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Vibrational measurements of Na/Ni(111) and (Na + CO)/Ni(111)

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Abstract The vibrational properties of Na atoms and of Na coadsorbed with CO on Ni(111) have been studied by high-resolution electron energy loss spectroscopy. Loss measurements showed a significant weakening of the alkali–substrate bond as a function of the alkali coverage. Moreover, we found that coadsorbed CO molecules dramatically influence the vibrational properties of Na adatoms. The Na–Ni stretching frequency (22 meV) measured on the Na/Ni(111) system shifted down to 13 meV for the (Na + CO)/Ni(111) surface. This unexpected result was ascribed to a charge transfer from Na to CO. Present findings give new insights on the nature of the alkali–substrate and alkali–CO bond.

Introduction

The adsorption and coadsorption properties of alkali metals on metal surfaces have motivated the experimental and theoretical research aimed at providing new insights into the alkali–substrate [1] and alkali–adsorbate interactions [2]. The alkali-metal atom is regarded as the prototype system for modeling chemisorption and coadsorption. Such processes are of great interest in several applications such as heterogeneous catalysis, corrosion, and oxidation [3, 4]. Despite the great effort, the nature of the alkali–substrate bond is still under investigation and no conclusive results have been reached. In the Gurney model [5], the alkali atoms transfer their valence charge to the substrate and the bonding is ionic; on the contrary, at higher coverages the alkali–alkali interaction dominates over the alkali–substrate interaction, and the overlayer assumes a metallic character. However, Ishida [6, 7] questioned the ionic model and demonstrated that, regardless of the coverage, the alkali–substrate bond has essentially a covalent character. Ishida's predictions were confirmed by the photoemission measurements [8]. Nonetheless, the covalent model was not accepted.

The coadsorption of CO with alkali metals on transition metal surfaces has also been extensively investigated [9]. High-resolution electron energy loss spectroscopy (HREELS) and infrared reflection absorption spectroscopy measurements revealed a notable lowering of the C–O stretching frequency in the CO-alkali coadsorbed phase [10, 11]. Such finding stimulated a great interest and several investigations aimed at understanding the chemical and physical origins of the softening of the C–O vibration were performed. The weakening of the C–O bond favors the dissociation and the reactions of CO with other species, i.e., the Fischer–Tropsch process. To date, many effects had been considered as responsible of the softening of the C–O stretching: electrostatic interactions [12, 13], surface states [14], direct [15], and indirect chemical interactions mediated by the substrate [16]. Furthermore, a recent [17] theoretical work reported that such lowering is caused by the alkali-induced electronic polarizability of the metal surface.

However, the achieved results have not yet been conclusive and new experimental investigations are needed to clarify the adsorption properties of alkali atoms on metal surfaces and the alkali–CO interaction.

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In this study, HREELS measurements taken for Na adsorbed on Ni(111) and for the (Na + CO)/Ni(111) coadsorbed phase are reported. First, the Na–Ni stretching vibration was measured as a function of the alkali coverage and, successively, we focused our attention on the effects of CO on the vibrational properties of Na atoms. This point is particularly important, as previous studies of the coadsorption of alkali atoms with CO were focused exclusively on the shift of the C–O vibration, while the effects caused by CO on the vibrational properties of alkali atoms were completely disregarded.

The Na–Ni stretching energy was found to decrease as a function of the alkali coverage. Moreover, the Na–Ni mode measured in the presence of coadsorbed CO molecules was unexpectedly found to downshift by about 10 meV with respect to the Na–Ni vibration measured for Na adsorbed on the clean Ni(111) surface (22 meV).

Experimental

High-resolution electron energy loss 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 of 3 eV and an energy resolution between 2.0 and 3.0 meV. The Ni(111) surface was prepared by repeated cycles of ion sputtering ($E_p =$ 1.5 keV) and annealing to 1,000 K. Low energy electron diffraction (LEED) and Auger electron spectroscopy were used to check surface order and cleanliness, respectively. Na atoms were deposited onto the Ni(111) surface by a dispenser, which was carefully degassed for several days at a pressure of 2–4 $\times 10^{-8}$ Pa. CO molecules were admitted in the chamber by means of a precise leak-valve. Alkali and CO coverages were determined from the exposure time taking as reference the coverage of well-known LEED structures: c(4 × 2)-CO and ($\sqrt{3} \times \sqrt{3}$)R30°-Na.

Results and discussion

Loss spectra of Na deposited on Ni(111) at 400 K are shown in Fig. 1a. The Na–Ni stretching vibration was revealed at about 25 meV for a very low coverage (0.01 ML). Increasing Na coverages (0.06 ML), this peak shifted down to 21–22 meV (Fig. 1b). No further variation of the Na–Ni stretching energy was observed for higher coverages. Previous loss measurements [18] and calculations [19] performed on Na/Cu(111) as a function of the Na coverage found a constant energy of 21–22 meV for the Na–Cu mode. During these measurements, we noticed that the presence of even small amounts of CO had a dramatic influence on the Na–Ni stretching vibration. Accordingly, much care was devoted to avoid any contamination of the surface. Very clean layers of alkali metals could be obtained with the Ni(111) surface held at 400 K during both deposition and measurements.

In order to accurately investigate the effects of CO molecules on the vibrational properties of Na, clean layers of Na were exposed to CO at room temperature. Unexpectedly, the loss spectrum of Na/Ni(111) changed upon CO exposure (Fig. 2). The Na–Ni stretching frequency shifted from 22 down to 13 meV and, moreover, the line

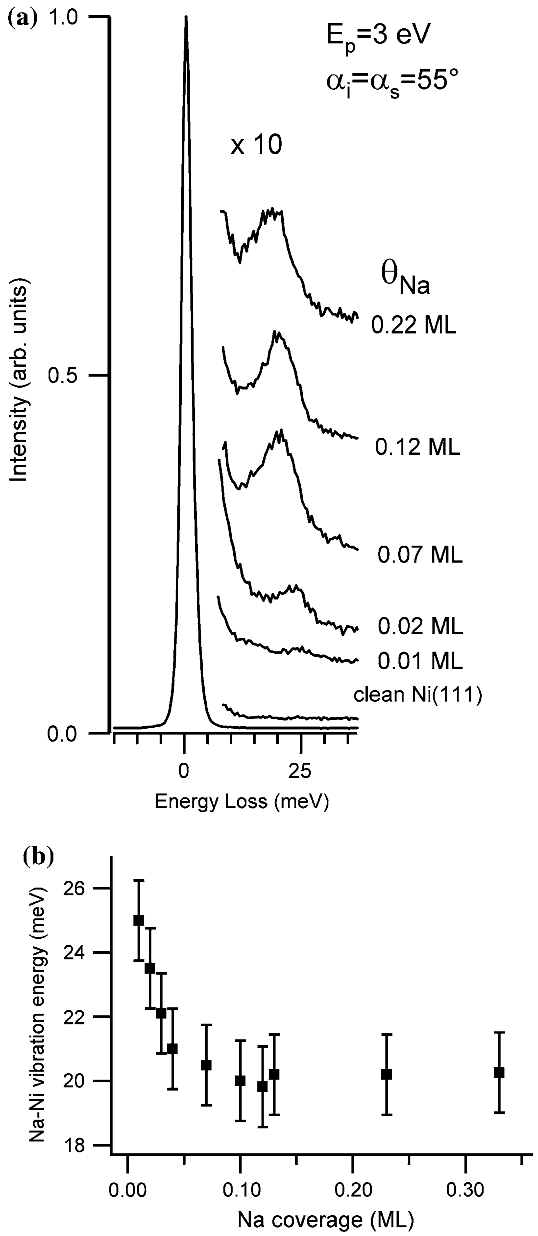

Fig. 1 (**a**) HREEL spectra of Na deposited at 400 K onto the Ni(111) surface as a function of the alkali coverage. (**b**) Na–Ni vibration energy as a function of the Na coverage

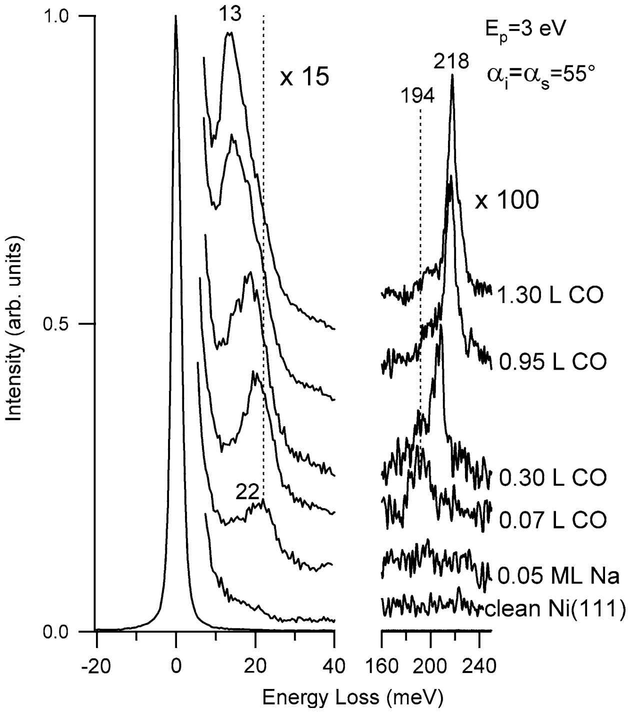

Fig. 2 HREEL spectra for 0.05 ML Na/Ni(111) at 400 K for different CO exposures at room temperature

shape of such peak became narrower. The C–O stretching energy, initially at 194 meV (0.07 L of CO), shifted upward to 218 meV (for higher CO exposure). As a comparison, the C–O stretching frequency is 235 meV for c(4 × 2)-CO/Ni(111) (0.5 ML of CO) [20]. Interestingly, the coadsorption process affected both the Na–Ni and the C–O vibrations and their frequencies were found to depend on the Na/CO ratio. We suggest that the energy shift of the Na–Ni mode induced by CO molecules should be taken into account in any realistic model describing the coadsorption of alkali and CO on metal surfaces.

The weakening of the Na–Ni bond induced by CO molecules was not previously reported and its observation may be the key to understand the basic mechanisms of the catalytic activity of alkali atoms. A remarkable increasing of the alkali–substrate bond length in the coadsorbed phase was observed in the investigation of the structural properties of K/CO on Ni(111) and K/CO on Ni(100) [21, 22]. This finding was not completely understood; nonetheless, it is in excellent agreement with the weakening of the alkali–substrate bond reported in this work.

The stretching frequency of CO adsorbed on metal surfaces is strictly related to the electronic population of the $2\pi^*$ orbitals as the occupation of such antibonding orbitals weakens the C–O bond. Most existing models interpreted the lowering of the C–O stretching frequency induced by the alkali coadsorption in the above framework.

Nevertheless, the physical mechanisms leading to the charge back-donation into the empty $2\pi^*$ orbital of CO are very different from each other. He and Jacobi [23] studied the coadsorption of Cs with CO on Ru(0001) and assumed a two-step process: pre-adsorbed alkalis donate their charge to the metal surface and then such charge is back-donated to CO coadsorbed molecules. Instead, calculations by Wimmer et al. [12] led to a picture of alkali s electrons polarized toward the surface. The alkali-induced dipole layer causes a shift of all CO electronic states toward the Fermi level favoring an enhanced charge transfer from the surface metal to the $2\pi^*$ orbital. In other “electrostatic models”, alkali atoms were assumed to be in an ionic state. A recent model explaining the softening of the C–O bond was proposed by Stolbov and Rahman [17]. It is based on an alkali-induced enhancement of the surface electronic polarizability. These authors showed that the strong electronic polarizability of Cu(111) and Pd(111) surfaces induced by the pre-adsorbed K atoms (0.25 ML) causes a red shift in the C–O and O–O stretching frequencies. Unfortunately, the effects of coadsorbed CO molecules on the vibrational properties of K atoms were not considered also in that study.

In order to investigate whether others effects (e.g., screening effects among coadsorbates) could be at the origin of the lowering of the Na–Ni vibration frequency, the (Na + CO)/Ni(111) surface was exposed to oxygen (Fig. 3). It is evident that oxygen atoms did not influence the Na–Ni stretching vibration.

Furthermore, in order to verify the possibility of the occurrence of alkali-induced promotion effects, the Na/Ni(111) surface was exposed to CO at 400 K (Fig. 4). We found the existence of a critical alkali-metal coverage for the CO dissociation. A partial dissociation of CO occurred at both 400 K and room temperature provided that the alkali coverage was sufficiently high.

For a CO exposure of only 0.20 L ($1\ \mathrm{L} = 1 \times 10^{-6}$ mbar s), the critical alkali precoverage for carbon monoxide dissociation at 400 K was 0.10 ML as revealed (Fig. 4) by the appearance of the Na–O vibration at 33 meV. For $\sqrt{3} \times \sqrt{3}R30^\circ$ − Na (0.33 ML) such vibration was found at 36 meV, while at the saturation of the first Na layer (0.44 ML) its loss energy shifted up to 38 meV. The presence of such vibrational mode unambiguously demonstrated the partial dissociation of carbon monoxide into atomic oxygen and carbon. Very likely, sodium atoms essentially interact with highly electronegative oxygen atoms rather than with carbon atoms, thus explaining the absence of a carbon-substrate vibrational mode. The presence of the Na–O bond did not influence the Na–Ni stretching energy, as any shift of Na vibration was measured. The direct alkali–oxygen interaction was found to reduce the dissociation barrier [9]

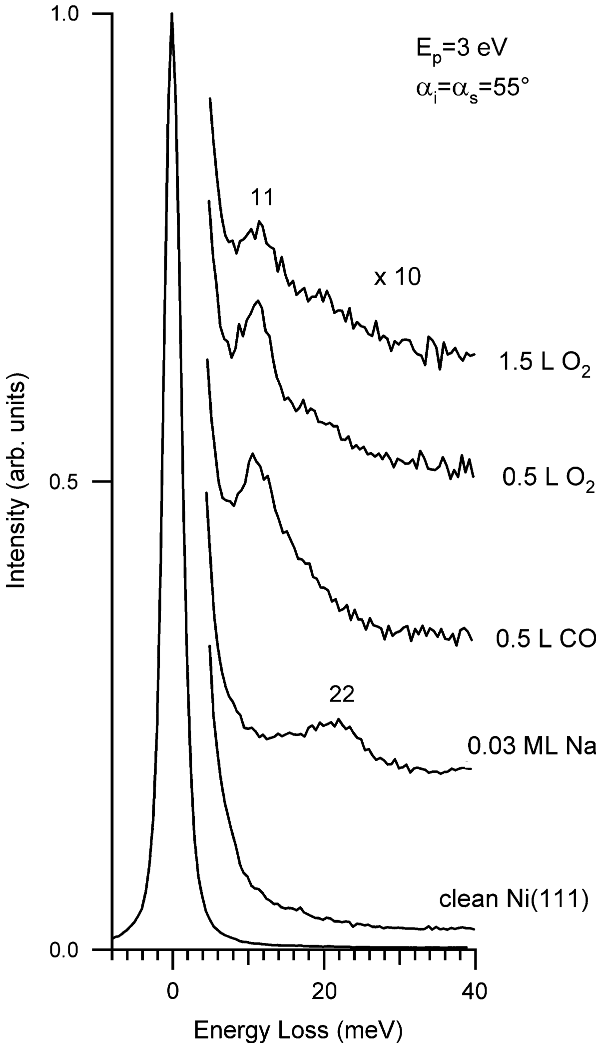

Fig. 3 HREEL spectra for 0.03 ML Na/Ni(111) exposed at room temperature to CO and successively to O_2

and was suggested to be the main physical origin of alkali-promoted CO dissociation.

Present loss measurements may simultaneously elucidate on the nature of the alkali–substrate and alkali–CO bond. The alkali–substrate bond is stronger at low coverages and becomes weaker as the alkali coverage was increased (Fig. 1). Such behavior is rather different from that reported in previous studies. For K on Pt(111) [24] and Na and K deposited on copper surfaces [18], the alkali-metal stretching energy was found to increase as a function of the alkali coverage. No convincing explanations were given for this unexpected finding. Instead, our results are in excellent agreement with Ishida's covalent model [6, 7]. As a matter of the fact, the adsorbate–substrate interaction dominated at low coverages and became less important as the alkali coverage increased. Moreover, the presence of CO molecules affected the Na–Ni stretching energy, which shifted toward lower energies. The energy shifts of the Na–Ni and C–O stretching vibrations were strictly related to each other (Fig. 2). We suggest that the shift of the alkali–substrate and C–O modes are correlated to the charge state of CO molecules and Na atoms. A significant charge transfer from Na atoms to CO molecules accompanied the adsorption of CO onto the Na-precovered Ni(111) surface. Loss measurements indicate that alkali atoms form a covalent bond at low coverages and a metallic bond at higher coverages. Strong support to this picture arises from the results of Figs. 1 and 2 which directly prove that initially the alkali atoms are almost in a neutral charge state and that their ionization occurs only if coadsorbed with CO. The transition from the covalent state to the metallic one occurs at very low coverages.

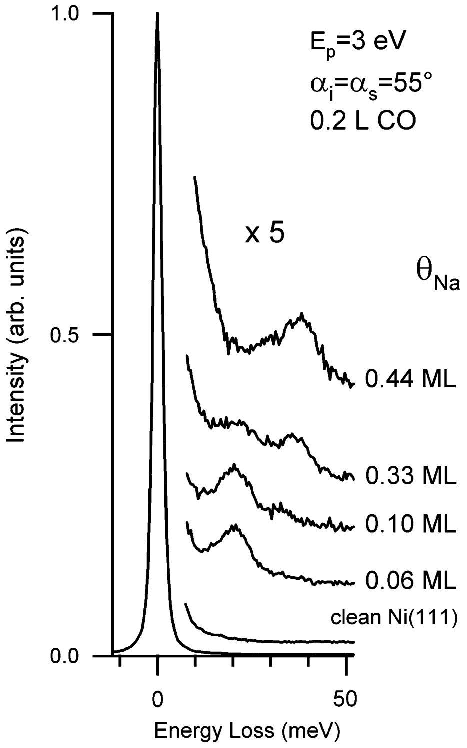

Fig. 4 HREEL spectra of 0.20 L of CO dosed at room temperature on different Na sub-layers prepared at 400 K on Ni(111)

Concluding remarks

In conclusion, we have presented loss measurements providing direct evidence of a dramatic lowering of the Na–Ni stretching frequency in the presence of coadsorbed CO. Alkalis adsorbed on clean Ni(111) donate almost no charge to the substrate (covalent bond). On the contrary, a charge transfer from Na to CO was found to occur in the (Na + CO) coadsorbed phase. Calculations including the new effects reported here (the weakening of the Na–Ni mode) are needed for elucidating the basic mechanisms of the alkali–CO bond and the alkali promotion effects.

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