Bonding and Bond Lengths of Chemisorbed Molecules from Near-Edge X-Ray-Absorption Fine-Structure Studies

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Intramolecular scattering resonances in near-edge x-ray-absorption fine-structure spectra of chemisorbed molecules are used to determine the molecular orientation, bonding, and bond length. In particular, we demonstrate that the position of the σ shape resonance relative to the Fermi level is directly correlated with the intramolecular bond length of the chemisorbed molecule. By comparison with the known molecular distances in the gas phase, changes induced by the chemisorption bond are revealed.

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Near-edge x-ray-absorption fine-structure (NEXAFS) studies of chemisorbed low-Z molecules focus on the energy region within ~ 30 eV of the C, N, or O 1s excitation threshold (K edge).[1] This energy region is typically dominated by multiple-scattering resonances and is therefore discarded in the single-scattering analysis of the extended x-ray-absorption fine structure (EXAFS).[2] However, although its quantitative analysis is often difficult, especially for chemisorbed atoms,[3] the NEXAFS spectrum contains the largest and most detailed absorption structures. The most pronounced near-edge effects are observed for chemisorbed *molecules*.[1,4] The NEXAFS is found to be dominated by intramolecular scattering resonances with surprisingly little influence from scattering contributions due to substrate surface atoms. The observed resonances arise from transitions of a 1s core electron to *bound* states (e.g., empty or partially filled molecular orbitals) and/or to *quasibound* states in the continuum which have an enhanced amplitude on the molecule (shape resonances). The transitions are governed by dipole selection rules and analysis of their intensity as a function of $\vec{E}$ vector orientation allows the precise determination of the molecular orientation on the surface.[1,4]

For molecules with π bonding the NEXAFS spectrum will exhibit a strong resonance which corresponds to a transition of a 1s electron into the antibonding π^* orbital. The presence or absence of the π^* resonance is thus a direct indication for the hybridization of the bond. Opposite to the π resonance, which is strongest when the $\vec{E}$ vector is parallel to the π orbital, the σ shape resonance is strongest if the $\vec{E}$ vector lies along the internuclear axis between two neighboring atoms and it is present for all molecules. Because it arises from resonant scattering of the excited 1s photoelectron between atoms within the molecule it has been proposed that, in analogy to EXAFS, its energy position bears a direct correspondence to the intramolecular bond length.[4-6]

It is the purpose of this paper to demonstrate that such a correlation indeed exists for *chemisorbed* molecules. Thus NEXAFS spectra allow the derivation of the intramolecular bond length for a chemisorbed molecule in a simple, straightforward way. By comparison with the known gas-phase distance, changes induced by the chemisorption bond are revealed. The significance of our results lies in the implied potential of NEXAFS to monitor chemical reaction processes on surfaces.

Experiments on a variety of chemisorption systems were carried out at the Stanford Synchrotron Radiation Laboratory with use of the grasshopper monochromator (1200 lines/mm holographic grating) on beam line I-1. The single crystals were cleaned by Ar^+ bombardment and oxygen treatments to remove C. Surface cleanliness and order after annealing were checked by Auger and low-energy electron-diffraction measurements. Temperature-programmed reaction spectroscopy was used to characterize the absorbates on the surface.[7] NEXAFS spectra were recorded in the 80–300 K range at a base pressure of $\sim 8\times10^{-11}$ Torr. In all cases the x-ray incidence angle on the sample could be varied from grazing incidence ($\vec{E}$ along surface normal) to normal incidence ($\vec{E}$ in surface plane).[4]

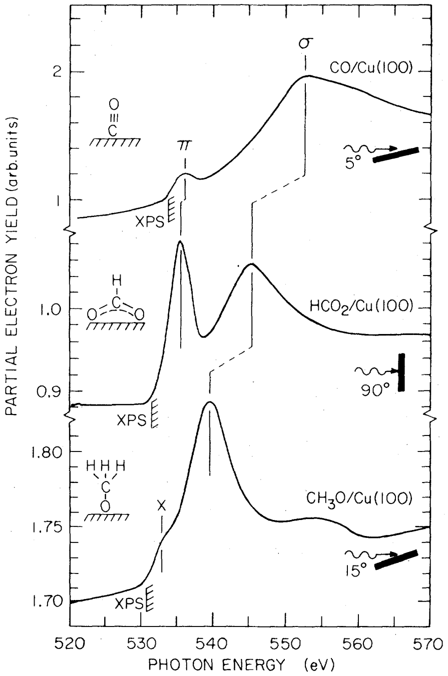

FIG. 1. NEXAFS spectra of the O K edge region for CO, formic acid (HCOOH), and methanol (CH_3OH) on Cu(100). HCOOH and CH_3OH were dissociated to formate HCO_2 and methoxy CH_3O, respectively, under controlled experimental conditions. Spectra were recorded at 90 K for CO and HCO_2 and 250 K for CH_3O. π and σ are two final-state intramolecular resonances. The O 1s binding energies determined by photoemission are labeled "XPS."

In Fig. 1 we show NEXAFS spectra above the O K edge for three molecules with carbon-oxygen bonds chemisorbed on Cu(100). The spectra are shown only for the x-ray incidence geometry which maximizes the σ-shape-resonance intensity.[7] In analogy with CO on Ni(100),[1] it is clear that at 90 K CO on Cu(100) also stands up along the surface normal. The σ shape resonance is centered at 552.5 eV. The π resonance is minimized for the grazing-incidence x-ray geometry. The second spectrum is for formic acid (HCOOH) which at 300 K chemisorbs as formate (HCO_2) on Cu(100) with two equivalent C-O bonds and the two oxygen atoms bonded to the surface.[8] In this case the σ shape resonance due to scattering between the absorbing O and neighbor C atoms is maximized for normal x-ray incidence. It occurs at 545.5 eV, a 7-eV shift relative to CO. Note that the backscattering contribution due to H is negligible compared to C and for the interpretation of the NEXAFS spectra the molecules can thus be viewed with missing H atoms. The C-O bond in the formate involves a π orbital as indicated by the narrow resonance at 535.5 eV. It arises from the C-O pseudo double bond with a π orbital parallel to the surface.[7] Methanol (CH_3OH) can be dissociated on Cu(100) to form the methoxy species CH_3O.[9,10] For CH_3O/Cu(100) measured at 250 K the σ shape resonance is observed most strongly at grazing incidence and its vanishing intensity for normal incidence determines the orientation of the O-C axis to be along the surface normal.[7] The σ resonance falls at 539.0 eV, 13.5 eV lower than for CO and 6.5 eV lower than for HCO_2. No π resonance is observed at any sample orientation[7] in good accord with the C-O single bond nature. The structure marked X in Fig. 1 is the atomiclike absorption step at the O K edge and the small peak around 555 eV is an EXAFS wiggle due to O-Cu scattering. We have also indicated in Fig. 1 the O 1s binding energies (E_B^{1s}) relative to the Fermi level determined by x-ray photoemission spectroscopy (XPS).[11] In all cases the XPS E_B^{1s} values coincide exactly with the K-edge threshold.

The position of the σ shape resonance in Fig. 1 decreases in energy with increasing C-O bond length R,[12] where $R = 1.13$ Å for triple-bonded CO gas, $R \sim 1.25$ Å for the pseudo-double-bonded formate ion $(HCO_2)^-$, and $R = 1.43$ Å for single-bonded CH_3OH. In a simple EXAFS-like picture, one would expect that the energy separation of the resonance (i.e., the first EXAFS wiggle) from threshold is inversely proportional to R^2. Indeed, such a correlation has previously been suggested by several authors.[5,6] Recently, Natoli[13] has given a theoretical justification within the framework of multiple-scattering theory. For the case of scattering between two atoms separated by R the scattering maximum will occur at a wave vector k_r of the photoelectron which is determined from an EXAFS-like expression, $k_r R = \text{const}$, where the constant depends on the atomic scattering phase shifts $\varphi_i(k)$. In the scattering theory k_r is referenced to the (constant) "muffin-tin" potential in the interstitial region, corresponding to $k=0$. If we define as Δ the energy difference between the σ-shape-resonance excitation energy (E_σ) and the 1s binding energy ($E_B{}^{1s}$) relative to the Fermi level E_F, we can rewrite the relation $k_r R = \text{const}$ as

$$(\Delta - V_0)R^2 = C_0 = \text{const} \qquad (1)$$

where the "inner potential" V_0 measures the muffin-tin potential relative to E_F. The value of $E_B{}^{1s}$ can be obtained from XPS or directly from the absorption onset in the NEXAFS spectrum (see Fig. 1). If V_0 and the atomic scattering phase shifts which determine the constant C_0 in Eq. (1) are known we can use Eq. (1) for the determination of an unknown bond length R.

For the chemisorption cases shown in Fig. 1 the σ resonance arises from scattering between the absorbing O atom and its nearest-neighbor C atom. Therefore the scattering phase shifts $\varphi(k)$ are identical in all three cases. Furthermore, because of the small energy range it will be a good approximation to neglect the k dependence of $\varphi(k)$. Thus the constant C_0 in Eq. (1) should be identical for all three cases of interest. The muffin-tin constant V_0 is also expected to be the same since the atoms in the molecule and the substrate are identical in all cases. If we take the two extreme cases CO/Cu(100) and CH_3O/Cu(100), with a change in bonding from triple to single bond ($\Delta R \sim 0.3$ Å),[12] as reference systems we can determine V_0 and C_0 in Eq. (1). We argue that for these two cases the intramolecular C-O chemisorption bond lengths are almost identical to those in the gas phase. This is supported by the small frequency shift in the C-O stretch relative to the gas phase[14] and the relatively weak chemisorption bond. The C-O bond lengths $R = 1.13 \pm 0.02$ Å for CO/Cu(100) and $R = 1.43 \pm 0.02$ Å for CH_3O/Cu(100) together with the respective measured values $\Delta = 18.8 \pm 0.5$ eV and $\Delta = 8.3 \pm 0.3$ eV lead to the values $V_0 = -9.2 \pm 1.6$ eV and $C_0 = 35.7 \pm 2.3$ eV Å^2.

By use of Eq. (1) we can now calculate that the value $\Delta = 13.8$ eV for HCO_2/Cu(100) corresponds to $R = 1.25 \pm 0.08$ Å. A simple linear approximation between Δ and R without invoking Eq. (1) yields the value $R = 1.27 \pm 0.04$ Å. These values are in excellent agreement with the value $R = 1.25 \pm 0.02$ Å[12] for the C-O bond length in formate ions coordinated by a variety of metals. With the above procedure intramolecular chemisorption bond lengths can typically be determined with an accuracy of ± 0.05 Å. A larger data base will decrease the potential error in R which by use of Eq. (1) is mainly determined by the error bars of V_0 and C_0. This uncertainty in R for chemisorbed molecules is comparable or smaller than that obtained with any other surface technique. Note in particular that SEXAFS studies of intramolecular bond lengths in low-Z molecules[15] are difficult because of the quickly decaying backscattering amplitudes above the edge and the short bond lengths which result in few EXAFS oscillations.

To illustrate the application of NEXAFS for the determination of bond length changes in a molecule upon chemisorption we show in Fig. 2 the spectrum of O_2 chemisorbed on Pt(111) at 90 K. For comparison the gas-phase O_2 spectrum[16] is also shown. In the spectra peak A is readily identified to be the π final-state resonance and peak B is the σ shape resonance. The dependence of the O_2/Pt(111) spectra on x-ray incidence unambiguously determines that the molecule lies down on the surface. The most dramatic difference from the gas-phase spectrum is the separation of peaks A and B which change from 11 eV (gas) to 4 eV (surface) indicating a substantial *increase* of the O-O bond length for chemisorbed O_2. We can estimate the intramolecular chemisorption bond length by means of Eq. (1) if we use the value $\Delta = 7.9$ eV for the separation of the σ resonance from the absorption onset, taken as $E_B{}^{1s} = 531.1$ eV from XPS.[17] We assume transferability of the muffin-tin constant V_0 and the phase-shift constant C_0. This is justified because the scattering phase shifts for C and O are very similar. Secondly, we have found empirically that *V_0 is surprisingly constant (~ 9 eV) for different low-Z molecules with bonds between C, N, and O atoms on various d-band metals.* By use of Eq. (1) we find $R = 1.45$ Å for the O-O bond length on Pt(111), a dramatic increase of 0.24 Å

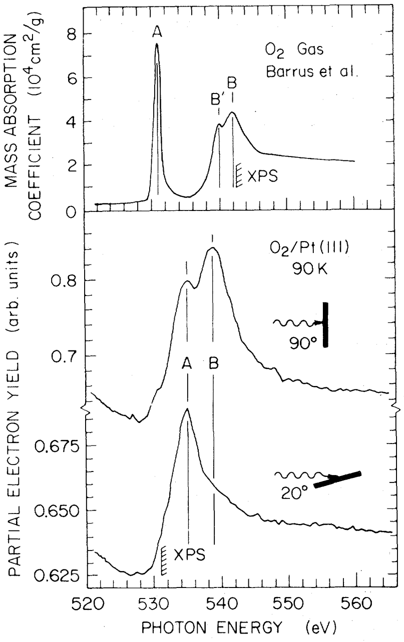

FIG. 2. Oxygen K edge NEXAFS spectra for gas-phase O_2 (Ref. 16) and O_2/Pt(111) for two directions of x-ray incidence. Peaks A and B are π and σ final-state resonances; peak B' is a multielectron feature. The O 1s binding energies relative to the vacuum level (gas) and Fermi level (surface) are denoted by "XPS."

over the value $R = 1.21$ Å for gas-phase O_2. The large O_2 bond length on the surface is close to the O-O single-bond length $R = 1.49$ Å in peroxide (H_2O_2) or in the $(O_2)^{2-}$ ion.[12] This is explained by π bonding of O_2 on Pt(111) with substantial charge transfer from the metal into the two antibonding π^* orbitals of O_2, rendering the molecule in a peroxylike $(O_2)^{2-}$ state. The π chemisorption bond is supported by the substantial broadening of the π resonance (peak A) in Fig. 2 with a full width at half maximum (FWHM) of 5.4 eV relative to a FWHM = 3.7 eV for chemisorbed CO or CHO_2 (Fig. 1). Note, however, that the antibonding π^* orbitals for O_2/Pt(111) are not filled completely since some π resonance intensity remains. Our findings here are in complete support of the interpretation of earlier electron-energy-loss measurements on the same system.[18]

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