

Adsorption and temperature-dependent decomposition of SO₂ on Cu(100) and Cu(111): A fast and high-resolution core-level spectroscopy study

M. Polcik,* L. Wilde, and J. Haase

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

B. Brena, D. Cocco, G. Comelli, and G. Paolucci
Sincrotrone Trieste, Padriciano 99, I-34012 Trieste, Italy

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The adsorption and temperature-dependent decomposition of SO₂ on Cu(100) and Cu(111) have been studied by fast and high-resolution core-level photoemission. The analysis of the S 2*p* and O 1*s* data shows that molecular SO₂ adsorption dominates at 170 K. On heating the SO₂-covered surfaces to about room temperature, SO₂ decomposes into SO+O+S. On further heating SO+O recombine to form SO₂, which is the only species detected in corresponding temperature-programmed desorption (TPD) experiments. From the temperature- (time-) dependent S and O coverages a "TPD curve" can be constructed.
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Due to its role as a major air pollutant, a catalyst poison, and a corrosive the adsorption of sulfur dioxide becomes increasingly important. From a number of studies performed so far on SO₂ adsorption on various metals, it can be concluded that at low enough temperature molecular adsorption usually dominates. On subsequent heating, however, SO₂ decomposes on most metal surfaces. Surface SO species on Pt(111) (Ref. 1) and Pd(100) (Ref. 2) as well as surface SO₄ species on Ni(poly) (Ref. 3), Fe(poly) (Ref. 4), and Pd(100) (Ref. 2) have clearly been identified in addition to atomic S and O. Sulfur dioxide does not decompose on the noble metals Au (Ref. 3) and Ag (Refs. 5–9).

A temperature-programmed desorption (TPD) study of SO₂ adsorbed on Cu(111) (Refs. 10 and 11) has shown that the only desorbing particles detected were SO₂ molecules although a small amount of atomic S left on the surface after each TPD run indicated a dissociation process. Similar effects are observed for SO₂ adsorbed on Cu(100). An x-ray absorption experiment¹² on the (2×2) phase obtained by heating a "thin" multilayer of SO₂ condensed on Cu(100) to about room temperature, however, unambiguously proved the existence of an SO_{*x*} (*x* ≠ 2) species on the surface with no more SO₂ left there.

We used high-resolution core-level photoemission [x-ray photoemission spectroscopy (XPS)] for identifying the SO_{*x*} species. This procedure is based on the fact that the core-level binding energy of an atom is dependent on its surroundings.^{13,14} From the core-level spectra it is thus possible to determine the number of different species by simply counting the number of peaks, provided that the shifts are not smaller than the measured peak width. In addition, by calibrating with known coverages for simple atomic-adsorbate systems the stoichiometry of a molecular adsorbate can be found. Finally, by making use of the high photon flux behind an undulator at a third generation synchrotron radiation source time-dependent XPS sweeps can mimic TPD results.

The fast and high-resolution XPS studies of SO₂ on Cu(110) and Cu(111) reported here indicate that on heating to about room temperature adsorbed sulfur dioxide SO₂(a)

decomposes into SO(a)+O(a)+S(a). Above a temperature of about 350 K the coadsorbed SO+O species recombine and desorb as SO₂ molecules. Both prominent TPD peaks above the multilayer desorption peak are thus fully understood.

The core-level photoemission experiments were conducted at the Super ESCA beamline¹⁵ at the storage ring ELETTRA in Trieste using the light from a 5.6-mm period undulator, a modified SX-700 monochromator,^{16,17} and a hemispherical electron analyzer equipped with a multichannel detector. The experimental resolution for the S 2*p* and O 1*s* spectra was approximately 100 and 300 meV, respectively. The characteristic time for taking XPS spectra as shown in this paper was of the order of 10 sec, making it possible to study the kinetics of surface processes.¹⁸ For the TPD experiment performed at BESSY in Berlin a quadrupole mass spectrometer (Leybold Inficon Transpector H100M) was used; masses 16, 32, 48, 64, and 80 were recorded simultaneously. The Cu(100) and Cu(111) crystals were cleaned by successive cycles of argon-ion bombardment and annealing at 650 K. Surface cleanliness was checked with XPS. SO₂ was dosed via a leak valve (isotropic dosing). The Cu(100)-(2×2)-S reference structure was obtained by dosing clean Cu(100) with ≥5 L H₂S at 300 K [where 1 L (Langmuir)=10⁻⁶ Torr s],¹⁹ whereas the Cu(100)-(√2×√2)R45°-O reference structure was prepared by dosing with ≥1200 L O₂ at 550 K.²⁰

In Fig. 1 S 2*p* and O 1*s* XPS spectra are depicted, taken during slow and continuous heating of the Cu(100) crystal initially dosed at 180 K with 5 L SO₂. The S 2*p* data clearly show three different spin-orbit split doublets located at binding energies (*p*_{3/2} component of the doublet) of about 160.2, 164.3, and 165.3 eV. Initially the 164.3-eV doublet dominates, which has been identified as SO₂ by x-ray absorption [near-edge x-ray absorption fine structure (NEXAFS)].¹² Upon heating to room temperature SO₂ disappears from the surface and the 165.3-eV doublet shows up together with the one at 160.2 eV. The latter can clearly be identified as atomic S by comparison with the spectrum measured on the Cu(100)-(2×2)-S reference structure. On the other hand,

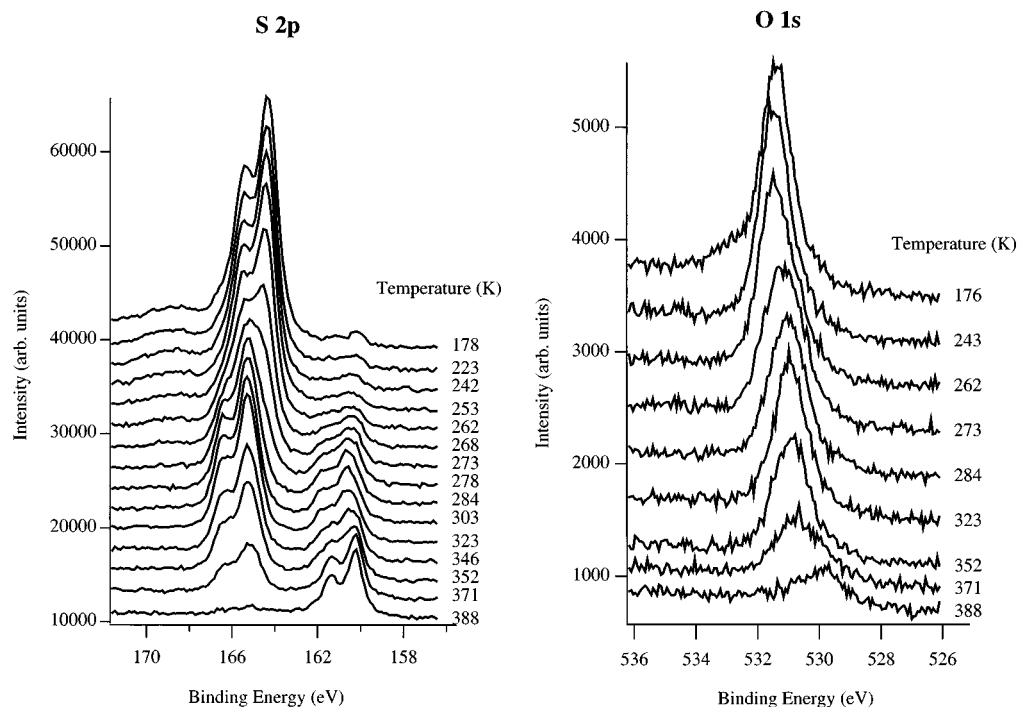


FIG. 1. S 2*p* (left) and O 1*s* (right) core-level photoemission data for Cu(100)-SO₂ with the sample temperature as parameter during continuous heating (~ 0.1 K/s).

x-ray absorption suggests an SO_{*x*} species with $x \neq 2$ for the 165.3-eV doublet. On further heating to about 390 K the SO_{*x*} species disappears nearly completely from the surface whereas the atomic S doublet hardly grows, but sharpens and shifts slightly in energy. Concerning different oxygen-containing species the O 1*s* data are less distinctive at first glance. Only one single peak is observed, which shifts to lower binding energy on heating and initially broadens on increasing the temperature to about 273 K.

In the first step of our analysis we fitted the individual S 2*p* and O 1*s* curves by assuming three main components each. In Fig. 2 the fits for four distinct temperatures are shown. As already discussed above, the three doublets used for the S 2*p* fits in Fig. 2, left, are assigned to SO₂, SO_{*x*} ($x \neq 2$), and atomic S. As can be seen from the S 2*p* data, there is already partial dissociation (decomposition) on SO₂ adsorption at 180 K indicated by small amounts of SO_{*x*} and atomic S. The O 1*s* data in Fig. 2 (right) are fitted with three main components located at 531.6, 530.9, and 530.2 eV. Within experimental accuracy the first one at 531.6 eV corresponds to both SO₂ (which dominates at 180 K) and SO_{*x*} (which is exclusively present near room temperature), whereas the components at 530.9 and 530.2 eV are assigned to atomic oxygen in different adsorption sites. The dominant atomic oxygen contribution at room temperature has clearly been identified as oxygen in bridge sites by x-ray absorption.¹² The component at 530.2 might be oxygen in hollow sites that are occupied on a clean Cu(100) surface.²⁰ Residual oxygen on the surface at temperatures of about 390 K and higher is assumed to be subsurface oxygen. The O 1*s* data also suggest partial dissociation (decomposition) on SO₂ adsorption at 180 K indicated by the small amount of atomic oxygen in the 176-K spectrum.

In order to identify the SO_{*x*} species we calibrated the

measured S 2*p* and O 1*s* intensities with intensities corresponding to the known coverages of 0.22 ± 0.01 ML for Cu(100)-(2×2)-S (Ref. 19) and of 0.48 ± 0.05 ML for Cu(100)-(√2×√2)R45°-O.²¹ The XPS spectra of the reference structures are not shown here. The results obtained for all measured temperatures are plotted in Fig. 3. In particular, in the bottom panel of Fig. 3 the coverages of S and O in the SO_{*x*} species are compared. Note that at room temperature and above there is no more SO₂ on the surface. From the comparison for coverages near room temperature (284, 303, and 323 K) an average of $x = 1.2 \pm 0.4$ is obtained, which clearly identifies the SO_{*x*} species as SO. Values of $x \geq 2$ are far outside the error bars and $x = 2$ has already been excluded by x-ray absorption. We emphasize here that by taking into account the small amount of SO in the O 1*s* signal for SO₂+SO below 250 K and comparing it with the S 2*p* signal for SO₂ (cf. Fig. 3) we get an independent (of NEXAFS) identification of the latter species. The ratio of the oxygen and sulfur coverages in this species below 250 K measures 2.1 ± 0.2 , showing that it is indeed SO₂. This result also demonstrates that within experimental accuracy the used calibration procedure is not affected by diffraction effects.

Finally, the processes taking place on SO₂ adsorption and subsequent heating will be reviewed and compared with the TPD spectrum shown in Fig. 4 (bottom), which was taken after SO₂ multilayer condensation on Cu(100) at 110 K. We should emphasize here that throughout the whole temperature range only desorbing SO₂ molecules are detected in TPD. As already mentioned above, molecular SO₂ adsorption dominates at 180 K. Small amounts of SO, atomic S, and atomic O, however, are already present on the surface (cf. Figs. 2 and 3) indicating the following decomposition pathways:

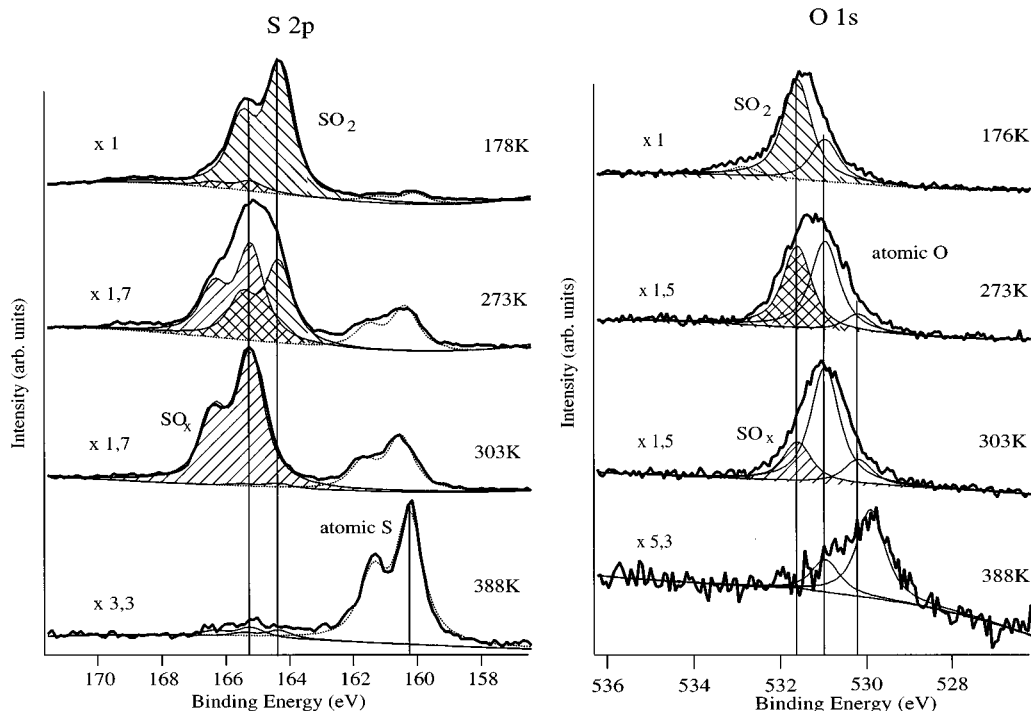


FIG. 2. Curve fits of the S 2p (left) and O 1s (right) data of Fig. 1 for four distinct temperatures. The S 2p spectra were fitted with three spin-orbit split doublets located at 165.3 eV (SO_x), 164.3 eV (SO₂), and approximately 160.2 eV (atomic S). The O 1s data were fitted with three components located at 531.6 eV (SO₂ and SO_x), 530.9 eV (atomic O), and 530.2 eV (atomic O). The shifted atomic O component at ~529.9 eV for 388 K is assigned to subsurface oxygen (cf. text).

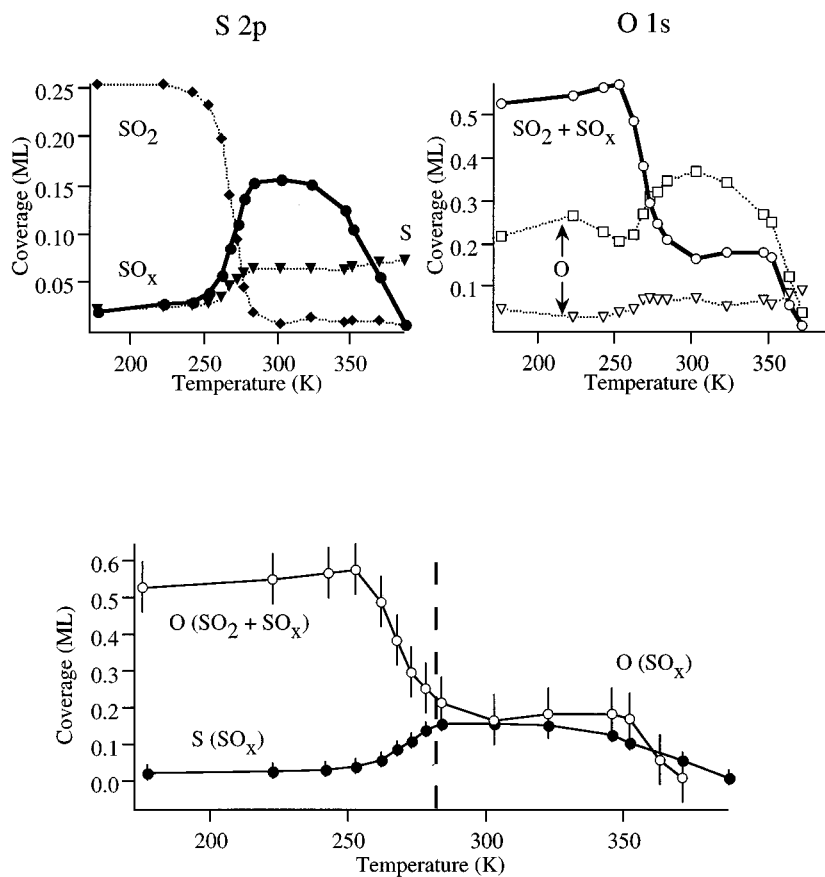


FIG. 3. Absolute S (top left) and O (top right) coverages of the different species detected on the Cu(100) surface as a function of temperature. In the lower panel the O(SO₂+SO_x) and S(SO_x) coverages are depicted, which show for temperatures above ~280 K (marked by a dashed line) that the SO_x species must be identified with SO.

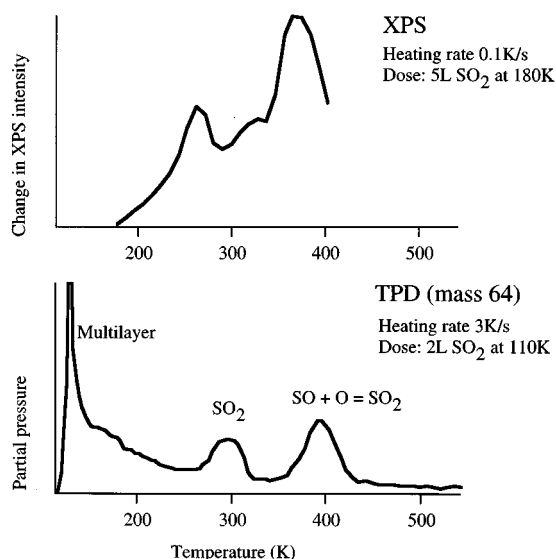
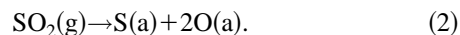
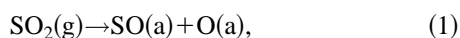
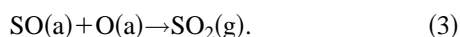


FIG. 4. "TPD curve" obtained by summing up all S and O coverages of Fig. 3 and forming the sign-inversed derivative (top) compared with the true TPD curve (bottom) for Cu(100)-SO₂.



Between about 250 and 300 K SO₂ is desorbing (cf. Fig. 3) giving rise to a prominent SO₂ desorption peak (cf. Fig. 4, bottom). At the same time the amounts of SO and atomic O as well as atomic S on the surface increase, showing that decomposition pathways (1) and (2) with SO₂(a) instead of SO₂(g) are active. Above a temperature of about 350 K the amounts of SO(a) and O(a) decrease while the amount of S(a) stays roughly constant (cf. Fig. 3). Because only SO₂ molecules are detected in the corresponding TPD peak (cf. Fig. 4, bottom), the following reaction pathway is suggested:



The alternative pathway 2SO(a) → SO₂(g) + S(a) must be excluded. Our XPS analysis on Cu(100)-SO₂ can thus fully explain the TPD experiment. Because only SO₂ molecules are detected in the latter, TPD can prove neither decomposition of SO₂ on Cu(100) nor the recombination of SO(a) + O(a) at higher temperatures, which results in desorbing SO₂ molecules.

Another interesting feature of the XPS experiment is depicted in Fig. 4. By adding up the S and O coverages (XPS intensities) for all detected surface species from Fig. 3 and forming the sign-inversed derivative of the sum (cf. Fig. 4, top) the TPD curve (cf. Fig. 4, bottom) is reproduced. The slight shift of the temperature scale is explained by the different heating rates (see numbers in Fig. 4).

The XPS data for Cu(111)-SO₂ are quite similar to those obtained for Cu(100)-SO₂ shown and discussed above. The most relevant results are summarized in Fig. 5. As can be seen from the figure, molecular SO₂ adsorption dominates at 170 K. Above a temperature of about 250 K the SO₂ coverage drastically decreases and the SO_x species shows up together with atomic S. Above about 280 K practically no more SO₂ is present on the surface. From a comparison of

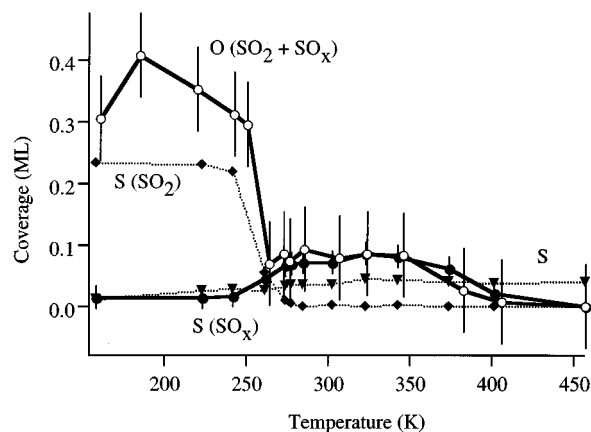


FIG. 5. Absolute S and O coverages for some species detected on the Cu(111) surface as a function of temperature. Above ~270 K the comparison of the S(SO_x) and O(SO₂+SO_x)≡O(SO_x) curves shows that SO_x must be identified with SO.

the absolute O and S coverages in the SO_x species above this temperature an x close to 1 is calculated (cf. Fig. 5), unambiguously identifying SO_x as SO. On further heating to about 450 K SO and also atomic O disappear nearly completely from the surface on which only a small amount of atomic S is left.

Finally, we note that because only SO₂ molecules are detected in a TPD experiment on Cu(111)-SO₂ (Refs. 10 and 11) and because the atomic S coverage stays constant for temperatures above about 300 K (cf. Fig. 5), the same reaction pathway (3) as on Cu(100) is suggested. This also explains the second-order desorption behavior of the corresponding TPD peak.¹¹

A comparison of the absolute SO₂ and SO coverages on Cu(100) and Cu(111) in Figs. 3 and 5, respectively, shows that on heating the SO₂-covered surfaces much less SO is formed on Cu(111) compared to Cu(100). This is probably due to different SO₂ bonding to the substrate on these two surfaces. On Cu(100) SO₂ stands upright and strongly bonds through both the S and O atoms with one of the S-O bonds being nearly parallel to the surface.¹² This definitely leads to more facile dissociation.² No structure determination has been performed for the Cu(111)-SO₂ system. An SO₂ bonding to Cu(111) mainly through the S atom similar to that found for Ag(110)-SO₂ (Ref. 22) could explain the quantitative differences of SO₂ decomposition observed for Cu(100) and Cu(111).

In summary, our fast and high-resolution XPS studies on SO₂ adsorption on Cu(100) and Cu(111) have shown that on both surfaces molecular adsorption dominates at 170 K. On heating the SO₂-covered surfaces to about room temperature SO₂ decomposes into SO+O+S. On further heating SO+O recombine to form SO₂, which is the only species detected in TPD studies. It has been shown for Cu(100)-SO₂ that the XPS experiment can reproduce the TPD curve.

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- *Permanent address: Institute of Physics of the Czech Academy of Sciences, Czkrovarnická 10, 16253 Praha 6, Czech Republic.
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