Vibrational Broadening in Core-Level Spectra from Adsorbates: C, N, and O on Ni(100)

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(Received 22 May 1989)

The x-ray-photoelectron core-level linewidths show pronounced differences between atomic C, N, and O adsorbed on Ni(100). Furthermore, the widths are temperature dependent. The observed effects are reproduced within a model based on the creation of vibrational excitations in the core-ionization process. This explains the large linewidths observed for many adsorbate systems. The results have important consequences for the general understanding of line shapes in core-level spectroscopies.

PACS numbers: 68.35.Ja, 73.20.Hb, 79.60.−i, 82.65.−i

Core-level spectroscopies are of major importance in the study of adsorbed atoms and molecules. XPS (x-ray photoelectron spectroscopy) is used to identify different adsorbate species, NEXAFS (near-edge extended x-ray-absorption fine structure) is used to study the initially unoccupied electron states of adsorbates, etc. To be able to use the full potential of these spectroscopies it is of fundamental importance that the intrinsic core-level line shapes are known for different situations. A broad spectral feature in XPS may, for instance, be caused by some broadening mechanism or it may be due to two or more shifted features indicating several types of adsorbates.

In the present Letter we show that vibrational effects give rise to major broadenings of adsorbate core levels. This provides a new explanation for the observed large variations in core-level linewidths for adsorbates. As a consequence this implies that electronic excitations which have previously been discussed as the origin of these effects[1-6] are of considerably less importance. With this understanding of the broadening mechanism it will be possible to account for the variations in linewidths between different adsorbates. Furthermore, these effects can be used to obtain information on adsorbate geometries.

We have investigated the core-level linewidths of ordered layers of C, N, and O adsorbed on Ni(100). It is found that the widths vary significantly between the three adsorbate systems. Furthermore, the O 1*s* line shows different widths for the *p*(2×2) and *c*(2×2) phases. The linewidths are also found to be temperature dependent. It is shown that the linewidths can be consistently explained using knowledge about equilibrium bond distances and vibrational energies for the adsorbates.

The spectra were excited with monochromatized x rays and recorded using a hemispherical analyzer (36-cm mean field radius), equipped with a multichannel detection system. The overall resolution was 0.4–0.5 eV. The adsorbate layers were prepared by decomposition of C_2H_4, NH_3, and O_2. The adsorbate structures were carefully monitored by LEED and XPS. Carbon[7,8] and nitrogen[9,10] form *c*(2×2) overlayers. In both cases there is a reconstruction of the substrate which gives rise to a *p*4*g* surface structure. Oxygen adsorbs without reconstruction[11] and both the p(2×2) (coverage 0.25 relative to the substrate) and *c*(2×2) (coverage 0.5) phases were investigated.

Figure 1 compares the 1*s* spectra from the *c*(2×2) overlayers of C, N, and O recorded at 150 K. The width (FWHM, full width at half maximum) is 0.67 eV for the C 1*s* line, 0.94 eV for the N 1*s* line, and 1.42 eV for the O 1*s* line. Figure 2 shows the spectra for the *p*(2×2) and *c*(2×2) phases of oxygen for two different temperatures, 150 and 600 K. The O 1*s* peak is significantly broader for the *c*(2×2) phase [1.42 eV compared to 1.18 eV for the *p*(2×2) phase as measured at 150 K]. Fur-

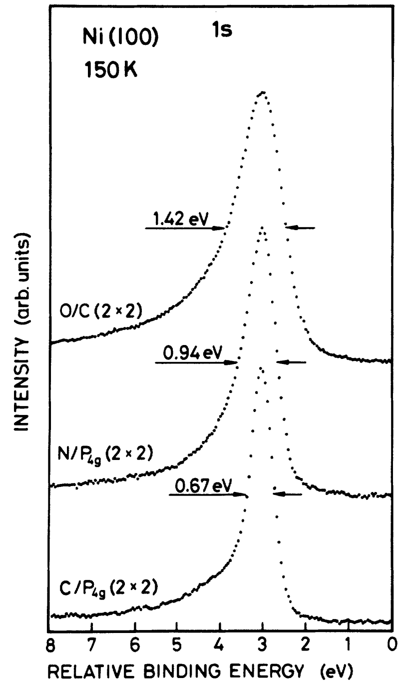

FIG. 1. C 1*s*, N 1*s*, and O 1*s* spectra for the *c*(2×2) adsorbate layers measured at 150 K.

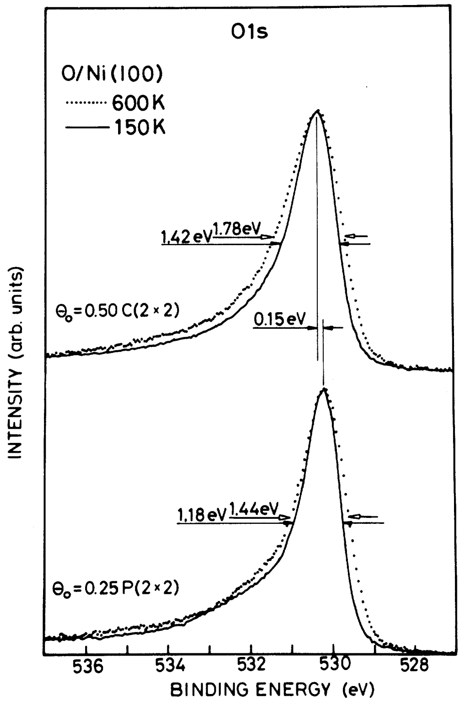

FIG. 2. O 1*s* spectra for the *c*(2×2) and *p*(2×2) phases recorded at 150 and 600 K.

thermore, the O 1*s* linewidth increases with temperature. For nitrogen there is also a temperature effect, whereas the C 1*s* linewidth is essentially independent of temperature. The measured widths are summarized in Table I.

The spectrometer function has in the present case a width of 0.4–0.5 eV. The intrinsic lifetime widths for the C 1*s*, N 1*s*, and O 1*s* levels (~0.1 eV)[12] can for practical purposes be neglected. The additional broadening observed for many adsorbates has previously been interpreted in terms of electronic shakeup processes related to the electronic screening of the core hole.[1-6] This type of broadening gives rise to asymmetric core line shapes in all metallic systems.[13] To some extent such shakeup processes may also occur for adsorbates. For the present systems the broadening can be expected to be largest for carbon and nitrogen since these adsorbates are most closely incorporated in the surface. In the following we therefore use the experimental C 1*s* width at 150 K (0.67 eV) as a reasonable estimate (upper limit) of the broadening due to these effects.

We propose that the additional broadening for nitrogen and oxygen is due to vibrational excitations. The basis for this effect is that the time scale of the photoionization process is much shorter than the time scale associated with geometrical relaxation. This implies that the photoionized site is produced with the same geometry as the initial state. The equilibrium geometry and interatomic force constant are generally different for the system before and after ionization. This leads to excitation of vibrational motion in the final state (Franck-Condon transitions).

In Fig. 3 potential-energy curves for an adsorbate before and after ionization are shown along some vibrational coordinate. This may be the vertical motion of an atomic adsorbate in a fourfold site on Ni(100). We assume that only the ground-state vibration is populated. Two different situations are considered. In Fig. 3(a) the equilibrium geometry changes very little as a result of the core ionization. The Franck-Condon principle then gives transitions mainly to the lowest vibrational final state ($v=1 \rightarrow v'=1$) and there is no broadening of the core electron line. Figure 3(b) represents a case where the core ionization leads to a substantial change in the equilibrium bond distance. The initial-state vibrational

TABLE I. Experimental and calculated 1*s* linewidths (FWHM) in eV. A width of 0.67 eV is quadratically added to the calculated widths. This reproduces the experimental C 1*s* FWHM at 150 K. The unbroadened values are given within parentheses.

	Experiment				Calculations			
	150 K	300 K	500 K	600 K	150 K	300 K	500 K	600 K
C *c*(2×2)	0.67			0.68	0.67 (~0)	0.67 (~0)	0.67 (~0)	0.67 (~0)
N *c*(2×2)	0.94			1.05	0.87 (0.55)	0.95 (0.67)	1.02 (0.77)	1.07 (0.84)
O *c*(2×2)	1.42	1.53	1.61	1.78	1.27 (1.08)[a]	1.42 (1.25)	1.64 (1.50)	1.75 (1.62)
O *p*(2×2)	1.18	1.33	1.40	1.44	1.21 (1.01)[a]	1.33 (1.15)	1.52 (1.36)	1.61 (1.46)

[a] The slope of the final-state curve is chosen to give a reasonable overall agreement over the whole temperature range. The same slope is used for the *c*(2×2) and *p*(2×2) phases.

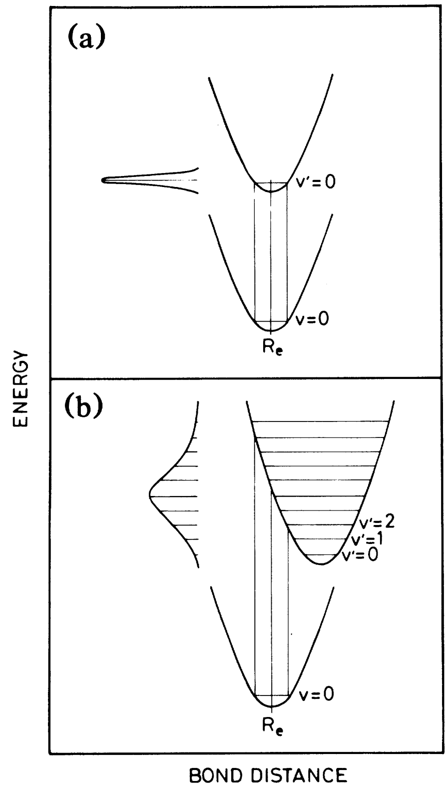

FIG. 3. Initial- and final-state potential-energy curves for situations with (a) a small or (b) a large geometry change.

wave function is then projected onto a steep part of the final-state potential-energy curve. This creates transitions to a number of vibrational states and a broadened core-level spectrum is observed. The linewidth depends on the spatial extention of the ground-state vibration and the slope of the final-state potential-energy curve in this region.[14,15] In the general case for a surface system a large number of vibrational modes should be treated. However, the discussion above shows that it is sufficient to consider those modes which correspond to the situation in Fig. 3(b). In general this simplifies the treatment considerably.

Another consequence of the vibrational effects is that the linewidths may depend on temperature.[16] This is easily seen from Fig. 3. A higher temperature leads to thermal population of excited vibrational states. If the initial- and final-state potential-energy curves are very similar [Fig. 3(a)] the excited vibrational states will core ionize to excited final states ($v=n \rightarrow v'=n$ transitions). The energies of these transitions are essentially the same as for the $v=1 \rightarrow v'=1$ transition and there is no additional broadening of the core electron line. However, if the potential-energy curves are different [Fig. 3(b)], a higher temperature will lead to a larger broadening.

If the initial- and final-state potential-energy surfaces are known, the vibrational line profiles can be calculated. The atomic adsorbates C, N, and O are most interesting in this respect since one has experimental knowledge about both the initial- and final-state potential-energy curves. For the final state the $Z+1$ approximation is employed. This approximation is based on the fact that the removal of a core electron from an atom leads to essentially the same change in the valence-electron properties as if an additional charge were added to the nucleus. In this way the C $1s$, N $1s$, and O $1s$ final states behave very much like adsorbed nitrogen, oxygen, and fluorine atoms, respectively. In particular, this implies that the potential-energy curves for the final states can be represented by the curves for the $Z+1$ elements.

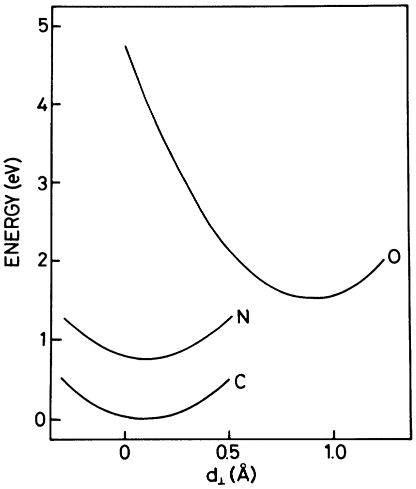

FIG. 4. Potential-energy curves for the vertical motion of the $c(2\times2)$ overlayers of C, N, and O on Ni(100) (harmonic approximation).

The presently investigated adsorbates occupy fourfold hollow sites. This implies that upon core ionization the equilibrium geometry does not change parallel to the surface. The parallel vibrational modes can therefore be neglected. The potential-energy curves for the vertical motion of C, N, and O in the $c(2\times2)$ overlayers are displayed in Fig. 4. The harmonic approximation is used and the substrate is assumed to be rigid. The bond distances are obtained from SEXAFS determinations[8,10,17] and the force constants have been derived from k-resolved electron-energy-loss data.[9,18,19] The vibrational energies have been averaged over the different k vectors. From the curves in Fig. 4 the C $1s$ and N $1s$ widths can be estimated. The vibrational progressions have been calculated using Ansbacher's method[20] and the results are shown in Table I. The C and N potential-energy curves are very similar and consequently the calculated C $1s$ broadenings are small. For the N $1s$ ionization, however, there is a substantially larger shift in equilibrium bond distance between the initial and final (oxygenlike) states. This leads to calculated vibrational broadenings of 0.55 and 0.84 eV for the N 1*s* line at 150 and 600 K, respectively. In order to compare the calculated widths to experiment, a FWHM of 0.67 eV is quadratically added to the results (see above). As can be seen the important trends of the C 1*s* and N 1*s* widths are well reproduced. The calculated C 1*s* width is independent of temperature. For N 1*s* the calculated values are 0.87 and 1.07 eV compared to the experimental values of 0.94 and 1.05 eV at 150 and 600 K, respectively.

For the O 1*s* ionization, detailed knowledge of the (fluorinelike) final state is lacking. However, the observed widths can be reproduced in a consistent way with the same type of model. A final-state curve (essentially a linear slope) is chosen in such a way that it gives linewidths in the observed range. The same curve is used for the $c(2\times2)$ and $p(2\times2)$ phases. As can be seen the temperature effects are reproduced in a reasonable way. The calculations also suggest that the larger widths and the more pronounced temperature effects for the $c(2\times2)$ phase are connected to the shallower potential-energy minimum for this phase.

We have demonstrated that there are large variations in linewidths among the atomic adsorbates C, N, and O on Ni(100). The broader lines also show pronounced temperature effects. The observed effects are consistently explained within a model based on excitations of vibrational motion, in the present case due to vertical adsorbate modes. Large broadenings have also been observed in other systems such as CO/Ni(100).[21] In that case the broadening is due to parallel vibrational modes. The present results are important for the general understanding of core-level spectroscopies for adsorbates. The utilization of this effect also provides a means for obtaining structural information on adsorbates.

The assistance of J. O. Forsell and H. Rydåker is gratefully acknowledged. This work was supported by the Swedish Natural Science Research Council and the Swedish Board for Technical Development.

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