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Orientation and bond length of molecular oxygen on Ag(110) and Pt(111): A near-edge x-ray-absorption fine-structure study

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Near-edge x-ray-absorption fine-structure studies of O_2 chemisorbed on Ag(110) and Pt(111) surfaces near 100 K reveal different predissociation stages of molecular oxygen. O_2 on Ag(110) exhibits only a σ^* resonance and resembles a single-bonded peroxo species. The O—O bond is aligned parallel to the surface, along the $[1\bar{1}0]$ aximuth, with a bond length of 1.47 ± 0.05 Å. O_2 on Pt(111) also lies down but is less perturbed from the gas phase as revealed by the presence of a π^* resonance and an O—O bond length of 1.32 ± 0.05 Å, characteristic of a superoxo species.

The bonding of molecular oxygen on surfaces is of interest in understanding the early stages of molecular dissociation, in general, and the oxidation of surfaces, in particular. Oxygen chemisorbs molecularly on relatively few metal surfaces, the most studied being Ag(110) (Refs. 1-7) and Pt(111) (Refs. 8-12). Despite the general consensus that a stretched lying-down O_2 species is present on both these surfaces, the detailed bonding and structure of the molecule, in particular on Ag(110), have been controversial. Previously, it was proposed from electron-energy-loss studies (EELS) that the O—O bond is oriented parallel to the surface along the $[1\bar{1}0]$ azimuth[2] with a stretched bond length of $\simeq 1.4$ Å.[1,2] The same general geometry was obtained from angle-resolved photoemission studies (ARPES).[4] This geometry is in contrast to that deduced from an electron-stimulated-desorption ion angular distribution (ESDIAD) study which favored a site with a component of the O—O bond along the [001] azimuth.[7] On the theory side, a molecular-dynamics study favored adsorption of oxygen in a site within the atomic troughs of the Ag(110) surface,[13] while a molecular-orbital cluster study favored an O_2 geometry above the long twofold bridge site with the O—O bond oriented parallel to the surface along either the [001] or the $[1\bar{1}0]$ azimuths.[14]

More agreement exists regarding the orientation of O_2 on the Pt(111) surface. From vibrational studies it was proposed that the O—O bond is oriented parallel to the surface and that it is a severely stretched single bond.[8-11] Valence-level photoemission studies indicated that the π_g level was at least partially filled[8,9] and this was taken as support of an O—O single bond. Early near-edge x-ray-absorption fine-structure (NEXAFS) studies of O_2 on Pt(111) agreed with these proposals by finding an O—O bond length 1.45 ± 0.05 Å oriented parallel to the surface.[12]

Here we report a detailed NEXAFS study of O_2 chemisorbed on Ag(110) to determine the molecular bonding and orientation and reexamine results for O_2 on Pt(111).[12] We find that on both surfaces O_2 is oriented parallel to the surface and that on Ag(110) it is ordered along the $[1\bar{1}0]$ azimuth. The O—O bond is lengthened with respect to gaseous O_2 (1.207 Å) to 1.47 Å on Ag(110) and to 1.32 Å on Pt(111). From these bond lengths and the respective π^* resonance intensities which are a direct measure of the degree of rehybridization, we find that O_2 can be characterized as peroxo-like on Ag(110) and superoxo-like on Pt(111) in contrast to previous beliefs.

The experiments were performed on beam line I-1 at the Stanford Synchrotron Radiation Laboratory with use of a grasshopper monochromator (1200 lines/mm holographic grating). The NEXAFS spectra were obtained by partial-Auger-yield detection with a retarding voltage of −400 V. The energy scale was calibrated to ±0.5 eV by assigning the inflection points of the respective absorption edges to the O(1*s*) binding energies which have been measured to be 529.3 eV for O_2 on Ag(110) (Ref. 6) and 530.8 eV for O_2 on Pt(111).[9] The raw spectra were corrected for the monochromator transmission function and the background signal from the "clean" surface. This background correction was necessary for Ag(110) because of subsurface oxygen which exhibited a peak at 537.5 eV.

The Ag(110) crystal which has been used in previous studies was cleaned (base pressure 2×10^{-10} Torr) by Ar^+ sputtering for 10 min, annealing momentarily to 775 K, and then performing several oxygen adsorption-desorption cycles until a reproducible recombinative oxygen thermal desorption peak was obtained at 600 K along with a minimum desorption of carbon dioxide in the range 300–500 K, indicating a carbon-free surface. Auger electron spectroscopy showed no indication of contamination, and a sharp low-energy electron diffraction pattern was observed indicating a well-ordered surface. The crystal could be cooled to 90 K, radiatively heated by a tungsten filament and rotated about a vertical axis, allowing the polar angle between the electric field vector **E** and the surface normal to be varied from 10° (grazing x-ray incidence) to 90° (normal x-ray incidence). In addition, the crystal was *in situ* rotatable azimuthally about a horizontal axis. For the NEXAFS studies the crystal at 90 K was exposed for 10 min to 2×10^{-8} Torr oxygen using a needle doser.

Figure 1 shows the oxygen *K*-edge absorption spectra for O_2 chemisorbed on Ag(110) at 90 K and at various polar and azimuthal **E** orientations. Additional experiments on H_2O, carbonate (CO_3), and atomic oxygen showed that the spectra in Fig. 1 were not affected by these frequent contaminants for Ag(110). Only one major peak at 532.6 eV is observed in the spectrum which is superimposed upon the atomiclike absorption step. The peak is assigned to a transition from the O(1*s*) core level to the unfilled σ^* antibonding orbital of the O—O bond based on *K*-shell spectra of gaseous species like O_2 (Ref. 15) and CF_3O-OCF_3.[16] For **E** along the [001] azimuth and $\theta=90°$ a second weak peak is observed around 542 eV. We attribute this feature to a scattering resonance due to the adsorbate-substrate bond.

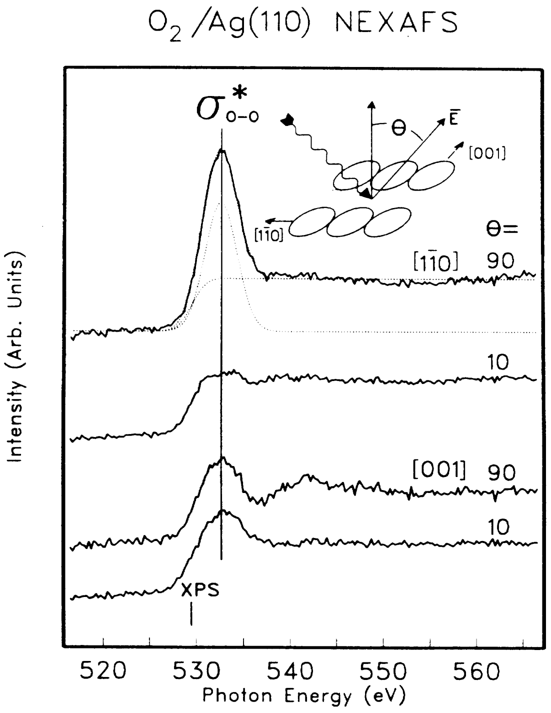

FIG. 1. Oxygen *K*-edge NEXAFS spectra for O_2 on Ag(110) at 90 K as a function of polar and azimuthal **E** orientations. The O-O σ^* peak at 532.6 eV is strongest when **E** lies along the O—O bond direction which occurs when **E** is along the [1$\bar{1}$0] azimuth and parallel to the surface ($\theta=90°$). The line at 529.3 eV marks the O(1*s*) binding energy relative to the Fermi level for O_2 on Ag(110).

The O-O σ^* peak in Fig. 1 is dominant in one orientation only, when the **E** vector of the x rays is parallel to the surface ($\theta=90°$) and parallel to the [1$\bar{1}$0] azimuth. Since the σ^* peak is maximized when **E** is parallel to the O—O bond, this is also the rough orientation of the O—O bond. Quantitative analysis of the angular dependence of the intensity of the O-O σ^* peak was accomplished by deconvolution of the spectra into a Gaussian peak for the O-O σ^* peak and a Gaussian-broadened absorption step as shown at the top of Fig. 1. Using measurements with **E** parallel to [1$\bar{1}$0] and at polar angles of 90°, 45°, 20°, and 10°, the O-O axis was determined to be parallel to the surface with a maximum error of 12°. A nearly constant 22 ± 2% remnant of the O-O σ^* peak is observed when **E** is along *any* polar angle of the [001] azimuth. This is accurately accounted for by the small vertical **E** component of the elliptically polarized synchrotron radiation which for this sample orientation lies along the [1$\bar{1}$0] azimuth.[17] Since the x-ray polarization is known we can accurately determine that the O-O axis lies directly along the [1$\bar{1}$0] azimuth with an uncertainty of 10°.

The NEXAFS spectrum of O_2 on Pt(111) at 100 K (Ref. 12) shown in Fig. 2 exhibits two resonances, a π^* resonance at 533.1 eV, which is absent for Ag(110), and a σ^* resonance at 538.0 eV, which relative to Ag(110) is shifted by 5.4 eV to higher energy. Previous studies have shown that a simple linear correlation can be established between the position of the σ^* resonance position and the intramolecular bond length for free and chemisorbed molecules.[18,19] In Fig. 3 such a correlation is made using the σ^* peak positions of gaseous O_2 (541.7 eV) (Ref. 15) with a bond length of 1.207 Å,[18] CF_3O-OCF_3 (533.6 eV) and $C(CH_3)_3O$-$OC(CH_3)_3$ (533.2 eV) (Ref. 16) with O—O bond lengths of 1.42 ± 0.02 and 1.48 Å, respectively.[20] Using this correlation we determine the O_2 bond length to be 1.32 ± 0.05 Å on Pt(111) and 1.47 ± 0.05 Å on Ag(110). The bond length derived here for O_2 on Pt(111) differs from that derived in previous NEXAFS studies.[12] This is due to the use of an empirical[18,19] rather than a parameter-dependent semitheoretical[12,21] correlation between bond length and resonance position.[22] Our error bar of ± 0.05 Å is due to uncertainties in transfering the *absolute* gas-phase resonance energies to the surface. The *relative* O—O bond-length difference on Ag(110) and Pt(111), corresponding to a 5.4-eV shift of the σ^* peak, can be estimated more accurately to be 0.15 ± 0.03 Å.

The O-O distance on Ag(110) correlates well with O—O single-bond lengths observed in normal peroxides like H_2O_2 (1.45–1.48 Å) (Ref. 20) and peroxo complexes bonded to metal atoms (1.40–1.52 Å).[23,24] The bond length on Pt(111), on the other hand, is close to that usu-

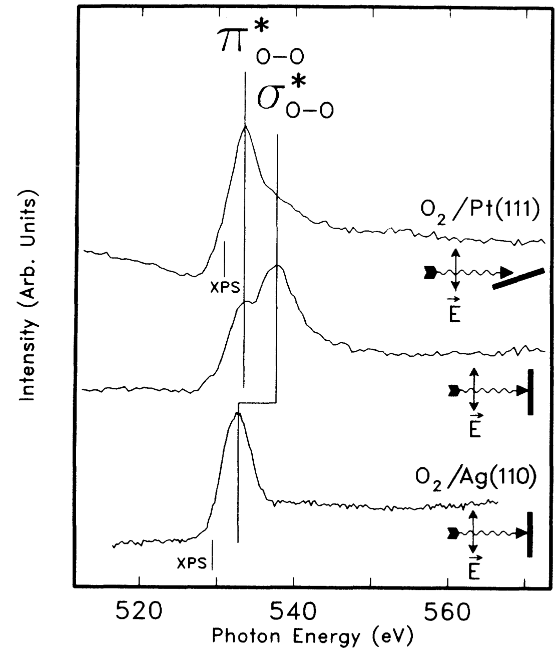

FIG. 2. NEXAFS spectra for O_2 on Pt(111) at 100 K (Ref. 12) as a function of polar **E** orientation and in comparison to O_2 on Ag(110). The two peaks in the O_2/Pt(111) spectra are assigned to the O-O π^* resonance at 533.1 eV and the O-O σ^* resonance at 538.0 eV and their angular dependence shows that the O—O bond is parallel to the surface. Comparison to O_2/Ag(110) reveals a shift of the σ^* resonance, indicating a shorter O—O bond for O_2 on Pt(111). The line at 530.8 eV marks the O(1*s*) binding energy of O_2 on Pt(111).

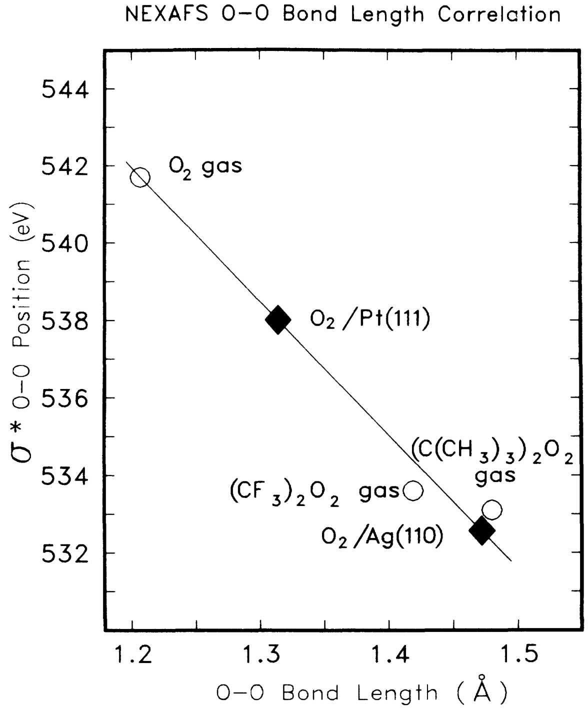

FIG. 3. Correlation between the O-O σ^* resonance position and the O—O bond length. The σ^* peak energies of O_2, CF_3O-OCF_3, and $C(CH_3)_3O$-$OC(CH_3)_3$ were obtained from gas-phase *K*-shell spectra (Refs. 15 and 16). Bond lengths of the chemisorbed O_2 species are obtained from this correlation.

ally associated with superoxo complexes with an O—O bond order of 1.5 and bond lengths in the range 1.10–1.30 Å.[23,24] The intramolecular bonding picture arising from the derived bond lengths is supported by the presence of a π^* peak for Pt(111), indicating a partly unfilled π^* orbital and a bond order *larger* than one, and the complete absence of the π^*resonance for Ag(110), signifying complete filling of the π^* orbital and a bond order of one.

Our bond lengths for O_2 on Ag(110) and O_2 on Pt(111) need to be compared with the previously reported vibrational frequencies of about 640 cm^{-1} for O_2 on Ag(110) (Refs. 1 and 2) and about 870 cm^{-1} for Pt(111).[8,10] These frequencies compare to the values 790–850 cm^{-1} (Refs. 23 and 24) for bidentate peroxo ligands in metal complexes and 1070–1120 cm^{-1} (Refs. 23 and 24) for bidentate superoxo ligands in metal complexes. Our results indicate therefore that there is a frequency shift of about 200 cm^{-1} between O_2 on Ag(110) and Pt(111) and the respective peroxo and superoxo metal complexes. In contrast, direct comparison of the frequencies for chemisorbed and metal-complex-bonded O_2 previously led to the proposal of peroxo-like species on *both* Ag(110) (Refs. 1 and 2) and Pt(111).[8-11]

The orientations for O_2 on Ag(110) and O_2 on Pt(111) are in agreement with the conclusions of previous vibrational and photoemission results. However, since the NEXAFS result can rule out any deviation of the O—O bond greater than 10° away from the $[1\bar{1}0]$ azimuth it is at variance with the ESDIAD result[7] which suggested that the O—O bond has a component along the [001] azimuth. Our study also contradicts the conclusion of the ESDIAD work that the O-O axis is nearly perpendicular to the surface. The discrepancy between the structural models derived by ESDIAD and the various other techniques, especially NEXAFS, casts doubts on the interpretation of the ESDIAD data. We suggest that in the ESDIAD spectra the ion trajectories do not follow the direction of the O-O axis and/or that the ion signal predominantly originates from a minority species.

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[22] In Ref. 12 we used results for O—C bond lengths in CO and CH_3O on Cu(100) and a simplified theoretical expression linking the bond length, the resonance position, a so-called "inner potential," and a phase-shift constant, to derive an O—O bond length of 1.45 Å. Later studies of possible correlations between the σ^* resonance position and the intramolecular bond length in gas-phase (Ref. 18) and chemisorbed (Ref. 19) molecules revealed that the approach used in Ref. 12 has severe limitations when transferred from one group of molecules to another. In particular, it involves parameters like the inner potential and the phase-shift constant which are not transferable. As proposed in Refs. 18 and 19, a direct empirical correlation between the resonance position and the bond length can be established which is also used here.

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