Beyond the Chemical Shift: Vibrationally Resolved Core-Level Photoelectron Spectra of Adsorbed CO

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Vibrational fine structure has been observed in the C1s and O1s photoelectron lines of CO adsorbed on Ni(100). This allows a detailed separation of vibrational and electronic contributions to the line profile. The main line is found to represent the fully screened final state. The width of the photoelectron lines is dominated by the intramolecular stretch mode, which strongly depends on the chemical state of the adsorbate. The identification of the adiabatic transition makes the determination of chemical shifts more precise. The equivalent core approximation is found to be highly accurate and electronic and geometric equilibrium properties of the core-ionized adsorbate are extracted. [S0031-9007(98)06752-0]

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The main reason for the impact of core-level photoelectron spectroscopy in its application to surfaces is the utilization of the chemical shift [1–5]. Different species and adsorption sites are often easily identified from their core-level binding energy positions [5]. However, there is additional, important chemical information available from a detailed study of the line profile of the main lines using high resolution x-ray photoelectron spectroscopy (XPS). In the present Letter we show how the adsorption of CO in different chemical states modifies the vibrational fine structure in the core-level spectra significantly.

The core-level line profile is due to electronic and vibrational contributions in a polyatomic system [5,6]. For solids, surfaces, and adsorbates the general assumption has been that no detailed separation of the various contributions can be made [5,7–9], as they were thought to be both larger and more complex than in free molecules, where this separation is possible and frequently done [10]. Recently, it has been shown that for adsorbates with hydrocarbon functional groups it is possible to resolve vibrational fine structure with large splittings [11]. The present work on CO adsorbed on Ni(100) shows that even much smaller core-level vibrational splittings in adsorbates can be clearly resolved and that electronic and vibrational contributions can be separated. This leads to a significantly enhanced understanding of the core-ionized adsorbate, allowing the extraction of additional information on the electronic and geometric structure exceeding what was possible with XPS previously.

The results show that the line profiles are dominated by the excitation of CO stretch vibrations. Other vibrational modes and electronic broadening contributions are small. The much larger linewidth for the O1s spectra can be traced back almost entirely to the higher excitation of the intramolecular stretch for a core hole on the oxygen atom than on the carbon atom. The XPS main line is found to represent the fully screened final state. By comparison to independent information for adsorbed NO we find that the equivalent core approximation [5] is valid to high accuracy; the electronic structure of the two species is nearly identical. Furthermore, the present findings provide a general applicable line-shape parametrization based on a few, physically relevant parameters, relating to ground state properties like bond lengths and force constants.

The XPS measurements were performed at the Advanced Light Source, Lawrence Berkeley National Laboratory, by combining monochromatic soft x rays from beam line 8.0 with a Scienta SES 200 electron analyzer [12]. The overall resolution was between 50 and 30 meV for 700 and 320 eV photon energy. All spectra were recorded at 80 K in normal emission with the electric field vector of the synchrotron radiation normal to the crystal surface. We prepared the CO/Ni(100) and CO/H/Ni(100) phases as described elsewhere [13]. An XPS spectrum of the clean Ni(100) surface was measured for each excitation energy and subtracted from the adsorbate covered one. For the least squares fits we employed Doniach-Sunjic line profiles [14,15] convoluted with Gaussian functions. For each vibrational progression the same line profile was used for all components. Vibrational energies and progressions were determined by evaluating numerous spectra with different excitation energies well above threshold averaging out possible effects due to photoelectron diffraction.

Figure 1 shows the C1s and O1s XPS spectra for $c(2 \times 2)$CO/Ni(100), obtained at $\hbar\omega = 320$ and 700 eV, respectively. The novel information is the well resolved fine structure due to the excitation of vibrational motion. The C1s spectrum is dominated by the first vibrational component, whereas the O1s spectrum shows a rich progression. The C1s main line has a splitting of 217.8 ± 2.2 meV with the adiabatic transition at 285.8 ± 0.1 eV; the O1s main line exhibits a splitting of 173 ± 8 meV with the adiabatic transition at 531.4 ± 0.2 eV. These splittings are significantly reduced compared to the gas phase values, where 300 ± 4 meV (C1s) and 226 ± 7 meV

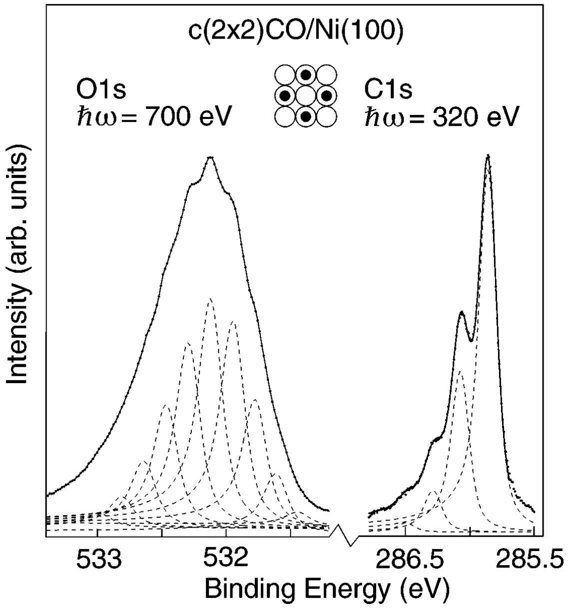

FIG. 1. C1*s* and O1*s* photoemission spectra of $c(2 \times 2)$ CO/Ni(100). Vibrational fine structure due to intramolecular stretch; C1*s* 217.8 ± 2.2 meV, O1*s* 173 ± 8 meV. Adiabatic transitions at 285.8 ± 0.1 eV (C1*s*) and 531.4 ± 0.2 eV (O1*s*).

(O1*s*) have been reported [16]. The relative intensities of the various vibrational levels of the C1*s* main line exhibit a strong photon energy dependence, which will be discussed elsewhere.

To determine which vibrational mode is excited in the core-ionization event, we look at the ground state vibrational modes of CO adsorbed on Ni(100) in the $c(2 \times 2)$ superstructure. In this phase the molecule occupies, in an upright position, on top sites with the carbon end down [17,18]. The carbon-oxygen stretch, molecule-substrate stretch, and frustrated rotation have been measured with electron energy loss spectroscopy (EELS) to 256, 59.5, and 35 meV, respectively [18]. The frustrated translational mode has been determined using inelastic helium scattering to 3.5 meV [19]. The vibrational energy of the core-ionized molecule will be slightly different but the only mode close to our observed splitting is the carbon-oxygen stretch mode. To fit the vibrational components the following parameters were used: The lifetime broadening in the C1*s* and O1*s* levels has a FWHM of 92 [20,21] and 180 meV [22], respectively. The asymmetry index [15] is $\alpha = 0.08$. Additional Gaussian contributions of 104 and 84 meV are needed to model the vibrational components in C1*s* and O1*s*, respectively. These Gaussian contributions are larger than the experimental bandwidth between 30 and 50 meV, especially in the carbon spectrum. The additional broadening comes mainly from the low energy frustrated translational mode, which contributes significantly to the line profile [23,24]. The electronic broadening contributions due to electron-hole pair shakeup processes are surprisingly weak for the $c(2 \times 2)$CO/Ni(100) system with relatively small asymmetric tails to higher binding energies, which is contrary to previous expectations [7–9]. However, electronic and vibrational broadening is system dependent (Fig. 3). No vibrational fine structure was resolved, i.e., for weakly adsorbed $c(2 \times 2)$CO/Cu(100) on top [17] with strong shakeup contributions [25,26].

The excitation of vibrational motion is due to the fact that the potential energy surfaces for the atomic motion are different before and after ionization. The ground state internuclear distance in $c(2 \times 2)$CO/Ni(100) has been determined with electron diffraction techniques to be 1.13 Å [27,28]. The shape of the final state potential energy surface is given by the observed positions of the vibrational sublevels in the XPS spectra. Within the Franck-Condon picture [29] the only remaining parameter, the displacement of the equilibrium distance, Δr, can then be determined from the shape of the vibrational envelope. The decreased vibrational splitting relative to the ground state adsorbate immediately shows that both ionizations lead to more shallow potential energy surfaces for the CO stretch vibration. The wider vibrational projection in the O1*s* spectrum is due to the fact that the bond is elongated more in this case, about 0.16 Å compared to 0.039 Å for C1*s* ionization.

The detailed mapping of the final state properties allows us to evaluate the equivalent core approximation [5] in a way not possible before. For adsorbates this approximation has been used only in a qualitative way. A major complication is that there is no time for geometric relaxation during the photoemission process. This implies that the final state species is produced in the nonequilibrium geometry defined by the initial state. Now that the vibrational fine structure is resolved, we can determine potential energy surfaces for the core-ionized species and extrapolate its equilibrium properties [30]. The accuracy of this approach is tested by comparing the intramolecular stretch energies between C1*s* ionized CO and ground state NO, which is the appropriate molecule in the equivalent core approximation. The NO molecule occupies on top sites in the NO/Ni(100)-6*L* phase [17] like the CO molecule on Ni(100) in the $c(2 \times 2)$ superstructure. In this phase the ground state N-O stretch mode has a vibrational energy of 208 meV [17,18]. When comparing the intramolecular stretch energies between C1*s* ionized CO and NO, one has to correct for the different atomic masses. This has been done using a triatomic (Ni,C,O) linear force model. We find excellent agreement between the measured vibrational energies of C1*s* core-ionized $c(2 \times 2)$CO/Ni(100) at 217.8 ± 2 meV and the renormalized ground state vibration in NO/Ni(100)-6*L* at 218 meV. This demonstrates the very high accuracy of the equivalent core approximation for the bonding properties. Furthermore, this proves in great detail the complete screening of the final state, yielding a neutralized core excited final state. Our results also suggest that in terms of adsorbate-adsorbate interactions and vibronic coupling an isolated NO impurity molecule amidst the CO adsorbate behaves essentially the same as being embedded in a full NO overlayer.

In the next step we have performed XPS measurements for CO in different chemical states, characterized through chemically shifted core-level binding energies [13]. In Fig. 2 the XPS spectrum of the carbon region of the $c(2\sqrt{2} \times \sqrt{2})R45^\circ$ CO/H/Ni(100) phase is shown. In this coadsorption phase CO molecules occupy in upright position to equal parts fourfold hollow and top sites [31,32]. The chemical shift of 1.1 eV clearly separates the C1s lines for CO on top and on hollow sites at 286.2 and 285.2 eV, respectively. The new feature is again that within each C1s line vibrational fine structure is observed.

In Fig. 3 the vibrational fine structure in the C1s line is investigated as a function of substrate coordination. The spectra in Fig. 3 are the C1s main lines for $c(2 \times 2)$ CO/Ni(100), CO/H/Ni(100) disordered, and $c(2\sqrt{2} \times \sqrt{2})R45^\circ$ CO/H/Ni(100) with the CO molecules occupying top sites [17,18], twofold bridge sites [31], and fourfold hollow sites [31,32], respectively. A lowering of the vibrational splitting in the C1s line is found with increasing substrate coordination. In higher coordination sites the vibrational sublevels are less resolved. This is due to smaller vibrational splitting, but also due to larger additional broadening. The results from the numerical fits are summarized in Table I. The displacement of internuclear equilibrium distance Δr upon C1s ionization for adsorption on bridge and hollow sites is 0.045 and 0.066 Å, respectively, in comparison to 0.039 Å for on top. As a result we find that Δr increases with substrate coordination.

Over the years, ground state vibrational spectroscopy has been used to derive local adsorption geometries of diatomic molecules on the basis of their intramolecular stretch frequency. However, it has been shown recently that the established correlation between adsorption site and intramolecular stretch frequency does not hold for all diatomic molecules [34–37], in particular, for NO [34,35,38]. For CO adsorbed on Ni(100) the relationship between adsorption site and intermolecular stretch frequency is established [17,31,39]. Employing the equivalent core approximation and the known adsorption geometry of CO/H/Ni(100) in bridge and hollow sites we attempt to assign NO adsorption sites by comparing vibrational splittings between C1s ionized CO and ground state NO. Adjusting for the different nuclear masses, we predict from our C1s XPS measurements that the NO vibrational stretch energies in the NO/H/Ni(100) system should be 175 and 150 meV for adsorption in bridge and hollow sites, respectively. EELS data for NO/H/Ni(100)-0.5L shows a loss peak between 160–180 meV [40]. This is consistent with NO molecules in bridge sites. For NO or NO/H on Ni(100) no adsorption phase is found which exhibits an EELS peak at 150 meV. This makes it—with all due caution—unlikely that NO would adsorb on fourfold hollow sites on this surface. However, for 0.5 L NO on Ni(510), which is essentially a stepped (100) surface, a loss feature at 150 meV has been observed and assigned to NO on highly coordinated step edges [40].

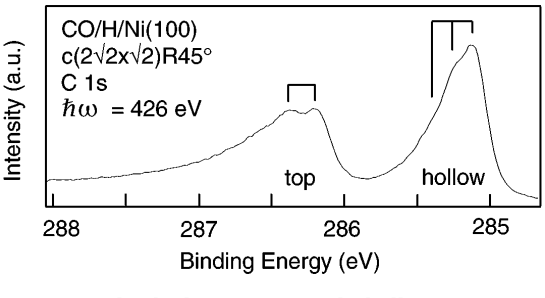

FIG. 2. CO adsorbed in top and hollow sites in the CO/H/Ni(100) $c(2\sqrt{2} \times \sqrt{2})R45^\circ$ superstructure. Chemical shift of 1.1 eV and additional vibrational fine structure.

In conclusion, we have observed vibrational fine structure in the C1s and O1s photoelectron lines of adsorbed CO and CO/H on Ni(100). This allows us to separate and quantify the most important contributions to the line profile. The XPS main line represents, in all essential details, the fully screened final state. The line profile is dominated by the intramolecular stretch mode, whereas electronic broadening contributions are surprisingly small. The vibrational energy of the intramolecular stretch is found to vary for core-ionized CO in different chemical states, which are characterized by chemical shifts. These can be determined more accurately as the adiabatic

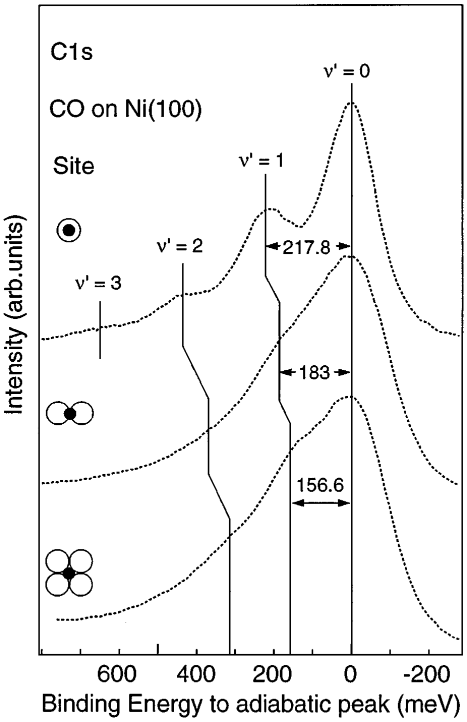

FIG. 3. Vibrational fine structure as a function of substrate coordination. The C1s line for CO molecules on top, bridge, and hollow sites. Photon energy $\hbar\omega = 320$ eV for on top and $\hbar\omega = 426$ eV otherwise.

TABLE I. Summary of C1s photoemission data and Franck-Condon analysis with Morse potentials. Anharmonicity values have been assumed from gas phase data [33] as 1.65 and 1.68 meV for the ground and C1s ionized states, respectively.

	Vibrational splitting E_{vib} (meV)		Branching ratio $\frac{\nu_0\to\nu_i'}{\nu_0\to\nu_0'}$ for $i = 1, 2$		Δr (Å)
	Ground state EELS	C1s ionized XPS	Experiment	Calculation	
CO/Ni(100) $c(2 \times 2)$ Top	256 [18]	217.8 ± 2.2	0.305 ± 0.047 0.039 ± 0.017	0.301 0.050	0.039
CO/H/Ni(100) Disordered Bridge	240 [31]	183.0 ± 5	0.379 ± 0.037 0.071 ± 0.032	0.379 0.069	0.045
CO/H/Ni(100) $c(2\sqrt{2} \times \sqrt{2})R45°$ Hollow	210 [31]	156.6 ± 4	0.624 ± 0.058 0.271 ± 0.079	0.654 0.232	0.066

transitions are identified. We find the equivalent core approximation to be highly accurate for the core-ionized adsorbate, and with the powerful tools of vibrational analysis potential energy surfaces and equilibrium geometries for the final state species are derived.

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