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CO/Rh(111): Vibrational frequency shifts and lateral interactions in adsorbate layers

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High resolution electron energy loss spectroscopy (HREELS), low-energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS) were used to study lateral interactions in the adsorbate layer of the CO/Rh(111) system. The vibrational spectra show that CO adsorbs exclusively on top at low coverage. At about half a monolayer a second adsorption site, the threefold hollow site, becomes occupied as well. A steady shift to higher frequencies of the internal C–O vibrations is observed over the whole coverage range. The frequency of the metal CO (M–CO) vibration in the on-top mode hardly shifts at low coverage. However, upon the emergence of the second adsorption site the M–CO vibrations experience a shift to lower frequencies. The population of the second site is also accompanied by the development of a low temperature shoulder in the TD spectra, indicating an increasingly repulsive interaction in the adsorbed CO layer. Vibrational spectra of isotopic mixtures of ¹²CO and ¹³CO were used to assess the origin of the observed frequency shifts. They confirm that frequency shifts of the C–O stretching vibration at total CO coverage of 0.33 ML in the ($\sqrt{3} \times \sqrt{3}$)R30° structure arise purely from dipole–dipole coupling. Dilution of an isotopic species effectively suppresses frequency shifts arising from dipole–dipole coupling. Therefore, experiments with a small amount of ¹³CO as a tracer to monitor the frequency shifts in the ¹²CO adlayer were carried out over the entire coverage range of ¹²CO. The results demonstrate that dipole–dipole coupling causes the frequency shifts at low coverage (<0.5 ML), whereas chemical effects set in at higher coverage (0.5–0.75 ML), connected with the population of the threefold sites. The results illustrate that HREELS in combination with isotopic dilution is a powerful tool in the assessment of lateral interactions between adsorbed molecules. © 2001 American Institute of Physics. [DOI: 10.1063/1.1355767]

I. INTRODUCTION

Adsorption of carbon monoxide on metal single crystals has been studied extensively as the archetype for the behavior of molecules on surfaces. Many investigations have focused on the determination of the different sites where CO may adsorb, by using vibrational methods such as high resolution electron energy loss spectroscopy (HREELS) and reflection-absorption infrared spectroscopy (RAIRS). Site identification has been based on the internal C–O vibration frequency, which is known to depend specifically on CO–metal coordination in metal-organic compounds. This method relies on transferring the concept of specific spectral regions in metal-organic chemistry to surface science, equating coordination numbers in carbonyl compounds with coordination on surface sites (ontop: 2130–2000 cm⁻¹, twofold bridge: 2000–1880 cm⁻¹, threefold hollow: 1800–1880 cm⁻¹, fourfold hollow: <1800 cm⁻¹).¹

The site-specific CO stretch frequencies were found to shift considerably with increasing CO coverage, for instance on Ni(111),² Ni(100),³ Pt(111),⁴ Cu(100),⁵ Rh(111),^{6,7} and

Rh(100).⁸ Such shifts reflect the interactions between the adsorbate molecules in the adsorption layer. The origin of these coverage-dependent frequency shifts can be twofold:

- (i) Dipole coupling caused by the interaction of CO dipoles vibrating at the same frequency, and
- (ii) Changes in chemical bonding caused by adsorbed molecules on neighboring sites.

Dipole–dipole coupling was first introduced by Hamaker *et al.*⁹ in surface vibrational spectroscopy to explain the C–O frequency shifts on silica-supported platinum. Crossley and King¹⁰ confirmed the existence of dipole–dipole coupling in vibrational spectra of CO on Pt(111) by using isotopic mixtures of ¹²CO and ¹³CO. As this type of coupling is a resonance effect between dipoles oscillating at the same frequency, an isolated ¹³CO molecule in an environment of ¹²CO molecules is not affected by dipole coupling. The original description of a vibrating CO adsorbate by Eischens *et al.*⁹ has been refined to include the interactions of a dipole and its own image, images of other dipoles, and screening of dipole images by the electronic polarizability of the adsorbate.^{15–17} The correctness of this description has been confirmed for CO on several metal single crystal surfaces in RAIRS experiments with isotopic mixtures, for

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instance on Pt(111),^{10,11} Pt(100),^{11,12} Pd(100),¹³ and in HREELS by analysis of the dispersion of the internal C–O mode in the $c(2\times 2)$ structure on Cu(100).¹⁴

Obviously, vibrational frequencies may also change when chemical bonding between metal and adsorbate is altered by the effect of neighbors. Such changes affect isotopes equally and shifts of chemical origin are thus straightforwardly revealed by isotope tracers.

Coverage-dependent frequency shifts complicate the determination of CO adsorption sites on the basis of the simple scheme for linear, bridged, and threefold adsorption geometry given above and may lead to erroneous assignments. Indeed, a photoelectron diffraction (PED) study by Schindler *et al.*¹⁸ in 1993 revealed that CO adsorbs on Ni(111) in the threefold hollow site, and not in the bridge site that was previously assigned on the basis of RAIRS, HREELS, and LEED. Here, the internal C–O frequency shifts from 1831 cm^{-1} at low coverage to 1905 cm^{-1} in the $c(4\times 2)$ structure at 0.50 ML, a value that at first sight would be associated with bridge sites.

Another example of an initially incorrect assignment of adsorption sites on the basis of vibrational spectroscopy in combination with LEED is provided by CO on Rh(111).^{6,7,19,20} A linear species was observed over the entire coverage range, with a CO stretch frequency increasing from 2016 cm^{-1} at low coverage to 2065 cm^{-1} in a (2×2) structure at saturation coverage.⁷ At higher coverage a second adsorption site was found with an initial internal C–O frequency of 1835 cm^{-1} shifting to 1855 cm^{-1} at saturation. This site was assigned to a bridge site based on the internal C–O frequency assisted by arguments from LEED¹⁹ and a subsequent tensor-LEED study.²⁰ From the relative peak intensities of the two CO species in EELS, the authors arrived at the conclusion that the (2×2) structure at saturation coverage contains two on-top and one bridged CO per unit cell. An investigation of the CO/Rh(111) system by high resolution core level spectroscopy (HRCLS)²¹ confirmed the on-top site in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ and (2×2) -3CO structures but revealed that the second site in the (2×2) -3CO structure is not a twofold bridge but a threefold hollow site. Reconsideration of the tensor-LEED experiments²² as well as a recent surface x-ray diffraction (SXRD) study²³ confirmed the new assignment.

The new structural analysis of CO/Rh(111) makes it worthwhile to reinvestigate this system by HREELS with the performance of a new generation of spectrometers, in order to assess the nature of the frequency shifts and interpret them in terms of lateral adsorbate interactions by using the isotopic dilution technique. First, we describe experiments at fixed total CO coverage as previously reported for other CO–metal combinations^{10,11,13,24} to confirm that dilution of an isotopic species (*viz.* ^{13}CO in ^{12}CO) suppresses the dipole coupling. Next, we report the use of ^{13}CO as a tracer to monitor frequency shifts of chemical origin in the ^{12}CO adlayer over the entire coverage range. In a subsequent publication we intend to compare these shifts to the results of density functional theory (DFT) calculations.

II. EXPERIMENT

The experiments were performed in a home-built, two-stage stainless-steel ultrahigh vacuum chamber with a base pressure of about 5×10^{-11} mbar. The first chamber is equipped with a sputter gun and can be sealed off by a gate valve from the main chamber. The latter houses the spectroscopic equipment, arranged in three levels. The first contains a quadrupole mass spectrometer (Prisma QME200, Balzers) for thermal desorption spectroscopy (TDS) and residual gas analysis. The second level has a four-grid, reverse-view low-energy electron diffraction (LEED) system (RVL2000/8/R, LK Technologies) which can also be used for Auger electron spectroscopy (AES). The last level contains the high resolution electron energy loss spectrometer (ELS3000, LK Technologies) housed in a double μ -metal shielding.

The rhodium crystal was oriented in the [111] direction within 0.5° and polished by standard procedures. The crystal was mounted with 0.3 mm tantalum wires on the sample holder, where it can be cooled to liquid nitrogen temperature and heated to 1400 K by ohmic resistance. Temperatures were measured with a type N thermocouple spot-welded on the back side of the crystal. Sample preparation was done by cycles of argon sputtering at 900 K (1.5 keV , $5\ \mu\text{A}/\text{cm}^2$) and annealing at temperatures between 900 and 1100 K and a finishing flash annealing to 1400 K. Surface cleanliness was initially checked by AES and controlled before every experiment by HREELS. The commonly used annealing procedure at elevated oxygen pressure was abandoned because this treatment often resulted in a loss peak at about 560 cm^{-1} caused by oxygen left on the surface.

Gas adsorption occurred by exposing the surface at 150 K to an increased CO background pressure of about 1×10^{-8} mbar using research grade ^{12}CO (Linde AG) and ^{13}CO (99% pure, Cambridge Isotope Laboratories). Exposures are given in Langmuir units ($1\text{ L}=1.33\times 10^{-6}$ mbar) and were not corrected for ion gauge sensitivity. CO coverage is reported in monolayers; isotopic ratios were checked with the mass spectrometer. In order to improve ordering of the adsorbate layer the sample was briefly heated to 200 K after CO adsorption. The HREELS spectra were recorded at 90 K and measured in specular scattering geometry with a resolution (elastic peak at full width half maximum) of about 16 cm^{-1} (2 meV). Reported primary energies are not corrected for contact potential differences.

III. RESULTS AND DISCUSSION

A. LEED experiments and site assignment

The HREELS spectrum of the clean Rh (111) surface, shown in Fig. 1 (bottom) together with the corresponding LEED pattern and structure model, consists of a smooth background spectrum of inelastically scattered electrons. The LEED pattern exhibits the threefold symmetry of the hexagonal 111-fcc surface.

After exposing a small amount (0.05 L) of CO, two loss peaks appear at 468 cm^{-1} (58.0 meV) and 2015 cm^{-1} (249.8 meV) in the M–CO and C–O stretching vibration region, respectively. Both frequencies clearly indicate that CO occupies the on-top site at low coverage, in agreement with a

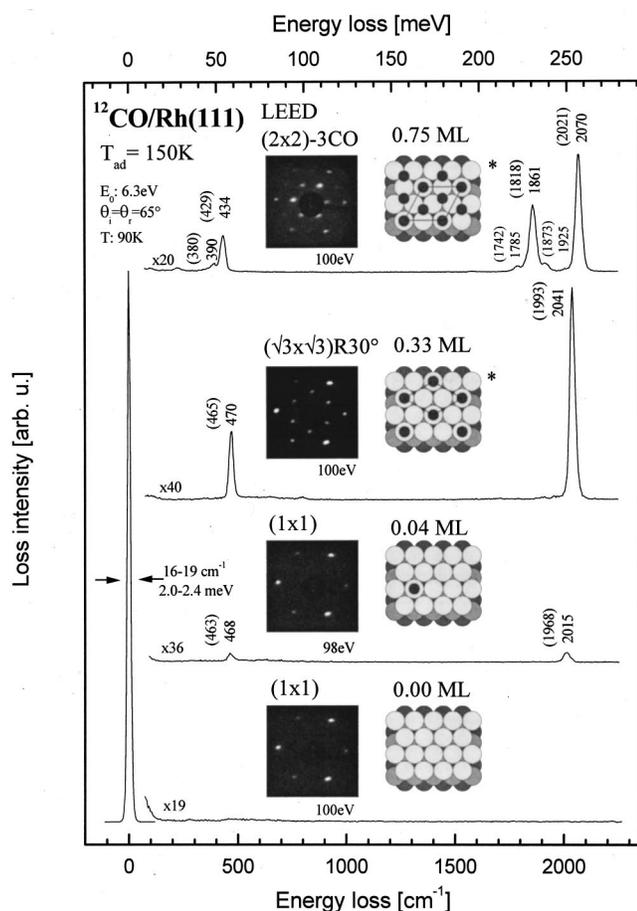


FIG. 1. HREELS, LEED, and corresponding structure models [* structural analysis by HRCLS (Ref. 20) and tensor-LEED (Ref. 21)] at selected ^{12}CO coverage from bottom to top: 0.00, 0.04, 0.33, and 0.75 ML. The frequencies in brackets are obtained at the same coverage of pure $^{13}\text{C}^{16}\text{O}$ adlayers.

coverage-dependent HRCLS study.²⁵ The LEED pattern hardly changes at such a low coverage. CO adsorbs on top without forming any ordered structures as visualized in the structure model beside the LEED pattern. Wave numbers given in brackets in Fig. 1 were obtained from $^{13}\text{C}^{16}\text{O}$ at the same coverage.

Exposure of the surface to about 1 L of CO yields a coverage of 0.33 ML and leads to the development of a sharp $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ LEED pattern. The HREELS peaks shift to 470 cm^{-1} (58.3 meV) and 2041 cm^{-1} (253.1 meV). These values are still characteristic of linear CO, in agreement with HRCLS^{21,25} and tensor-LEED;²² the resulting structure model is depicted in Fig. 1.

After an exposure of about 4 L of CO the $(2\times 2)\text{-}3\text{CO}$ LEED pattern appears corresponding to the saturation coverage of 0.75 ML under UHV conditions (Fig. 1, top spectrum). The on-top C–O stretching frequency is further shifted to 2070 cm^{-1} (256.6 meV), whereas the M–CO stretching frequency is subjected to a significant opposite shift towards 434 cm^{-1} (53.8 meV). In addition, a second major vibrational state is observed in both frequency regions at 1861 cm^{-1} (230.7 meV) and 390 cm^{-1} (48.3 meV), indicating the occupation of a second site. Recent HRCLS,²¹ tensor-LEED,²² and SXRD²³ studies have identified this site

as a threefold hollow site. The corresponding structure has been included in Fig. 1. At the low- and high-energy side of the threefold hollow C–O loss peak, two further minor losses are observed at 1785 cm^{-1} (221.3 meV) and 1925 cm^{-1} (238.7 meV) that cannot be assigned straightforwardly from the structure model. We note that the fact that these peaks develop at higher coverage makes it unlikely that they are associated with defects. We therefore tentatively attribute the 1925 cm^{-1} (238.7 meV) peak to a twofold bridge site, since its frequency lies within the range found for bridged sites on Rh(100).^{8,26,27} Adsorption of CO on bridge sites of the (111) surface might occur in domain boundaries between regions of $(2\times 2)\text{-}3\text{CO}$ structure. The other minor vibrational state at 1785 cm^{-1} may be assigned to the antisymmetric dipole–dipole coupling of the CO in the two inequivalent threefold sites in the 2×2 unit cell (one hcp and one fcc site). Detailed theoretical calculations of the frequencies are required to clarify this interpretation. We will ignore these two small peaks in the rest of this paper.

The spectra obtained by dosing pure ^{13}CO show the same loss features, but shifted to lower frequencies due to the isotopic effect (Fig. 1, frequencies in brackets). We also tried to reproduce other reported CO-induced superstructures.^{25,28} Above 0.5 ML the so-called “split (2×2) ” structure was observed which develops into the $(2\times 2)\text{-}3\text{CO}$ structure at exposure of about 4 L. Annealing the $(2\times 2)\text{-}3\text{CO}$ structure to 240 K (still below the desorption temperature of CO), converted it irreversibly into a diffuse split (2×2) LEED pattern. For this reason the sample temperature was always kept below 200 K for the HREELS experiments after the surface had been exposed to CO.

The $p(2\times 2)$ structure at 0.25 ML, first reported by Thiel *et al.*,²⁸ could not be reproduced. This structure has not been observed in subsequent investigations^{19,20,29} and it was even suggested³⁰ that the $p(2\times 2)$ does not exist on Rh(111). However, Beutler *et al.* reported the existence of the $p(2\times 2)$ structure, albeit at temperatures below 120 K.²⁵ We also could not reproduce the (4×4) structure that these authors reported.²⁵ It remains unclear whether this is because we could not realize the delicate conditions required for these structures or perhaps because our LEED-CCD camera has insufficient sensitivity.

B. TDS experiments

TDS experiments (Fig. 2) were performed in order to obtain the calibration of the coverage versus exposure and to determine the kinetic parameters of the CO desorption. The spectra were measured with a linear heating rate β of 5 K/s. At low coverage a single desorption peak is observed with its peak maximum around 520 K. This peak shifts towards lower temperature and broadens slightly with increasing coverage. At CO coverages above 0.5 ML a shoulder develops at the low temperature side of the desorption peak, showing a maximum at approximately 415 K for saturation coverage.

The inset in Fig. 2 shows the TDS peak areas versus coverage. The almost perfectly linear dependence points to a coverage-independent sticking coefficient, suggesting precursor-mediated adsorption kinetics. This is in agreement with molecular beam experiments by Beutl *et al.*,³¹ who

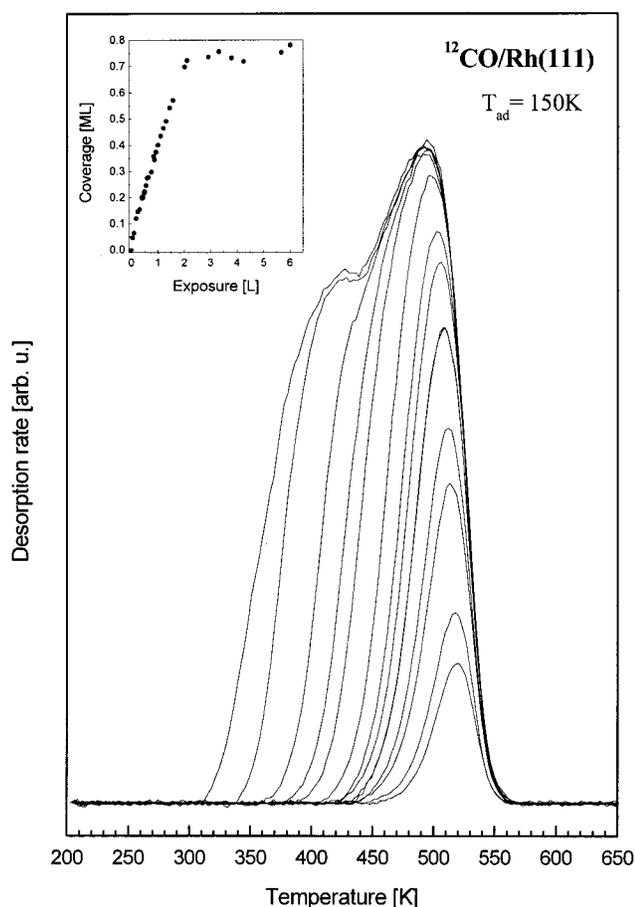


FIG. 2. TPD spectra of ^{12}CO adsorbed at 150 K. The heating rate β was 5 K/s. The inset shows the uptake curve.

found evidence for an extrinsic precursor on the condensed adsorption phases above 0.25 ML at temperatures below 140 K, which is close to the adsorption temperature used in the experiments reported here.

In order to extract kinetic parameters for desorption of CO we used the method proposed by Chan, Aris, and Weinberg,³² yielding $E_{\text{des}} = 151 \pm 5$ kJ/mole and $\nu = 10^{15 \pm 1} \text{ s}^{-1}$ and the coverage-corrected leading edge method,³³ yielding $E_{\text{des}} = 159 \pm 5$ kJ/mole and $\nu = 10^{15 \pm 1} \text{ s}^{-1}$, both in the limit of zero coverage. These values agree reasonably well with those determined by Wei *et al.*,³⁰ who found desorption energies between 160 and 165 kJ/mole and pre-exponential factors of $10^{16} - 10^{17} \text{ s}^{-1}$. Previous TDS work has yielded lower desorption energies, however, in combination with lower pre-exponential factors.²⁸ The differences are most likely due to the different methods used for deriving kinetic parameters from TDS spectra.^{34,35}

C. HREELS of ^{12}CO at different coverages

Figure 3 shows how the HREELS spectra develop with increasing ^{12}CO coverage. The frequencies of the main loss features are given in Fig. 4(a) and the relative loss intensities as ratio of loss peak to elastic peak area in Fig. 4(b).

The coverage sequence starts with the lowest observed on-top CO frequencies at 468 and 2015 cm^{-1} for the M-CO and C-O stretching vibration, respectively. With increasing

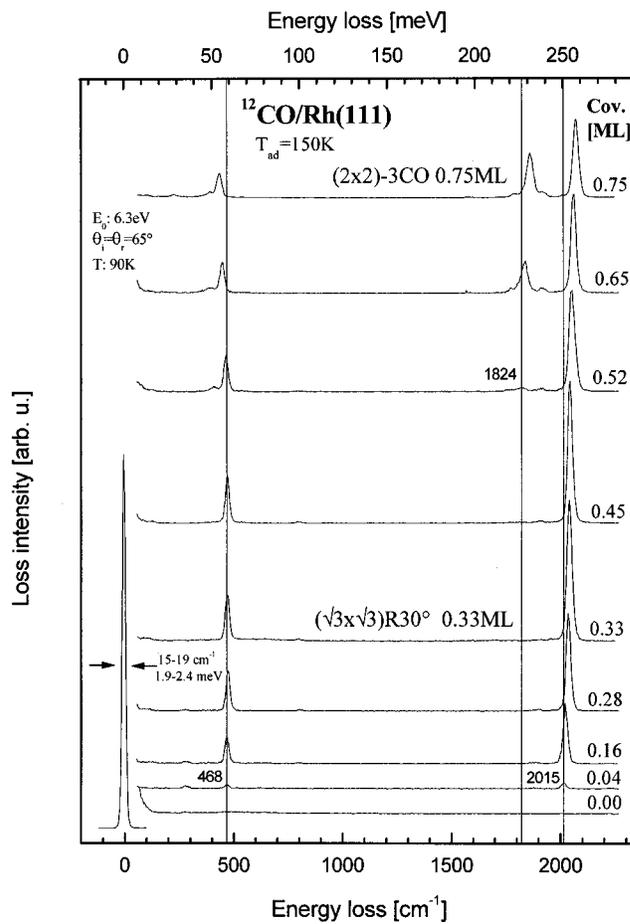
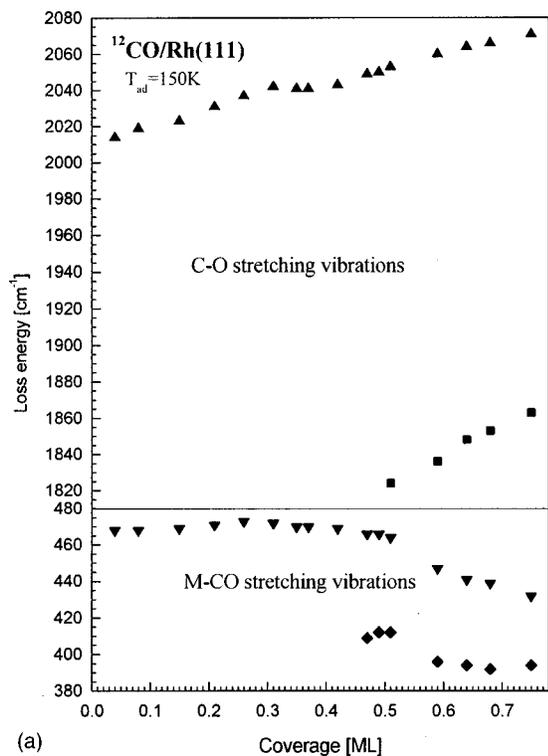


FIG. 3. HREELS spectra with increasing ^{12}CO coverage. The lines are at the frequency of the first emergence of the respective loss peak.

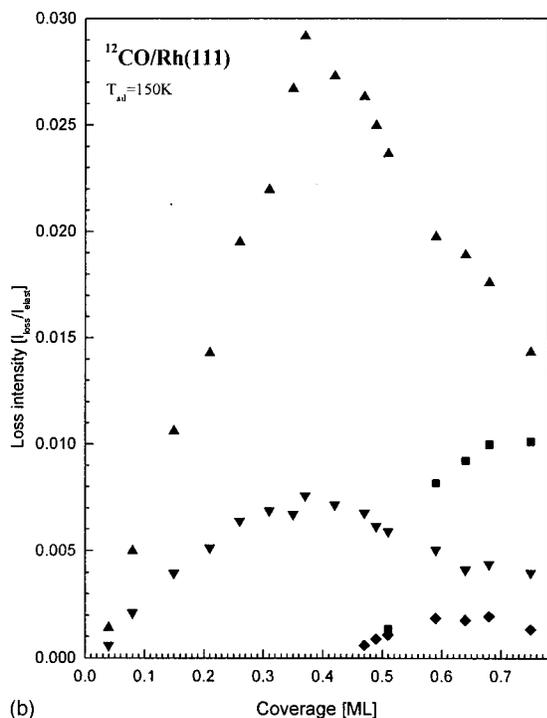
coverage the internal C-O frequency shifts continuously to 2070 cm^{-1} at saturation coverage (0.75 ML), with a range between 0.33 and 0.5 ML where the frequency is constant at 2040 cm^{-1} . The M-CO stretching vibration hardly changes between 0 and 0.5 ML of CO, but decreases strongly between 0.5 and 0.75 ML, i.e., in the range where the second major adsorption site, the threefold hollow site, also becomes populated. The C-O stretch frequencies of the threefold CO shifts from 1815 to 1861 cm^{-1} and the metal-carbon vibration from 410 to 394 cm^{-1} , as the coverage increases from 0.5 to 0.75 ML [Fig. 4(a)].

The HREELS intensities of the linearly adsorbed CO [Fig. 4(b)] increase monotonously with coverage up to 0.5 ML and decrease to approximately 50% of their maximum value when the threefold sites have been filled at saturation. This agrees well with the site occupation of CO at 0.5 ML (all CO linear) and 0.75 ML (0.5 ML in threefold and 0.25 ML in linear sites). Figure 4(b) also shows that threefold CO on Rh(111) appears approximately a factor of 3 less intense in HREELS than linear CO, as can be deduced from the respective intensities at saturation coverage.

Note, however, that peak intensities in HREELS are in general unreliable as a measure of fractional coverage, the reason being that the dynamic dipole moment of CO varies for different sites, while it usually changes with coverage too. In addition, loss intensities in HREELS are even more



(a)



(b)

FIG. 4. (a) Vibrational frequencies of the principal adsorption sites as function of the ^{12}CO coverage; \blacktriangle : internal C–O vibrations on-top site; \blacksquare : threefold hollow site. M–CO stretching vibrations: \blacktriangledown : on-top site; \blacklozenge : threefold hollow site. (b) Relative loss intensities expressed of the principal adsorption sites as function of the ^{12}CO coverage expressed as ratio of loss peak and elastic peak area; \blacktriangle : internal C–O vibrations on-top site; \blacksquare : threefold hollow site. M–CO stretching vibrations: \blacktriangledown : on-top site; \blacklozenge : threefold hollow site.

difficult to quantify than, e.g., reflectance changes in RAIRS because changes in adsorbate layer can affect the measured elastic and inelastic intensity differently due to the finite acceptance angle of the spectrometer.^{36,37} In addition, intensi-

tytransfer phenomena may play a role, as we will see in the next section.

Upon filling the Rh(111) surface with CO, half of the already adsorbed CO molecules are forced to change site from linear to threefold hollow. This is qualitatively recognized in the plot of HREELS intensity versus coverage in Fig. 4(b). Note that the strongest increase in threefold CO is observed between 0.51 and 0.6 ML. The observed site occupation is in agreement with the coverage and temperature dependent HRCLS study of Beutler *et al.*²⁵ These authors reported an increase of the fractional coverage of CO on threefold hollow sites from 0.02 to 0.21 ML in the total coverage range from 0.50 to 0.56 ML. This is indeed the coverage range where we observe the strongest increase in the threefold CO intensity [Fig. 4(b)] and where large shifts occur in the Rh–CO frequencies of both linear and threefold sites [Fig. 4(a)].

D. HREELS at 0.33 ML CO with variable $^{12}\text{CO}/^{13}\text{CO}$ composition

The frequency shifts of Fig. 4(a) can have two causes, namely dipole–dipole coupling between CO molecules vibrating at the same frequency, and changes in chemical bonding due to the effect of neighboring molecules. As explained in the Introduction, dilution of isotopically labeled ^{13}CO in an environment of ^{12}CO provides a means to suppress the dipole–dipole coupling in the ^{13}CO without affecting its chemical environment.^{10,11}

Figure 5 shows a series of HREELS spectra at a fixed total CO coverage of 0.33 ML, corresponding to the ordered $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ structure, but at varying $^{12}\text{CO}/^{13}\text{CO}$ ratio. All C–O stretch frequencies are given in Fig. 6. The spectra show two loss peaks in the internal C–O vibration region, the ^{13}CO at lower and the ^{12}CO at higher energy. Two lines indicate the experimental C–O singleton frequencies of both isotopic species. The conclusion from Figs. 5 and 6 is that small amounts (9%) of CO in the environment of isotopically different CO in the $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ structure vibrate at their individual singleton frequencies, i.e., as if they were present as isolated molecules. This proves that the shift of the internal CO frequency between 0 and 0.33 ML is entirely due to dipole–dipole coupling between neighboring molecules, and that chemical bonding effects play no role.

As Fig. 5 shows, ^{12}CO in 0.33 ML of CO yields much higher intensities than equal coverages of ^{13}CO do. Intensity transfer from the low- to the high-energy loss peak causes this. The effect can be described qualitatively by assuming that in-phase ^{12}CO – ^{12}CO and ^{12}CO – ^{13}CO modes contribute intensity to the high frequency band while the less intense out-of-phase ^{12}CO – ^{13}CO and in-phase ^{13}CO – ^{13}CO modes contribute to the low frequency band.^{9–11}

Thus, the internal C–O frequency shift on Rh(111) at 0.33 ML arises purely from dipole–dipole coupling. In the following we use a small amount of ^{13}CO as a tracer to investigate the nature of frequency shifts in ^{12}CO over the entire coverage range up to 0.75 ML.

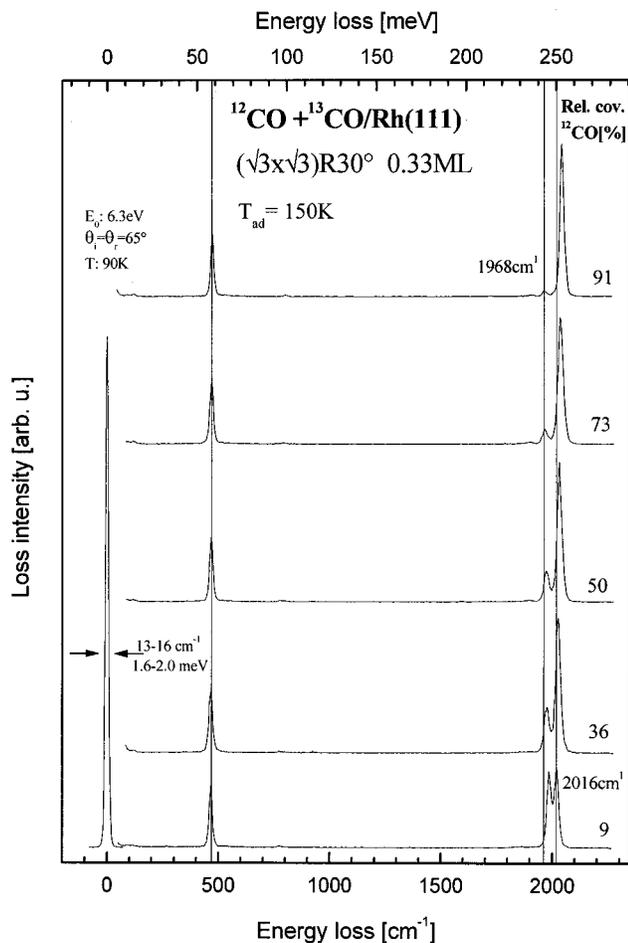


FIG. 5. HREELS spectra at total CO coverage 0.33 ML with different fractional coverage of ^{12}CO and ^{13}CO . The lines mark the singleton frequencies of both isotopic species.

E. HREELS at fixed low fractional ^{13}CO and variable fractional ^{12}CO coverage

The spectra of ^{12}CO at increasing coverages between 0.08 and 0.75 ML along with a small amount of ^{13}CO (0.04 and 0.08 ML as indicated) as a tracer are shown in Fig. 7. All frequencies of the internal C–O vibrations are given in Fig. 8. Although the phenomenon of intensity transfer argues in favor of choosing the tracer at the higher frequency and the majority species at the lower, we have nevertheless chosen ^{13}CO as the diluted component, to prevent overlap of dipole–dipole shifted ^{13}CO peaks with the ^{12}CO peak at its singleton frequency. The disadvantage of this choice is that the intensity of the ^{13}CO tracer is small. Low fractional ^{12}CO coverages were measured with 0.04 ML coadsorbed ^{13}CO , whereas we doubled the amount of ^{13}CO to 0.08 ML at higher ^{12}CO coverages (0.5 ML and up) to gain sufficient intensity in the ^{13}C –O peak. To assess the difference in dipole–dipole coupling between 0.04 and 0.08 ML of ^{13}CO , a control experiment was done with 0.08 ML ^{13}CO in the low coverage regime of ^{12}CO (filled symbols in Fig. 8). The experiment shows that dipole–dipole coupling in 0.08 ML of ^{13}CO in the environment of ^{12}CO may safely be ignored.

As Figs. 7 and 8 show, the ^{13}CO tracer vibrates at its singleton frequency over the coverage range up to 0.5 ML,

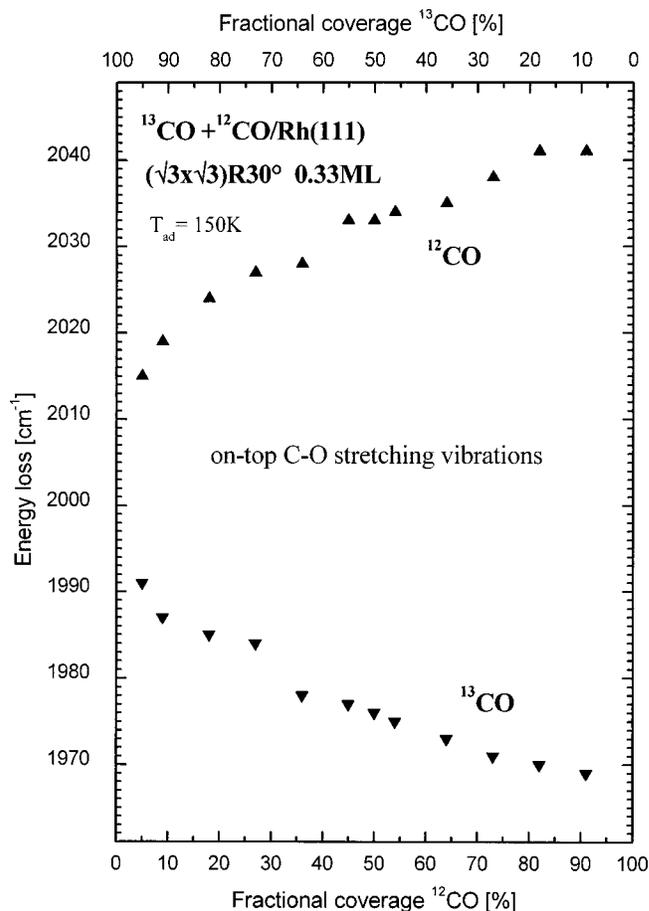


FIG. 6. Loss frequencies of the internal C–O vibrations of ^{12}CO (\blacktriangle) and ^{13}CO (\blacktriangledown) as function of the isotopic composition at 0.33 ML total CO coverage.

i.e., where CO is adsorbed exclusively at on top sites, although the frequency of the ^{12}CO shifts considerably upward. The Rh–CO stretching frequency hardly shifts in this range. However, as HREELS cannot resolve the contributions of the two isotopic species to this loss feature, we leave it out of the discussion. We conclude that dipole–dipole coupling causes the entire shift in the ^{12}CO frequency for coverages between 0 and 0.5 ML.

Dipole–dipole shifts are quantitatively described by the model of Persson and Ryberg.¹⁷ The frequency, ω , depends on coverage as

$$\left(\frac{\omega}{\omega_0}\right)^2 = 1 + \frac{\alpha_v U \Theta}{1 + \alpha_e U \Theta},$$

in which ω_0 is the vibrational frequency of the loss at zero coverage (singleton frequency: 2009 cm^{-1}), Θ is the coverage, α_v is the vibrational polarizability of the adsorbed molecule, α_e is its electronic polarizability, and U is the summation term of the dipoles ($U = 0.67\text{ \AA}^{-3}$). The experimentally observed shifts are reproduced quantitatively up to 0.4 ML when we use the following polarizabilities $\alpha_v = 0.22\text{ \AA}^3$ and $\alpha_e = 2.57\text{ \AA}^3$. The small shift of the on-top Rh–CO vibration is negligible.

For CO coverages increasing from 0.5 to 0.75 ML, where the threefold hollow sites become occupied, the inter-

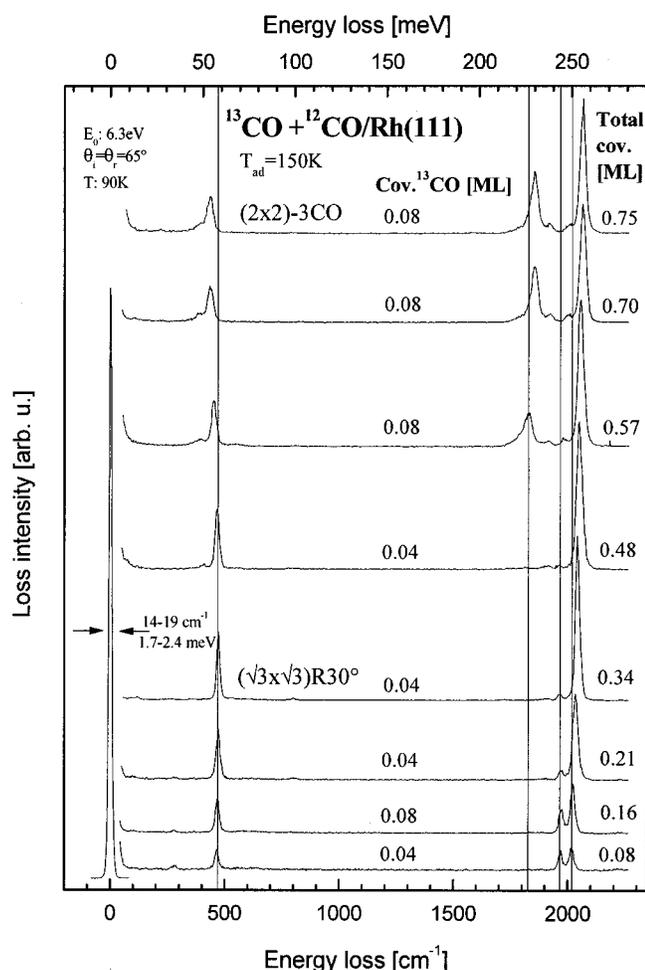


FIG. 7. HREELS spectra of two low (0.04 and 0.08 ML) fractional ^{13}CO coverage with increasing ^{12}CO coverage.

nal ^{13}C -O on-top vibration shifts to higher frequencies. The frequency increases steeper than that of the on-top ^{12}C -O vibration and reaches approximately 2015 cm^{-1} at 0.75 ML. The low intensity and the shift closer to the base of the intense ^{12}C -O on-top loss reduces the accuracy of the frequency determination somewhat.

We attribute the observed frequency shift of about 45 cm^{-1} of the on top ^{13}CO between 0.5 and 0.75 ML to changes in the adsorption bond caused by the densification of the adsorbate layer into the (2×2) -3CO structure. These changes lead to a destabilization of the on-top CO as compared to its bonding at lower coverages. The fact that this chemical shift of approximately 45 cm^{-1} between 0.5 and 0.75 ML exceeds the total shift in the linear ^{12}CO of only about $15\text{--}20\text{ cm}^{-1}$, is attributed to reduced dipole-dipole coupling, as the coverage of linear ^{12}CO molecules decreases by a factor of 2. In addition, the dipole-dipole coupling in the (2×2) network of linear CO may be affected by the presence of the other 2×2 nets of CO in hcp and fcc sites, which together make up the (2×2) -3CO structure. A brief calculation shows the magnitude of the effects. In the absence of chemical interaction, we expect a frequency of approximately 2035 cm^{-1} for the (2×2) network of linear ^{12}CO [Fig. 4(a), measurement at 0.25 ML]. If this were the only

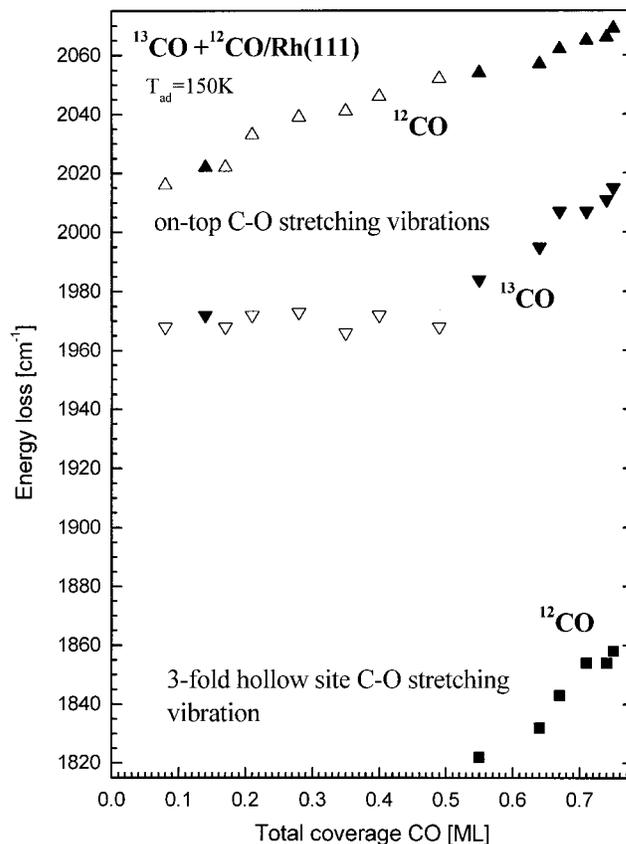


FIG. 8. Internal C-O frequencies of the principal adsorption sites as function of the total CO coverage, \blacktriangle , Δ ^{12}CO on-top, and \blacktriangledown ^{13}CO on-top; open symbols at 0.04 ML ^{13}CO coverage, closed symbols at 0.08 ML of ^{13}CO .

correction, we would find a chemical shift of $2070\text{--}2035 = 35\text{ cm}^{-1}$, as compared to the experimentally determined shift of 45 cm^{-1} . This indicates that the attenuating effect of the threefold CO on the dipole-dipole coupling between the linear CO molecules, suggested above, is small (at most 10 cm^{-1}), if present at all.

We intend to verify the above assignments in a theoretical study of the CO/Rh(111) system by *ab initio* DFT calculations, which are currently in progress.

IV. CONCLUSIONS

CO adsorption on Rh(111) at coverages between zero and saturation (0.75 ML) were studied by HREELS, LEED and TDS with the following results:

- At low coverage CO adsorbs only on top. The singleton frequencies are found at 2015 cm^{-1} (249.8 meV) and 468 cm^{-1} (58.0 meV) for the C-O stretching and Rh-CO stretching vibration, respectively. TDS analysis yields an activation energy of desorption of $155 \pm 5\text{ kJ/mole}$ and a pre-exponential factor of $10^{15 \pm 1}\text{ s}^{-1}$.
- The frequencies shift to 2041 cm^{-1} (253.1 meV) and 470 cm^{-1} (58.3 meV) at 0.33 ML, where a sharp $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ LEED pattern of linear CO is observed. Experiments with isotopic mixtures of ^{12}CO and ^{13}CO reveal that the internal C-O vibration frequencies depend only on the fractional coverage of

the respective isotopic species, proving that the frequency shift of 26 cm^{-1} (3.2 meV) in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ CO structure arises purely from dipole-dipole coupling.

- (iii) At about 0.5 ML CO starts to occupy the threefold hollow site, which is accompanied by the development of a low temperature shoulder in the TDS.
- (iv) At saturation coverage of 0.75 ML, the LEED pattern exhibits a (2×2) -3CO structure, in which CO occupies one linear and two threefold hollow sites. The threefold CO vibrations appear at 1861 cm^{-1} (230.7 meV) and 390 cm^{-1} (48.4 meV), and those of the linear C-O at 2070 cm^{-1} (256.6 meV) and 434 cm^{-1} (53.8 meV).
- (v) Experiments with small amounts of ^{13}C O as a vibrational tracer show that all frequency shifts in the HREELS spectra of CO up to 0.5 ML are due to dipole-dipole coupling. At coverages higher than 0.5 ML, however, the ^{13}C O tracer reveals that the filling of the surface to the (2×2) -3CO structure causes significant chemical effects, leading to the destabilization of both linear and threefold CO. These repulsive lateral interactions in the (2×2) -3CO structure correspond to a frequency shift of approximately 45 cm^{-1} . The total frequency shift of the linear CO in the adsorbate layer at saturation coverage can largely be understood as the consequence of dipole-dipole coupling in an isolated (2×2) network of CO, plus the effect of the modified adsorbate bonding due to neighboring CO molecules.

The results illustrate that HREELS in combination with the use of isotopic mixtures is a powerful tool in the assessment of lateral in adsorbate layers, in particular in combination with theoretical calculations which are currently in progress.

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