

# Vibrational analysis of the (Cs+CO)-(2×2) compound layer on Ru(0001)

Cite as: J. Chem. Phys. **104**, 8118 (1996); <https://doi.org/10.1063/1.471526>

Submitted: 06 November 1995 • Accepted: 09 February 1996 • Published Online: 31 August 1998

Peimo He, Yabo Xu and Karl Jacobi



View Online



Export Citation



Chemical Physics Reviews

First Articles Now Online!

READ NOW >>>



# Vibrational analysis of the (Cs+CO)-(2×2) compound layer on Ru(0001)

Peimo He

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*

Yabo Xu

*Physics Department, Zhejiang University, Hongzhou 310027, People's Republic of China*

Karl Jacobi<sup>a)</sup>

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*

(Received 6 November 1995; accepted 9 February 1996)

On a Ru(0001) surface Cs and CO form a very well ordered (Cs+CO)-(2×2) compound layer whose structure was analyzed recently (Cs on-top, CO in threefold sites). Here we present a vibrational analysis of the same system using high-resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS), and low-energy electron diffraction (LEED). The bonding of CO to Ru is both local and nonlocal. Two (C–O) stretch frequencies are observed depending on whether there are one or two CO molecules in the 2×2 cell. They change in energy between 155 and 204 meV depending on CO coverage  $\theta_{\text{CO}}$ . Setting  $\theta_{\text{CO}}^{\text{max}}=1.0$ , the evolution of the C–O stretch intensities indicates that up to  $\theta_{\text{CO}}=0.22$  the 1-CO-(2×2) phase is formed exclusively implying some mobility of the Cs layer. For  $\theta_{\text{CO}}>0.22$  the 2-CO-(2×2) phase grows additionally until at  $\theta_{\text{CO}}=1.0$  only the 2-CO-(2×2) phase is found. Two Ru–CO stretch modes are observed for the first time and are assigned to adsorption in the hcp and fcc hollow sites within the 2×2 unit cell. They are very weak in intensity which is attributed to the threefold-hollow site and some screening in the 2D compound. With CO adsorption a change of the electronic structure of the Cs adlayer is observed; the adlayer loses metallicity and the Cs–Ru stretch becomes visible. Strong changes of the Cs–Ru stretch energies are observed with CO coverage. © 1996 American Institute of Physics. [S0021-9606(96)02818-1]

## I. INTRODUCTION

Alkali-metal overlayers adsorbed on transition-metal surfaces play an important role as electronic promoters in heterogenous catalysis.<sup>1</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. Recently, it was demonstrated how these interactions in turn also affect the properties of the adsorbed alkali-metal atoms.<sup>2</sup> The vibrations of Cs atoms adsorbed on a Ru(0001) surface can 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 an 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, thus corroborating more indirect conclusions of a recent calorimetric study with a related system.<sup>3</sup>

The Cs+CO coadsorption system is very interesting. It

forms a well ordered two-dimensional compound whose structure was determined recently.<sup>4,5</sup> Figure 1 shows a schematic top view of the Cs-(2×2) adlayer on Ru(0001) the structure of which is also known from an independent study.<sup>6</sup> As one can see, the 2×2 unit cell exhibits two adsorption sites of high symmetry which are the hcp and fcc threefold-hollow sites. In the (Cs+CO)-(2×2) compound CO occupies these two sites giving rise to a 1-CO- or a 2-CO-phase if only the hcp-site or both sites are occupied, respectively.<sup>4,5</sup> It is interesting to note that CO has changed its adsorption site from on-top in the CO/Ru(0001) system<sup>7,8</sup> to the threefold-hollow site in the Cs+CO compound layer. Whereas in many vibrational studies conclusions on adsorption sites are drawn we are here in the good position to investigate how the known structure influences the vibrational pattern.

Using high-resolution electron energy loss spectroscopy (HREELS) we have been able to measure the complete set of dipole-active modes including the internal stretch mode of C–O and the Ru–CO and the Cs–Ru modes.<sup>9</sup> Two different C–O stretch modes are found due to the occupation of the 2×2 unit cell by one or two CO molecules. We have found two Ru–CO modes which we assign to the two different (hcp and fcc) threefold-hollow sites. The Cs–Ru mode shows characteristic differences for the three phase [Cs-(2×2), 1-CO-Cs, 2-CO-Cs].

## II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) apparatus with a base pressure of  $1 \times 10^{-11}$

<sup>a)</sup> Author to whom correspondence should be addressed.

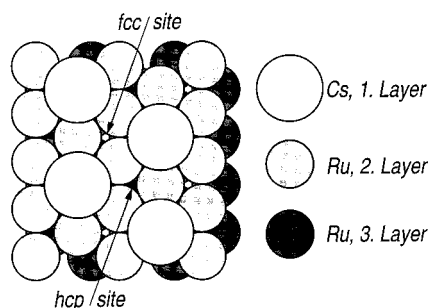


FIG. 1. Schematic sketch of a Cs-(2×2) unit cell on a Ru(0001) surface.

mbar which was achieved by a pumping line completely free of oil consisting of a Ti sublimation pump, a turbomolecular pump with magnetic bearing (Leybold, NT340M), a drag pump (Balzers, TCP015), and a diaphragm pump. The apparatus consisted of two chambers—the upper chamber contained an argon ion gun, a quadrupole mass spectrometer, and a LEED optics. The lower chamber housed a high-resolution electron energy loss spectrometer for recording vibrational spectra. The two chambers were separated by a valve, in order to keep the lower chamber at a pressure of  $3 \times 10^{-11}$  mbar during preparation of the sample in the upper chamber. The HREEL spectrometer was developed and mounted at the laboratory of Ibach.<sup>10</sup> HREEL spectra were taken at a  $60^\circ$  angle of incidence with respect to the surface normal and in a specular geometry. The primary energy was 1.5 eV and the energy resolution was set to 3.8 meV. Typically, count rates in the elastic peak of about  $3 \times 10^5$  counts per second were achieved. Energy loss intensities are normalized against the intensity of the elastic peak.

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 low-energy electron diffraction (LEED) and HREELS as in previous work.<sup>11</sup> Cs was evaporated from a break seal ampoule. Thermal desorption spectroscopy (TDS) was used for the determination of the CO coverage  $\theta_{\text{CO}}$ .

In the following the HREEL spectra will be presented depending on CO coverage  $\theta_{\text{CO}}$  which 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 maximum CO coverage found for the Ru(0001)-Cs-(2×2) surface is two CO molecules per 2×2 unit cell. We define this value of two CO molecules per four Ru surface atoms as  $\theta_{\text{CO}}=1.0$  throughout this contribution. Our calibration is in agreement with that of Over *et al.*<sup>4,5</sup> for the same system.

### III. RESULTS

Figure 2 exhibits a set of HREEL spectra with the full energy window between 0 and 250 meV in which energy losses were observed. Parameter is the coverage of CO. The

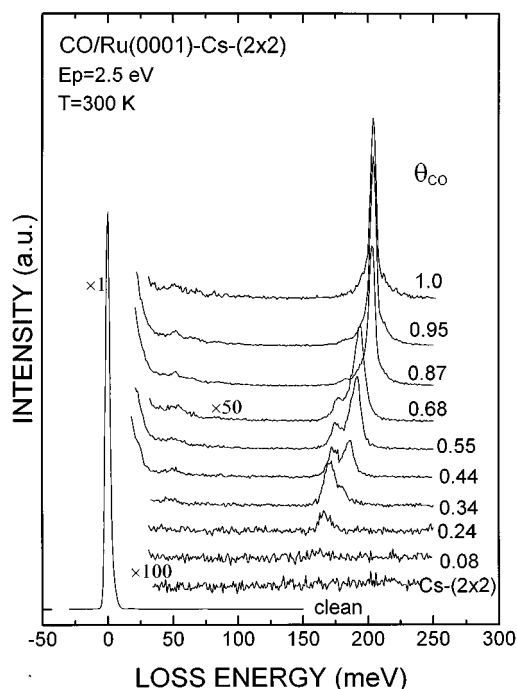


FIG. 2. HREEL spectra of a Ru(0001)-Cs-(2×2) surface onto which different amounts of CO—as given by the relative coverage  $\theta_{\text{CO}}$  (see text)—have been adsorbed. Primary energy  $E_p$  and temperature  $T$  for preparation and measurements are indicated. Clean surface means without CO. The spectra have been measured in specular geometry.

first spectrum is for the clean surface, i.e., the Ru(0001) surface covered by Cs with  $\theta_{\text{Cs}}=0.25$  and exhibiting a 2×2 LEED pattern. The Cs-(2×2) HREEL spectrum is known to exhibit a continuous background of electron-hole pair excitation, throughout the whole window of Fig. 2, including an equivalent noise as can be seen from the figure.<sup>12</sup> The noise and the background decrease when  $\theta_{\text{CO}}$  increases from 0 to about 0.3. Interestingly, nearly no vibrational signal of CO can be recognized in this coverage regime. For  $\theta_{\text{Cs}} \geq 0.24$  the CO intramolecular stretch vibration is observed; it changes in energy and line shape with increasing  $\theta_{\text{CO}}$ . For the Ru–CO stretch mode which is expected at energies between 40 and 60 meV only very weak signals are observed. This contrasts the CO adsorption on the bare surface (without any Cs) for which a strong Ru–CO stretch signal is observed.<sup>13,14</sup> This mode is completely suppressed in the 0.08 curve in Fig. 2 although, as checked by TDS, there is CO on the surface with a coverage of  $\theta_{\text{CO}}=0.08$ . In HREELS this CO can only be detected by using the impact mode in electron scattering as, e.g., by choosing an angle of  $10^\circ$  off-specular for the analysis. In Fig. 3 we compare the results for specular and off-specular geometry. For the two sets of spectra and for small coverages of CO the CO stretch mode is clearly observed at about 160 meV.

#### A. The CO stretch mode

First we analyze the CO stretch mode because it gives rise to the strongest signal. The loss energy as function of  $\theta_{\text{CO}}$  is given in Fig. 4. For small  $\theta_{\text{CO}}$  there is only one fre-

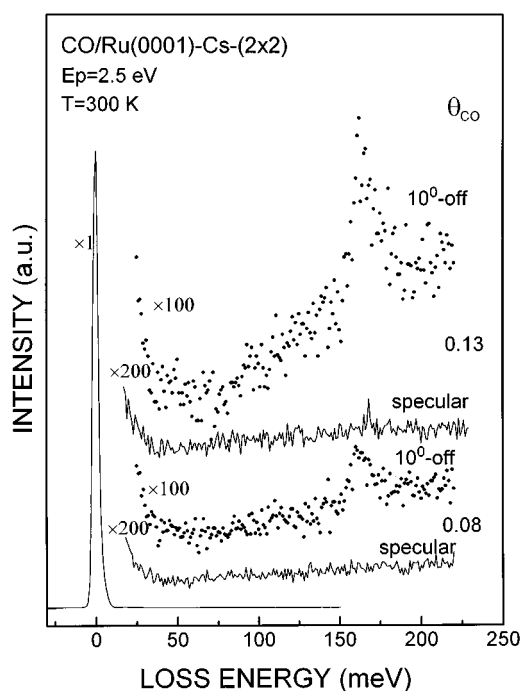


FIG. 3. Specular and off-specular HREEL spectra for small CO coverages  $\theta_{\text{CO}}$ . The other parameters are as for Fig. 2.

quency which is 155 meV in the limit  $\theta_{\text{CO}} \rightarrow 0$ . Very soon two losses are observed. Following the LEED structure analysis we assign these two losses to CO with one CO molecule or two CO molecules in the Cs-(2×2) unit cell. We will call this the 1-CO- and the 2-CO-phase in the following. The integrated intensity of these modes is plotted in Fig. 5. First, there is a remarkable delay in the appearance of the CO stretch intensity. Quite obviously CO is embedded within the metallic Cs adlayer which screens the CO stretch mode excitation. In this region basically one single CO stretch frequency is observed which smoothly is connected with the lower frequency branch in Fig. 4 assigned to the 1-CO-phase. Second, there is a regime where two frequencies are

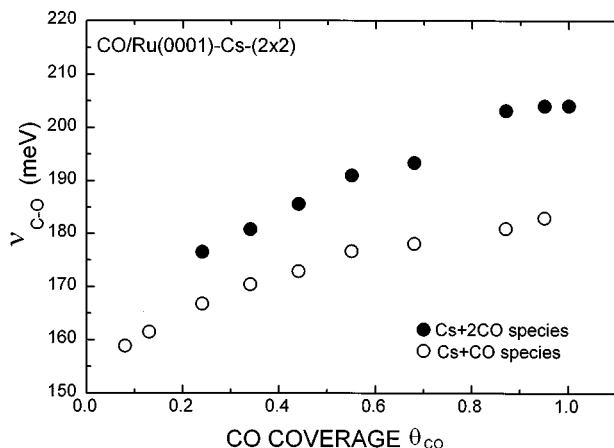


FIG. 4. Internal stretch-mode frequency of CO  $\nu_{\text{C-O}}$  as a function of the CO coverage  $\theta_{\text{CO}}$ .

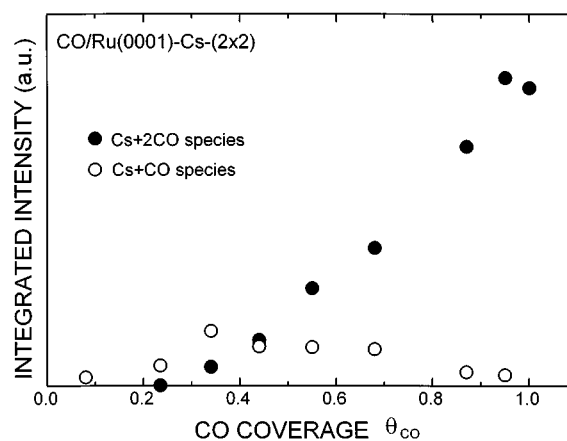


FIG. 5. Integrated intensity of the internal stretch mode of CO as a function of the CO coverage  $\theta_{\text{CO}}$ .

observed. This part starts already at about  $\theta_{\text{CO}}=0.22$ , i.e., much earlier than at  $\theta_{\text{CO}}=0.5$ . The latter value is expected for a situation when a complete 1-CO-phase is formed first and later the 2-CO-phase. Quite obviously there is an overlapping regime, i.e., the 2-CO-phase starts forming earlier than the 1-CO-phase has been completed. For CO saturation at  $\theta_{\text{CO}}=1$  one single loss remains at 204 meV. This shows that the CO stretch mode frequency is not influenced by the difference between the hcp and fcc hollow site. If there is an influence, it is smaller than about 1 meV. The linewidth of the CO stretch mode was 4.2 meV for  $\theta_{\text{CO}}=1$  and the FWHM of the elastic peak was 3.3 meV in this experiment. For the CO/Ru(0001) system (without Cs) we have observed<sup>14</sup> an inhomogeneous broadening of 1.85 meV, a value which is larger than that observed here. This confirms the high degree of order in the CO+Cs layer.

## B. The Ru-CO stretch mode

The most surprising result is the very weak intensity of the Ru-CO stretch mode. This is contrary to the CO/Ru(0001) system (i.e., without Cs) for which the intensity of this mode is as high as for the intramolecular stretch mode.<sup>13,14</sup> In the latter system CO is adsorbed at an on-top site up to a coverage of  $\theta_{\text{CO}}=0.33$ . In the Cs+CO compound, on the other hand, CO is shifted to the threefold-hollow site and the Ru-CO mode intensity is weaker than for the internal CO stretch mode by a factor of 20.

We have studied the Ru-CO loss peak furthermore in greater detail. Some spectra are shown in Fig. 6. The loss energies are plotted in Fig. 7. Most interestingly one observes two losses which we assign to the hcp and fcc sites. According to the LEED structure analysis the hcp site is occupied first and we assign the higher-lying loss to the hcp site. In agreement with the appearance of a second line in the C-O stretch mode signal the fcc-site loss is observed only for  $\theta_{\text{CO}}>0.2$ . As can be seen from Fig. 6 the two losses differ in character; whereas the hcp-site loss is dipole active the fcc-site one is not. From Fig. 6 one also notices that for  $\theta_{\text{CO}} \leq 0.26$  the (dipole-active) hcp-site mode cannot be ex-

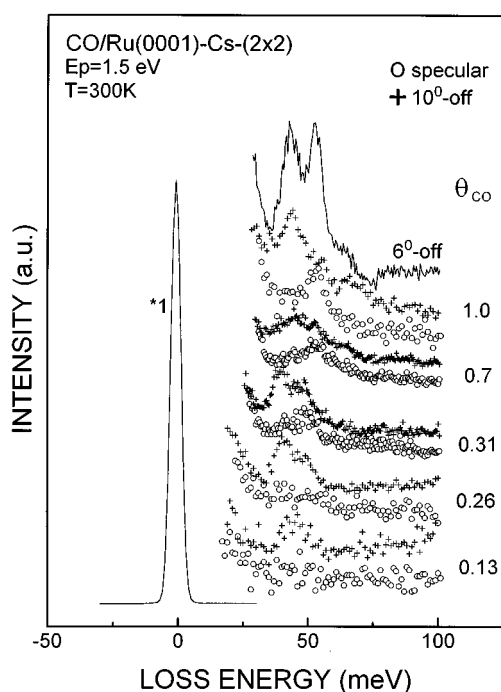


FIG. 6. The Ru–CO stretch-mode region of HREEL spectra of CO adsorbed on the Ru(0001)-Cs-(2×2) surface. The CO coverage  $\theta_{\text{CO}}$  is indicated. The spectra are measured in the dipole mode (specular) and in the impact mode ( $10^\circ$  off). The other parameters are as for Fig. 2. The sensitivity factors are 1000 (specular), 50 ( $10^\circ$  off-specular), and 400 ( $6^\circ$  off-specular).

cited in specular geometry due to the screening of the Cs layer. Furthermore, the hcp-site loss energy increases somewhat stronger with  $\theta_{\text{CO}}$ . We also varied the surface temperature from 300 K to 85 K which did not change the spectra very much.

### C. The Cs–Ru mode

We have already shown that we can resolve the Cs–Ru vibration  $\nu_{\text{Cs}}$  at about 8–10 meV with our spectrometer.<sup>2,12,15</sup>

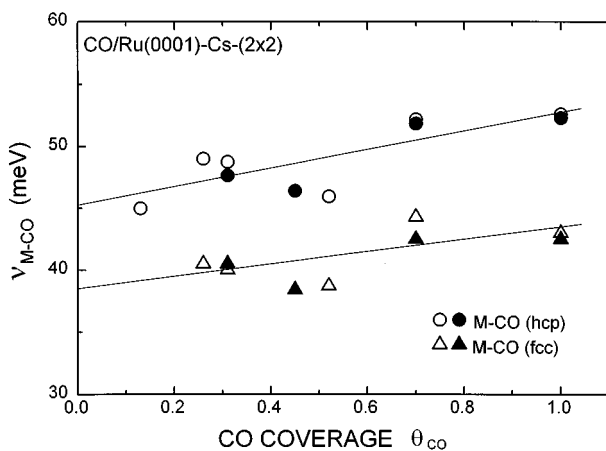


FIG. 7. Ru–CO stretch-mode frequencies  $\nu_{\text{M-CO}}$  as a function of CO coverage  $\theta_{\text{CO}}$ . Circles are for the hcp threefold-hollow site and triangles for the fcc threefold-hollow site at which CO is adsorbed. The open and the full symbols are for two different runs of the experiment.

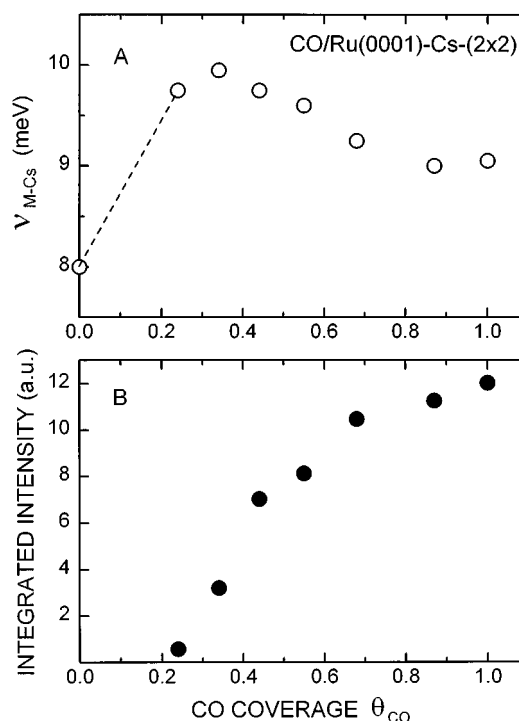


FIG. 8. (a) Ru–Cs stretch-mode frequency  $\nu_{\text{M-Cs}}$  as a function of CO coverage  $\theta_{\text{CO}}$ . (b) Integrated intensity of  $\nu_{\text{M-Cs}}$  as a function of  $\theta_{\text{CO}}$ .

The Cs–Ru vibration is observed if the Cs atom is somewhat positively charged which is the case at submonolayer coverages or within a compound layer, i.e., in coadsorption with an electronegative species. If the Cs monolayer becomes metallic, the Cs–Ru mode cannot be excited since the delocalized charge screens out any dipole fluctuation. Interestingly, the energy of the Cs–Ru mode varies strongly with Cs coverage which we have interpreted as a change of the bond strength to the surface.<sup>15</sup>  $\nu_{\text{Cs}}$  varies from 6.7 to 8.9 meV and falls back to 8.0 for  $\theta_{\text{Cs}}=0.25$ . Our second observation was that any interaction with chemically active gases leads to a reappearance of the  $\nu_{\text{Cs}}$  mode. In this contribution we have studied the latter effect in detail for the coadsorption with CO. Energy and intensity of the  $\nu_{\text{Cs}}$  mode are plotted in Figs. 8(a) and 8(b). The raw data have been published elsewhere.<sup>9</sup> The  $\nu_{\text{Cs}}$  mode becomes observable for  $\theta_{\text{CO}}>0.2$ , i.e., behaves similarly as the CO stretch mode. The delocalized charge of the Cs layer screens every dipole-active vibrational mode including the Cs–Ru mode for coverages  $\theta_{\text{CO}}<0.2$ .

The energy of the Cs–Ru mode is maximal at about  $\theta_{\text{CO}}=0.34$ , i.e., for the 1-CO-phase. We argue that there is a real maximum since we know that  $\nu_{\text{Cs}}=8.0$  meV for  $\theta_{\text{CO}}=0$ .<sup>15</sup> The value for  $\nu_{\text{Cs}}$  in Fig. 8(a) rises from 8.0 meV for  $\theta_{\text{CO}}=0$  to 10.0 meV for  $\theta_{\text{CO}}=0.34$ . At  $\theta_{\text{CO}}=1.0$  we have only the 2-CO-phase and  $\nu_{\text{Cs}}=9.0$  meV. The intensity of the Ru–Cs vibration increases up to  $\theta_{\text{CO}}=1.0$ . This increase is not proportional to the CO coverage.

Finally, we mention that we also have reproduced the known<sup>5</sup> thermal desorption spectra of the Cs+CO compound. Both Cs and CO are thermally stabilized within the Cs+CO compound and part of the Cs and all CO desorb at

the same temperature within a sharp desorption peak at about 640 K. Qualitatively, the desorption spectra look like spectra of order 1/2 compatible with desorption from the perimeter of 2D islands. Under the assumption of island formation at small  $\theta_{\text{CO}}$ , this is in agreement with the observation that the peak temperature shifts by only 15 K to higher values between  $\theta_{\text{CO}}=0.08$  and 1.0.

#### IV. DISCUSSION

According to the structure analysis of the Cs-(2×2)-Ru(0001) surface<sup>6</sup> Cs is adsorbed at the on-top position. The Ru atom below the Cs moves inwards by 0.1 Å. This structure gives rise to two different adsorption sites within the 2×2 unit cell; the hcp and the fcc site (see Fig. 1) which may be occupied by CO. Compared to the Cs free surface the CO adsorption site is changed from on-top to threefold hollow. Due to the existence of these two different sites and the observation of two distinct phases (the 1-CO- and the 2-CO-phase) it is straight forward to assign the two different C–O stretch frequencies to a difference in occupation of these two sites.

##### A. Formation of the CO+Cs phases with $\theta_{\text{CO}}$

In order to explain the intensity variation of the C–O stretch mode we have set-up the following simple model. We define in addition to  $\theta_{\text{CO}}$  the relative coverage  $\theta_1$  of the 1-CO-phase and  $\theta_2$  of the 2-CO-phase. We differentiate between the two coverage regimes  $\theta_{\text{CO}} < 0.22$  and  $\theta_{\text{CO}} \geq 0.22$ .

##### 1. $\theta_{\text{CO}} < 0.22$

From our measurements we conclude that within the Cs-(2×2) structure, Cs is mobile so that always the 1-CO-phase is formed only. It follows

$$\theta_1 = 2\theta_{\text{CO}}, \quad (1)$$

and

$$\theta_2 = 0. \quad (2)$$

##### 2. $\theta_{\text{CO}} \geq 0.22$

The existing Cs+CO phase is immobile so that additional CO is adsorbed statistically on an empty threefold-hollow site independent of whether or not there is already one CO molecule adsorbed in the 2×2 unit cell. This gives

$$\frac{d\theta_1}{dt} = k_1(1 - \theta_1 - \theta_2) - \frac{d\theta_2}{dt}, \quad (3)$$

$$\frac{d\theta_2}{dt} = k_2\theta_1, \quad (4)$$

$$\frac{d\theta_{\text{CO}}}{dt} = k(1 - \theta_{\text{CO}}), \quad (5)$$

$$\theta_{\text{CO}} = 0.5\theta_1 + \theta_2, \quad (6)$$

Under the assumption of

$$k_1 = k_2 = k, \quad (7)$$

this reduces to

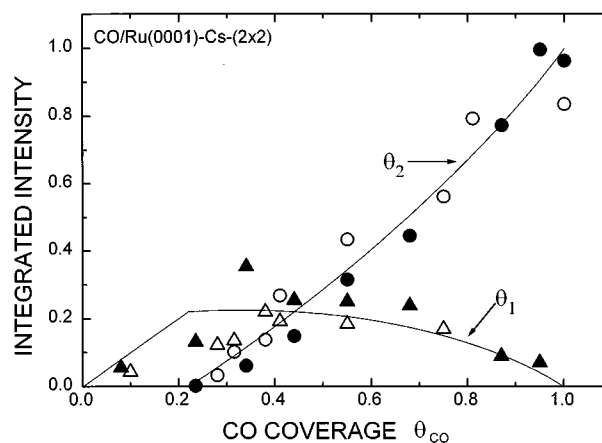


FIG. 9. Integrated intensity of the internal stretch mode of CO as a function of the CO coverage  $\theta_{\text{CO}}$ . The lines are from a model calculation (see text). Open and filled circles are for two different runs of the experiment.

$$\frac{d\theta_1}{d\theta_{\text{CO}}} = 1 - \frac{3\theta_1}{2(1 - \theta_{\text{CO}})} \quad (8)$$

and

$$\theta_2 = \theta_{\text{CO}} - 0.5\theta_1. \quad (9)$$

Equations (8) and (9) were numerically integrated and the result is shown as lines in Fig. 9. One recognizes that the data are reproduced quite well. The data points are from two runs of the experiment. The data points for  $\theta_1$  are multiplied by a factor of 2 in order to meet the calculated lines. This may indicate that the excitation cross section of the CO stretch mode is smaller by this factor in the 1-CO-phase compared to the 2-CO-phase. There may also be some intensity transfer from the low-energy mode to the high-energy mode. The assumption (7) implies equal sticking coefficients for the two CO species. One could make the reasonable assumption that  $k_2 < k_1$  but one realizes that the factor, the  $\theta_1$  data have to be multiplied with, becomes larger than 2 instead of smaller. From this modeling of our experiment we conclude that the 1-CO- and the 2-CO-phase do not develop one after the other but there exists some coexistence for  $0.22 \leq \theta_{\text{CO}} \leq 1$ . This conclusion is different to that one of Over *et al.*<sup>4</sup> who concluded that the 2-CO-phase forms only after completion of the 1-CO-phase at  $\theta_{\text{CO}} \geq 0.5$ . A recent LEED calculation has indicated that a CO occupation in fcc and hcp sites according to the HREELS results of the 1-CO-(2×2) phase improved indeed the agreement between experimental and calculated LEED spectra.<sup>16</sup>

##### B. The CO intramolecular stretch mode

According to the above intensity analysis the two different branches of the CO intramolecular stretch mode are due to different local Cs:CO ratios in the Cs-(2×2) unit cell. This follows directly from the observation that the low-energy branch appears first and loses intensity for  $\theta_{\text{CO}} > 0.4$ , whereas the high-energy branch grows strongly in intensity and is left finally as the only one when both sites in each unit

cell are filled with CO. The energy of CO internal stretch modes depends on stoichiometry and on  $\theta_{\text{CO}}$ , but not on the kind of the threefold-hollow site since for  $\theta_{\text{CO}}=1$ , when both fcc and hcp sites are occupied, we observe one single stretch frequency only. According to our energy resolution the influence on the stretch frequency from the two different hollow sites is smaller than 1 meV. The low-lying branch of the 1-CO-phase can be extrapolated for  $\theta_{\text{CO}}\rightarrow 0$  to 155 meV and to 184 for  $\theta_{\text{CO}}\rightarrow 1$ . This energy agrees with the value found by Kondoh and Nozoye who adsorbed CO onto a Cs layer with  $\theta_{\text{Cs}}=0.33$  at 85 K.<sup>17</sup> The CO seems to push some Cs out of the surface layer into the second layer under these conditions.

The high-energy branch varies from 177 meV at  $\theta_{\text{CO}}=0.22$  to 204 meV at  $\theta_{\text{CO}}=1$ . So, the coverage dependencies of the CO stretch mode exhibit both a local and nonlocal aspect of the CO bond to the surface. For a given  $\theta_{\text{CO}}$  the frequency jumps to the high-energy branch if a second CO is adsorbed in the unit cell. This is the local aspect. On the other hand, for the given Cs concentration  $\theta_{\text{Cs}}=0.25$  the frequency of a given CO molecule either in the 1-CO-phase or in the 2-CO-phase increases strongly with  $\theta_{\text{CO}}$ , i.e., depends on the occupation of all other CO sites whether they are at far distances or not. This long-range interaction may be explained by a sharing of a given charge among an increasing number of CO molecules. With increasing  $\theta_{\text{CO}}$  the charge back-donated into the  $2\pi^*$  orbital decreases and the internal stretch mode frequency rises. As the coverage of CO increases, more molecules will compete for the available charge and the effect on the individual molecule will be smaller. This nonlocal interaction between Cs and CO is likely to operate through the metal. Such a smooth change of frequency with  $\theta_{\text{CO}}$ , as observed here for the internal CO stretch mode, is also evident for the Cs–Ru and the Ru–CO modes discussed below.

### C. The Cs–Ru stretch mode

The energy resolution of the used spectrometer is so high that we could resolve the Cs–Ru stretch vibration  $\nu_{\text{Cs}}$ . The energy of this mode is 8.0 meV for the Cs-(2×2) structure at  $\theta_{\text{CO}}=0$ .<sup>2,12,15</sup> This value was derived by extrapolation for  $\theta_{\text{Cs}}\rightarrow 0.25$ . At  $\theta_{\text{Cs}}=0.25$  the Cs–Ru vibration cannot be observed since it is screened by the 2D delocalized charge. We cannot decide whether  $\nu_{\text{Cs}}$  moves continuously up to 10.0 meV at about  $\theta_{\text{CO}}=0.3$  or whether it jumps to this value since in this range of  $\theta_{\text{CO}}$  the adlayer is metallic and any vibration is screened out. The data show a weak maximum around  $\theta_{\text{CO}}=0.33$  which is consistent with a continuous change. At  $\theta_{\text{CO}}=0.33$  there is only the 1-CO-phase on the surface whereas at  $\theta_{\text{CO}}=1$  there is the 2-CO-phase. From  $\theta_{\text{CO}}=0.33$  to 1.0 the energy of  $\nu_{\text{Cs}}$  changes from 10 to 9 meV. These changes of vibrational energy are consistent with the data from the structure evaluation making the reasonable assumption that a stronger bond is connected with a shorter bond length. The Cs–Ru layer distances are  $3.15 \text{ \AA} \pm 0.08 \text{ \AA}$  for Cs-(2×2) (Ref. 6),  $3.12 \text{ \AA} \pm 0.04 \text{ \AA}$  for the 1-CO-phase, and  $3.16 \text{ \AA} \pm 0.04 \text{ \AA}$  for the 2-CO-phase.<sup>4</sup> In the

1-CO-phase the Cs–Ru bond is stronger than in the Cs-(2×2) phase and becomes weaker than in the 2-CO-phase. The latter effect is in accordance with chemical intuition. The bond to the substrate becomes weaker if the components in the 2D adlayer form a stronger bonding network with each other. Since the energy of the Cs–Ru mode differs by only 1 meV between the 1-CO-phase and the 2-CO-phase it is not possible to clearly decide whether the frequency change observed is due to a local or nonlocal interaction.

### D. The Ru–CO stretch mode

The small intensity of the Ru–CO stretch mode is the most surprising result of this investigation. We know already from the development of the CO stretch mode with  $\theta_{\text{CO}}$  that the screening is observed only for  $\theta_{\text{CO}} < 0.24$ . For  $\theta_{\text{CO}} \geq 0.24$  the CO stretch mode intensity is as large as on the bare Ru surface. In contrast, the Ru–CO mode intensity is small throughout the whole coverage regime. Furthermore, we know also for the (Cs+O) split (2×2) compound coadsorption system that the O–Ru mode is clearly observed within the Cs matrix.<sup>11</sup> Therefore it seems to us that the weak intensity of the Ru–CO mode in the (Cs+CO)-(2×2) compound is mainly caused by the adsorption in the hollow site. We are not aware of any other surface for which CO is adsorbed on-top in one phase and in threefold-hollow sites in the other. From the literature the following general trend can be derived for the relative intensities of the C–O and metal–CO stretch modes; it is  $\approx 1$  for on-top, 2–3 for bridge (or top bend), and 5–6 for threefold-hollow sites. For the latter case we know only one example, which is Ni(111), for which HREELS data<sup>18</sup> and independent structural data<sup>19–21</sup> are known. For Pd(111), at which CO adsorbs also at the threefold-hollow site,<sup>22</sup> the intensity ratio is about 9.<sup>23</sup> For our case, the above noted intensity ratio is about 20, i.e., much larger than in any other case. We conclude that part of the weak Ru–CO stretch mode intensity is due to some screening of the mode by the neighboring Cs ions and the C–O dipole. This may also be the difference to the Cs+O coadsorbate case. The O–Ru mode may be better accessible for the electric field of the incoming electron than the Ru–CO mode.

Finally, we note that the (K+CO)-(2×2) compound layer on Ru(0001) exhibits also a very weak intensity ratio<sup>24,25</sup> which has been discussed in terms of side-on-bonded CO (Ref. 24) and upright, bridge-bonded CO shielded by K.<sup>25</sup> In the meantime it was shown that the adsorption geometry is the same as for (Cs+CO)-(2×2) (Ref. 26) so that our interpretation of the influence of the threefold-hollow site seems also important for K+CO system.

Despite its weak intensity we have been able to investigate the Ru–CO stretch mode in detail and to differentiate between the fcc and hcp sites here for the first time. The observation that the vibrational energy quantum is larger for the hcp site than for the fcc site in accordance with the idea that the Ru atom in the third layer is taking part in the bonding. In the limit  $\theta_{\text{CO}}\rightarrow 0$  the frequencies of the Ru–CO

stretch mode are 54.2 meV (on-top)<sup>14</sup> 45.3 meV (hcp) and 38.5 meV (fcc). Interestingly, the Ru–CO modes of the hcp- and fcc-site differ not only in energy but also in the dynamical dipole moment perpendicular to the surface which is small for the hcp-site but below the detection limit for the fcc-site. So, the Ru atom in the second substrate layer seems to enhance the bonding strength and the dynamic dipole moment perpendicular to the surface.

The Ru–CO stretch modes exhibit a strong increase in binding energy with  $\theta_{\text{CO}}$ . This result is difficult to understand since with  $\theta_{\text{CO}}$  there is a strong increase of the C–O stretch mode which is connected with a reduction of backdonated charge. If one assumes, that backdonation and  $\sigma$ -donation are somehow in balance, a reduction of  $\sigma$ -donation, i.e., a reduction of the Ru–CO bond strength, has to be anticipated with increasing  $\theta_{\text{CO}}$ . At this point the calculations of Schultz *et al.*<sup>27</sup> are of importance which showed that a pure electrostatic picture of a  $\text{K}^+$  interacting with  $(\text{CO})^-$  locally would lead to a stable bonding configuration. They pointed out that the  $2\pi$  orbital of CO filled with 1 electron would be much less diffuse than in the gas phase thus leading to a much stronger reduction of the CO stretch mode as observed experimentally. In this picture also the bonding of the  $\text{CO}^-$  is mainly to the  $\text{Cs}^+$  and only to a lesser degree to the surface leading to a reduction of the Ru–CO stretch mode frequency. Although this model explains some of the trends in our experiment—including the weak dipole perpendicular to the surface giving rise to the weak Ru–CO stretch mode intensity—it is right only to some extent since it predicts also an extended C–O bond distance of 1.27 Å for the  $\text{CO}^-$  species compared to the 1.15 Å gas phase value. According to the recent structural analysis the bond length is  $1.15 \pm 0.13$  Å for the 1-CO-phase and  $1.10 \pm 0.07$  Å for the 2-CO-phase.<sup>4</sup> Both values are much nearer to the gas phase value than to that of  $\text{CO}^-$  and the pure ionic bonding picture has to be discarded for this reason. Nevertheless, the model calculations mentioned show an important aspect of the bonding situation. The increase of the Ru–CO stretch mode energy with  $\theta_{\text{CO}}$  could mean a reduction in the ionic part of the bonding between  $\text{Cs}^{\delta+}$  and  $\text{CO}^{\delta-}$ .

## V. CONCLUSION

Using HREELS we collected a complete set of the dipole-active vibrational modes of the well ordered (Cs+CO)-(2×2) 2D compound layer on Ru(0001). The different vibrational modes exhibit characteristic changes in energy and intensity with CO coverage  $\theta_{\text{CO}}$ .

### A. The intermolecular CO stretch mode

For  $\theta_{\text{CO}} \rightarrow 0$  there is one single loss peak observed at 155 meV. This energy is strongly reduced compared to the value for gas phase CO (265 meV) or to that for chemisorbed CO on Ru(0001) (245 meV for  $\theta_{\text{CO}} \rightarrow 0$ ). The Cs atoms lower the local potential so that strong backdonation into the  $2\pi^*$  orbital becomes possible. For  $\theta_{\text{CO}} \geq 0.22$  a second frequency is observed varying from 177 meV to 204 meV. The lower branch is assigned to the 1-CO-phase (1 CO within the 2×2

unit cell) and the upper branch to the 2-CO-phase (2 CO within the 2×2 unit cell). The occurrence of two frequencies at a given  $\theta_{\text{CO}}$  value is a clear indication that the CO stretch mode frequency depends on the local CO concentration. The strong and continuous shift of this frequency to higher values with  $\theta_{\text{CO}}$ , on the other hand, documents the aspect of delocalization of the Cs–CO–Ru interaction. For a given Cs coverage, which is  $\theta_{\text{Cs}} = 0.25$  in our case, the individual CO molecule gets less charge backdonated if the number of CO molecules increases.

For  $\theta_{\text{CO}} = 1$  there remains only one line at 204 meV which means that the difference of the two adsorption sites (hcp and fcc threefold hollow) influences the intramolecular stretch mode energy by less than 1 meV. The two CO stretch mode branches can be used to differentiate between the two phases. From modeling of the CO stretch mode intensities we conclude the following: For  $\theta_{\text{CO}} < 0.22$  the adlayer is mobile to such a degree that only the 1-CO-phase grows. At about  $\theta_{\text{CO}} = 0.22$  the adlayer becomes immobile so that the 2-CO-phase grows in addition. This finding differs from the interpretation of the LEED result in terms of a sequential formation of the 1-CO-phase and the 2-CO-phases.<sup>4</sup>

### B. The Cs–Ru mode

The Cs–Ru mode is observed at 8 meV loss energy for  $\theta_{\text{Cs}} = 0.25$  and  $\theta_{\text{CO}} = 0$ . Keeping  $\theta_{\text{Cs}}$  constant  $\nu_{\text{Cs}}$  increases to 10.0 meV at  $\theta_{\text{CO}} = 0.3$  where the 1-CO-phase prevails. For  $\theta_{\text{CO}} \rightarrow 1.0$ , i.e., in completing the 2-CO-phase it decreases again to 9.0 meV. The bond of Cs to the Ru surface is strengthened by the interaction with CO. This strengthening is larger in the 1-CO-phase. In the 2-CO-phase the lateral bond network weakens the Cs bond to the Ru substrate.

### C. The Ru–CO mode

The ratio of the C–O and the Ru–CO stretch mode intensities is about 20, i.e., larger than any ratio found for CO species adsorbed on different sites at a given surface. We argue that both the weak dipole moment of the Ru–CO bond perpendicular to the surface at the threefold-hollow site and some screening by Cs atoms and CO explains the large ratio. Furthermore, we observe for the first time different frequencies for the two different hcp and fcp threefold-hollow sites. Surprisingly, the Ru–CO stretch energies increase with CO coverage whereas from the increase of the C–O stretch mode energy a decrease is expected. As an explanation we consider that an increase of the Ru–CO bond strength may occur in order to counterbalance the Cs–Ru bond strength decrease.

Finally, we underline that the CO bonding within the Cs–CO–Ru compound is both localized and delocalized in character. The observation of two C–O stretch mode frequencies at a given Cs coverage supports a local picture. The smooth changes of all the modes with  $\theta_{\text{CO}}$ , on the other hand, indicate some nonlocal character, i.e., some gradual change of the charge distribution between the different bonds. The charge backdonated to the individual CO mol-



ecule depends on the total number of CO molecules on the surface. It is straight forward to assume that this delocalization proceeds via the electronic charge near to the Fermi level of the Ru substrate.

## ACKNOWLEDGMENTS

The support of Professor G. Ertl and the technical assistance of P. Geng and M. Richard are gratefully acknowledged. We thank Dr. H. Bludau, H. Dietrich, and Dr. H. Over for fruitful discussions. P. He is grateful to the Max-Planck-Gesellschaft for a postdoctoral fellowship. Y. Xu thanks the Alexander-von-Humboldt Stiftung for a stipend.

<sup>1</sup>W. D. Mross, *Catal. Rev. Sci. Eng.* **25**, 591 (1983).

<sup>2</sup>K. Jacobi, H. Shi, M. Gruyters, and G. Ertl, *Phys. Rev. B* **49**, 5733 (1994).

<sup>3</sup>N. Al-Sarraf, J. T. Stuckless, and D. A. King, *Nature* **360**, 243 (1992).

<sup>4</sup>H. Over, H. Bludau, R. Kose, and G. Ertl, *Phys. Rev. B* **51**, 4661 (1995).

<sup>5</sup>H. Over, H. Bludau, R. Kose, and G. Ertl, *Surf. Sci.* **331–333**, 62 (1995).

<sup>6</sup>H. Over, H. Bludau, M. Skottke-Klein, G. Ertl, W. Moritz, and C. T. Campbell, *Phys. Rev. B* **45**, 8638 (1992).

<sup>7</sup>G. Michalk, W. Moritz, H. Pfnür, and D. Menzel, *Surf. Sci.* **129**, 92 (1983).

<sup>8</sup>H. Over, W. Moritz, and G. Ertl, *Phys. Rev. Lett.* **70**, 315 (1993).

<sup>9</sup>A short version of some of the results has been presented at the ECOSS15

conference, Lille, France, Sept. 1995; P. He, Y. Xu, and K. Jacobi, *Surf. Sci.* (in press).

<sup>10</sup>H. Ibach, *Electron Energy Loss Spectrometers - The Technology of High Performance* (Springer, Berlin, 1991).

<sup>11</sup>H. Shi, K. Jacobi, and G. Ertl, *Surf. Sci.* **269/270**, 682 (1992).

<sup>12</sup>K. Jacobi, H. Shi, H. Dietrich, and G. Ertl, *Surf. Sci.* **331–333**, 69 (1995).

<sup>13</sup>G. E. Thomas and W. H. Weinberg, *J. Chem. Phys.* **70**, 1437 (1970).

<sup>14</sup>P. He, H. Dietrich, and K. Jacobi, *Surf. Sci.* **345**, 241 (1996).

<sup>15</sup>P. He and K. Jacobi, *Phys. Rev. B* **53**, 3658 (1996).

<sup>16</sup>H. Over, (1996) unpublished LEED spectra calculations of the (Cs +1CO)(2×2) phase assuming 28% fcc and 72% hcp site occupation.

<sup>17</sup>H. Kondoh and H. Nozoye, *J. Phys. Chem.* **98**, 390 (1994).

<sup>18</sup>W. Erley, H. Wagner, and H. Ibach, *Surf. Sci.* **80**, 612 (1979).

<sup>19</sup>L. Becker, S. Aminpirooz, B. Hillert, M. Pedio, J. Haase, and D. L. Adams, *Phys. Rev. B* **47**, 9710 (1993).

<sup>20</sup>M. E. Davila, M. C. Asensio, D. P. Woodruff, K.-M. Schindler, P. Hoffmann, K.-U. Weiss, R. Dippel, P. Gardner, V. Fritzsche, A. M. Bradshaw, J. C. Conesa, and A. R. González-Elipe, *Surf. Sci.* **311**, 337 (1994).

<sup>21</sup>M. Filali Baba, C. Mijoule, N. Godbout, and D. R. Salahub, *Surf. Sci.* **316**, 349 (1994).

<sup>22</sup>H. Ohtani, M. A. v. Hove, and G. A. Somorjai, *Surf. Sci.* **187**, 372 (1987).

<sup>23</sup>F. Cemic (private communication).

<sup>24</sup>F. M. Hoffmann and R. A. d. Paola, *Phys. Rev. Lett.* **52**, 1697 (1984).

<sup>25</sup>J. J. Weimer, E. Umbach, and D. Menzel, *Surf. Sci.* **155**, 132 (1985).

<sup>26</sup>H. Over, H. Bludau, S. Schwegmann, R. Kose, and G. Ertl (unpublished).

<sup>27</sup>P. A. Schultz and C. H. Patterson, *J. Vac. Sci. Technol. A* **5**, 1061 (1987).