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Influence of CO adsorption on the alkali-substrate bond studied by high-resolution electron energy loss spectroscopy

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The coadsorption of Na/CO on Ni(111) has been investigated using high-resolution electron energy loss spectroscopy. Loss measurements showed that coadsorbed CO molecules dramatically affect the vibrational properties of Na adatoms. The Na-Ni vibration energy at 22 meV measured on the Na/Ni system shifted down to 12 meV for the CO/Na/Ni surface. This result was ascribed to a charge transfer from Na to CO. On the contrary, no appreciable shift of the Na-Ni stretching frequency was observed for the coadsorption of Na with oxygen.

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The knowledge of chemical reactions at surfaces is one of the main aims of surface science studies in ultrahigh-vacuum conditions. Alkali-metal atoms are promoters of a wide variety of catalytic reactions such as oxidation of metal and semiconductor surfaces and dissociation of various molecules (CO,N_2,NO).[1–4] Because of its fundamental and technological importance, the alkali+CO system received a great attention.

High-resolution electron energy loss spectroscopy (HREELS) and infrared reflection absorption spectroscopy (IRAS) measurements revealed a significant lowering of the C-O stretching frequency in the alkali+CO coadsorbed phase.[5,6] To date, many effects are supposed to be responsible for the softening of the C-O internal bond: Electrostatic interactions,[7–10] surface states,[11] direct,[12] and indirect (substrate-mediated)[13] chemical interactions. A recent theoretical work suggests that the shift of the C-O energy vibration is caused by an enhanced alkali-induced electronic polarizability of the metal surface.[14]

Despite the wealth of efforts, the achieved results have not yet been conclusive and new experimental investigations are needed to shed more light on this area and, in general, on the microscopic mechanisms governing the surface reactivity. So far, many of the previous experimental studies[2,5,6] on the alkali-CO coadsorption were performed within a common approach; that is, first, alkali atoms were deposited onto the metal surface and only successively the surface was exposed to CO molecules. This procedure was based on the assumption, taken for granted, that preadsorbed alkalis change the electronic properties of the underlying surface and, as a consequence, the adsorption properties of CO molecules. Accordingly, the softening of the C-O bond was mainly ascribed to the action of preadsorbed alkali atoms. Theoretical investigations were performed within the same assumption.[14] As a matter of fact, all previous studies were focused on the alkali-induced shift of the C-O stretching vibration, whereas any effect of CO on the alkali-substrate bond was completely disregarded. As alkali atoms affect the vibrational properties of CO, likewise CO molecules should influence the nature of the alkali-substrate bond. So far, the effects of CO on the vibrational properties of alkali atoms have not been investigated.

In this Brief Report, we show that CO molecules dramatically affect the chemical bond of alkali-metal atoms with the substrate. The Na-Ni stretching mode measured in the presence of coadsorbed CO molecules was found to shift to lower energies by about 10 meV with respect to the Na-Ni stretching energy (22 meV) measured for Na adsorbed on the clean Ni(111) surface. Same results were obtained for the coadsorption of K and CO. By contrast, the Na-Ni vibration was slightly reinforced for Na coadsorbed with oxygen atoms. Our results suggest that the basic mechanisms of the catalytic promotion of alkali atoms are still poorly understood and claim for new theoretical approaches.

HREEL measurements were performed using a spectrometer (Delta 0.5, SPECS) operating at a base pressure of 5×10^{-9} Pa. Loss spectra were acquired in the specular geometry (incidence angle of 55°) using a primary electron beam energy of 3 eV and an energy resolution of about 2 meV. The Ni(111) surface was prepared by repeated cycles of ion sputtering (E_p=1.5 keV) and annealing at 1000–1200 K. Low energy electron diffraction (LEED) and Auger electron spectroscopy were used to check surface order and cleanliness, respectively. Na (K) atoms were deposited onto the Ni(111) surface by a well degassed dispenser (SAES GETTERS). Preadsorbed alkali layers free of any contamination could be obtained only by keeping the Ni(111) surface at 400 K during deposition. Alkali, CO, and oxygen coverages were estimated from the exposure time taking as reference the coverage of well-known LEED structures; that is, $(\sqrt{3} \times \sqrt{3})R30°$-Na, $p(2\times2)$-K, $c(4\times2)$-CO, and $p(2\times2)$-O, respectively. The coverage θ is given as the ratio between the number of adsorbed atoms and the number of atoms of the topmost layer of the Ni(111) substrate. Furthermore, a clear $(3/2\times3/2)$-Na LEED pattern appeared at full Na monolayer coverage, i.e., 0.44 ML.

First, the vibrational spectra of alkalis, CO, and oxygen separately adsorbed on the Ni(111) surface were recorded in order to have well-established reference data. As known, CO molecules occupy threefold hollow sites on Ni(111) and at the coverage of 0.5 ML they form a $c(4\times2)$ LEED structure.[15] For this phase, the CO-Ni mode and the C-O stretching energy were observed at 50 and 235 meV, respectively.[16] As far as oxygen atoms, they form a p(2

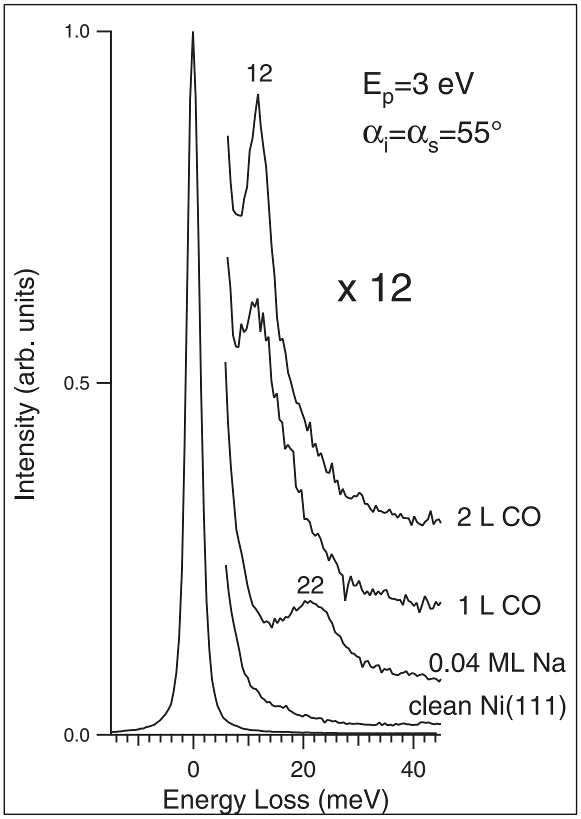

FIG. 1. Electron energy loss spectra of 0.04 ML of Na deposited at 400 K onto the Ni(111) surface and after CO exposures. After CO exposures, the Na-Ni vibration energy shifted from 22 meV down to 12 meV.

×2) structure and the O-Ni vibration was found at 70 meV.[17] As concerns the adsorption of Na, the Na-Ni stretching energy assumed values between 25 meV (for Na coverage less than 0.01 ML) and 22 meV (for Na coverage above 0.04 ML).

The loss spectrum of 0.04 ML of Na deposited on Ni(111) showed the Na-Ni stretching energy at about 22 meV (Fig. 1). The latter result is in excellent agreement with loss measurements[18] and calculations[19] performed on Na/Cu(111) and it provides a direct evidence that the differences between the electronic structure of Ni(111) and Cu(111) play only a negligible role on the Na-substrate bonding. The Na-Ni stretching energy shifted from 22 meV down to 12 meV upon CO exposure (Fig. 1); moreover, the Na-Ni loss peak became narrower than that measured on the Ni(111) clean surface. The behavior of the Na-Ni and C-O stretching energies for 0.08 ML of preadsorbed Na as a function of CO exposure is shown in Fig. 2. The Na-Ni vibration was observed to continuously shift towards lower energies while the C-O stretching energy initially remained at 208 meV (0.3 L of CO) and then shifted upward to 218 meV for 1.6 L of CO (highest CO coverage and saturation). Interestingly, both the Na-Ni and the C-O vibration energies were mutually affected upon coadsorption. The energy shift of the Na-Ni and C-O vibrations was found to be dependent on the Na/CO ratio. Similar results were obtained by coadsorbing K and CO on the same surface.

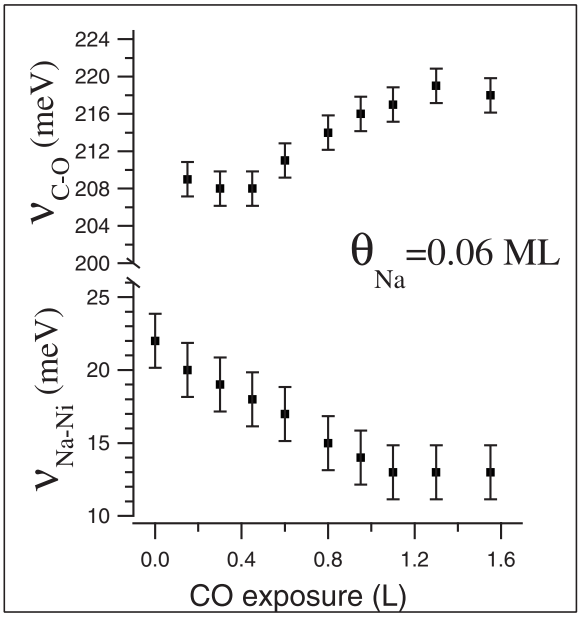

FIG. 2. Behavior of the C-O internal stretching and the Na-Ni vibration energies as a function of CO exposure. The Na layer was prepared at 400 K, whereas CO exposures were made at room temperature.

More details on the Na-CO interaction could be obtained by adsorbing Na on the $c(4\times2)$-CO/Ni(111) surface. The $c(4\times2)$ structure was prepared by exposing the surface to 1 L of CO at 200 K. The CO-Ni and the C-O vibrational modes were measured at 50 meV and 235 meV, respectively (Fig. 3). Such modes were significantly affected by Na deposition (at 200 K). The CO-Ni vibration strengthened and shifted to higher loss energies up to 72 meV; moreover, a new feature arose at 220 meV, close to the C-O stretching vibration. Both modes at 220 and 235 meV evolved with the alkali deposition and merged into a single feature at 220 meV for a Na coverage of 0.22 ML. The Na-Ni stretching energy for the CO/Na phase was observed between 12 meV and 14 meV (Na coverages above 0.22 ML). As regards the structural side of the investigation, the initial $c(4\times2)$-CO LEED pattern slightly degraded with the Na deposition but no new ordered structures were observed. The existence of two distinct C-O frequencies for Na coverages between 0.07 and 0.13 ML indicated the presence of two different species of adsorbed CO molecules; the former was essentially unaffected being the C-O stretching energy at 235 meV; the latter, instead, interacted with Na atoms and moved to 220 meV. The interaction between sodium and carbon monoxide influenced also the CO-Ni loss as its line shape appeared broadened. At the highest Na coverage (0.22 ML), a uniform layer with about one atom of Na for each two CO molecules should exist on the surface and only a single C-O stretching energy at 220 meV was observed in the loss spectrum.

Loss measurements taken for the Na/CO coadsorbed phase (Figs. 1–3) showed a simultaneous weakening of the Na-Ni and C-O bonds and a strengthening of the CO-Ni bond. The weakening of the Na-Ni bond caused by CO mol-

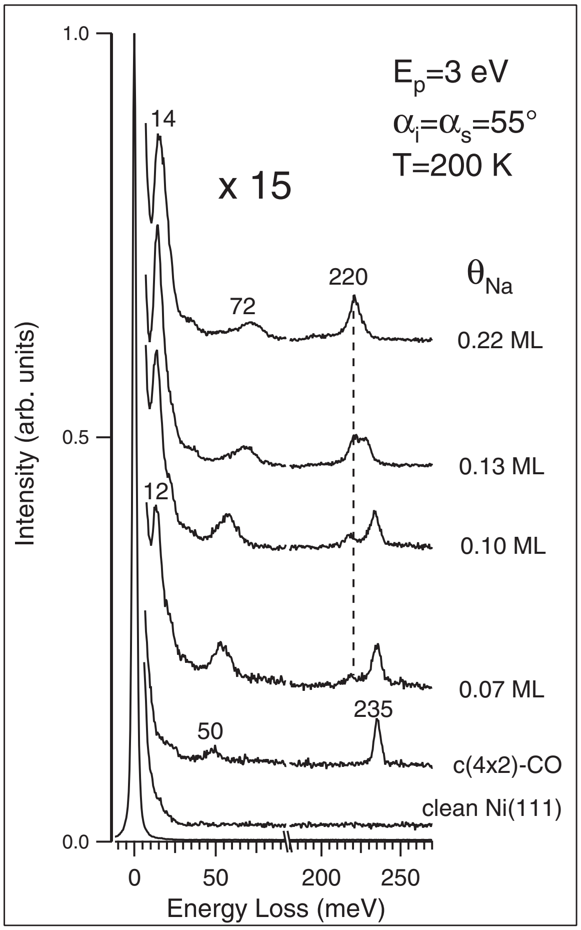

FIG. 3. Electron energy loss spectra of $c(4\times 2)$-CO prepared at 200 K and after deposition of different amounts of Na at the same temperature.

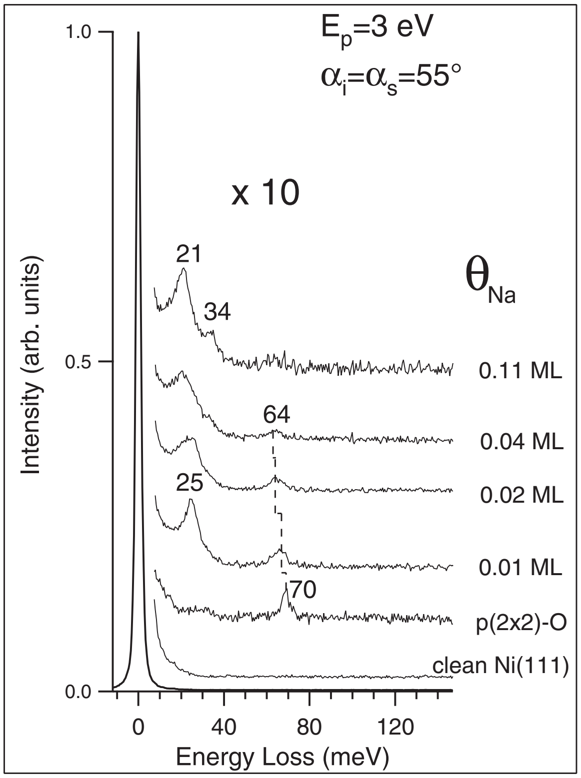

FIG. 4. Electron energy loss spectra of p(2-2)-O prepared at 400 K and after deposition of different amounts of Na at the same temperature.

ecules was unexpected and never observed before. During the investigation of the structural properties of K/CO on Ni(111) and on Ni(100),[20,21] a significant increasing of the alkali-substrate bond length was revealed with respect to the case of K/Ni(111) and K/Ni(100). Such finding was not completely understood, but it is in excellent agreement with the weakening of the Na-Ni bond reported in this work.

The bond of CO with metal surfaces is explained within the donation-backdonation model.[22,23] The stretching frequency of CO strongly depends on the population of the $2\pi^*$ orbitals as occupied antibonding orbitals weakens the C-O bond.[24] On the other hand, the CO-Ni bond depends on the electron donation from the CO-5σ orbitals to the Ni surface and the back-donation from the substrate into the $2\pi^*$ orbitals of CO.[24] The alkali-induced lowering of the C-O stretching frequency has been ascribed to an enhanced back-donation from the substrate into the $2\pi^*$ molecular states promoted by alkalis.[25,26] Nevertheless, the physical mechanisms describing the charge donation are very different one from each other. He and Jacobi[27] studied CO/Cs on Ru(0001) and assumed a two-step process: Preadsorbed alkalis donate their charge to the metal surface and then such charge is back-donated to coadsorbed CO molecules. Their measurements were interpreted assuming a long-range interaction between CO and Cs. Instead, calculations by Wimmer *et al.*[25] led to a picture of alkali s electrons polarized towards the surface. The alkali-induced dipole layer causes a shift of all electronic states of CO towards the Fermi level, favoring a charge transfer from the metal surface into the $2\pi^*$ orbitals. In others "electrostatic models,"[9,28] the electric field causing the enhanced electron back-donation was assumed to be arising from alkali atoms adsorbed in a full ionic state. Recently, Stolbov and Rahman[14] showed that the softening of the internal bond in diatomic molecules, such as CO and O_2 adsorbed on Cu(111) and Pd(111), was caused by an enhancement of the surface electronic polarizability induced by preadsorbed K atoms (nonlocal model). Unfortunately, in all these studies the vibrational properties of alkali atoms were not considered either before or after the coadsorption with molecular species.

Our loss spectra provide direct evidences that the shifts of the Na-Ni and C-O stretching frequencies are related to each other and we suggest that they are correlated to the charge state of both CO molecules and Na atoms. The adsorption of CO on the Ni(111) surface precovered with Na and vice versa is accompanied by a significant donation of charge from Na atoms into CO molecules. Moreover, the strengthening of the CO-Ni bond (Fig. 3) confirms experimentally the alkali-induced charge transfer from CO-5σ to the metal surfaces induced by alkali atoms, as found by Wimmer *et al.*[25] and by Jenkins and King.[26] Present measurements indicated that Na and CO should be in close contact on the metal surface for charge transfer to take place. Accordingly, we suggest that the action of CO on the Na adatoms is a local effect. The similar Na+CO/Cu(111) system studied by Svensson[29] exhibited an analogous behavior, i.e., the action of Na on CO molecules was found to be very local, in disagreement with the nonlocal electron transfer process (Wimmer and Stolbov models).

In order to ascertain whether the same mechanisms, i.e., charge transfer processes, apply for other systems, we investigated the coadsorption of Na with oxygen. Carbon monoxide and oxygen are both electronegative species with respect to Na atoms and they could behave in the same way. A $p(2\times2)$-O structure was prepared at 400 K and several coverages of Na were deposited on this phase at the same temperature. The loss spectrum of the $p(2\times2)$-O showed the O-Ni mode at 70 meV and an induced phonon at 30 meV (Fig. 4). After the deposition of Na on the oxygen layer, the Na-Ni stretching appeared at 25 meV while the O-Ni vibration shifted from 70 meV down to 64 meV. For Na coverages between 0.04–0.11 ML, a new feature appeared at 34 meV and the Na-Ni peak shifted to 21 meV. The feature at 34 meV was assigned to the O-Na stretching mode. The weakening of the O-Ni bonding may be due to the formation of Ni-oxygen-Na bonds or a charge transfer from the metal surface to the antibonding states of adsorbed oxygen atoms, as found for K/O/Rh(111).[30] No other changes were observed for higher Na coverages. Hence, present results unambiguously indicated that Na atoms donate charge to CO molecules, but they do not donate any charge to oxygen atoms.

In conclusion, we have presented loss measurements providing direct evidences of a dramatic lowering of the Na-Ni stretching frequency in the presence of coadsorbed CO. The effect was ascribed to a local charge transfer between the coadsorbed species. Such charge donation is responsible of the weakening of the C-O and Na-Ni stretching vibrations and of the strengthening of the CO-Ni bond. Calculations including the effects reported here (the CO-induced weakening of the Na-Ni mode) are needed to clarify the basic mechanisms of the alkali-CO bond and alkali promotion effects.

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