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Interaction of Cs and CO on Ru(0001) for Cs submonolayer coverages

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The interaction of Cs and CO was studied for submonolayer coverages of Cs on Ru(0001) by means of high-resolution electron energy-loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS), and low-energy electron diffraction (LEED). From the HREEL spectra and the 2×2 LEED pattern it is concluded that two-dimensional islands of Cs+2CO stoichiometry are formed first. For high CO doses CO adsorbs on the bare Ru surface between the islands as concluded from the $\nu(\text{C-O})$ stretch-mode frequency and the $(\sqrt{3}\times\sqrt{3})R30^\circ$ LEED pattern. Besides some local interaction between CO and Cs, there is strong evidence found for a long range, through substrate interaction. Our data can be understood in terms of a charge redistribution model; Cs donates a given amount of charge to the surface which is then backdonated to and shared between the adsorbed CO molecules within the (Cs+2CO)-islands and outside of them on the bare surface. The desorption temperature of CO with $\theta_{\text{CO}}\rightarrow 0$ increases nearly linearly with θ_{Cs} indicating CO desorption out of a two dimensional Cs gas in which the lateral interaction increases with θ_{Cs} .
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I. INTRODUCTION

The coadsorption of Cs and CO molecules on transition metal surfaces is of great importance as this system is thought to model the promotion effect in heterogeneous catalysis.^{1,2} There have been several models discussed in the past. Some of them consider that the surface potential is locally lowered by the alkali metal which enhances the backdonation of charge to the CO molecule.¹⁻⁵ Others propose a direct interaction between the alkali metal and the CO through the formation of a surface complex.^{6,7} Finally, a polarization model was proposed which involves pure electrostatic interaction.⁸⁻¹¹ Besides a local, short-range effect we believe that our experiment gives strong evidence for a long-range effect; Cs donates a given amount of charge to the surface which is then backdonated to and shared between the different CO molecules on the surface. Our analysis is based on recent structure analyses of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ -CO,^{12,13} 2×2 -Cs,¹⁴ and 2×2 -(Cs+2CO) Ref. 15 structures and their associated vibrational spectra for CO,^{16,17} Cs,^{18,19} and Cs+2CO.²⁰⁻²²

Two further topics are discussed; HREELS and LEED clearly indicate that, for submonolayer amounts of Cs, CO forms two dimensional islands first. Due to the high lateral mobility of Cs we suppose that this cannot easily be shown by scanning tunneling microscopy (STM). Furthermore, the analysis of the thermal desorption spectroscopy (TDS) results shows that, in the composite layer, CO desorbs from a two-dimensional Cs gas.

II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) apparatus with a base pressure of 1×10^{-11} mbar which was achieved by a pumping line free of oil con-

sisting of a Ti sublimation pump, a turbomolecular pump with magnetic suspension (NT340M, Leybold), a drag pump (TCP015, Balzers), and a diaphragm pump (MD4T, Vacu-brand). The apparatus consisted of two chambers. The upper chamber contained an argon ion gun, a quadrupole mass spectrometer, a low-energy electron diffraction (LEED) optics, and a Cs effusion cell. The lower chamber housed a high-resolution electron energy-loss (HREEL) spectrometer for recording vibrational spectra. The two chambers were separated by a valve in order to keep the lower chamber at a pressure of 3×10^{-11} mbar during preparation of the sample in the upper chamber.

The HREEL spectrometer was developed and mounted at the laboratory of Ibach.²³ HREEL spectra were taken at an angle of incidence of 60° with respect to the surface normal for specular geometry. The primary energy was 2.5 eV and the energy resolution was set to 3.8 meV. Typically, count rates in the elastic peak of about 3×10^5 counts per s were achieved. Energy loss intensities are normalized against the intensity of the elastic peak. The HREELS data were taken at 300 K.

The sample was mounted using W wires in narrow slits at the edges of the sample. The wires were resistively heated. The temperature was measured by a Ni-CrNi thermocouple spot-welded to the back of the crystal. The Ru(0001) surface was prepared and its cleanliness was checked by LEED and HREELS as in previous work. Cs was evaporated from a break seal ampoule. The Cs adlayers were prepared by evaporating about one monolayer onto the sample at room temperature and subsequent annealing to characteristic temperatures from Ref. 14 given in Ref. 24. The amount of Cs was always checked with HREELS by the intensity of the Cs-Ru stretch mode as shown in Fig. 1. Coverages are given relative to the number of substrate surface atoms.

The mass spectrometer was used to perform thermal desorption spectroscopy (TDS) measurements with a heating rate of 3 K s^{-1} . For this purpose the sample was positioned

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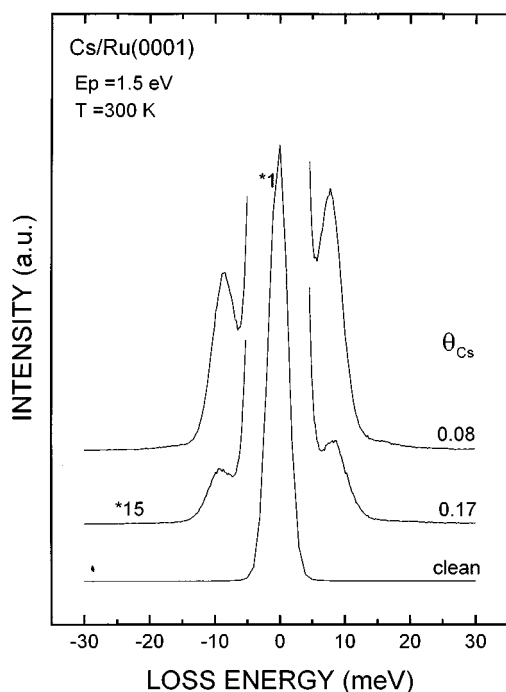


FIG. 1. HREEL spectra for the clean Ru(0001) surface and two different Cs coverages θ_{Cs} . Energy E_p of the incoming electrons and sample temperature T are given.

in front of a short stainless-steel tube with a diameter of about the sample size so that the ionizer of the mass spectrometer accepted molecules only after desorption from the sample surface. The coverage θ_{CO} was determined independently by TDS measurements. The TDS signals were calibrated with the help of the Ru(0001) $\sqrt{3}$ CO structure which is known to consist of one CO molecule per 3 Ru surface atoms. The gas doses are given in units of langmuir (1 langmuir (L) = 1.33×10^{-6} mbar \times s).

III. RESULTS

The Cs overlayer on Ru(0001) is characterized by repulsive lateral interaction giving rise to a liquidlike behavior and ringlike diffraction patterns in LEED. At appropriate coverages, the Cs atoms lock into commensurate adsorption sites and give rise to, e.g., a 2×2 LEED pattern for $\theta_{\text{Cs}} = 0.25$, and a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern for $\theta_{\text{Cs}} = 0.33$, when a complete monolayer is reached. The Cs submonolayers with $\theta_{\text{Cs}} = 0.08$ and 0.17 were prepared by evaporation of a full monolayer and subsequent annealing to characteristic temperatures.²⁴ The HREEL spectra of these Cs coverages are depicted in Fig. 1. The Cs–Ru stretch mode at about 8 meV is resolved and both gain (negative energy loss) and loss are observed. The Cs–Ru stretch mode and its coverage dependence has been discussed elsewhere.¹⁹ For the data presented in this work the Cs coverage was controlled by the Cs–Ru stretch-mode intensity relative to the elastically scattered intensity.

Before we present the results of the interaction of CO with Cs at submonolayer coverages we recall the results for

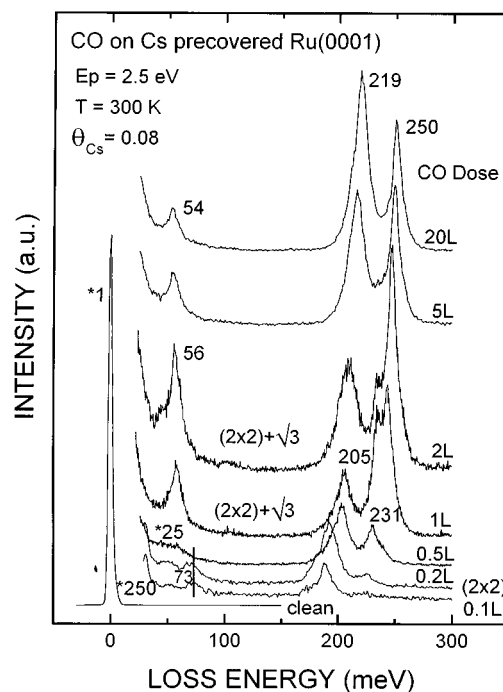


FIG. 2. HREEL spectra for a Ru(0001) surface precovered by an amount of $\theta_{\text{Cs}} = 0.08$ and different doses of CO in units of langmuir (L) (1 langmuir = 1.33×10^{-6} mbar \times s). Energy E_p of the primary electrons and sample temperature T are given. The observed LEED patterns are given.

the borderline cases, namely, $\theta_{\text{Cs}} = 0$ and $\theta_{\text{Cs}} = 0.25$. For the clean Ru(0001) surface the HREEL spectra show one C–O stretch mode increasing in energy from 245 to 252 meV with CO coverage.^{16,17} Recently, we observed also coverage-dependent changes in frequency of the Ru–CO stretch mode between 54 and 55.5 meV. For $\theta_{\text{Cs}} = 0.25$, CO adsorption leads to a well ordered two-dimensional composite layer in which Cs remains at the on-top position evaluated for the bare Cs phase and CO adsorbs at the two threefold-hollow sites within the Cs- 2×2 unit cell.¹⁵ From our analysis of the C–O stretch mode spectra with increasing CO coverage²¹ we have drawn the following conclusion: First, a $\nu(\text{C–O})$ peak appears which shifts continuously from 158 to 182 meV and is attributed to the local stoichiometry $\text{Cs}(\text{CO})_1$, i.e., a stoichiometry with one CO within the Cs- 2×2 unit cell. At somewhat higher CO coverages a second peak appears shifting from 177 to 204 meV with θ_{CO} which is attributed to the local stoichiometry $\text{Cs}(\text{CO})_2$. This assignment is supported through the observation that for $\theta_{\text{Cs}} \rightarrow 0$ and $\theta_{\text{Cs}} \rightarrow 0.25$ only one C–O stretch mode is observed.

In Figs. 2 and 3 HREEL spectra are shown for submonolayer coverages of Cs and increasing amounts of coadsorbed CO. Both sets of spectra show similar changes of peak positions up to the coverage at which the C–O stretch mode is found at 204 meV. The low-lying C–O stretch mode lines—150 meV in Fig. 2 and 162–170 meV in Fig. 3—are assigned to the local $\text{Cs}(\text{CO})_1$ stoichiometry. They shift in frequency and disappear finally when their intensity is transferred into the higher lying frequency due to the $\text{Cs}(\text{CO})_2$ stoichiometry. This indicates that during the early stages of CO adsorption

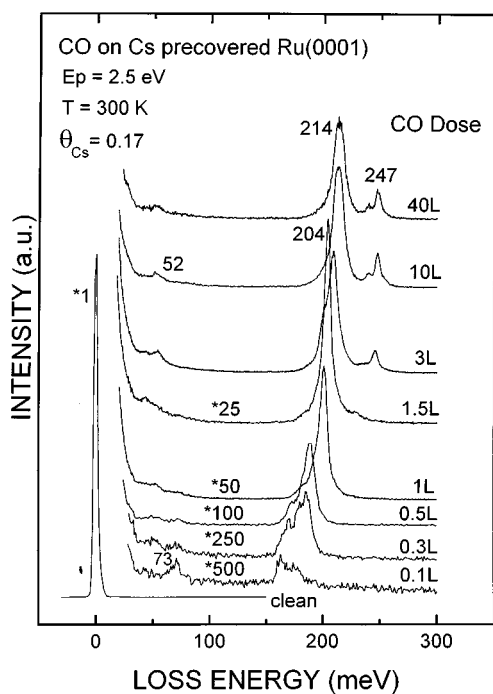


FIG. 3. Same as for Fig. 2 with $\theta_{\text{Cs}}=0.17$.

(Cs+2 CO)- 2×2 islands are formed. During adsorption all Cs atoms are collected into the $\text{Cs}(\text{CO})_n$ ($n=1, 2$) islands due to attractive interaction between Cs and CO. The frequencies of both species shift with CO coverage which indicates an appreciable amount of long-range interaction. All Cs atoms are rearranged and all incoming CO molecules are collected to built-up (Cs+2 CO)-islands with a single frequency at 204 meV.

The only difference with CO adsorption on the Cs-(2×2) precovered surface is the observation of a new peak at 73 meV. We attribute this peak to a bending mode of CO since a tilted CO seems to be likely at least at the borderlines of the anticipated (Cs+2 CO)-islands.

Upon further adsorption of CO up to saturation coverage, the HREEL spectra are governed in the C–O stretch-mode region by two peaks of which one is due to CO adsorbed at the bare Ru surface and the other one develops directly from the 204 meV peaks, i.e., is due to CO in the (Cs+2 CO)-islands. The latter observation is very remarkable. The stretch-mode frequency of the CO in the islands increases in frequency although there is no reason to assume any structural change within the CO islands. The frequency for CO on the bare surface is smaller than for CO/Ru(0001) and the frequency for CO in the (Cs+2 CO)-islands is higher than in the case when the whole surface is covered by Cs+2 CO.

In addition to the two main peaks there is a third peak at intermediate coverages. Since it is observed before the mode from CO on the bare surface is seen, one may speculate that it is due to adsorption at the edges of the (Cs+2 CO)-islands. The M–CO stretch mode around 55 meV exhibits also changes in energy and intensity with the CO coverage. We

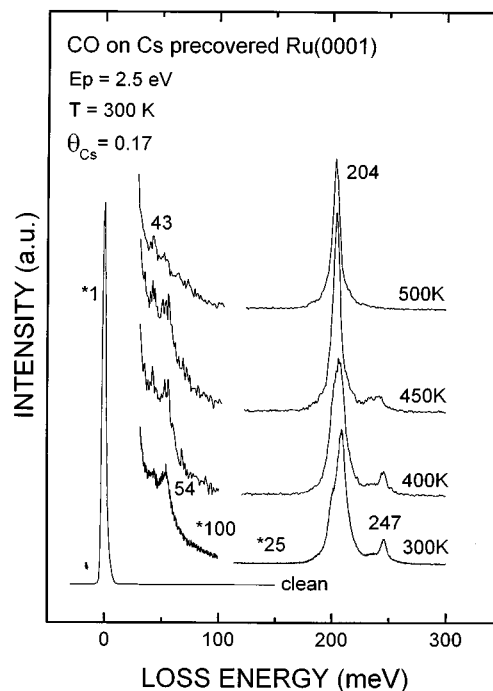


FIG. 4. HREEL spectra for a Ru(0001) surface covered with Cs ($\theta_{\text{Cs}}=0.17$) and dosed to CO (dose of 3 L) which was annealed to different temperatures as indicated. Sample temperature T during preparation and measurement is indicated. E_p is the primary energy of the electrons.

will not discuss this mode in detail here. We briefly mention that, similar to the CO adsorption on the bare surface,¹⁷ the M–CO stretch mode shifts up in energy and shifts downwards later which is interpreted as due to a dipole–dipole interaction onto which at higher coverages a chemical shift into the opposite direction is superimposed. Figure 4 shows HREEL spectra after annealing at different temperatures which clearly indicate that the adsorption process is reversible. The CO from the bare surface desorbs first. After annealing to 500 K a HREEL spectrum is observed typical for the (Cs+2 CO)- 2×2 phase; one single CO stretch mode loss at 204 meV and faint peaks in the Ru–CO mode range.

The formation of the (Cs+2 CO)-islands and their coadsorption with CO on the bare surface were also checked by LEED. At the very early stages of CO adsorption a 2×2 LEED pattern can be observed which becomes more intense with CO dose until the (Cs+2 CO)-islands have been fully developed. Upon further CO adsorption, CO molecules adsorb on the bare Ru surface, where they form a $\sqrt{3}$ structure, so that a superposition of the 2×2 and $\sqrt{3}$ is expected for the LEED pattern which is actually observed in the LEED pattern. These observations are also indicated in Fig. 2. Thus, the LEED pattern supports our conclusion, derived from the HREEL spectra, that the (Cs+2 CO)-islands are surrounded by areas which are covered by CO alone.

Figures 5 and 6 show some TD spectra of CO adsorbed on Cs-precovered surfaces. For comparison the spectra from a Ru surface without Cs and from the (Cs+2 CO)- 2×2 composite layer are shown additionally. For the pure CO adsorption the TD spectrum exhibits two peaks due to the $\sqrt{3}$ phase

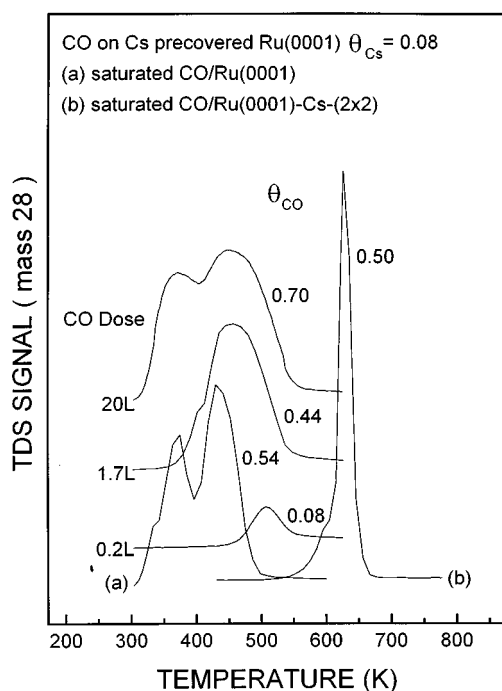


FIG. 5. Thermal desorption spectra from a Ru(0001) surface, precovered by Cs ($\theta_{\text{Cs}}=0.08$) and subsequently covered with different amounts of CO (θ_{CO}). For comparison the TD spectra of (a) the bare Ru surface saturated with CO and of (b) the saturated (Cs+2 CO)- 2×2 phase are also given. The LEED pattern for the 1.7 L CO dose is $2\times 2+\sqrt{3}$. Preparation and measurements are performed at $T=300$ K.

at higher temperature (430 K) and due to the compressed phase at lower temperature (370 K) which are well known.²⁵ This spectrum is used for the calibration of CO coverages in the coadsorbed phases. The TD spectrum for the Cs+2 CO coadsorption layer is also shown for comparison. It is in agreement with a previously published one.²¹ The peak is shifted by about 200 K to higher temperature and $\theta_{\text{CO}}=0.5$ was verified.

The TD spectra for the coadsorption with submonolayer amounts of Cs exhibit features known from other alkali metal on transition metal surfaces.^{1,2} Some amount of the CO is shifted to higher desorption temperatures, another part is found at the same temperature as known from the pure CO phase. In Fig. 5, for the CO dose of 1.7 L, $\theta_{\text{CO}}=0.44$ was found. From $\theta_{\text{CO}}=0.08$ we would expect that 0.33 of the surface is covered by Cs+2 CO with $\theta_{\text{CO}}=0.5$ and 0.66 of the surface by CO- $\sqrt{3}$ with $\theta_{\text{CO}}=0.33$ giving rise to $\theta_{\text{CO}}=0.39$ which compares reasonably well with the value of $\theta_{\text{CO}}=0.44$ as derived from TDS if one takes into account that no special care was taken to exactly meet the composite (Cs+2 CO)+ $\sqrt{3}$ phase.

In both figures, one can see that the amount of CO adsorbed at saturation is larger than the amount of CO adsorbed on the bare surface. Such an increase in the amount of adsorbed CO was also observed for K-promoted CO adsorption on Pt(111).²⁶

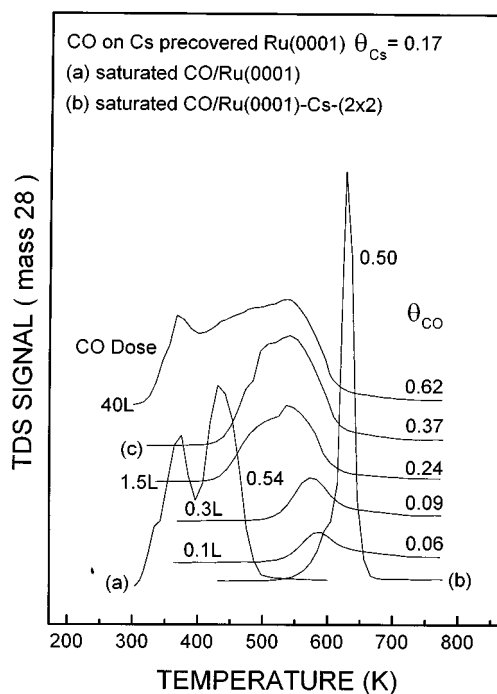


FIG. 6. Same as for Fig. 5 with $\theta_{\text{Cs}}=0.17$. Curve (c) is for a 3 L CO dose and annealing to 200 °C.

IV. DISCUSSION

A. The (Cs+2 CO)- 2×2 island formation

As it is well known, Cs submonolayers on Ru(0001), like other alkali metal on transition metal surfaces,¹ form liquidlike structures due to repulsive interaction between the Cs atoms. This behavior changes in case of coadsorption with other adsorbates, especially, if the coadsorbed species is more electronegative than Cs which is the case for many adsorbates. So far it has been proven for oxygen²⁷ and CO (Refs. 20, 21) that a composite layer can be formed with a well defined stoichiometry. One of these cases is the (Cs+2 CO)- 2×2 composite layer on Ru(0001) which has been already well characterized by structural¹⁵ and vibrational^{17,21} analyses. In the (Cs+2 CO)- 2×2 overlayer Cs maintains its on-top position, known from the 2×2 -Cs overlayer, whereas CO is shifted to the two hcp threefold-hollow sites. It is characterized by one single C–O stretch-mode frequency at 204 meV and two Ru–CO modes of very weak intensity. More interesting for our discussion is the dependence of the vibronic properties on CO coverage θ_{CO} . For $\theta_{\text{CO}}\rightarrow 0$ one C–O stretch-mode is observed at 155 meV. Up to $\theta_{\text{CO}}=0.22$ the adlayer is mobile and only a Cs+1 CO phase is formed. For $\theta_{\text{CO}}>0.22$ the mobility gets lost and statistically more 2×2 cells are filled with 2 CO molecules which show a second C–O stretch mode shifted to a higher value by 15–20 meV. The second frequency is interpreted as due to the Cs+2 CO phase which locally starts forming. For $\theta_{\text{CO}}\rightarrow 0.5$ only the higher-lying branch remains. Interestingly, its energy is shifted up to 204 meV.

In the investigation, which we discuss here, both from the 2×2 LEED pattern and the HREELS frequencies we

conclude that islands of the Cs+2 CO phase are formed. It is a reasonable assumption then that these Cs+2 CO islands possess locally the same structure as the saturated phase for $\theta_{\text{Cs}}=0.25$. The driving force for the formation of islands is the increased binding energy in the composite layer which can be recognized in the TD spectra shown in Figs. 5 and 6 for the pure CO, Cs+2 CO islands, and the Cs+2 CO phase. This difference in binding energy is probably due to electrostatic interaction between the differently charged CO and Cs species. After formation of the (Cs+2 CO)- 2×2 islands, CO is adsorbed on the bare part of the surface for which one expects a $\sqrt{3}$ ordered CO adlayer. At this stage, actually one observes a LEED pattern which is a superposition from the 2×2 and $\sqrt{3}$ domains from the two different phases.

For small alkali-metal coverages some authors have proposed the formation of chainlike nuclei [CO+Cs/Pt(111),²⁸ CO+K/Ru(0001),⁴ and CO+K/Pt(111) (Ref. 29)]. In our LEED investigation we did not find any indication for such structures and, therefore, conclude that 2D-islands are formed from the very beginning. Our findings are in agreement with those of Murray *et al.*³⁰ who observed a dense network of small K+CO islands on Ni(100) in scanning tunneling microscopy (STM). The STM image was in very good agreement with the observed $p(2\times 2)$ LEED pattern. Chain formation was not observed. It is not known whether the islands are so small in our case too. For the (Cs+CO)-Ru(0001) system STM always shows very large 2×2 islands even at θ_{Cs} in the percent region³¹ indicating that the STM tip is helping for island formation. From this observation it seems that Cs+CO is more mobile on Ru(0001) than K+CO on Ni(100) giving rise to larger islands in our case.

Kondoh *et al.*²² observed also island formation for the Cs+CO on Ru(0001) system. We agree with their conclusion on the stoichiometry within the islands which is CO:Cs =2:1. They always worked at CO saturation so that they could not observe the $\nu(\text{C}-\text{O})$ level splitting for smaller CO coverages. We do not agree with their finding of a 4:3 stoichiometry for $\theta_{\text{Cs}}=0.25$. Both their CO dose of 10 L (compared to 40 L in our case) and their $\nu(\text{C}-\text{O})$ frequency of 188 meV (from Fig. 9 in Ref. 25) at $\theta_{\text{Cs}}=0.25$ (which is lower than our value of 204 meV) indicate that they have not reached saturation.

So far we have discussed the island formation. Now we turn to the decomposition of the islands. Inspection of Figs. 5 and 6 show—from the TD spectra for small CO coverages—that the CO desorption peak temperature shifts to higher values with increasing Cs coverage as shown in Fig. 7. The desorption temperature changes nearly linearly with θ_{Cs} . Using the Readhead formula for first order desorption and assuming a frequency factor of 10^{13} , one can calculate the CO binding energy as follows: 1.17 eV ($\theta_{\text{Cs}}=0.0$), 1.38 eV ($\theta_{\text{Cs}}=0.08$), 1.60 eV ($\theta_{\text{Cs}}=0.17$), and 1.71 eV ($\theta_{\text{Cs}}=0.25$). The CO binding energy increases strongly (but not linearly) with Cs coverage. This observation can be qualitatively explained in the following way: Before CO desorption, the Cs+2 CO islands are dissolved and CO is embedded in a 2D Cs gas. There is still lateral attractive interaction which may well be understood on electrostatic grounds.¹¹ This in-

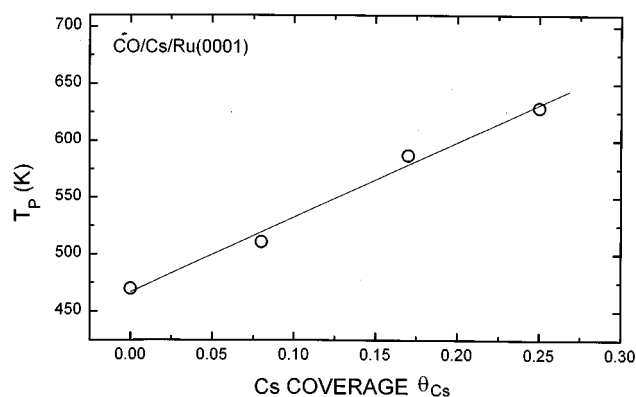


FIG. 7. CO desorption temperature for small amounts of CO ($\theta_{\text{Cs}} \rightarrow 0$) as a function of Cs precoverage θ_{Cs} .

teraction increases strongly with Cs coverage leading to an increase of the desorption temperature of CO with θ_{Cs} .

B. Charge redistribution in the adlayer

CO chemisorption is discussed in the widely accepted Blyholder model.³² Charge from the 5σ orbital of CO is donated to the metal surface which backdonates some charge into the antibonding $2\pi^*$ orbital of CO. This charge redistribution weakens the internal CO bond. As a result the C–O stretch mode frequency decreases from 265 meV in the gas phase to, e.g., 245 meV for CO on Ru(0001) in the limit $\theta_{\text{CO}} \rightarrow 0$. This decrease is called the chemical shift. The stabilization of the Ru–CO bond is thought to be due to a lowering of the potential near to the alkali metal which may enhance the backdonation. With this background the enormous experimental material on alkali-promoted CO adsorption is discussed under the aspect of the range of interaction, i.e., long range vs short range. Both aspects are found also in our results but most remarkable is the strong evidence for long-range interaction. The most evident effect of a short range interaction is the occurrence of two slightly different CO stretch mode frequencies for CO coverages smaller than saturation. If there is only one CO molecule in the 2×2 unit cell its stretch frequency is smaller than for the case that there are two molecules in the unit cell.

As we pointed out recently,²¹ the long-range or nonlocal effects can be qualitatively discussed in the following picture: Depending on θ_{Cs} a given amount of charge is donated to the Ru surface. This donated charge can be backdonated to the adsorbed CO molecules. If, for a given donated charge, the number adsorbed CO molecules increases, the amount which can be backdonated per molecule decreases. So, the chemical shift is large at small θ_{CO} and gets smaller with increasing θ_{CO} . The $\nu(\text{C}-\text{O})$ stretch-mode frequency rises from 155 to 182 meV for the Cs+1 CO phase and from 175 to 204 meV for the Cs+2 CO phase. This charge-redistribution model is furthermore supported by the results for the Cs submonolayer coverages presented above.

- (i) The frequency for the saturated island (Cs+2 CO phase) increase further if additional CO is adsorbed

on the bare surface. These molecules cannot directly interact with those in the island. Instead—indirectly—they take part in the overall charge thus reducing the part backdonated to the molecules in the island.

- (ii) The CO molecules on the bare parts of the surface, i.e., between the Cs+2 CO islands, show a stronger chemical shift than on the bare Ru surface. That they are adsorbed at the bare surface, is strongly supported through the occurrence of the $\sqrt{3}$ LEED pattern. They exhibit a stronger chemical shift to smaller $\nu(\text{C-O})$ frequency since the whole surface participates in the charge donated to the surface by the Cs atoms.

The charge-redistribution model qualitatively accounts for every detail in the different spectra. For $\theta_{\text{Cs}}=0.08$ the part of the bare Ru surface is larger than for $\theta_{\text{Cs}}=0.17$. Therefore, more CO can be adsorbed there and the reduction in chemical shift for the CO in the islands is larger for $\theta_{\text{Cs}}=0.08$ as compared to the spectra for $\theta_{\text{Cs}}=0.17$. The observed effect also depends on the amount of donated charge, i.e., on θ_{Cs} . It is smaller for $\theta_{\text{Cs}}=0.08$ and, therefore, both CO frequencies are not shifted so much to lower values (219 and 250 meV) as they are for $\theta_{\text{Cs}}=0.17$ (214 and 247 meV).

Our interpretation is in agreement with that given in a number of other contributions. For the coadsorption of K and CO on Ru(0001) de Paola *et al.*⁴ observed an upward shift of $\nu(\text{C-O})$ with θ_{CO} and attributed this to a long-range through substrate interaction between K and CO. Using IR reflection adsorption spectroscopy, Tüshaus *et al.*^{28,29} observed for the coadsorption of K and CO on Pt(111) a number of different bands each of them shifting with CO coverage. They attributed the different bands to different local stoichiometries and the shifts of the individual bands to some long-range effect.

V. CONCLUSION

On the base of our recent study of the (Cs+2 CO)-2×2 composite layer on Ru(0001), we have observed clear spectroscopic evidence that (Cs+2 CO)-2×2 islands are formed when dosing with CO a Ru(0001) surface precovered by submonolayer amounts of Cs. After completion of the (Cs+2 CO)-islands, CO adsorbs on the bare surface left between the islands. In this stage the $\nu(\text{C-O})$ frequency of the island CO is increased further although we can give arguments that the tightly packed islands are not undergoing a structural change. The $\nu(\text{C-O})$ frequency for the CO on the bare surface is smaller than that one for the bare surface. These observations strongly support the following charge redistribution model: Cs adsorption delivers a certain amount of charge which can backdonated to the $2\pi^*$ orbital of CO. In this model the CO outside of the islands also participates on the charge and reduces the amount of charge backdonated to the CO within the island.

We find a nearly linear dependence of the CO desorption temperature from the Cs coverage. This indicates that TDS does not measure the binding energy of CO which is stabilized within the Cs+2CO composite layer but measures the desorption energy of CO within a 2D Cs+CO gas phase in which the lateral stabilization increases with the Cs density.

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