

## Adsorbate-induced electronic modification of alkali-metal overlayers

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For submonolayer coverages of Cs on Ru(0001) surfaces, the Cs-Ru vibration is observed at 7.8 meV ( $63 \text{ cm}^{-1}$ ) by means of high-resolution electron-energy-loss spectroscopy. At Cs coverages near the complete monolayer the adlayer becomes metallic as indicated by screening of the Cs-Ru vibration and the occurrence of an electronic excitation (plasmon) at 580 meV. Coadsorption of CO as well as of oxygen leads to the reappearance of the Cs-Ru vibration and the disappearance of the electronic excitation which is interpreted as a demetallization through chemical interaction with the coadsorbed species.

Alkali-metal overlayers adsorbed on transition-metal surfaces play an important role as “electronic” promoters in heterogeneous catalysis<sup>1</sup> and have been extensively studied in the past.<sup>2</sup> Frequently, they facilitate bond breaking of adsorbed particles involved in the catalytic reaction, and the related modifications of the electronic properties of these coadsorbates have been studied in detail, mainly by using carbon monoxide as a test molecule.<sup>3</sup> Here we demonstrate how these interactions in turn also affect the properties of the adsorbed alkali-metal atoms. The vibrations of Cs atoms adsorbed on a Ru(0001) surface against the substrate may be excited by impinging low-energy electrons and are monitored as characteristic energy losses as long as the coverage is small. At higher coverages, the closer distances between the Cs adatoms cause the overlayer to become metallic, and as a consequence, dipole fluctuations are screened very efficiently by the two-dimensional electron gas so that excitation of the vibrations via dipole scattering is no longer feasible. This becomes possible again, however, after subsequent adsorption of CO or oxygen, which is the way the electronic coupling between the alkali adatoms is suppressed. In addition, observed shifts of the Ru-Cs vibration to higher energies indicate substantial strengthening of this bond, and thus corroborates more indirect conclusions of a recent calorimetric study with a related system.<sup>4</sup>

The experiments were performed with an ultrahigh-vacuum apparatus working at a base pressure of  $3 \times 10^{-11}$  mbar, which was equipped with a high-resolution electron-energy-loss-spectrometer (HREELS) enabling us to record vibrational spectra with a resolution of about 3 meV ( $24 \text{ cm}^{-1}$ ).<sup>5</sup> The primary energy of the electron was 2.5 eV. The measurements were performed in specular geometry at an angle of  $60^\circ$  with respect to the surface normal. The surface of the single-crystal Ru sample with (0001) orientation was cleaned by standard techniques, and the state of the surface was probed by low-energy electron diffraction (LEED) and photoelectron spectroscopy. Cs atoms were deposited onto the surface by evaporation from a breakseal ampoule. Their coverage  $\Theta$  is defined as the ratio of the densities of adatoms over that of Ru atoms in the top-most layer of the substrate. Saturation of the first monolayer is achieved around  $\Theta=0.33$  where the nearest-

neighbor distance is 4.64 Å; the Cs atoms are located in threefold-coordinated sites and form an ordered  $\sqrt{3} \times \sqrt{3} R30^\circ$  superstructure.<sup>6</sup>

The HREEL spectra of Fig. 1 are recorded at 300 K from a Ru(0001) surface with a Cs overlayer of  $\Theta=0.08$ . At this coverage, the dipole-dipole repulsion between the adparticles causes the formation of a liquidlike configuration exhibiting short-range order with a mutual Cs-Cs separation of about 9.5 Å.<sup>7</sup> In this range of coverages, there is still a continuous decrease of the work function with  $\Theta$ , indicating the “ionic” character of the substrate-adsorbate bond, and the distances between neighboring Cs atoms exceed by far those in the bulk metal, so that not yet substantial mutual orbital overlap takes place. A peak at a loss energy of 7.8 meV in the HREEL spectrum is attributed to excitation of the Cs-Ru vibration. This Cs vibration is resolved here. (There is likewise an anti-Stokes peak at  $-7.8 \text{ meV}$  due to deexcitation of this vibrational mode.) A comparison with vibrational energies of other alkali-metal atoms adsorbed

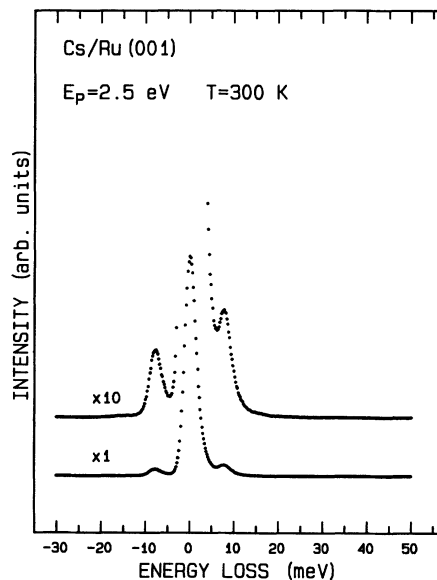


FIG. 1. HREELS for a Ru(0001) surface covered with a fraction of a monolayer of Cs ( $\Theta_{\text{Cs}}=0.08$ , with respect to the number of surface atoms).

TABLE I. Energies  $E_x$  for an alkali metal  $x$  against surface vibration as calculated from  $E_x = E_{Na} (m_a/m_x)^{1/2}$  where  $m_x$  is the atomic mass of the alkali metal and  $E_{Na} = 20$  meV is assumed. Experimental values are also given.

Alkali $x$	$E_x$ (meV)	exp. value (meV)	Reference
Li	36	35–38	8,12
Na	20	18–21	8–11
K	15.4	12–18	8,9,13,14
Rb	10.4		
Cs	8.3	7.8	this work

on transition-metal surfaces as reported in the literature<sup>8–14</sup> is given in Table I. It shows furthermore that the vibrational energies scale approximately with the square root of the mass, indicating similar force constants, and hence also similar binding properties, which are essentially governed by the high-lying valence levels of the alkalis.

The Cs-Ru vibration observed for  $\Theta_{Cs} = 0.08$  weakens in intensity and finally disappears completely at higher Cs coverages. This is shown in Fig. 2 in which curves *A* and *B* are recorded for  $\Theta = 0.25$ , which is about 75% of the saturation of the monolayer. No vibrational energy loss is observed at 7.8 meV from Cs or at higher energies from any adsorbate. At  $\Theta = 0.25$ , the Cs atoms form an ordered  $2 \times 2$  overlayer in which the nearest-neighbor separations have decreased to 5.4 Å. In this range, the work function attains its minimum caused by strong mutual depolarization of the dipoles and the overlayer becomes metallic in nature. The increasing dipole-dipole repulsion causes, in addition, a strong decrease of the adsorption energy with increasing coverage as reflected by thermal-desorption-spectroscopy data, and hence also a lowering of the vibrational frequency is to be expected. However, HREELS features are no longer discernible due to the pronounced screening of dipole excitations by the laterally delocalized valence electrons. This is observed here for

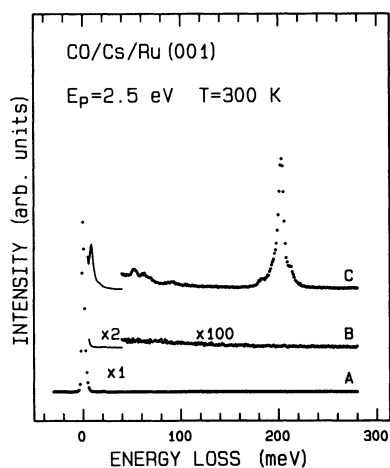


FIG. 2. HREEL spectra for a Ru(0001) surface covered with Cs at  $\Theta_{Cs} = 0.25$  (curves *A* and *B*) and for the same surface after saturation with CO at a dose of  $6 \times 10^{-6}$  mbar s (curve *C*). The energy of the primary electrons  $E_p$  is given.

a Cs adsorbate in full agreement with the finding for the lighter alkalis.<sup>8–12</sup> The delocalized valence electrons manifest themselves in addition by the emergence of an electronic (plasmon) excitation at 580 meV. Electronic excitations in adsorbed alkali-metal layers on Al, Ag, and Cu surfaces have been studied thoroughly in recent years.<sup>15–19</sup> These studies can help to qualitatively understand the behavior of the Cs layer on a transition-metal surface like Ru(0001), but we will not discuss this point here in greater detail.

The spectrum *B* of Fig. 2 changes completely after subsequent adsorption of CO. In curve *C* of Fig. 2, one recognizes the strong C-O stretching vibration at 203 meV ( $1637 \text{ cm}^{-1}$ ), a weak loss at 52 meV ( $420 \text{ cm}^{-1}$ ) due to the CO-Ru vibration, and a very strong loss at about 8 meV ( $64 \text{ cm}^{-1}$ ). (Note that the scaling factor is only 2 at this energy in curves *B* and *C*.) From its energy and intensity we attribute this loss to the Cs-Ru vibration, which reappeared during coadsorption of CO.

Due to the interaction with Cs, the C-O stretching mode is lowered in energy from 252 meV at the bare Ru(0001) surface<sup>20</sup> to 203 meV in the coadsorbate layer. For a number of other surfaces, it was found that the actual value of the C-O stretching frequency varies with the CO:Cs ratio<sup>21</sup> and that the value of 203 meV is compatible with a 1:1 ratio for CO to Cs in the coadsorbate layer. This is supported from a qualitative analysis of the LEED pattern: The  $2 \times 2$ -Cs structure rearranges into a sharp  $(2 \times 2)$ -(Cs+CO) structure. Since at least one Cs atom and one CO molecule are required in the unit cell, at first sight it appears somewhat surprising that a Cs layer with a density of 75% of its maximum value is able to accommodate about  $\frac{3}{4}$  of a full monolayer of CO, which exhibits a  $\sqrt{3}$  structure on the bare Ru(0001) surface at saturation coverage. Obviously, there occurs some lateral attraction in the coadsorbate, which leads to a very densely packed  $(2 \times 2)$ -(Cs+CO) coadsorbate phase. Future studies have to determine the structure of the  $(2 \times 2)$  layer in detail. The main C-O stretching loss at 203 meV in curve *C* of Fig. 2 is accompanied by some weak satellite lines, which are assigned to CO minority species (184 meV) and to combination losses ( $203 + 8 = 211$  and  $203 - 8 = 195$  meV). Finally, we note that the intensity of the CO-Ru vibration is smaller by about a factor of 10 compared to the intensity found at the bare Ru surface. Obviously, the excitation of this vibration is strongly shielded in the coadsorbate layer.

The strong change in the vibrational properties of Cs on Ru(0001) induced by coadsorbed CO is not peculiar to the interaction with CO, but is even more pronounced upon coadsorption of oxygen, as shown in Fig. 3. In curves *A* and *B*, the data of Fig. 1 are reproduced for comparison. Curve *C* shows the result for the Cs+CO coadsorbate system discussed above at better energy resolution. Besides the loss, the gain is also resolved. Curve *D* in Fig. 3 was recorded after admission of  $O_2$  onto the Cs layer with  $\Theta_{Cs} = 0.25$ . The energy of the Ru-Cs vibration now is increased to 10 meV, while the peak at 23 meV originates from the Cs-O vibration indicating dissociative adsorption.<sup>22</sup>

The reappearance of the Cs-Ru vibration in the

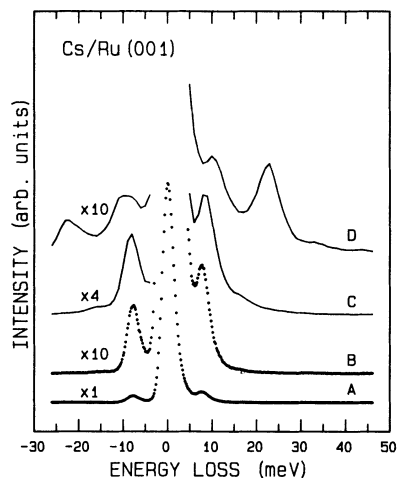


FIG. 3. HREEL spectra for Ru(0001) surfaces at 300 K. Curves *A* and *B*: The Cs coverage is  $\Theta_{\text{Cs}}=0.08$ . Curve *C*:  $\Theta_{\text{Cs}}=0.25$  and subsequent saturation with CO ( $10^{-5}$  mbar s). Curve *D*:  $\Theta_{\text{Cs}}=0.25$  and subsequent saturation with O<sub>2</sub> ( $4 \times 10^{-6}$  mbar s).

HREEL spectra has to be attributed to a “demetallization” of the Cs adlayer through the presence of interstitial coadsorbed species as sketched schematically in Fig. 4. Panel *A* shows the Cs layer at low coverage. The bonding is basically “ionic,” and the charge accumulation between the surface and the center of the Cs atom is due to the response of the metal surface in order to screen the Cs<sup>+</sup> core.<sup>23,24</sup> Panel *B* depicts the situation for the rather densely packed Cs layer, which is metallic as indicated through the delocalized electron density. In this state we observe an interface plasmon centered at 580 meV, which vanishes during coadsorption of CO as well as of O. The latter situation is sketched in panel *C*: The Cs cores are kept at the same lateral distance, the delocalized charge is withdrawn, and coadsorbed species, which is CO in panel *C*, are “squeezed” in between the Cs<sup>+</sup> cores. The reappearance of the alkali-metal-substrate vibration was also observed for the interaction of H<sub>2</sub>O with an Na layer of Cu(111) recently.<sup>25</sup> Arguments were given that NaOH is formed bonded to the Cu substrate with its axis in an upright position. For the Cs + CO coadsorbate on Ru(0001), the adsorbate-induced electronic modification is similar, but the process itself is completely different since no direct bond between Cs and CO is formed.

For CO, the Cs-Ru vibration appears at nearly the same energy as in Fig. 1, suggesting also comparable bond strengths of the Cs atoms to the Ru substrate. Since now, however, the Cs coverage is much higher (0.25 compared to 0.08), we have to conclude that the addition of CO increases the effective strength of the Ru-Cs bond. This conclusion is nicely confirmed by the results of a recent calorimetric study.<sup>4</sup> Adsorption of CO on a K-precovered Ni surface yielded a net energy gain of about 180 kJ mol<sup>-1</sup>, which was attributed only in part to the formation of the Ni-CO bond, while the remaining

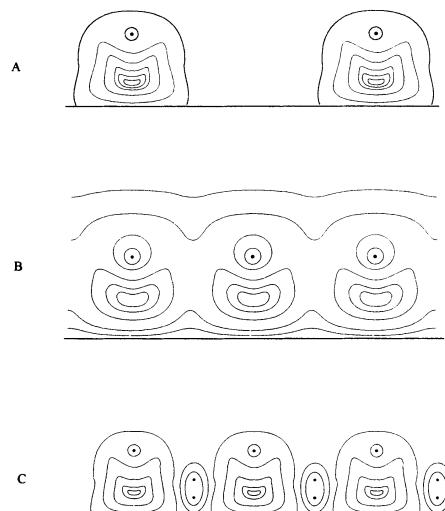


FIG. 4. Schematic charge densities induced by different adsorbates: (a) isolated, essentially ionically bound Cs atoms, (b) more densely packed Cs layer at a coverage of  $\Theta_{\text{Cs}}=0.25$  in the metallic state with delocalized charge distribution, and (c) the Cs+CO coadsorbate layer. The Cs<sup>+</sup> cores are indicated by a dot surrounded by a small circle. While the pictures of the Cs-induced charge densities are inspired by recent charge-density calculation for alkali atoms at Al surfaces (Refs. 23 and 24), the picture of CO is even more schematic.

substantial fraction was suggested to be due to strengthening of the Ni-K bond. For oxygen, the effect in the vibrational spectrum is even more pronounced as the Cs-Ru vibration is now shifted to 10 meV. A LEED analysis with the related  $\sqrt{3} \times \sqrt{3} R 30^\circ$ -Ru(0001) phase with  $\Theta_{\text{Cs}}=\Theta_{\text{O}}=0.33$  had revealed that the O atoms are located in threefold hollow sites below the plane formed by the Cs atoms.<sup>26</sup> A reduction of the effective Cs radius (if compared with the oxygen-free phase) by about 0.1 Å signaled a depletion of electronic charge from the Cs atoms, which thus become more “ionic.” Quite a similar “demetallization,” for which we give spectroscopic evidence here, was suggested in modeling work-function changes of O<sub>2</sub> (CO) and Na coadsorbate layers recently.<sup>27</sup>

We have already noted that the intensity of Cs-Ru vibration found in the spectra of Fig. 1 is very large. Using the measured loss intensity, one may determine a dynamic dipole moment  $\mu$  from dipole-scattering theory. An effective dynamic charge  $Q$  can then be calculated from  $\mu=Q(\hbar/2M_r\omega)^{1/2}$ .<sup>28,29</sup> For a rigid Ru lattice, the reduced mass  $M_r=M_{\text{Cs}}$  and the following dynamic charges are calculated:  $Q=1.36 e^-$  for  $\Theta_{\text{Cs}}=0.08$ ,  $1.3 e^-$  for the Cs+CO coadsorbate, and  $0.85 e^-$  for the Cs+O coadsorbate. These values are larger than, e.g., the value of  $0.5 e^-$  found for Na on Cu(111) at  $\Theta_{\text{Na}} \rightarrow 0$  (Ref. 11) as becomes plausible from the different size of the ions. The size of  $Q$  in the case of Cs also underlines the fact that it is a dynamic charge, which is considered here.

In conclusion, we have found spectroscopic evidence

that a metallic Cs layer is demetallized through the interaction with coadsorbed species at a transition-metal surface. While the influence of an alkali-metal (promoter) on the coadsorbed molecule has already been extensively discussed in the literature, we have demonstrated spec-

troscopically that these interactions in turn also affect the properties of the adsorbed alkali-metal atom.

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