

Adsorption Sites and Bond Lengths of Iodine on Cu{111} and Cu{100} from Surface Extended X-Ray-Absorption Fine Structure

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The unambiguous identification of adsorption sites is demonstrated by using absolute and relative polarization-dependent surface extended-x-ray-absorption fine-structure amplitude functions. This empirical procedure is generally applicable to all oriented adsorbates on single-crystal substrates.

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With the improved capabilities of photoemission for providing detailed electronic structure of adsorbates on single-crystal substrates, there has recently been increasing interest in developing similar capabilities for more detailed characterization of their geometrical structure.¹ The precise determination of *both* the adsorbate-substrate bond length and the adsorption site is essential for realizing this goal. We have previously shown^{2,3} that the technique of surface extended-x-ray-absorption fine structure (SEXAFS) can provide adsorbate-substrate bond lengths that are accurate to within $\pm 0.03 \text{ \AA}$ by using well-established empirical procedures. This involves evaluation of the sinusoidal frequency of interfering outgoing and backscattered adsorbate core photoelectron waves. In systems exhibiting only one frequency (corresponding to a single distance), the adsorption site must be inferred by evaluation of the sinusoidal amplitude, a procedure fraught with potential difficulties and questions of inherent reliability.³⁻⁵ We report here the first results of a purely empirical procedure using absolute and relative SEXAFS amplitudes by which we unambiguously determine adsorption sites. The prototypical study involves iodine adsorbed on copper in the structures Cu{111} $(\sqrt{3} \times \sqrt{3})R30^\circ$ and Cu{100} $p(2 \times 2)$. We show that in these systems I occupies the highest symmetry threefold and fourfold sites and that the I-Cu bond lengths are larger than that in γ -CuI by $0.04 \pm 0.02 \text{ \AA}$ and $0.07 \pm 0.02 \text{ \AA}$, respectively. The present results represent the most precisely determined surface bond lengths and adsorption sites and demonstrate the general applicability of SEXAFS for obtaining both types of information.

The SEXAFS experiments were performed at the Stanford Synchrotron Radiation Laboratory under dedicated conditions of 3 GeV and 60 mA. The ultrahigh-vacuum chamber ($\sim 10^{-10}$ Torr) in which the samples were cleaned, characterized, and prepared using low-energy electron diffraction (LEED) and Auger spectroscopy was modified

from our previous system^{2,3} to include an adjustable electron multiplier detector, a differentially pumped directional iodine doser, a mechanism for *in vacuo* exchange of up to four samples, and a sample manipulator for performing decoupled motions of x , y , z , and two orthogonal sample rotations operational 10 cm off the main azimuthal axis of the sample arm.⁶ The independent sample rotations proved essential for the polarization-dependent SEXAFS amplitudes reported here. We investigated three different detection schemes for measuring the SEXAFS signal, namely, Auger,^{2,7} partial yield,^{3,8} and total yield,^{8,9} and on the basis of significantly greater collection efficiency in our electron multiplier geometry the latter was adopted. The I overlayer structures were prepared as previously described^{2,3} and measured by SEXAFS at least two independent times, with each measurement consisting of the synchrotron polarization direction $\vec{\epsilon}$ both parallel and nearly perpendicular ($\sim 70^\circ$) to the surface in question. In all cases adsorbate-substrate bond lengths for a given system were reproducible to better than $\pm 0.015 \text{ \AA}$. Data accumulation times for each polarization measurement typically consisted of 3 h of summed 10-min scans. Signal improvements by as much as a factor of 25 over earlier measurements^{2,3} were achieved and made possible the previously impractical study of the $\frac{1}{3}$ -monolayer Cu{100} $p(2 \times 2)$ system.

The relevant steps in the EXAFS analysis procedure using the $\frac{1}{3}$ -monolayer system Cu{111} $(\sqrt{3} \times \sqrt{3})R30^\circ$ -I (with $\vec{\epsilon}$ parallel to the surface) and the polycrystalline bulk model compound γ -CuI are given in Fig. 1. Details of the procedures appear elsewhere.^{2,10,11} The filtered surface and bulk data are compared in Fig. 1(d) to show the difference in frequencies (distances) and amplitudes (effective coordination numbers) between the two systems. The filtered SEXAFS data from Fig. 1(d) are also compared in Fig. 2 with the same surface measured nearly perpendicular to $\vec{\epsilon}$ to show the polarization dependence of the

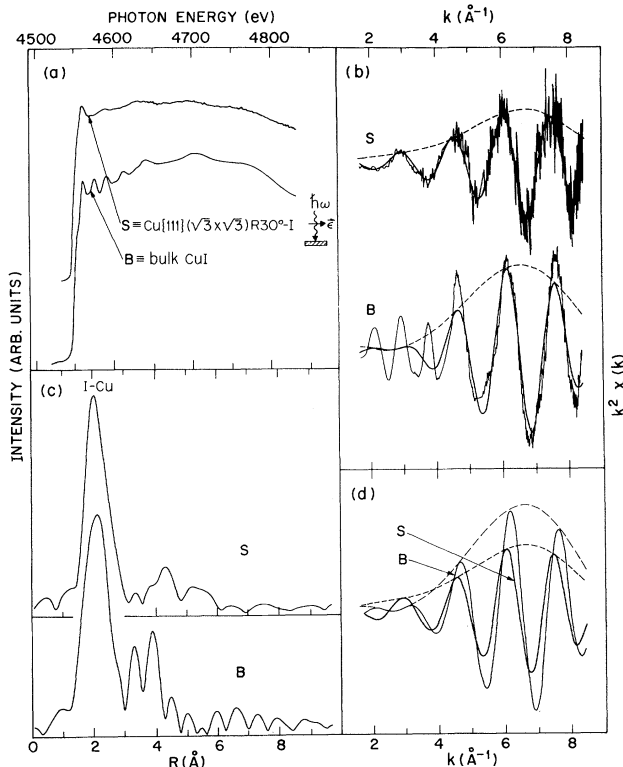


FIG. 1. (a) Raw EXAFS and SEXAFS data in energy space for bulk CuI (**B**) and I adsorbed on Cu{111} (**S**). (b) Raw data in k space after background subtraction and multiplication by k^2 . The amplitudes have been normalized to the edge heights. (c) Fourier transforms of data from (b). The double peaks at $R \sim 3.3$ and ~ 3.9 Å in CuI are due to I-I. (d) Retrtransformed data from (c), after filtering with a window function from $k = 0.8$ to 3.6 Å $^{-1}$. The filtered data are also shown in (b).

SEXAFS amplitudes. We first address the distance.

The precision of the adsorbate-substrate bond length is determined by the reproducibility of the frequencies shown in Fig. 2 (the distances agree to ± 0.01 Å). The accuracy of the surface bond lengths is assessed from the fact that the procedure of phase shift transferability¹² applied to a wide variety of bulk compounds (gaseous, solid, liquid, covalent, and ionic)^{4, 10-12} provides bond lengths that are typically within ± 0.01 Å of those determined from x-ray and electron diffraction measurements. In the absence of comparably accurate independent measurements of surface structures we estimate the accuracy of the SEXAFS results to be ± 0.02 Å. Using the I-Cu distance of 2.617 ± 0.005 Å in γ -Cu^{13, 14} we determine the I-Cu bond length in Cu{111} $(\sqrt{3} \times \sqrt{3})R30^\circ$ -I to be 2.66 ± 0.02 Å.

The evaluation of surface bond lengths with use

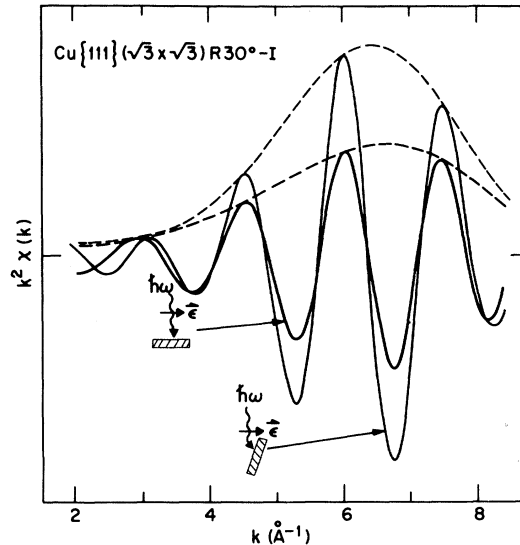


FIG. 2. Comparison of filtered SEXAFS data from Cu{111} $(\sqrt{3} \times \sqrt{3})R30^\circ$ -I with synchrotron polarization $\vec{\epsilon}$ parallel and nearly perpendicular ($\sim 70^\circ$) to the surface. Note agreement in phase and difference in amplitude.

of phase shifts from chemically different bulk model compounds is on firm theoretical ground because energetic photoelectron waves of $k \geq 4$ Å $^{-1}$ (~ 60 eV) are predominantly scattered by chemically insensitive core electrons of the adsorbing and neighboring atoms. The evaluation of adsorption sites in systems where second nearest-neighbor substrate distances are not readily distinguishable from the noise, e.g., see Fig. 1(c), necessitates the use of EXAFS amplitudes from (usually) chemically different model compounds and this procedure is by no means on firm theoretical footing.^{4, 5} Indeed, the assumption of amplitude transferability would appear to be doomed to failure because the Debye-Waller and inelastic loss terms in the EXAFS amplitude function (see below), even at $k > 4$ Å $^{-1}$, are inherently determined by the chemically sensitive valence electrons.

The important advantage of surface-EXAFS over bulk-EXAFS amplitude measurements which permits surface-atom coordination numbers (adsorption sites) to be determined with a high degree of confidence is that SEXAFS amplitude functions from spatially oriented adsorbates can be evaluated as a function of polarization direction.^{2, 3} Taking the ratio between two different polarization-dependent SEXAFS amplitudes within the same system, e.g., see Fig. 2, thus eliminates the use of model compounds and greatly enhances

the reliability of the adsorption site determination because the need for invoking absolute amplitude transferability is completely removed.¹⁵

The top half of Table I summarizes the SEXAFS amplitude and site determination data for the I-Cu{111} system. For the three most symmetric one, two, and threefold adsorption sites we have calculated as a function of polarization direction the absolute magnitude of the effective surface coordination number $N_S = \sum_i (\frac{1}{3} + |\vec{\epsilon} \cdot \vec{r}_i|^2)$,¹⁶ where \vec{r}_i is the unit vector connecting the absorbing atom (I) to the i th atom in the coordination sphere. Denoting the surface and bulk systems by S and B , the absolute experimental N_S values are determined from^{2,3}

$$\ln[A_S(k)/A_B(k)] = \ln(N_S R_B^2 / N_B R_S^2) + 2k^2(\sigma_B^2 - \sigma_S^2) + 2[R_B/\lambda_B(k) + R_S/\lambda_S(k)], \quad (1)$$

where $A(k)$ is the measured amplitude function, R is the distance, σ is the rms displacement, and $\lambda(k)$ is an effective inelastic mean free path. Empirically we have found that the Debye-Waller term is negligibly small¹⁷ [see Fig. 1(d)] and for simplicity we have assumed that the inelastic-loss term is also negligible (in general it need not be³). For tetrahedrally coordinated I in polycrystalline CuI, $N_B = 4(\frac{1}{3} + \frac{1}{3}) = 2.66$, and thus knowledge of R_B and R_S gives N_S straightforwardly. Comparison between the calculated and both experimental *absolute* N_S values in Table I strongly suggests that I occupies the threefold hollow.

The amplitude uncertainties quoted in Table I include the precision (based on reproducibility of different measurements) and our estimation of possible experimental systematic errors. Of the latter, the most important one arises from the sensitive positioning of the sample with respect to the synchrotron beam. With scanning energy the monochromatized beam moves slightly, and particularly at grazing angles of incidence, modifications in the SEXAFS amplitudes had been observed as a result of adsorbate concentration gradients near the edges of the samples. While this problem has been essentially removed in the present measurement by using adjustable beam slits and phosphorescent markings along the sample perimeter, we nevertheless quote conservative error limits of $\pm 20\%$ for N_S with $\vec{\epsilon}$ nearly perpendicular to the surface and $\pm 10\%$ for $\vec{\epsilon}$ parallel to the surface.

The small differences between the calculated and experimental absolute N_S values for the {111} surface are likely fortuitous, since they include the inherent uncertainties in absolute amplitude transferability mentioned above via our simplify-

TABLE I. Calculated versus experimental N_S values for I on Cu.

	atop	bridge	hollow	Expt.
Cu{111}:				
$\vec{\epsilon}_{\parallel}$	0.33	0.90	1.46	1.6 ± 0.2
$\vec{\epsilon}_{\perp}$	1.22	2.05	2.89	3.0 ± 0.6
$\vec{\epsilon}_{\perp}/\vec{\epsilon}_{\parallel}$	3.65	2.28	1.98	1.9 ± 0.4
Cu{100}:				
$\vec{\epsilon}_{\parallel}$	0.33	0.89	2.24	1.9 ± 0.2
$\vec{\epsilon}_{\perp}$	1.22	2.04	3.38	2.8 ± 0.6
$\vec{\epsilon}_{\perp}/\vec{\epsilon}_{\parallel}$	3.65	2.29	1.51	1.5 ± 0.3

ing neglect of the last two terms in Eq. (1). Further consideration of these terms is certainly of interest from a fundamental point of view, but for determining adsorbate sites the need for this is clearly obviated by taking the ratio of the surface amplitude functions within the same system.¹⁵ The excellent agreement between the experimental *relative* amplitudes and those calculated for the threefold site, see Table I, is testimony to this simple and important fact. The point to emphasize here is that while a single amplitude measurement alone can indeed strongly suggest an adsorption site, it is actually the combination of *both* the absolute and the relative amplitudes which allows the adsorption site to be determined unambiguously.

Measurement and analysis of the Cu{100}p(2 × 2)-I structure is in all respect analogous to that given for the Cu{111}(√3 × √3)R30°-I system. The I-Cu{100} bond length is determined to be 2.69 ± 0.02 Å. The *absolute* accuracies of the bond lengths in the I-Cu{111} and I-Cu{100} systems are limited by the lack of an independent calibration, but the *relative* surface bond lengths are considerably more precise, with the I-Cu{100} distance being larger than the I-Cu{111} distance by 0.03 ± 0.015 Å. The experimental absolute amplitudes shown in the bottom half of Table I suggest the fourfold site and differ from the calculated values to a degree similar to that found for bulk systems.⁴ Together with the relative amplitudes, they clearly establish the adsorption site to be the fourfold hollow.

Previous LEED studies¹⁸ of O, S, Se, and Te on Ni, Cu and Ag {111} and {100} surfaces all showed occupation of the respective threefold and

fourfold sites and, where studied, showed the first nearest-neighbor $X-M\{111\}$ bond lengths to be shorter than those of $X-M\{100\}$. Both trends are consistent with the present results. Unlike our findings, however, the LEED bond lengths were significantly shorter than the corresponding distances in the stable bulk analogs. The similarities between the earlier LEED and present SEXAFS systems, viz., ordered submonolayer electronegative adsorbates on the same surfaces of fcc transition (noble) metal substrates, should be contrasted with the bonding differences expected between chalcogenides and halides. Furthermore, only two systems have been studied thus far by both SEXAFS^{2,20} and LEED,^{19,21} $\text{Ag}\{111\}(\sqrt{3}\times\sqrt{3})R30^\circ\text{-I}$ and $\text{Al}\{111\}(1\times 1)\text{-O}$, with the former^{2,19} showing good agreement and the latter^{20,21} showing poor agreement. Given the limited data on identical systems with which to check the LEED results, meaningful generalizations of surface chemical trends must await further data of accuracy comparable to or higher than that reported here.

In summary, we have shown that SEXAFS can now be expected to provide both accurate distance and site information. The determination of both surface structural parameters from a variety of adsorbate systems, along with a detailed knowledge of their electronic structure, should considerably enhance our understanding of surface bonding.

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¹⁵Possible anisotropies in the Debye-Waller and inelastic-loss terms for the surface system should be negligible compared to the leading term in Eq. (1).

¹⁶The isotropic factor of $\frac{1}{3}$ arises from the $p \rightarrow d$ dipole selection rule appropriate for the $I(L_z)$ edge; the $p \rightarrow s$ probability is negligible (see Ref. 2).

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