Bond Lengths and Bond Strengths in Weak and Strong Chemisorption: N_2, CO, and CO/H on Nickel Surfaces

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New chemical-state-specific scanned-energy mode photoelectron diffraction experiments and density functional theory calculations, applied to CO, CO/H, and N_2 adsorption on Ni(100), show that chemisorption bond length changes associated with large changes in bond strength are small, but those associated with changes in bond order are much larger, and are similar to those found in molecular systems. Specifically, halving the bond strength of atop CO to Ni increases the Ni-C distance by 0.06 Å, but halving the bond order (atop to bridge site) at fixed bond strength causes an increase of 0.16 Å.

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A key challenge in the quantitative determination of surface adsorption structures is to determine interatomic bond lengths with chemically significant precision. The general understanding of interatomic bond lengths in molecular systems has been well established for many years [1], and some of the general concepts of bond order have been shown to be quite effective to describe atomic chemisorption at metal surfaces [2]. Far less attention has been paid to understanding the trends in bond lengths associated with molecular chemisorption at metal surfaces, such as the relationship between bond strength and bond length. Weak bonds are assumed to be longer than strong ones, yet there is a dearth of data to allow quantitative evaluation of this idea. Here we show, using both chemical-state specific scanned-energy-mode photoelectron diffraction (CS-PhD) experiments and density functional theory (DFT) calculations, that chemisorption bond length changes associated with different bond strengths are actually very small, but that those associated with changes in bond order are very similar to those found in molecular systems. Ni(100)/N_2 is a weak chemisorption system in which an unusually long (2.25 Å) Ni-N bond length [3] had been attributed to this weak bonding, but we show that the true bond length (1.81 Å) is not anomalously long. Moreover, by comparing experimentally determined Ni-C bond lengths for CO adsorbed on Ni(100) with and without coadsorbed hydrogen, we show that CO weakly chemisorbed in the $c(2 \times 2)$-CO/H phase in an atop site has a Ni-CO bond length only marginally (0.06 Å) longer than when it occupies the same atop site in the strongly chemisorbed $c(2 \times 2)$-CO phase despite a change in the chemisorption bond strength of a factor of 2 or more. By contrast, we show that changing the CO bonding coordination from onefold to twofold (halving the bond order) in strongly chemisorbed CO and CO/H bridging phases has a far larger effect (0.16 Å).

The adsorption of CO on nickel surfaces is a model chemisorption system which has been studied extensively, in part due to its relationship to a range of chemically significant catalytic reactions. Several investigations of the adsorption of the isoelectronic molecule N_2 have focused on the similarities and differences in the electronic structure and bonding character [4]. These are typically described through refinements of the original Blyholder model of σ donation from the molecule to the metal combined with back donation from the metal into the molecular π states. CO forms a moderately strong chemisorption bond on Ni surfaces (heat of adsorption approximately 1.2 V per molecule [5,6]), whereas N_2 is bonded much more weakly (falling from 0.4 to 0.2 eV with increasing coverage [7]). Both species form $c(2 \times 2)$ ordered phases with the molecular axes perpendicular to the surface and located atop a surface Ni atom on Ni(100). On a Ni(100) surface predosed with hydrogen, CO adsorption at low temperature also leads to a $c(2 \times 2)$ phase [8], for which vibrational spectroscopy indicates occupation of the same atop site, but the CO restructures at around 140 K, and desorbs at 210 K, indicating an adsorption energy for the coadsorbed atop state of 0.4–0.6 eV, a factor of 2–3 times less than with no coadsorbed hydrogen. Comparison of the Ni-C bond lengths for atop CO on Ni(100) with and without coadsorbed hydrogen thus provides a direct measure of the influence of changes in the bond strength.

The experimental technique of scanned-energy mode photoelectron diffraction (PhD) [9] exploits the coherent interference between the directly emitted component of

the photoelectron wave field from an adsorbate core level and components of the same wave field elastically scattered by neighboring atoms. As the photoelectron energy (and wavelength) vary, the substrate scattering paths switch in and out of phase, leading to intensity modulations which are characteristic of the emitter atom site. Photoelectron binding energy "chemical shifts" can be exploited to obtain PhD modulation spectra which are not only element specific, but also chemical-state specific. Here this CS-PhD [10] technique has been used to extract separate structural data from the 2 N atoms of the N_2 adsorbate which are rendered inequivalent by the end-on bonding to the surface, showing a N 1*s* chemical shift of 1.3 eV; we denote the 2 N atoms as "inner" and "outer" relative to the underlying substrate. This same chemical-state specificity separated the C 1*s* emission from atop CO and from small amounts of coadsorbed CO in local bridging sites on Ni(100) both with and without hydrogen predosing [11] (having atop-bridge chemical shifts of 0.8 and 0.4 eV, respectively). An undulator on the BESSY II synchrotron radiation facility provides the high spectral resolution and high flux needed for these measurements.

The Ni(100) sample was prepared *in situ* by Ar ion bombardment and annealing to produce a clean well-ordered surface as judged by low energy electron diffraction (LEED) and soft x-ray photoelectron spectroscopy. A well-ordered $c(2 \times 2)$-N_2 surface was prepared by exposing the clean surface to N_2 at a pressure of 1×10^{-7} mbar while cooling the sample from 150 to 75 K. The $c(2 \times 2)$-CO-H structure was prepared by cooling the Ni(100) surface to 65 K in a hydrogen partial pressure of 1×10^{-7} mbar and then exposing at this temperature to 10×10^{-6} mbar · s CO. PhD modulation spectra were obtained by recording a sequence of photoelectron energy distribution curves (EDCs) around the N 1*s* or C 1*s* peaks at 4 eV steps in photon energy in the photoelectron energy range $\approx$ 80–400 eV in a series of different emission directions. The individual EDCs were fitted by Gaussian peaks (in the case of N 1*s* separate peaks for emission from the two inequivalent N atoms and for the unscreened satellite peak), together with a step and a template background. The integrated peak areas were then plotted as a function of photoelectron energy and the final PhD modulation spectrum was obtained by subtraction and normalization by a smooth spline function representing the nondiffractive intensity and instrumental factors. Quantitative structure determination was effected by comparing these experimental PhD spectra with the results of multiple scattering simulations [12] for a succession of refined structural models, the optimum structure being established by minimizing an objective reliability factor (*R* factor) [9] which quantifies the level of theory-experiment agreement.

In the case of the Ni(100)$c(2 \times 2)$-N_2 surface, analysis of our full CS-PhD data [13] confirms that the molecule occupies a site atop an outermost layer Ni atom with the N-N axis perpendicular to the surface to within $\pm 10°$. A subset of the experimental PhD spectra are compared with the results of the calculations for the best-fit structure in Fig. 1. The N-N bond length is found to be 1.13 ± 0.03 Å and the Ni-N bond length, $d_{\text{Ni-Ni}}$, is 1.81 ± 0.02 Å. Figure 2 shows the variation of the *R* factor as a function of $d_{\text{Ni-Ni}}$; a second minimum occurs at a bond length of approximately 2.25 Å, corresponding to that obtained in the earlier study [3], but the value of the *R* factor is larger than that of the true minimum by 6 times the estimated standard deviation. Other minima at even longer and shorter bond lengths show even larger *R* factors. This problem of "multiple coincidences" in fitting both PhD [14] and LEED [15] intensity-energy data is well known, but with sufficiently large datasets the true minimum can be established reliably. The dataset used here comprises 13 chemical-state specific spectra in different emission directions; the earlier analysis was based on a single spectrum without separation of the two inequivalent emitters.

Nevertheless, in order to provide a wholly independent check on the value of $d_{\text{Ni-Ni}}$ for this structural phase we have conducted DFT calculations based on a 5-layer Ni(100) slab with the CASTEP computer code [16] in the generalized gradient approximation (GGA) using revised PBE functionals [17] and ultrasoft pseudopotentials, taking full account of electron spin in the final optimization. The outermost two Ni layers adjacent to the adsorbed N_2 were allowed to relax in the structural optimization,

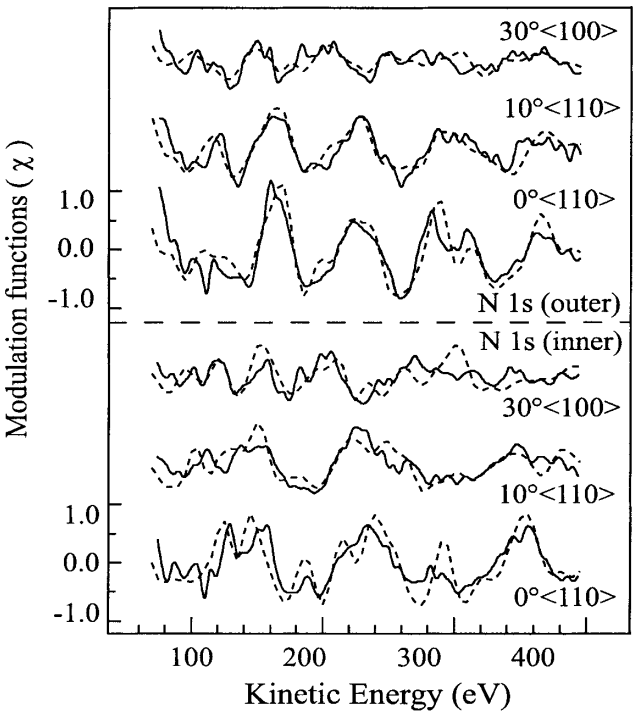

FIG. 1. Comparison of a subset of the experimental (full lines) chemical-state-resolved N 1*s* PhD spectra obtained from a Ni(100)-$c(2 \times 2)$-N_2 surface with the results of multiple scattering calculations (dashed lines) for the best-fit structure.

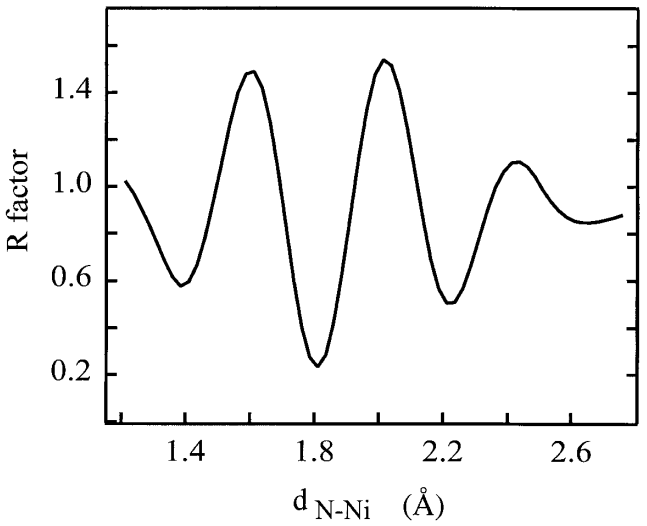

FIG. 2. Variation of the R factor as a measure of experiment/theory agreement for the Ni(100)-$c(2 \times 2)$-N_2 surface, with the parameter $d_{\text{Ni-Ni}}$.

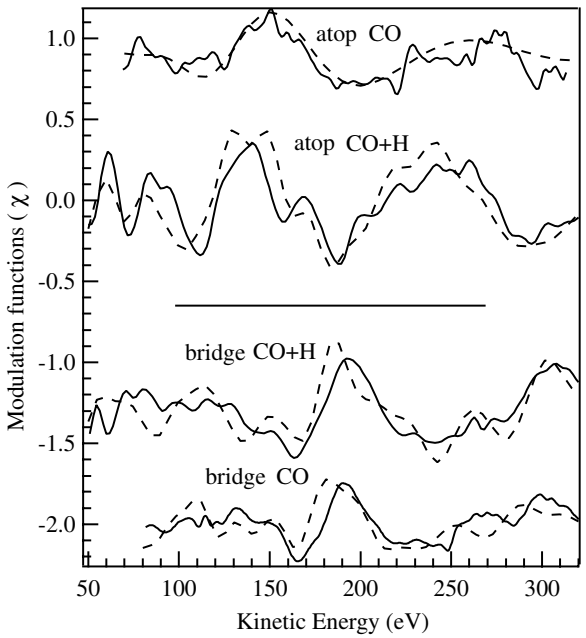

FIG. 3. Comparison of the normal emission C 1s PhD spectra from the atop and bridge species adsorbed on Ni(100) with and without coadsorbed hydrogen. Shown in each case is the experimental data (full line) and the results of the calculation for the best-fit structure (dashed line).

while the lower layers were constrained to the geometry obtained from an equivalent bulk Ni calculation. These calculations yielded a value for $d_{\text{Ni-Ni}}$ of 1.79 Å, in excellent agreement with experiment. The adsorption energy was calculated to be 0.51 eV per molecule, similar to the experimental value at low coverage and entirely consistent with weak chemisorption. For the $c(2 \times 2)$ phase the experimental value is significantly lower, but the experiments also indicate an unusually large vibrational entropy [7] not included in the calculation.

Similar fitting of the C 1s PhD spectra recorded from the weakly chemisorbed Ni(100)$c(2 \times 2)$-CO + H surface [18] confirmed atop site occupation of the CO and yielded a Ni-C bond length of 1.79 ± 0.02 Å. The strongly chemisorbed $c(2 \times 2)$ phase formed by pure CO on Ni(100) was studied extensively in the early development of quantitative LEED, and while the atop site is universally agreed, values for the Ni-C bond length fall in the range 1.7–1.8 Å with typical estimated errors of ± 0.1 Å [19]. To provide a more precise reference value in a common methodology we have therefore conducted a C 1s PhD study of this phase, concentrating only on normal emission and one off-normal direction, sufficient to provide a clear Ni-C distance for a well-established site. The value we obtain is 1.73 ± 0.03 Å. Figure 3 shows a comparison of the normal emission C 1s PhD spectra obtained from these two $c(2 \times 2)$-CO (CO atop) phases with and without coadsorbed H. The difference in the electron energies of the maxima reflects the change in Ni-C bond length, but the change from strong to weak chemisorption effected by the coadsorbed hydrogen causes an increase in the Ni-C bond lengths of only 0.06 ± 0.04 Å. DFT calculations, performed in the same fashion as those for the Ni(100)$c(2 \times 2)$-N_2 system described above, provide strong support for these experimental values. For the pure Ni(100)$c(2 \times 2)$-CO system we find the optimal value of the Ni-C distance to be 1.74 Å, while for a Ni(100)-$c(2 \times 2)$-2H + CO phase (with the H atoms occupying all the hollow sites) we find the equivalent bond length to be 1.79 Å, both in excellent agreement with experiment. Note that while there are known to be problems with the accuracy of DFT calculations (even using the revised RPE functional) in determinations of exact adsorption energies for CO adsorbed in different sites [notably on Pt(111)], the interatomic distances are generally far more reliable.

On Ni surfaces CO can bond in one-, two-, and threefold coordinated sites depending on the orientation and the coverage. It is therefore instructive to compare the Ni-C bond lengths in this situation. On Ni(100) one can change the adsorption site from atop to bridge either by increasing the coverage in a pure CO layer, or by raising the temperature (to around 270 K) with coadsorbed hydrogen. Using the same PhD methodology we find that for these two states, which have very similar (intermediate) adsorption energies, the Ni-C bond lengths with and without coadsorbed H are 1.88 ± 0.03 Å and 1.89 ± 0.03 Å, respectively [18]. Figure 3 shows that the normal emission C 1s PhD spectra from these two surfaces are almost identical, reflecting this common geometry. On Ni(110) one also finds bridge site adsorption, with experimental LEED and published DFT calculations both yielding Ni-C bond lengths in the range 1.85–1.89 Å [21,22]. Finally, on Ni(111) CO adopts threefold coordinated hollow sites both in the 0.5 ML $c(4 \times 2)$ phase and at lower coverage; PhD measurements find the Ni-C distance on

TABLE I. Summary of Ni-C bond lengths and adsorption energies on various Ni surfaces.

Surface	Coordination	Bond length (Å)	Adsorption energy (eV)
Ni(100)/H	1	1.79	0.4–0.6
	2	1.88	≈1.0
Ni(100)	1	1.73	1.2 [6]
	2	1.89	1.1 [6]
Ni(100)	2	1.85–1.89 [21,22]	1.1 [6]
Ni(111)	3	1.93 [23]	1.2 [6]

this surface to be 1.93 ± 0.03 Å [23], in excellent agreement with a quantitative LEED study which gives 1.94 ± 0.03 Å [24]. Averaging over these various measurements on the different surfaces there is thus a systematic increase in this bond length of 0.15 ± 0.04 Å from onefold to twofold coordination, and of approximately 0.07 ± 0.04 Å in going from twofold to threefold coordination for pure CO-covered Ni surfaces. For comparison, the simple expression given for bond length changes in fractional bonds by Pauling for intermetallic compounds [1] would predict values 0.18 and 0.09 Å, respectively, closely similar despite the very different bonding character. These results highlight the fact that for Ni-CO surface bonding, halving the bond order has a much larger effect on the bond length than does halving the bond energy (despite the fact that the adsorption energies in the one-, two-, and threefold coordinated sites on the three low index faces of Ni are closely similar [6]).

Unlike CO adsorption, there is very little comparative data for N_2 adsorption, and indeed it seems that N_2 almost always forms singly coordinated bonds to metals in coordination compounds, so there is no information on bond order changes even from molecular systems. An interesting comparison does exist with adsorption on Ru(0001), however, because both CO and N_2 are known to bond at atop sites on this surface and, as on Ni(100), CO is strongly chemisorbed and N_2 is weakly chemisorbed. In these phases the Ru-N bond length is 0.08 Å longer that the Ru-C bond length; on Ni(100) the equivalent difference in the metal molecule bond length reported here is the same, 0.08 ± 0.04 Å.

In conclusion, our experimental determination of the local geometry of CO chemisorbed on Ni(100) in atop and bridge sites, with and without coadsorbed hydrogen, shows that while changes in chemisorption bond order lead to changes in the associated bond lengths closely consistent with simple Pauling rules, large changes in the chemisorption energy have a far more modest influence on the bond lengths (Table I). Similar data for the weakly chemisorbed isoelectronic N_2 species on Ni(100) reinforce the view that weak chemisorption does not lead to substantial increases in bond lengths, contrary to prior suggestions. DFT-GGA total energy calculations reproduce these key findings regarding strong and weak chemisorption bond lengths.

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