Determination of Intramolecular Bond Lengths of Low-Z Molecules in the Gas Phase, Condensed, and Chemisorbed States Using Extended X-Ray Absorption Fine Structure

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Extended x-ray absorption fine structure studies have been performed above the oxygen K edge for SO_2 in the gas phase as well as condensed and chemisorbed on Cu(100) and for CO chemisorbed on the same surface. The analysis of the pronounced oscillations shows that intramolecular bond lengths of low-Z molecules can be directly determined with high accuracy. The extended x-ray absorption fine structure technique thus possesses the unique capability of measuring these bond lengths in gas phase, condensed, and chemisorbed molecules.

Surface extended x-ray absorption fine structure (SEXAFS) is ideally suited for determining adsorbate-substrate bond lengths and positions of adsorbates on single-crystal surfaces with high accuracy [1,2]. This also holds for chemisorbed low-Z molecules containing C, N, and O atoms [3–7]. A complete structure analysis involving the direct determination of intramolecular bond lengths between low-Z atoms is, however, a rather challenging and as yet unsolved problem. Two factors inherently limit the information content of the SEXAFS data of chemisorbed low-Z molecules. First, the backscattering amplitudes of low-Z atoms are relatively weak compared to those of other atoms in the system, such as the substrate atoms, and they rapidly decay with increasing kinetic energy of the photoelectron. Second, the shorter intramolecular bond lengths relative to adsorbate-substrate distances reduce the number of complete SEXAFS oscillations, which critically affects the reliability of a bond length determination. In addition to these inherent features of EXAFS of low-Z molecules, there are also limitations in the SEXAFS detection schemes for the soft x-ray region [1]. So it has been assumed that information on intramolecular bond lengths in low-Z molecules would have to be obtained from other techniques [2].

The first critical tests to explore the detection limits of intramolecular EXAFS were performed on gaseous low-Z molecules using EXAFS [8] and the related inner-shell electron energy loss spectroscopy (ISEELS) [9] techniques. In addition to the inherently limiting factors discussed above, both of these studies suffered from the polarization-independent, and thus "averaged," small signal and certainly also from the large vibrational amplitudes in the gas phase. Nevertheless, EXAFS oscillations were clearly observed. The results of the ISEELS analysis, however, turned out to be strongly dependent on the background subtraction procedure [9]. A substantial step forward in determining intramolecular bond lengths of chemisorbed low-Z molecules was made by Comelli and Stöhr [10], who carried out EXAFS experiments on condensed hydrocarbons using SEXAFS detection modes. Because of a longer data range and larger EXAFS amplitudes compared to the gas phase data [8], the authors were able to determine C-C bond lengths with the high accuracy of ± 0.02 Å. Although Comelli and Stöhr also explored the possibility of measuring intramolecular bond lengths of chemisorbed molecules at submonolayer coverage by model calculations, no experiments have yet been performed.

An accurate determination of intramolecular bond lengths of chemisorbed low-Z molecules is a still unattained, but extremely desirable goal. Such information is an important part of the complete geometric structure of the adsorbate complex which together with its experimentally determined electronic structure provides the basis for a convincing theory of chemisorption. Special emphasis is therefore placed on the changes in intramolecular bonding compared to the gas phase as a result of chemisorption. Of course, other structural techniques such as low-energy electron diffraction (LEED) and photoelectron diffraction (PED) also yield information on intramolecular bond lengths of chemisorbed molecules. These techniques are, however, not applicable to gas phase studies and their accuracy—concerning intramolecular bond lengths—is not extremely high.

In this Letter we report for the first time on the direct determination of intramolecular bond lengths in chemisorbed low-Z molecules at submonolayer coverages. Our analysis of the polarization-dependent oxygen K edge data of SO_2 and CO on Cu(100) shows that O-S and O-C SEXAFS is clearly observable and even dominant for certain x-ray incidence angles according to the orientation of the molecules on the surface. We find that under careful and critical inspection of the background subtraction procedure in the SEXAFS analysis, in conjunction with a stable storage ring, intramolecular bond lengths of chemisorbed low-Z molecules can be determined with the same high accuracy as adsorbate-substrate distances. In conjunction with measurements performed on gaseous SO_2, our results thus demonstrate that the (S)EXAFS technique has the unique capability of measuring intramolecular bond lengths of low-Z molecules in the gas phase as well as in the condensed and chemisorbed state.

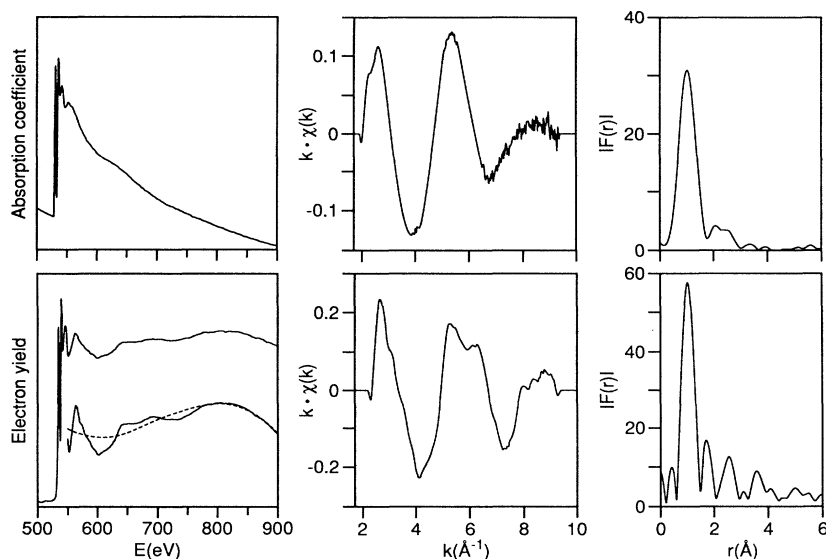The experiments were conducted at the electron

FIG. 1. Left: Oxygen K-edge EXAFS spectra of gaseous SO_2 (top) and of SO_2 condensed on Cu(100) (bottom) together with the spline-polynomial background (dashed line) fitted to the (enlarged) signal. Middle: Background-subtracted data converted into the k scale and multiplied by k. Right: Fourier transform of the background-subtracted data.

storage BESSY in Berlin with the grazing-incidence plane-grating monochromators HE-PGM-2 and SX-700-I [11] and the toroidal grating monochromator HE-TGM-1. The gas-phase EXAFS data were taken above the oxygen K edge in the transmission mode using a gas cell equipped with silicon-nitride windows. The SEXAFS data were taken above the oxygen K edge in both the partial and total electron yield mode at normal ($\theta=90°$, E vector parallel to the surface) and near-grazing ($\theta=20°$) x-ray incidence at a sample temperature of 100 K. The Cu(100) crystal was cleaned by successive cycles of argon-ion bombardment and annealing at 600 K. It was characterized by Auger electron spectroscopy and LEED. Multilayers of sulphur dioxide were condensed at a crystal temperature of 100 K. Partial desorption of SO_2 resulted in a (2×2) structure. Carbon monoxide exposures were also performed at 100 K and yielded a high-contrast c(2×2) LEED pattern. All SEXAFS spectra were normalized by dividing the yield of the covered sample by that of the clean Cu crystal measured immediately prior to exposure. A corresponding normalization procedure was applied to the gas-phase data by dividing the signal from the filled gas cell by that from the empty cell.

In Fig. 1 the oxygen K-edge EXAFS spectra of gaseous SO_2 (top, left) and condensed SO_2 (bottom, left) are shown together with the corresponding background subtracted data (middle) and their Fourier transforms (right). As can be seen from the figure, the EXAFS oscillations are rather large, at least up to a photon energy of 900 eV. At this energy we had to truncate our data because of the interfering Cu $L_{2,3}$ absorption edges. The Fourier transforms in Fig. 1 (right) are dominated by a peak corresponding to the nearest-neighbor (nn) O-S distance, i.e., the intramolecular O-S bond length. For background subtraction we used a conventional spline-polynomial fit. A characteristic three-section quadratic

spline fit yielding a smooth background is depicted in the bottom-left panel (inset) of Fig. 1. It is well known that, in general, by increasing the number of sections (polynomials) and/or increasing the power of the polynomials a "modeling" of the oscillations finally sets in (see also below) so that the overall shape of the fitted background is no longer smooth. Testing different spline fits and applying this criterion, the position of the dominating Fourier peak in Fig. 1 turns out to be accurate to within ±0.02 Å, with the average peak position for the gas phase and condensed state being identical (1.03 Å). This means that there is no bond length change on condensing SO_2 on Cu(100). Assuming an intramolecular O-S bond length of 1.43 Å [12], an empirical O-S phase shift is determined as $\psi=-0.81k+2.3$, which is in remarkably good agreement with the theoretical phase shift of $\psi=-0.80k+0.70$ taken from the calculations of McKale et al. [13]. We are thus led to the conclusion that (S)EXAFS can reliably determine intramolecular bond lengths of low-Z molecules not only in the condensed state [10], but also in gas phase.

As a next step we studied the system Cu(100)-(2×2)-SO_2 in which SO_2 is chemisorbed at a submonolayer coverage. In Fig. 2 the corresponding oxygen K-edge SEXAFS data for normal ($\theta=90°$) and near-grazing ($\theta=20°$) x-ray incidence and their Fourier transforms are shown. As can be seen from the figure, both spectra are characterized by the contributions of two different distances: the nn O-Cu distance with a Fourier peak at about 1.7 Å and the intramolecular O-S bond length giving rise to the peak at about 1.0 Å. Using the same smooth backgrounds as for the analysis of the multilayer spectrum, the O-S distance was determined as R_{O-S} = 1.48 ± 0.03 Å. Compared to the result for the SO_2 multilayer, this value indicates an increase of the O-S bond length as a consequence of chemisorption. This is a
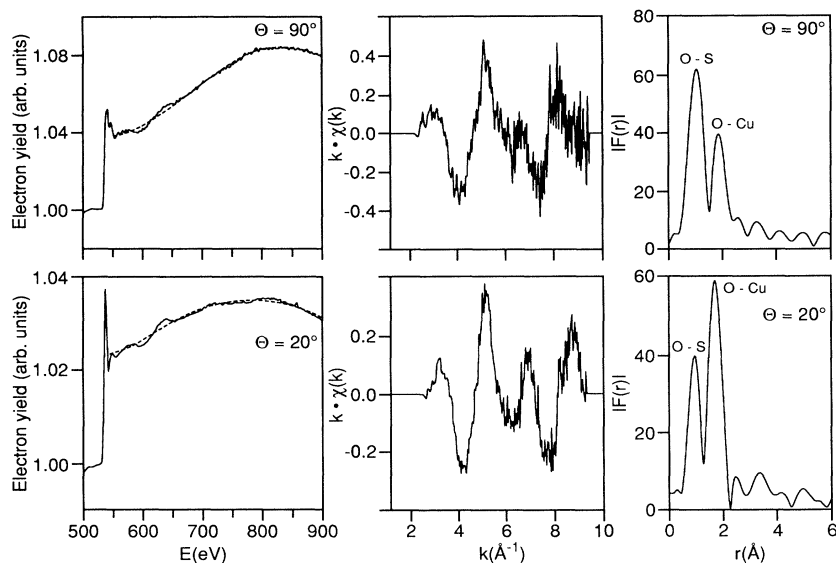
FIG. 2. Oxygen K-edge SEXAFS data of Cu(100)-(2×2)-SO$_2$ taken at normal (top) and near-grazing (bottom) x-ray incidence. Left: SEXAFS spectrum with spline-polynomial background. Middle: Background-subtracted data as a function of k. Right: Fourier transform of the background-subtracted data.

striking example for the potential of the SEXAFS technique. Our result can be explained in terms of a charge donation from the substrate valence orbitals into the antibonding $3b_1$ molecular orbital [14]. The most important conclusion from our experiment, however, is the fact that the intramolecular O-S bond length could be directly determined from the SEXAFS data with high accuracy. In the Cu(100)-(2×2)-SO$_2$ system studied, the nn O-S and the nn O-Cu Fourier peaks are separated by about 0.7 Å so that only a slight interference occurs. This was confirmed by SEXAFS simulations, which showed that only the weaker peak in both spectra was slightly shifted due to interference. But even in the case of overlapping distances the intramolecular bond length can be determined with high accuracy—though less directly—by a

SEXAFS simulation, as it is possible for overlapping adsorbate-substrate distances. Using the empirical O-Cu phase shift [1], the nn O-Cu distance was determined as $R_{\text{O-Cu}} = 1.95 \pm 0.03$ Å. The data presented here (bond lengths and SEXAFS amplitudes) are consistent with an adsorption geometry similar to that suggested for SO$_2$ chemisorbed on Ni(110) [15].

In addition to SO$_2$ we also studied CO adsorbed on Cu(100) with carbon as the low-Z backscattering atom. In the system Cu(100)-c(2×2)-CO carbon monoxide is known to adsorb in on-top positions with a nn C-Cu bond length of about 1.91 Å [16,17] and an intramolecular bond length of 1.15 ± 0.1 Å [16]. The contribution of the intramolecular O-C bond length as well as the contribution of the nn O-Cu distance to the SEXAFS is, there-
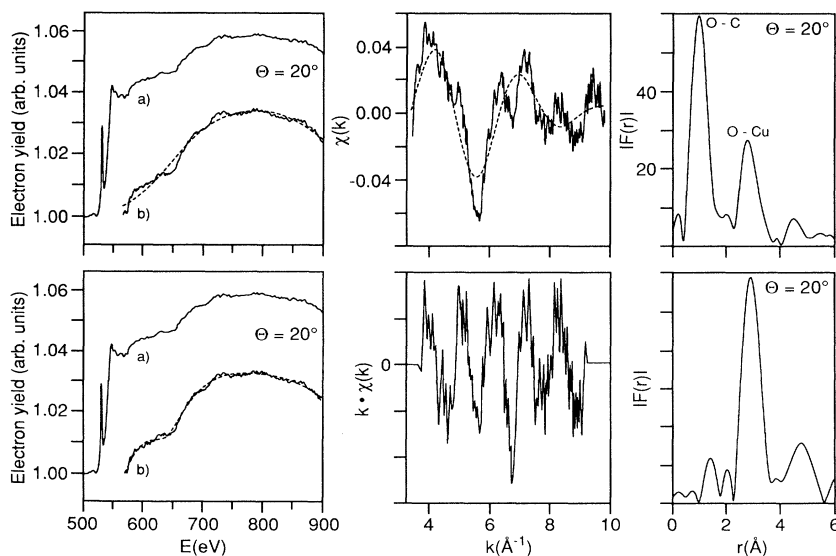

FIG. 3. Oxygen K-edge SEXAFS data for Cu(100)-c(2×2)-CO taken at near-grazing x-ray incidence. Left: SEXAFS spectra (a) with spline-polynomial backgrounds (dashed lines). (b) In the top panel the correct background is depicted. The fictitious background in the bottom panel represents the correct background modulated by the intramolecular O-C SEXAFS. Middle: Background-subtracted data as a function of k. The dashed line shows the backtransform of the O-C Fourier peak. Right: Fourier transforms of the background-subtracted data.

fore, largest at grazing x-ray incidence and zero at normal incidence. In agreement with this predicted polarization dependence, no oscillations were observed in the experimental data for $\theta = 90°$. Figure 3 (top) shows the $\theta = 20°$ SEXAFS spectrum (left) and the signal obtained after background subtraction and conversion to the k scale (middle). As in the previous analyses we used a smooth spline fit (inset of left panel). The corresponding Fourier transform is depicted in the (top) right panel of Fig. 3. It is dominated by the intramolecular O-C bond length yielding a peak at about 1 Å. At higher R values a second peak corresponding to the nn O-Cu distance of about 3 Å is observed. From an inspection of different spline fits which gave smooth backgrounds, the reproducibility of the nn O-C peak position is found to be ± 0.03 Å. As already mentioned, by applying a spline fit with a higher number of polynomials a "modeling" of the SEXAFS oscillations is possible with the low-frequency oscillations being modeled first. Using a four-section spline fit we were able to completely suppress the O-C contribution to the SEXAFS so that the first peak in the corresponding Fourier transform now is due to the nn O-Cu distance. This is shown in Fig. 3 (bottom, right). Accordingly, the fictitious background (Fig. 3, bottom left) then represents the true background modulated by the SEXAFS due to the O-C bond length. These modulations are large and result—as we have already seen—in the dominant O-C Fourier peak of Fig. 3 (top right) if the correct background is subtracted from the SEXAFS raw data. In Fig. 3 (top, middle) the backtransform of this peak is depicted (dashed line) which is now modulated by the SEXAFS of the nn O-Cu distance. Finally, we also tested the stability of the storage ring concerning the overall shape of the SEXAFS spectra, i.e., their background. Immediately after taking the data for the CO-covered surface, CO was desorbed and after subsequent oxygen exposure the SEXAFS of the oxygen-covered surface was measured. The reliable smooth background of the latter analysis was taken as a confirmation of the choice of the similarly smooth background in the CO experiment. Using the slightly modified empirical O-C phase shift of Ref. [8], $\psi = -0.50k + 5.1$ [18], we calculated an intramolecular bond length of $R_{O-C} = 1.16 \pm 0.03$ Å. This value is close to the gas phase value of 1.13 Å [19] and in good agreement with the result of the LEED study [16] $R_{O-C} = 1.15 \pm 0.1$ Å. Future measurements on chemically similar compounds are desirable, however, to establish the reliability of the O-C phase shift used here [18]. Finally we should mention that by using the empirical (single scattering) O-Cu phase shift, a nn O-Cu bond length of 3.16 Å is calculated, which differs from the LEED value [16] by 0.10 Å. We attribute this discrepancy to multiple scattering effects due to the on-top position of

the chemisorbed CO.

In conclusion, we have demonstrated the reliability of gas-phase EXAFS measurements on low-Z molecules and we have shown that with the presently available storage rings and electron detection schemes in SEXAFS also intramolecular bond lengths of chemisorbed low-Z molecules can be determined with high accuracy.

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[18] As the CO data of Ref. [8] suffered from background subtraction problems, we chose as our linearized reference phase shift $\psi = -0.50k + 5.1$, the average of the nearly identical phases of CO_2 and OCS, and modified the k-independent term to give a best fit to our data.

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