extramolecular scattering in the cluster. It is also found that cluster calculations for the two different polar scans of Fig. 1(b) are essentially identical for $\theta = 30^{\circ} - 100^{\circ}$, in agreement with experiment. Thus, within the context of this model, it can be concluded that the orientation of the CO molecule (perhaps as vibrationally averaged) is no more than $\sim 12^{\circ}$ from normal.

From the $I_{\text{max}}/I_{\text{back}}$ values given in Fig. 3(b) it is clear, however, that this model overestimates the degree of anisotropy by a factor of 2-4, as has been noted previously.² Such overestimates could be due to several effects acting either to depress the primary peak relative to the low- θ background or to increase the background: (1) socalled "small atom" corrections due to the spherical nature of the waves incident on O,¹⁰ (2) vibrational motion of the CO, (3) the occurrence of enhanced inelastic scattering for emission directions near O^{1, 2} (4) the presence of some CO in different adsorption sites or in dissociated form, and (5) residual errors in our methods of measuring absolute peak intensities or normalizing out the instrument function. The first two of these effects we have investigated quantitatively by carrying out calculations on a free CO molecule with and without allowing for spherical wave character, and with and without a vibrational motion in θ_t of the "frustated-rotation" type about an average position along the surface normal ($\overline{\theta}_t = 0^\circ$). This motion was approximated by averaging over

a ground-state harmonic oscillator in θ_t , with the probability of a given tilt then being $\exp(-2\theta_t^2/\theta_{\rm rms}^2)$, where $\theta_{\rm rms}$ is the rms tilt angle. For each value of θ_t , full averaging over azimuths was included, as before. Also, somewhat more accurate O scattering potentials allowing for the redistribution of charge with bonding in CO were used in these calculations,^{7, 11} but within the spherical-wave approximation the results were not found to be particularly sensitive to the choice of potential. These calculations are summarized in Figs. 3(c) and 3(d).

Figure 3(c) indicates that the inclusion of spherical wave fronts reduces the predicted anisotropies for $0^{\circ} \leq \theta_t \leq 10^{\circ}$ to only approximately 1.8–2.3 times the observed values, and thus demonstrates that this is one major cause of the overestimates based upon plane-wave fronts. However, the overall shapes and positions of the various peaks and minima are not much different from the cluster plane-wave results in Fig. 3(b), including the presence of weak first-order peaks at $\theta \approx 45^{\circ}$ for $\theta_{\star} \leq 10^{\circ}$. The primary peak shape and width are also in very good agreement with experiment for $0^{\circ} \leq \theta_t \leq 10^{\circ}$, although a small minimum is predicted at $\theta = 90^{\circ}$ that is not observed experimentally. Figure 3(d) illustrates the effect of increasing the rms vibrational amplitude $\theta_{\rm rms}$ from zero, and this also is found to decrease $I_{\rm max}/I_{\rm back}$, but without a significant change in the width or shape of the principal peak. A value of $\theta_{\rm rms} = 35^{\circ}$ is, in fact, found to yield very nearly the same anisotropy as observed experimentally, although it is very large in comparison to prior estimates for this motion based on carbonyl vibrations,^{4, 12} which which yield values closer to 10°. These results thus suggest that vibrational motion of this type may be a principal reason that a prior LEED analysis of this system has led to the proposal of a tilted CO geometry,⁷ as the rms vertical spacing of C and O would also be reduced by such motion. However, the other possible sources of uncertainty in $I_{\text{max}}/I_{\text{back}}$ prevent comparing experiment and theory so as to conclude anything

beyond $\theta_{\rm rms} \lesssim 35^{\circ}$ from the present study. It *is* clear, however, that the vibrationally averaged orientation of CO is within ~12° of normal, a result consistent with prior analyses of angle-resolved photoemission from valence levels.^{3, 4, 6}

Thus, intramolecular scattering processes in XPS core-level emission from adsorbates should be very directly relatable to bonding geometries, and a simple single-scattering model also appears to provide a good description of these phenomena, particularly when it is corrected for sphericalwave effects and possible vibrational motion.

Part of this study was supported by the National Science Foundation (Grant No. CHE 76-24506) and The Petroleum Research Fund administered by the American Chemical Society. One of us (C.S.F.) also gratefully acknowledges the support of the Science Research Council, Daresbury Laboratory, United Kingdom, during part of this work.

^(a) Permanent address: Department of Chemistry, University of Hawaii, Honolulu, Haw. 96822.

¹S. Kono, C. S. Fadley, N. F. T. Hall, and Z. Hussain, Phys. Rev. Lett. <u>41</u>, 117 (1978).

²S. Kono, S. M. Goldberg, N. F. T. Hall, and C. S.

Fadley, Phys. Rev. Lett. <u>41</u>, 1831 (1978).

³R. J. Smith, J. Anderson, and G. J. Lapeyre, Phys. Rev. Lett. <u>37</u>, 1081 (1976).

 4 C. L. Allyn, T. Gustafsson, and E. W. Plummer, Chem. Phys. Lett. <u>47</u>, 127 (1977), and Solid State Commun. <u>28</u>, 85 (1978).

⁵S. Andersson, Solid State Commun. <u>21</u>, 75 (1977). ⁶C. H. Li and S. Y. Tong, Phys. Rev. Lett. <u>40</u>, 46

(1978). ⁷S. Andersson and J. B. Pendry, Surf. Sci. <u>71</u>, 75

(1978), and references therein. ⁸M. Fink and J. Ingram, At. Data 4, 129 (1972).

⁹R. J. Baird and C. S. Fadley, J. Elect. Spectrosc. and Relat. Phenom. <u>11</u>, 39 (1977).

¹⁰P. A. Lee and J. B. Pendry, Phys. Rev. B <u>11</u>, 2795 (1975).

¹¹L. F. Mattheiss, Phys. Rev. <u>134</u>, A970 (1964), and B 10, 995 (1974).

¹²L. H. Jones, R. S. McDowell, and M. Goldblatt, J. Chem. Phys. <u>48</u>, 2663 (1968).