Coadsorbate effects on adsorbate vibrational properties

P. Jakob\textsuperscript{a,b,}\textsuperscript{*}, A. Schiffer\textsuperscript{b}

\textsuperscript{a}Fachbereich Physik und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, D-35032 Marburg, Germany
\textsuperscript{b}Physik-Department E 20, Technische Universität München, D-85747 Garching, Germany

\textbf{A R T I C L E   I N F O}

Article history:
Received 16 July 2008
Accepted for publication 26 February 2009
Available online 9 March 2009

Keywords:
Carbon monoxide
Infrared absorption spectroscopy
Low index single crystal surfaces
Metal surfaces
Ruthenium
Oxygen
Vibrations of adsorbed molecules

\textbf{A B S T R A C T}

A quantitative analysis of infrared absorption spectra to determine coadsorbate induced relative changes of the vibrational polarizability \( \chi \) of an adsorbate mode and of the dielectric screening \( \epsilon \) due to this extra species is presented. Four (ternary) coadsorption systems consisting of the Ru(0001)-(2 \times 2)-(X + CO + O) layer with additional coadsorbates X + H, NO, CO, or O (all of them occupying the remaining empty fcc site) have been studied with FT-IRAS, TDS, LEED and work function change measurements. On-top CO is thereby used as a probe molecule to monitor coadsorbate effects on the dielectric properties of the layer. The vibrational polarizability \( \chi \) associated with the internal C–O stretch mode \( (\nu_{C-O}) \) of on-top CO is lowered by all coadsorbates. The dielectric screening \( \epsilon \) within the adsorbate layer is reduced in the presence of the atomic coadsorbates O and H whereas an increase of \( \epsilon \) is found for the molecular coadsorbates; three-fold coordinated CO and NO. The derived changes of \( \chi \) and \( \epsilon \), as well as the involved line shifts \( \nu_{C-O} \) and \( \nu_{\text{MB}}\text{-CO} \) can be understood in terms of the standard Blyholder backbonding model, i.e. CO 5\( \sigma \) charge donation to the metal combined with a backdonation to electronic states with 2\( \pi^* \) character.

\textsuperscript{\textcopyright} 2009 Elsevier B.V. All rights reserved.

1. Introduction

The aim of the present study is to compare the influence of various coadsorbates X = H, NO, CO, or O at identical locations on the vibrational properties of a probe molecule, namely on-top CO on Ru(0001). In order to stabilize these coadsorbate systems, an oxygen \( (2 \times 2) \) overlay has been used as a template. It is essential for the present work to precisely accommodate specific atoms or molecules into this Ru(0001)-(2 \times 2)-(CO + O) layer. This way a well ordered ternary coadsorbate system is formed which contains oxygen, on-top CO, and a third species X, a quarter monolayer (ML) each.

The line position \( \nu \) of an adsorbate vibration represents the primary quantity of observation for surface vibrational spectroscopies such as infrared reflection absorption spectroscopy (IRAS) or high resolution electron energy loss spectroscopy (HREELS)\textsuperscript{[1,2]}. It contains valuable information regarding adsorbate–substrate and adsorbate–adsorbate interactions. Specifically, from the observation of the C–O stretch modes \( (\nu_{C-O}) \) of a mixed layer containing \textsuperscript{12}C\textsuperscript{16}O and \textsuperscript{13}C\textsuperscript{16}O isotopic species, the respective C–O stretch resonances frequencies with and without dynamical lateral interactions included can be specified\textsuperscript{[3,4]}. Along with the isotopic shift factor \( k_{is} \) of vibrational modes, (static) chemical shifts and (dynamical) dipole coupling shifts can be disentangled\textsuperscript{[3–7]}.

\textsuperscript{*} Corresponding author. Address: Fachbereich Physik Philipps-Universität Marburg, D-35032 Marburg, Germany, Tel.: +49 6421 2824328.
E-mail address: peter.jakob@physik.uni-marburg.de (P. Jakob).

Related quantities which are less straightforward to derive from spectroscopic data are the vibrational and electronic part of the polarizability, \( \chi_e \) and \( \chi_r \), respectively (both of them referring to oscillators including their image dipoles). In principle, their magnitudes can be extracted from (i) the integrated absorption intensity \( I \), (ii) the experimentally observed line position \( \nu \) and (iii) the hypothetical singleton line position \( \nu_{\text{single}} \) using the relations\textsuperscript{[8–11]}:

\[ I = \frac{G(\nu)}{1 + \chi_{e}U} \frac{\nu_{\text{single}}}{\nu^2} \]

and

\[ \frac{\nu^2 - \nu_{\text{single}}^2}{\nu_{\text{single}}^2} = \frac{\chi_{e}U}{1 + \chi_{e}U} \quad \text{with} \quad U = \sum_{i,j} \frac{1}{|R_i - R_j|^3} \]

In our analysis the singleton frequency \( \nu_{\text{single}} \) refers to the imaginary line position of an infrared active vibrational mode \( \nu \) for switched-off dynamical dipole–dipole coupling\textsuperscript{[4,12–14]}. We note that the term ‘singleton frequency’ is not defined uniquely in the literature. Quite generally, it is used to characterize oscillating species isolated from their surroundings and serves as a reference to specify dynamical lateral coupling within dense layers\textsuperscript{[3,4]}. Two different meanings of the term singleton exist: first, it may refer to isolated species, isolated meaning adsorbed on an otherwise bare surface, i.e. with neither static, nor dynamical interactions acting on them\textsuperscript{[15,16]}; second, it may correspond to an isolated species embedded in a layer of other (or identical) species, and with isolated meaning disregarding any dynamical interactions, but with static (chemical) interactions included\textsuperscript{[4,12–14]}.
Only in the second case it may be used as a reference value to quantify dynamical lateral coupling; this is why we adhere to this interpretation. In order to avoid confusion (and in accordance with the early paper of Crossley and King [4]), we will use the term “isolated singleton” whenever single species on bare surfaces are meant, and “surrounded singleton” (or simply “singleton”), when a species embedded within its surroundings, but lacking any vibrational coupling is meant. Note that, quite naturally, the isolated singletons represent trivial cases of (surrounded) singletons.

The dynamical lateral coupling within the adsorbate system is characterized by the lattice sum \( U \) of interacting oscillators (dipoles including self image dipoles) and a dielectric constant \( \varepsilon = 1 + x_{\varepsilon} U \), with \( x_{\varepsilon} \) denoting the non-resonant, electronic part of the polarizability. The position vectors of interacting adsorbate species within the ordered array are given by \( \vec{R}_i \) and \( \vec{R}_j \), the density of the layer (molecules/m²) by \( N_L \). In our analysis we will be primarily using the macroscopic parameter \( \varepsilon \) instead of the microscopic quantity \( x_{\varepsilon} \), since the various contributions to \( \varepsilon \) are manifold and their proper consideration difficult.

In order to obtain absolute intensities from Eq. (1), the function \( G(\theta) \) containing the geometrical information of the experimental setup must be known too. In our case (and most others alike) \( G(\theta) \) is difficult to quantify, as the infrared radiation impinges onto the sample within a cone rather than at a well defined angle \( \theta \). For glancing incidence (\( \theta \approx 85^\circ \)) \( G(\theta) \) depends very sensitively on the (mean) angle of incidence \( \theta \) [17,18].

To a good approximation \( G(\theta) \) is proportional to \( \sin^2\theta/\cos\theta \) [19]; a change of \( \theta \) by 0.5° then alters \( G(\theta) \) by \pm 10%.

As will be detailed in Section 3, relative changes of \( x_{\varepsilon} \) and of the ‘dielectric constant’ \( \varepsilon \) of the adlayer associated with coadsorption of atoms or molecules can be determined without knowing \( G(\theta) \), simply by evaluation of absorption intensities and of the dynamical dipole–dipole coupling shifts with and without coadsorbates. This procedure works well as long as the sample position remains unchanged during collection of both data sets, i.e. the geometric factor \( G(\theta) \) cancels out.

As a model system, the Ru[0001]-(2 \( \times \) 2)-(CO + O) coadsorption system was chosen. This layer contains linearly bound CO molecules at on-top sites and oxygen atoms in hcp sites as revealed by a LEED-IV analysis by Narloch et al. [20]. A recent investigation of our group has already shown that, using very high (\( \sim 10^5 \) L) CO exposures, a second CO species can be integrated into the Ru[0001]-(2 \( \times \) 2)-(CO + O) layer, more precisely, into the empty fcc sites [21]. This second CO species will be labeled \( \Delta\)CO; the respective \( v_{CO} \) line position is located at about 1850 cm\(^{-1}\). In the present work these data will be supplemented by replacing \( \Delta\)CO with H, NO, or O. As the perfection and reproducibility of the layers are crucial to minimize uncertainties of derived \( x_{\varepsilon} \) and \( \varepsilon \) values, particular care has been devoted to the layer preparation.

A brief outline of the experimental setup, as well as a detailed description of the recipes how to prepare the various ternary coadsorbate systems, will be given in Section 2. In this section a detailed description of the preparation of the various coadsorbate layers, i.e. the procedure of filling the empty fcc hollow site within the (2 \( \times \) 2)-(CO + O) unit cell (Fig. 1) with either H, NO, CO, or O will be given. The applicability of our approach to extract relative changes of the vibrational polarizability \( x_{\varepsilon} \) and the dielectric constant \( \varepsilon \) (see Section 3.3) requires a careful characterization of the used coadsorbate systems with appropriate surface techniques. Another point of concern is the reproducibility of experimental settings and of the prepared layers. Therefore, the characteristics of the resulting layers, namely (2 \( \times \) 2)-(H + CO + O), (2 \( \times \) 2)-(NO + CO + O), (2 \( \times \) 2)-(2CO + O), and (2 \( \times \) 2)-(CO + 2O), as well as of the reference (2 \( \times \) 2)-(CO + O) layer on Ru[0001], will be described as well.

Since the coadsorbate layers under investigation represent ternary systems, it is quite understandable that their preparation requires a definite adsorption sequence and that each individual step has to be characterized properly. This is particularly true in cases of the atomic coadsorbates H and O: in order to provoke a dissociation of impinging H\(_2\) or O\(_2\) molecules, ‘extended’ (larger than just a single site) empty surface areas are required. Obviously, this is rarely encountered when approaching saturation of the respective (2 \( \times \) 2)-(X + CO + O) layers. Dissociative adsorption processes should therefore be avoided as the final layer preparation step.

It should be mentioned beforehand that the long range order of the various layers is maintained after each of the preparation steps, as is confirmed by LEED observations showing sharp (2 \( \times \) 2) reflexes throughout the described preparation procedures. The over-
all geometries of some of the layers thus prepared have been confirmed by LEED-IV analysis, and the respective atomic relaxations of substrate and adsorbate layer quantified [20,25].

In the following the individual preparation steps are described. With the exception of the (2×2)-(CO + 20) layer the starting point of the preparation is always a Ru(0001)-(2×2)-O layer, which represents an immobile, stabilizing ‘cage’ for the other coadsorbates. Due to possible errors in the thermocouple readings, the quoted annealing temperatures may need some individual adjustments to obtain optimum results. We emphasize that all quoted vibrational frequencies in this section refer to the experimentally observed line positions at T = 100 K.

2.2.1. Ru(0001)-(2×2)-(X + CO + O) (layer A)

1. Exposure of the sample to about 10 L oxygen at T = 300 K produces a (2×1)-O overlayer with θO ≈ 0.5 ML [26].
2. Heating to 1250 K leaves a coverage of about 0.3 ML oxygen on the surface, consisting of small patches with a (2×2)-O and (2×1)-O local structure.
3. Exposure to 10 L hydrogen at 350–400 K leads to an efficient titration of oxygen in excess of θO ≈ 0.25 ML [27,28]; the resulting ‘inert’ (2×2)-O layer should not be exposed further to H2, since there is a slow, but still measurable removal of oxygen leading to defective layers with θO < 0.25 ML; it is thus advisable to monitor the progress of the titration process, e.g. using work function change measurements.
4. In order to remove possible CO or hydrogen contaminants and to induce proper ordering of the (2×2)-O layer the sample is heated to 750 K; slow cooling (about 1 K/s) further improves the layer homogeneity, by increasing domain sizes and reducing the relative fraction of domain boundaries.

The quality of the prepared Ru(0001)-(2×2)-O layer is crucial for the following preparation steps and should always be analyzed by appropriate means [21,29]. The (2×2) unit cell contains one oxygen atom (hcp site; \(v_{\text{Ru-O}} = 526.5 \text{ cm}^{-1}\)); the work function change with respect to the clean Ru(0001) surface amounts to +220 meV.

2.2.2. Ru(0001)-(2×2)-(CO + O) (layer B)

1. Layer (A) exposed to 10 L of CO at 100 K.
2. Annealing to 350 K to desorb CO in excess of 0.25 ML [21,29].

The (2×2)-(CO + O) layer is thermally stable up to 350 K, limited by CO-desorption. The (2×2) unit cell now contains one oxygen atom (hcp site; \(v_{\text{Ru-O}} = 524.5 \text{ cm}^{-1}\)) and one CO molecule (on-top site; \(v_{\text{C-O}} = 2050.7 \text{ cm}^{-1}\)); the work function change with respect to the clean Ru(0001) surface amounts to +425 meV.

2.2.3. Ru(0001)-(2×2)-(H + O) (layer C)

1. Layer (A) exposed to 10 L of H2 at 100 K.
2. Annealing to 160 K to desorb H in excess of 0.25 ML [30].

The (2×2)-(H + O) layer is thermally stable up to 160 K, limited by H2-desorption at higher T. The (2×2) unit cell now contains one oxygen atom (hcp site; \(v_{\text{Ru-O}} = 534.5 \text{ cm}^{-1}\)) and one H atom (fcc site); the work function change with respect to the clean Ru(0001) surface amounts to +195 meV.

2.2.4. Ru(0001)-(2×2)-(H + CO + O)

Layer (C) exposed to 10 L of CO (up to saturation) at 100 K [30]. Note, that a reversal of the Ru(0001)-(2×2)-(H + CO + O) layer preparation procedure, i.e. post-adsorption of hydrogen onto the (2×2)-CO layer was not practicable as the sticking coefficient for H2 molecules on the (2×2)-(CO + O) layer is very small; an estimate gives an upper limit of ~10−4 [30]. The Ru(0001)-(2×2)-(H + CO + O) layer is thermally stable up to 210 K, limited by H2-desorption. The enhanced stability of the (2×2)-(H + CO + O) as compared to the less dense (2×2)-(H + O) layer is attributed to a caging effect imposed on the H-atoms for the former; despite a lateral distance of only 5.4 Å, neighboring H-atoms cannot merge and recombine to form H2. By employing detailed balance arguments [31], the delayed H-desorption may also be associated with the negligible sticking coefficient of H2 on Ru(0001)-(2×2)-(CO + O) [30].

The (2×2) unit cell now contains one oxygen atom (hcp site; \(v_{\text{Ru-O}} = 534 \text{ cm}^{-1}\)), one H atom (fcc site) and one CO molecule (on-top site; \(v_{\text{C–O}} = 2055.3 \text{ cm}^{-1}\), \(v_{\text{C–O}} = 2061 \text{ cm}^{-1}\)). The work function change with respect to the clean Ru(0001) surface amounts to +415 meV.

2.2.5. Ru(0001)-(2×2)-(NO + CO + O)

Layer (B) exposed to 2 L of NO (up to saturation) at 100 K. The (2×2) unit cell now contains one oxygen atom (hcp site; \(v_{\text{Ru-O}} = 523 \text{ cm}^{-1}\)), one NO molecule (fcc site; \(v_{\text{N–O}} = 1546 \text{ cm}^{-1}\)), and one CO molecule (on-top site; \(v_{\text{C–O}} = 2061 \text{ cm}^{-1}\)). The work function change with respect to the clean Ru(0001) surface amounts to +930 meV. The Ru(0001)-(2×2)-(NO + CO + O) layer is thermally stable up to 220 K, limited by CO-desorption. CO desorption leads to an immediate site change of NO fcc → on-top, as evidenced by a \(v_{\text{N–O}}\) band evolving at 1800–1805 cm−1. For impinging NO at 100 K (2 L) the possible replacement of on-top CO, as well as a thermally induced exchange after adsorption is below 0.0005 ML. Such processes would inevitably produce on-top NO with a N–O frequency at about 1800 cm−1 which is not observed at all.

It is usually advisable to anneal to about 200 K before starting the measurements in order to desorb tiny amounts of unwanted physisorbed species associated with the NO exposure, e.g. (NO)2, N2O, or NO2. These latter species should be avoided beforehand by leading the NO gas through a lqN2 cooled trap before exposing the sample; this is actually recommended for any of the described gas dosing procedures.
2.2.6. Ru(0001)-(2×2)-(CO + O)

Layer (A) exposed to 10^12 L of CO at 150 K; note that, while 0.25 ML of on-top CO is easily adsorbed (see preparation of layer B), the second quarter monolayer (Δ-CO) requires very high exposures due to a vanishing sticking coefficient [21]. The layer is thermally stable up to 220 K, limited by CO-desorption. The (2×2) unit cell now contains one oxygen atom (hcp site; ν_Ru–O = 534.5 cm⁻¹), one CO molecule (fcc site; ν_C–O = 2517.7 cm⁻¹) and one CO molecule (on-top site; ν_Ru–CO = 2068.6 cm⁻¹). The work function change with respect to the clean Ru(0001) surface amounts to +960 meV.

2.2.7. Ru(0001)-(2×2)-(CO + 2O)

(1) Preparation of a (2×1)-O phase of oxygen on Ru(0001) with Θ_O = 0.5 ML by exposing the Ru-surface to 20 L of O₂ at T = 350 K.
(2) Annealing of the layer to 420 K.
(3) Exposure to CO while slowly cooling down to 300 K (total CO dosage during cool-down about 10 L). As a result of CO being incorporated into the layer, the original (2×1)-O phase transforms into a c(2×2)-(CO + 2O) honeycomb structure, with on-top CO surrounded by six oxygen atoms occupying hollow sites.

The layer is thermally stable up to 300 K, limited by CO-desorption. The (2×2) unit cell now contains one oxygen atom each on the hcp and the fcc sites, as well as one CO molecule (on-top site; ν_Ru–CO ≈ 390 cm⁻¹, ν_C–O = 2090 cm⁻¹). The work function change with respect to the clean Ru(0001) surface amounts to +870 meV.

The system Ru(0001)-(2×2)-(CO + 2O) has been subject to a number of investigations [25,23,22]. A very narrow vibrational peak and a high preexponential factor in thermal desorption spectra led Hoffmann et al. [33] and Kostov et al. [32], respectively, to suggest a honeycomb structure for the Ru(0001)-(2×2)-(CO + 2O) coadsorbate system. A LEED-IV analysis by Narloch et al. [25] confirmed the overall long range order and the local adsorption geometries of CO and oxygen. Scanning tunneling microscopy investigations demonstrated that the proposed phase transformation (2×1)-(CO + O) → (2×2)-(CO + 2O) does in fact occur; according to these images a fair number of domain boundaries is produced, though, leading to a non-perfect long range order [34]. This latter finding is, however, at least partially affected by the room temperature restriction during STM imaging. Thermal desorption spectroscopy identified a total CO coverage of the Ru(0001)-(2×2)-(CO + 2O) layer of 0.23–0.24 ML, i.e. slightly less than the ideal 0.25 ML value.

3. Results

3.1. Work function change measurements induced by coadsorbed H, NO, CO, or O

The evolution of the sample work function with increasing amounts of coadsorbate X within the Ru(0001)-(2×2)-(X + CO + O) layer and their thermal evolution are displayed in Fig. 2A and B, respectively. In order to ensure reproducibility of the derived work function changes, the vibrating (reference) electrode in our experimental setup was coated (passivated) by graphite (Φ_graphite = 4.5 eV [33]). All work function values are therefore offset according to Φ = Φ样品 − Φ_graphite.

In (A), Φ vs. coverage curves are shown for adsorbing CO and NO at 100 K. For hydrogen and oxygen molecules impinging on Ru(0001)-(2×2)-(CO + O) no adsorption traces have been recorded because of a vanishing sticking coefficient s for dissociative adsorption (see Section 2.2). A special situation is encountered for X = CO for which we detected a sudden drop of s as soon as the on-top sites within the (2×2)-O unit cell had been fully occupied by CO and only fcc sites were left. Based on curve (a) of Fig. 2 on-top CO increases Φ by 205 meV to reach a value of 1.755 eV for the complete Ru(0001)-(2×2)-(CO + O) layer. Continued (high) CO exposures lead to a steady but (due to the sharp drop of s) very slow Φ-increase.

In Fig. 2B, thermal evolution traces have been used to obtain equivalent work function change values associated with coadsorbates X; this approach works fine as long as X desorbs at lower temperatures than our probe molecule, on-top CO, which is the case for X = H and Δ-CO, but not for X = NO or O. In the latter case, a c(2×2)-(CO + 2O) honeycomb lattice is formed which transforms into a (2×1)-O structure upon desorption of CO, introducing an extra Φ-shift at T = 300 K (see Fig. 2d).

We can circumvent the various limitations encountered with the described continuous measurements of work function changes ΔΦads by taking advantage of the constant surface potential of our passivated reference electrode. Φ values obtained from the various Ru(0001)-(2×2)-(X + CO + O) layers can therefore be compared directly with the Ru(0001)-(2×2)-(CO + O) layer, i.e. they need not be measured in a single experiment (such as depicted in Fig. 2). This way a complete set of ΔΦads values has been obtained, which is summarized in Table 1. With the exception of H, all coadsorbates X lead to notable increases of Φ.

3.2. Frequency shifts of on-top CO induced by coadsorbed H, NO, CO, or O

As mentioned above, the ν_C–O mode of on-top CO is used to study the effect of various neighboring species occupying the fcc hollow site within the (2×2) unit cell of the Ru(0001)-(2×2)-(CO + O) layer. Our analysis generally comprises both, the ν_C–O mode of the 99% 12C16O majority species, as well as of the 1% 13C16O minority species (see Fig. 3). The respective line positions are influenced by static (chemical), as well as dynamical shifts (dipole coupling). The essential physical reason for the dynamical shift Δνdyn is the electrodynamic coupling of the oscillating dipoles of neighboring CO species with virtually identical vibrational frequencies. A static shift arises, for example, when the chemical bond of the on-top CO molecule is affected by the presence of a coadsorbate. Specifically, the chemical shift due to coadsorbate X corresponds to the associated shift of the respective singleton frequencies Δνchem = ν_chem − ν_chem(X) and Δνchem = ν_chem − ν_chem(X) for 12C16O.

In Fig. 3 the hypothetical 12C16O and 13C16O line positions in the absence of dynamic dipole coupling are labeled ν_chem and ν_chem(X).
Table 1
Compilation of the work function changes $\Delta \phi_{\text{ex}}$ and $\Phi'_{\text{ex}}$, and $\Phi'_{\text{ex}}$ associated with the different coadsorbates $X$ (see Fig. 2), and the corresponding dipole moments (per coadsorbate atom or molecule). The dipole moments were calculated assuming a coverage of 0.25 ML for species $X$.

<table>
<thead>
<tr>
<th>Layer $\text{Ru}(0001)$-(2 $\times$ 2)-(CO + O)</th>
<th>Work function change $\Delta \phi_{\text{ex}}$ (eV)</th>
<th>Dipole moment (debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = H</td>
<td>$-0.01$</td>
<td>$-0.007$</td>
</tr>
<tr>
<td>X = NO</td>
<td>$0.50$</td>
<td>$-0.34$</td>
</tr>
<tr>
<td>X = $\Delta$-CO</td>
<td>$0.53$</td>
<td>$-0.36$</td>
</tr>
<tr>
<td>X = $\sigma$</td>
<td>$0.44$</td>
<td>$-0.31^a$</td>
</tr>
</tbody>
</table>

For the $\text{Ru}(0001)$-(2 $\times$ 2)-(CO + O) layer CO has been post-adsorbed onto a (2 $\times$ 1)-O overlayer; the resulting (2 $\times$ 2)-(CO + O) honeycomb structure contains quite a few phase boundaries so that the maximum amount of deposited CO was 0.24 ML only; the calculated value of $-0.30$ debye (assuming a perfect layer) is therefore multiplied by 25/24 to yield $-0.31$ debye.

In order to avoid dynamical coupling between the vibrational modes of the coadsorbates X and the C–O stretch mode of on-top CO, it is essential that their frequencies are sufficiently separated from each other. These assumptions are well fulfilled for the used coadsorbates H, NO, $\Delta$-CO, and O.

In our analysis we will be comparing spectra with and without the coadsorbate X within the $\text{Ru}(0001)$-(2 $\times$ 2)-(CO + O) ordered layer; therefore, we need to label the respective values by superscripts $^x$ and $^o$, respectively. It is thereby assumed that the overall adsorption geometry and the long range order of the layer (see Fig. 1) is not modified by the coadsorbate X, which is confirmed by LEED [20,25]. Since LEED is not necessarily a good indicator for a well ordered homogeneous system, other methods have additionally been employed. Specifically, IRAS and TDS spectra have been searched for spurious features, which may indicate defective layers. Regarding this matter we like to stress that vibrational bands associated with the $^{12}$C$^{16}$O majority species usually do not provide adequate evidence for a sufficiently high homogeneity of an adsorbate layer (due to dynamical dipole coupling and a line narrowing effect [37,38]); this is why the spectral width of the minority $^{13}$C$^{16}$O isotope has additionally been examined. Special care has been generally taken to avoid the creation of structural defects during preparation; for example, critical preparation steps have been performed at low sample temperatures to suppress any mobility, e.g. of oxygen atoms within the (2 $\times$ 2)-O template, and to avoid possible site exchange of coadsorbate X and on-top CO.

In the following, we will be analyzing influences affecting the vibrational line positions of our probe molecule (on-top CO). The aim is to determine the extent of the dynamical dipole coupling shift of $\Delta_{\text{chem}}$, from single and experimentally observed line positions. Usually, the mere presence of a nearby coadsorbate species X, or of a structural or chemical heterogeneity of the substrate causes a (chemical) line shift [7,39,40], i.e.

$$
\Delta_{\text{chem}} = \tilde{\nu}^x_{\text{single}} - \tilde{\nu}^o_{\text{single}} = k_{\text{iso}} (\tilde{\nu}^x_{\text{single}} - \tilde{\nu}^o_{\text{single}}) = k_{\text{iso}} \Delta_{\text{chem}}
$$

In Fig. 3, $\Delta_{\text{chem}}$ can, as a first approximation, be estimated from the difference of the observed on-top CO line positions of naturally abundant (1.1%) $^{13}$C$^{16}$O in the spectra (a) and (b); this procedure provides reliable numbers as long as dynamical coupling among the dilute species is negligible. For the example shown in Fig. 3, the presence of X = $\Delta$-CO leads to a positive value of $\Delta_{\text{chem}}$, along with a decrease of $\Delta_{\text{dip}}$, i.e. $\Delta_{\text{dip}} < \Delta_{\text{chem}}$.

From our IRAS experiments the wave numbers $\tilde{\nu}^x_{\text{single}}$ and $\tilde{\nu}^o_{\text{single}}$ (as well as $\tilde{\nu}^x_{\text{chem}}$ and $\tilde{\nu}^o_{\text{chem}}$) can be calculated using $\Delta_{\text{dip}}$ and $k_{\text{iso}}$

$$
\tilde{\nu}^x_{\text{single}} = \tilde{\nu} - \Delta_{\text{dip}}
$$

$$
\tilde{\nu}^o_{\text{chem}} = \tilde{\nu}^x_{\text{chem}} - \tilde{\nu}^x_{\text{single}} = k_{\text{iso}} (\tilde{\nu}^x_{\text{chem}} - \tilde{\nu}^x_{\text{single}}) = k_{\text{iso}} \Delta_{\text{chem}}
$$

$$
\Delta_{\text{dip}} = \tilde{\nu} - \tilde{\nu}^o_{\text{chem}} = \tilde{\nu} - \tilde{\nu}^x_{\text{chem}} - \tilde{\nu}^x_{\text{single}} + \Delta_{\text{dip}}
$$

which leads to

$$
\Delta_{\text{dip}} = \frac{\tilde{\nu} - \tilde{\nu}^o_{\text{chem}}}{1 + 0.05 \cdot k_{\text{iso}}}
$$

where $\Delta_{\text{dip}} < 0$. From model calculations of the dynamical dipole coupling with ‘impurities’ of the heavier $^{13}$C$^{16}$O isotopic species it is found that $\Delta_{\text{dip}} \approx -0.05 \times \Delta_{\text{dip}}$ for on-top CO on $\text{Ru}(0001)$ [36]. This scaling factor of $-0.05$ may change slightly depending on the extent of electronic screening of surface electric fields. As $\Delta_{\text{dip}}$ is much smaller than $\Delta_{\text{chem}}$, such delicate effects will be neglected here.
served after H, NO, and O, taken with a spectral resolution of 4 cm⁻¹ at T_{\text{meas}} = 100 K. For each spectrum, 1000 scans were added. Depicted is the region of the ν_{C–O} mode of linearly bound on-top 12C16O. For comparison, the spectrum of the Ru(0001)-(2 x 2)-(CO + O) is displayed as well.

In Figs. 4–6 infrared absorption spectra of the four investigated systems are displayed in the ranges of the ν_{C–O} species (1.1% natural abundance) is displayed. For comparison, the spectrum of the Ru(0001)-(2 x 2)-(CO + O) is displayed as well. The spectra were taken with a spectral resolution of 4 cm⁻¹ at T_{\text{meas}} = 100 K using a lq. He cooled Si:B detector. Depicted is the region of the ν_{Ru–CO} mode. For comparison, the spectrum of the Ru(0001)-(2 x 2)-(CO + O) is displayed as well.

The majority 12C16O isotopic species the experimentally observed ν_{C–O} mode shift is highest for O (39.6 cm⁻¹) and smallest for H (4.6 cm⁻¹). NO and Δ-CO lead to intermediate shifts of 10.4 cm⁻¹ and 17.9 cm⁻¹, respectively. According to Figs. 4 and 5 the observed ν_{C–O} shifts differ for the 13C16O and the 12C16O isotopic species, which is due to dynamic dipole coupling primarily contributing to the former (see Table 2 for details). For the dilute 13C16O isotopic species the ν_{C–O} blueshift amounts to 49.2 cm⁻¹ for O and 6.7 cm⁻¹ for H; the molecular coadsorbates both induce moderate shifts of 24.3 cm⁻¹ (NO) and 25.4 cm⁻¹ (Δ-CO). Using the equations above, the (static) chemical line shifts A_{\text{chem}} can be separated from the (dynamical) dipole coupling related shifts. As summarized in Table 2 the respective A_{\text{chem}} are 6.8, 24.2, 25.6, and 49.8 cm⁻¹ for the coadsorbates X = H, NO, Δ-CO and O. Our detailed analysis clearly demonstrates that, to a first approximation, the ν_{C–O} line shift of the minority 13C16O isotopic species may be used to determine chemical shifts of vibrational modes. More accurate values, however, need to take into account the residual dynamical interaction with the surrounding regular CO, as well as the isotopic shift factor k_{iso}. According to Table 2 and Eq. (7), the dynamic dipole shift A_{dip} for on-top CO is reduced by each of the coadsorbates. Two influences may contribute: (i) a decreased vibrational polarizability α, and (ii) an enhanced ε (electronic screening); see below for a more qualitative analysis.

Before we analyze our results on ν_{C–O} in more detail, we turn to the external Ru–CO stretching mode, ν_{Ru–CO} (Fig. 6). It is apparent that the coadsorbates H and Δ-CO lead to ν_{Ru–CO} redshifts by 7.3 cm⁻¹ and 15.5 cm⁻¹, respectively. Owing to the low frequency cut-off of ~390 cm⁻¹ the minority ν_{Ru–CO} mode is not visible. Using the high resolution electron energy loss spectroscopy (HREELS) at a resolution of 8 meV and at T = 90 K [32]; the ν_{Ru–CO} redshift of on-top CO associated with the presence of the second oxygen atom within the (2 x 2) unit cell therefore amounts to 20–25 cm⁻¹. Note that the ‘first’ oxygen atom already caused a 35–40 cm⁻¹ redshift with respect to isolated CO on Ru(0001) or CO within the well ordered Ru(0001)-(√3 x √3)-CO layer [21,24].

There is another elegant way to determine ν_{Ru–CO} frequencies by means of detecting the combination band ν_{comb} of the internal and external stretch modes of on-top CO. By introducing an approximate correction term ∆ν (about 5 cm⁻¹), it is straightforward to
calculate the $\nu_{Ru-CO}$ frequencies according to: $\nu_{Ru-CO - single} = \nu_{comb} - \nu_{Ru-CO - single} + \delta \nu$. $\delta \nu$ accounts for the intermode coupling anharmonicities of $\nu_{Ru-CO}$ and $\nu_{C-O}$ (about $-2$ cm$^{-1}$ for on-top CO), as well as line shape effects which affect the respective absorption maxima [41–43].

Following this procedure we have extracted $\nu_{Ru-CO - single}$-values of 403, 396, 396, and 385 cm$^{-1}$ for the on-top CO species when $X = H$, NO, $\Delta$-CO, or O, respectively, are coadsorbed; the $\nu_{Ru-CO - single}$ line position for the Ru(0001)-(2 $\times$ 2)-(CO + O) layer has similarly been determined to be 410 cm$^{-1}$, reasonably close to the directly observed wave number of 412 cm$^{-1}$ (see Fig. 6). Similarly, the derived $\nu_{Ru-CO - single}$ line positions for $X = H$ and $\Delta$-CO agree favorably with the directly accessible values [21,30]; the accuracy of these indirectly obtained $\nu_{Ru-CO - single}$ line positions is estimated to be ±3 cm$^{-1}$. More accurate numbers would require dedicated spectra (optimized experimental conditions, lower sample temperatures and longer data accumulation times) and an intricate line shape analysis for $\nu_{comb}$ [36,41–43].

### 3.3. Quantitative determination of relative changes of $C_2$ and $C_4$

Using Eqs. (1) and (2), the intensity of an IR absorption line and the shift induced by dynamical dipole coupling can be rewritten [8–11]:

$$I \propto \frac{2x_2}{\epsilon} \cdot \nu^{2}_{single}$$

and

$$\delta = \frac{\sqrt{\nu^2 - \nu^{2}_{single}}}{\nu^{2}_{single}} \cdot \frac{X}{\epsilon}$$

$\nu$ and $\nu_{single}$ on the left side of Eq. (9) can be derived from the experiment so that the ratio

$$\delta^{oo} = \frac{\delta^2}{\delta} = \frac{\left(\frac{\nu^{2}_{single}}{x_2^2}\right)^2 - 1}{\left(\frac{\nu^{2}_{single}}{x_2^2}\right)^2 - 1} = \frac{x_2^2 \cdot U}{\epsilon} \cdot \frac{\nu^{2}_{single}}{x_2^2 \cdot \epsilon} = \frac{x_2^2 \cdot U}{\epsilon^2}$$

can be calculated. The essential point here is that, due to the retained structural arrangement of on-top CO with and without coadsorbate X, the dipole sum $U$ of oscillating on-top CO remains unchanged and cancels out.

The ratio $\gamma^{oo} = I/I'$ of the absorption intensities in the presence or absence of coadsorbate X, respectively, is accessible from the experiment as well. Using Eq. (8), $\gamma^{oo}$ may be expressed as:

$$\gamma^{oo} = \frac{I}{I'} = \frac{\gamma^{oo}_{C_2}}{\gamma^{oo}_{C_4}} \left(\frac{\epsilon}{\epsilon^0}\right)^2 \left(\frac{\nu^{2}_{single}}{\nu^{2}_{single}}\right)^2 = \delta^{oo} \cdot \frac{\epsilon^0}{\epsilon} \left(\frac{\nu^{2}_{single}}{\nu^{2}_{single}}\right)^2$$

### Table 2

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\nu_{Ru-CO}$</th>
<th>$\nu_{C-O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer Ru(0001)-(2 $\times$ 2)-(X + CO + O)</td>
<td>$\nu_{Ru-CO}$</td>
<td>$\nu_{C-O}$</td>
</tr>
<tr>
<td>Layer Ru(0001)-(2 $\times$ 2)-(CO + O)</td>
<td>$\nu_{Ru-CO}$</td>
<td>$\nu_{C-O}$</td>
</tr>
<tr>
<td>X = H</td>
<td>404.7</td>
<td>1984.3</td>
</tr>
<tr>
<td>X = NO</td>
<td>396.5</td>
<td>2003.0</td>
</tr>
<tr>
<td>X = $\Delta$-CO</td>
<td>304.5</td>
<td>2003.0</td>
</tr>
<tr>
<td>X = O</td>
<td>304.5</td>
<td>2003.0</td>
</tr>
<tr>
<td>Ru(0001)-(2 $\times$ 2)-(CO + O)</td>
<td>404.7</td>
<td>1984.3</td>
</tr>
</tbody>
</table>

* The value for X = O was determined by Kostov et al. using HREELS [32].

### Table 3

<table>
<thead>
<tr>
<th>Layer Ru(0001)-(2 $\times$ 2)-(X + CO + O)</th>
<th>$\gamma^{oo}$</th>
<th>$\delta^{oo}$</th>
<th>$\epsilon^2/\epsilon^0$</th>
<th>$x_2^2/x_4^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = H</td>
<td>0.95</td>
<td>0.911</td>
<td>0.97</td>
<td>0.88</td>
</tr>
<tr>
<td>X = NO</td>
<td>0.45</td>
<td>0.458</td>
<td>1.04</td>
<td>0.48</td>
</tr>
<tr>
<td>X = CO</td>
<td>0.65</td>
<td>0.691</td>
<td>1.09</td>
<td>0.75</td>
</tr>
<tr>
<td>X = O</td>
<td>0.70</td>
<td>0.589</td>
<td>0.88</td>
<td>0.54</td>
</tr>
</tbody>
</table>

* For the Ru(0001)-(2 $\times$ 2)-(CO + 2O) layer CO has been post-adsorbed onto a (2 $\times$ 1)-O overlayer; the resulting (2 $\times$ 2)-(CO + 2O) honeycomb structure contains quite a few phase boundaries so that the maximum amount of deposited CO was 0.24 ML only; the derived value of 0.52 for $x_2^2/x_4^2$ (assuming a perfect layer) is therefore multiplied by 25/24 to yield 0.54.

Combining Eqs. (10) and (11) leads to our final result:

$$\frac{\epsilon^2}{\epsilon^0} = \frac{\delta^{oo}}{\gamma^{oo}_{C_2}} \left(\frac{\nu^{2}_{single}}{\nu^{2}_{single}}\right)^2 = \frac{\delta^{oo}}{\gamma^{oo}_{C_4}} \cdot \left(K_0\right)^2$$

and

$$\frac{x_2^2}{x_4^2} = \frac{\delta^{oo}}{\gamma^{oo}_{C_2}} \cdot \frac{\epsilon^2}{\epsilon^0} = \left(\frac{\delta^{oo}}{\gamma^{oo}_{C_4}}\right)^2 \cdot \left(K_0\right)^2$$

This way we can determine quantitatively the relative changes of $x_2$ and $\epsilon$ induced by a coadsorbate X, starting from the Ru(0001)-(2 $\times$ 2)-(CO + O) layer. We find that each of the coadsorbates leads to a lowering of the $\nu_{C-O}$ mode absorption intensity. This cutback is substantial for NO (−55%), $\Delta$-CO (−35%) and O (−30%); H causes a comparatively small decrease of only −5%. Similar to the variations of $A_{dip}$ this reduction may be ascribed to both, a modified dielectric screening introduced by the coadsorbates X and a decreased oscillating dipole moment (vibrational polarizability $\alpha_x$) associated with $\nu_{C-O}$ excitation. A more quantitative evaluation on the basis of the equations outlined above thereby allows us to disentangle the two contributions. The resulting ratios $x_2^2/x_4^2$ and $\epsilon^2/\epsilon^0$ are compiled in Table 3, together with $\delta^{oo}$ and the ratio of integrated intensities $\gamma^{oo}_{C_2}$ of the $\nu_{C-O}$ modes. Interestingly, the atomic coadsorbates H and O cause a decrease of $\epsilon$. The effect is noteworthy for O (−12%) and almost negligible for H (−3%). The molecular coadsorbates, on the other hand, increase the dielectric constant $\epsilon$. Here, the screening enhancement is significant for $\Delta$-CO (+9%) and relatively small for NO (+5%); we stress that the effect on $x_2$ is considerably larger than the marginal modifications of $\epsilon$ seem to suggest.

The vibrational polarizability $\alpha_x$ is reduced by each of the coadsorbates. The effect is much stronger for coadsorbed oxygen (−46%) and NO (−52%), as compared to H (−12%) and $\Delta$-CO (−25%).
4. Discussion

Contrary to the variations of \( \tilde{\nu} \) and \( \epsilon \), the vibrational frequency of our probe molecule, on-top CO, represents an easy to detect quantity to monitor lateral interactions in adsorbate layers. In order to attribute the associated shifts to characteristic properties of the studied system, e.g. of the used materials and adsorbed species, it is essential to discriminate between static and dynamical shifts. In the present work a systematic analysis has been conducted for the ternary coadsorbate systems Ru(0001)-(2×2)-(X + CO + O) with X = H, NO, \( \Lambda \)-CO, or O.

4.1. Chemical shifts induced by \( X = H, NO, \Lambda-CO, or O \)

According to our investigation, each of the coadsorbates X leads to a \( v_{C-O} \), single, blueshift of the on-top CO species. In a simplified picture the chemical bond of the CO molecule to a metal surface can be described as an interaction of the occupied \( 5\sigma \) and the unoccupied \( 2\pi^* \) CO orbitals with electronic states of appropriate symmetry in the metal. Key elements of the model suggested by Blyholder [44,45] comprise a \( 5\sigma \) donation of charge into the metal and a backdonation into electronic states with \( 2\pi^* \) character [44–48].

In particular the latter process has to be borne in mind, when slight variations in the environment of adsorbed on-top CO by nearby species are being investigated [49–51]. The role of \( 5\sigma \) for \( v_{C-O} \) is of lesser importance; its primary role is to impose a Pauli-exclusion type of repulsion between CO and the metal substrate, thereby reducing orbital overlap and the adsorbate–substrate interaction strength. Charge in the \( 2\pi^* \) state, on the other hand, strengthens the metal–CO bond and, in particular, weakens the internal C–O bond. A reduced backdonation into the CO \( 2\pi^* \) orbital will therefore result in a less pronounced C–O bond weakening and a diminished strengthening of the metal–CO bond, implying a blueshift of \( v_{C-O} \) and a redshift of \( v_{\text{cm,CO}} \) on for top CO, in accordance with our experimental findings. Such a scenario could be implemented using electronegative coadsorbates, e.g. oxygen, which attracts charge from the metal, and thereby results in a lowering of the local charge density in the metal substrate. This simplified view, however, neglects local electrostatic fields, which influence both, the shape and energetic position of the relevant (e.g. \( 2\pi^* \)) orbitals, again modifying their occupancy. It has been stressed that the various effects are closely intertwined and accurate numbers on the resulting line shifts can be derived only by consideration of the self-consistently calculated surface fields [50].

Surface electrostatic fields may be estimated from the respective change in the work function \( \Delta \phi \) (see Fig. 2 and Table 1, above). However, there is no one-to-one correlation of the two physical quantities, since there is a multitude of effects contributing to \( \Delta \phi \), often with yet unclear relevance:

(i) Permanent dipole moment of a molecular adsorbate.
(ii) Simple polarization of the outer electron cloud in the dipole field of the (metal) surface (generally reducing the work function \( \phi \)).
(iii) Charge transfer between adsorbate and the substrate.
(iv) Induced dipole moment due to charge redistribution within an adsorbate, caused by orbital shift and/or hybridization with substrate electronic states.
(v) Relaxation or reconstruction of the surface layer.

Only in rather simple cases a straightforward interpretation appears justified and even then, things are usually more complex than conjectured. For example, Ar or Xe atoms adsorbed on Ru(0001) lead to \( \Delta \phi \) reductions by \(-220 \) and \(-505 \) meV, respectively. Obviously, process (ii) is dominant, while (i) and probably (v) should not contribute at all. All-electron calculations reveal, that rare gases located in a surface potential do participate in a (weak) hybridization with metal orbitals, i.e. process (iv) and possibly (iii) contribute as well, enhancing the fields caused by (ii) alone [50]. Single CO molecules embedded in these layers and acting as probe particles, experience substantial \( v_{C-O} \) line shifts of \(-17 \text{ cm}^{-1} \) (Ar) and \(-39 \text{ cm}^{-1} \) (Xe) [50,51]. These shifts were attributed to a Stark shift, induced by the static electric fields of the polarized Ar or Xe atoms. As pointed out in Ref. [50], it is inappropriate to simply assume an effective constant field; instead, the detailed, self-consistently determined field distribution should be used.

For a dipole field pointing in the opposite direction, as is the case for electronegative adsorbates, one would accordingly expect a blueshift of the \( v_{C-O} \) line position; on clean Ru(0001), such shifts have indeed been observed for individual CO molecules surrounded by increasing amounts of oxygen and, to a lesser extent, for hydrogen [50].

Considering the fact that simple polarization corresponding to process (ii), always leads to a negative \( \Delta \phi \), the positive contribution to \( \phi \) arising from chemical interactions of X = H, NO, \( \Lambda \)-CO, or O with the metal substrate is expected to be substantial. For electronegative coadsorbates such as analyzed here, this chemical interaction would imply a local depletion of charge in the metal substrate, leading to a reduced charge backdonation into the \( 2\pi^* \) orbital of nearby on-top CO, in accordance with the observed \( v_{C-O} \) blueshift.

Cluster calculations by Bagus and Müller [52,53] have shown that the vibrational polarizability \( \tilde{\nu}_v \) of adsorbed CO increases with the amount of charge that is transferred into the \( 2\pi^* \) orbital. The weaker backdonation suggested by our observation of a \( v_{C-O} \) blueshift of on-top CO coadsorbed with X = H, NO, \( \Lambda \)-CO, or O is therefore corroborated by the smaller \( \tilde{\nu}_v \) derived for each of these systems.

A detailed analysis of various Ru(0001)-(2×2)-(m·CO + n·O) layers (with m, n = 1 or 2) using density functional theory has been provided by Stampfl and Scheffler [54]. Specifically, their calculated CO binding energies and adsorption barriers agree nicely with our observations. In addition, shifts of CO molecular orbitals upon adsorption and correlated differential electron densities, as well as the projected density of states have been determined. Interestingly, they also could trace the negligible sticking of \( \Delta \)-CO onto the Ru(0001)-(2×2)-(CO + O) layer [21] back to an activation barrier of about 0.2 eV in the adsorption pathway.

4.2. Electronic screening induced by \( X = H, NO, \Lambda-CO, or O \)

The quantity \( \epsilon = 1 + \tilde{\nu}_e U \) is a measure for the non-resonant electronic response of the surface layer (at the frequency of the \( v_{C-O} \) vibration), \( \tilde{\nu}_e \) is the sum of the individual polarizabilities \( \tilde{\nu}_e^i \) of the various electrons \( i \) in the system. It can be changed either by changing the number of electrons in the system and/or by changing the individual polarizabilities \( \tilde{\nu}_e^i \). In our experiments the atomic coadsorbates H and O were found to decrease \( \epsilon \) of the layer. As the number of electrons in the system is increased upon O or H adsorption, the reduced \( \tilde{\nu}_e \) provides clear evidence for a reduction of the \( \tilde{\nu}_e^i \); one can think of the electronegative atomic coadsorbates as pinning the charge in the direction normal to the surface (with respect to the relatively free-moving substrate electrons near the Fermi level of the bare metal surface). The molecular coadsorbates NO and \( \Lambda \)-CO, on the other hand, increase \( \epsilon = 1 + \tilde{\nu}_e U \). Qualitatively speaking, one can imagine that the NO and \( \Lambda \)-CO molecules which are adsorbed upright on the surface enhance the mobility of the electrons near the Fermi level in the direction normal to the surface. The mere presence of additional electrons, however, cannot be the sole cause for the observed increase, because the effect of extra NO on \( \tilde{\nu}_e^i \) is quite a bit smaller than for \( \Lambda \)-CO.
4.3 Absolute numbers of $\zeta_0$ and $\epsilon$ for Ru(0001)-(2 x 2)-(CO + O) and Ru(0001)−($\sqrt{3} \times \sqrt{3}$)-CO layers

A quantitative analysis of the $v_{\text{C-O}}$ oscillator strength and electronic screening factors of on-top CO in different environments will be presented in the following. As outlined above, the determination of the geometrical factor $G(\theta)$ in Eq. (1), to extract absolute numbers for $\zeta_0$ and $\epsilon$ from spectroscopic data is rather cumbersome. A work-around solution is to consider the coverage dependencies of the absorption intensity and of dynamic shifts [10,55]. Some. A work-around solution is to consider the coverage dependencies of the absorption intensity and of dynamic shifts [10,55]. The respective CO coverages have been accurately and independently determined using TDS. In accordance with similar analysis performed earlier [10,55] we thereby presume that $\zeta_0$ of on-top CO remains constant over the relevant coverage range, i.e. up to $\Theta_{\text{CO}} = 0.25$ ML. Using Eq. (1) we then obtain

$$I' / I = \frac{N_i}{N_s} \left( \frac{\epsilon_i}{\epsilon} \right)^2 \left( \frac{\rho_i}{\rho_{\text{single}}} \right)^2 - \epsilon = \frac{N_i}{N_s} \left( \frac{\epsilon_i}{\epsilon} \right)^2 \left( \frac{\rho_i}{\rho_{\text{single}}} \right)^2 \left( \frac{I'}{I} \right)^2 \left( \frac{I}{I} \right)^2 \left( \frac{I''}{I} \right)$$ (14)

Here it is supposed that the screening factor $\epsilon_i$ is close to unity for the dilute layer (i); this implies that our value for $\chi_2^{(2-2)}$ already includes chemical and screening effects due to 0.25 ML of pre-adsorbed oxygen. On the right hand side of Eq. (14) the coverage dependency of the $\zeta_0$-electron frequency has additionally been neglected; for Ru(0001)-(2 x 2)-(CO + O) this is well justified, since this shift amounts to less than 1 cm$^{-1}$ for 0 < $\Theta_{\text{CO}}$ < 0.25 ML.

From our TDS and IRAS data (not shown) the screening effect arising from 0.25 ML on-top CO added to the Ru(0001)-(2 x 2)-O layer can then be calculated to yield $\epsilon^{(2-2)} = 1.21$. According to Eq. (2) the quantity $\delta = \chi_2 - \chi_2$ depends solely on the dynamic shift ($\Delta_d = 25.8$ cm$^{-1}$, see Table 2) and we derive a value of $\delta^{(2-2)} = 0.0256$ for the Ru(0001)-(2 x 2)-(CO + O) layer. The microscopic quantities $\chi_2$ and $\chi_2$ can be accessed by means of calculating the dipole lattice sum $U$. With $\epsilon^{(2-2)} = 0.0697$ Å$^{-3}$ for Ru(0001)-(2 x 2)-(CO + O), we obtain $\chi_2^{(2-2)} = 0.445$ Å$^3$ and $\chi_2^{(2-2)} = 3.0$ Å$^3$ for the resonant (vibrational) and the non-resonant (electronic) polarizabilities, respectively.

A similar analysis may be performed for CO on clean Ru(0001). Again comparing (i) a low coverage layer, $\Theta_{\text{CO}} = 0.01$ ML, and (ii) a ‘complete’ Ru(0001)-( $\sqrt{3} \times \sqrt{3}$)-CO layer, $\Theta_{\text{CO}} = 0.33$ ML, we obtain $\epsilon^{(3-x)} = 1.47$ and $\delta^{(3-x)} = 0.0430$. Taking into account the dipole lattice sum $U^{(3-x)} = 0.107$ Å$^{-3}$, we attain $\chi_2^{(3-x)} = 1.59$ Å$^3$ and $\chi_2^{(3-x)} = 1.44$ Å$^3$.

The derived value for $\epsilon$ agrees favorably with literature data [10,55]; the respective value for $\delta^{(3-x)} = 0.0333$, on the other hand, differs substantially, which we attribute to more accurate quantification of the $v_{\text{C-O}}$ dynamic dipole coupling shift ($\Delta_d = 42.3$ cm$^{-1}$ versus $\Delta_d = 33$ cm$^{-1}$ in Ref. [55]). Another discrepancy, the calculation of the dipole sum $U^{(3-x)}$ requires a more detailed discussion: in Ref. [10] the dipole sum contained contributions due to neighboring image dipoles, while these extra terms have been omitted in our analysis. Our value of $U^{(3-x)} = 0.107$ Å$^{-3}$ is therefore distinctly lower than used earlier ($U^{(3-x)} = 0.17$ Å$^{-3}$) [10]; this difference reflects itself in lower values for $\zeta_2^{(3-x)}$ (0.28 Å$^3$) and $\zeta_2^{(3-x)}$ (2.8 Å$^3$), as compared to our analysis (see above). This neglect of neighboring image dipoles is equivalent to reducing the somewhat arbitrary parameter $d$ (location of dipoles above the image plane of the metal substrate) to zero, i.e. placing all oscillating dipoles in the image plane [56]; of course, the oscillator strength ($-\chi_2$), as well as the screening properties ($-\chi_2$) of our oscillators then refers to CO molecules including the response of the substrate, i.e. both are considered an entity. We note that in cases that $\zeta_0$ predominantly arises due to an internal (oscillating) dipole of an adsorbed molecule, the placement of the dipoles at a distance $d$ above the image plane of a metal substrate is a reasonable thing to do. For adsorbed CO, however, the gas phase value $\chi_2^{\text{gas}} = 0.053$ Å$^3$ for $v_{\text{C-O}}$ [57] is considerably enhanced, most likely due to associated charge oscillations between the 2$p^*$ molecular orbital and the metal [10,11,58]. The resulting dynamic dipoles will therefore be located not too far from the image plane and setting $d = 0$ is well justified. Interestingly, the macroscopic screening quantity $\epsilon$ is negligibly affected by the different summation procedures of $U^{(3-x)}$, as $\epsilon = 1 + \chi_2$. $U = 1.48 [10]$ is virtually identical to $\epsilon = 1.47$ in our analysis.

The lower value of $\chi_2^{(2-2)}$ as compared to $\chi_2^{(3-x)}$ is attributed to a chemical effect due to nearby oxygen atoms. In accordance with the calculations of Bagus and Müller [52,53] coadsorbed oxygen reduces the charge backdonation into the CO 2$p^*$ orbital which, as a consequence, will also reduce $\chi_2$. Note that this charge backdonation also affects the C-O stretch frequency $v_{\text{C-O}}$, causing a redshift. The high value of $\chi_2^{(3-x)}$ (compared to layers with coadsorbed oxygen on Ru(0001) and to CO on Cu surfaces [55]) therefore should not surprise too much, since $v_{\text{C-O}}$ of on-top CO on Ru(0001) is fairly low, indicating a pronounced occupation of the 2$p^*$ orbital.

In order to cross-check the extracted numbers we can also calculate the ratio of the $\chi_2$ and $\epsilon$ for the Ru(0001)-( $\sqrt{3} \times \sqrt{3}$)-CO and the Ru(0001)-(2 x 2)-(CO + O) layers directly. Thereby possible experimental errors in the determination of the low density CO coverages (using TDS) are avoided, since the respective ‘high’ coverages are well known from their (2 x 2) and ( $\sqrt{3} \times \sqrt{3}$) long range orders. Such a procedure, however, requires a very accurate repeatability of the measurement geometry, in particular of the incident angle $\theta$. Combining Eqs. (1) and (2) then leads to:

$$\frac{\chi_2^{(3-x)}}{\chi_2^{(2-2)}} = \frac{\left( \frac{\chi_2^{(3-x)}}{\chi_2^{(2-2)}} \right)^2}{\left( \frac{\chi_2^{(3-x)}}{\chi_2^{(2-2)}} \right)^2} \frac{U^{(2-2)}}{U^{(3-x)}} \frac{I^{(2-2)}}{I^{(3-x)}} \frac{N^{(3-x)}}{N^{(2-2)}} = 1.22$$ (15)

and

$$\chi_2^{(3-x)} = \frac{\chi_2^{(3-x)}}{\chi_2^{(2-2)}} \frac{U^{(2-2)}}{U^{(3-x)}} \frac{I^{(2-2)}}{I^{(3-x)}} = 1.32$$ (16)

In accordance with the findings outlined above, the presence of oxygen decreases both quantities, i.e. $\chi_2$ as well as $\epsilon$.

The respective relative ratios, as derived from the $\Theta_{\text{CO}}$ dependencies above, yield

$$\frac{\chi_2^{(3-x)}}{\chi_2^{(2-2)}} = \frac{\chi_2^{(3-x)}}{\chi_2^{(2-2)}} = 1.47 \frac{1.21}{1.21} = 1.21$$

and

$$\frac{\chi_2^{(3-x)}}{\chi_2^{(2-2)}} = \frac{\chi_2^{(3-x)}}{\chi_2^{(2-2)}} = 0.59 \frac{1.44}{1.44} = 1.33$$

in perfect agreement with the values obtained from the direct comparison of the non-dilute layers.

On the basis of a LEED–IV analysis a static tilt of 13° of linearly bound (on-top) CO within the Ru(0001)-(2 x 2)-(CO + O) coadsorbate layer has been suggested [20,59]. This misorientation supposedly arises due to repulsive interactions between the (three) oxygen atoms and CO in their center. The effect seems to be delicate and DFT [60], as well as HREELS [29] so far cannot verify this experimental finding. In any case, a change of the CO adsorption geometry will also affect the $v_{\text{C-O}}$ vibrational absorption strength. It is quite reasonable to assume that this tilt is going to be altered
(or very likely even gets lifted) by the different coadsorbates X. As, out of steric reasons, an increase of the tilt angle does not seem likely when the empty site within the $2 \times 2$ unit cell gets filled, the overall geometrical effect on the $v_{C-O}$ oscillator strength will be rather small (an estimate gives $\cos^2 13^\circ = 0.95$). For metal surfaces the parallel component of a molecules' dynamic dipole moment is largely compensated by an image dipole, i.e. our IR radiation solely couples to its normal component (as do local dipolar fields associated with the C–O vibration). Consideration of a non-zero tilt therefore leads to a simple renormalization (or reinterpretation) of the $\varepsilon_p$ for on-top CO within the Ru(0001)-$(2 \times 2)$(CO + O) coadsorbate layer.

5. Summary

To summarize, the influence of various coadsorbates X = H, NO, Δ-CO, and O on the vibrational properties of a probe molecule, namely linearly bound (on-top) CO within the Ru(0001)-(2 $\times$ 2)-(X + CO + O) layer, has been investigated in detail. The experimental accessibility of the $v_{C-O}$ mode of $^{13}$CO thereby has been used to accurately determine the respective (surrounded) singleton frequencies $v_{\text{angle}}$ and evaluate the dynamical shifts $\Delta_D$. Along with quantitative measurements of absorption line strengths, the relative changes of $\varepsilon_p$ and $\varepsilon$ caused by the coadsorbates have been extracted.

We found that each of the coadsorbates X causes a chemical blueshift of $v_{C-O}$, as well as a redshift of $v_{Ru-CO}$ of linearly bound CO. These shifts can largely be understood within the framework of the Blyholder backbonding model. This model predicts a close antibonding $2\pi^*$ orbital. In agreement with our work function interpretation) of the vibration fields associated with the C–O vibration). Consideration of a radiation solely couples to its normal component (as do local dipoles)

Acknowledgement

Financial support by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 338 is gratefully acknowledged.

References