

Surface Science Letters

Using IR intensities as a probe for studying the surface chemical bond

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Abstract

Infrared (IR) intensities as determined by a combination of temperature dependent IR spectroscopy and temperature programmed desorption (TPD) were used to identify adsorption sites on Co and Co–Pd nano particles. It is shown that CO adsorption to metal atoms with a low metal coordination exhibits a strong intensity enhancement of the IR absorption as compared to regular surface sites. Density functional theory (DFT) calculations show that this intensity enhancement is due to a decoupling of the low coordinated metal atom bound to CO from those metal atoms embedded in the metal surface.

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1. Introduction

The properties of the chemical bond between a molecule and a solid surface have been discussed extensively since the early days of surface science (see e.g. [1] and references therein). From comparisons of infrared stretching frequencies between metal carbonyls and chemisorbed CO molecules at solid surfaces it was concluded that a highly localized description of surface chemical bonds is appropriate. This comparison also forms the basis for the so called cluster approach. Several theo-

retical models based on the local description of the surface chemical bond of carbon monoxide (CO) such as the Blyholder model or modifications thereof have been used to interpret the infrared observations. Also, photoelectron spectra have been interpreted on the basis of a localized description. Simple molecular orbital considerations have led to a classification of stretching frequencies with respect to the number of metal atoms involved in the bonding. Regions of stretching vibrations are separated into linearly, bridged and higher coordinated molecules schematically shown for CO adsorption to transition metal surfaces in Fig. 1 (see e.g. Ref. [2] and references therein). According to this classification experimentally observed IR frequencies can be assigned to specific adsorption geometries. It is, however, important to

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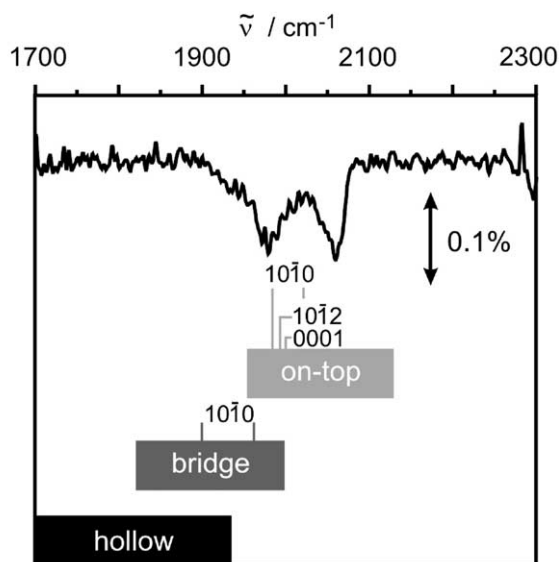


Fig. 1. IR spectra of medium coverage of ^{12}CO adsorbed to 2 \AA Co deposited at 300 K. Bottom: Schematic classification of IR stretching frequencies of CO on various transition metals with respect to adsorption geometries. Frequencies on various Co single crystal surfaces are shown for comparison.

notice that assignments based on this scheme have led to misinterpretations as shown recently via photoelectron diffraction experiments [3]. For less ordered surfaces as e.g. on deposited metal particles more than one species classified as linearly bound species may be observed in the IR spectra as exemplified by the IR spectrum of CO on Co particles shown in Fig. 1. While one of the species is assignable to on-top adsorption on regular sites the other is due to adsorption to low coordinated metal atoms. (The term low coordinated metal atom is used throughout this paper to classify metal atoms with lower metal–metal coordination than surface atoms in regular, low index surfaces.) Although, the IR frequencies are sufficiently different in the present case to discriminate the two species, this difference does not exist in the case of bimetallic Co/Pd particles as will be discussed below. Therefore, an alternative strategy is required to discriminate between such sites. IR intensities of molecules adsorbed on low coordinated metal sites are significantly enhanced as compared to molecules on regular surface sites. The physical reason

being connected with the dynamic response of the system will be discussed in this paper.

For the present study, a thin alumina film grown on a metallic NiAl(1 1 0) single crystal surface was used [4], which was studied with reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). On this film nanometer sized Co and Co–Pd particles were grown by means of atomic vapor deposition.

2. Experimental section

The UHV system used in this study has been described in detail elsewhere [5]. The NiAl(1 1 0) crystal was cleaned by cycles of sputtering and annealing to 1300 K until no impurities were found using Auger spectroscopy. The alumina film was prepared by previously described methods [6,7] and the quality of the film was checked using low energy electron diffraction. A commercial triple metal evaporator (Focus/Omicron EFM 3T) was used to deposit Pd and Co; the deposited amount was calibrated in situ by a quartz microbalance. The deposited amount of metal is given as the average thickness of a metal film in Ångströms. Co and Pd were deposited at room temperature. High purity CO was passed through a liquid nitrogen trap for further purification before being introduced into the vacuum system.

RAIR spectra were recorded with a Bio-Rad FT spectrometer operating at 4 cm^{-1} resolution. Thousand scans were accumulated for each spectrum, requiring about 10 min. Background spectra were recorded with the same settings after deposition of the metals and cooling to 44 K. Depending on the flow rate of the liquid helium used for cooling, the temperature measured by a W/Re 5/26% thermocouple and a high precision temperature controller (Schlichting Physikalische Instrumente) varies by $\pm 5 \text{ K}$. During experiments, the chamber pressure was usually $5 \times 10^{-11} \text{ mbar}$.

DFT calculations were performed using Gaussian 98 [8]. The calculations were done using the B3LYP exchange correlation functional. All core electrons have been replaced by large core ECPs, and for an accurate description of the valence electrons, a double-zeta basis set turns out to

be sufficient (Pd: 3s3p4d/2s2p2d [9]; Co: 5s5p5d/3s3p2d [10]). Calculations with larger basis sets and higher level of theoretical treatment were carried out on the CO gas phase molecule to estimate the error induced by the method used. Additional calculations with larger clusters were performed to check convergence of the shown results.

3. Results and discussion

The IR spectrum of an intermediate coverage of ^{12}CO adsorbed at 44 K to 2 Å Co deposited at 300 K (Fig. 1) reveals two bands in agreement with the TPD spectrum shown in Fig. 2a. Coverage dependent IR spectra (data not shown) [11] show a shift of the low frequency peak from 1967 cm^{-1} (1924 cm^{-1} for ^{13}CO) to approximately 2015 cm^{-1} (1970 cm^{-1}) at saturation coverage, becoming the asymmetric tail of a band at 2068 cm^{-1} (2022 cm^{-1}) which sets in at higher coverage and shows only a small blue shift with increasing coverage. The low frequency peak can be assigned to on-top bound CO in agreement with single crystal data [12]. However, the peak at 2068 cm^{-1} has no counterpart on smooth single crystal surfaces. On single crystal surfaces only red shifted bands were observed which have been assigned to bridge bound species [12,13]. It is noteworthy that the desorption temperature of these bridge bound species coincide with the low temperature desorption peak observed for the particles (see Fig. 2). Therefore, this feature was previously assigned to species in bridge positions [14].

However, investigations on sputtered single crystals as well as on powder catalysts show comparable bands around 2068 cm^{-1} . These peaks were attributed to defect site adsorption and carbonyl formation, respectively [13,15]. Isotope exchange experiments (Fig. 2b lower, black trace) were performed to elucidate the nature of the species in more detail. As compared to the pure ^{12}CO spectrum a pronounced feature at lower frequencies evolves with a low frequency cut off at the position expected for the ^{13}CO analog.

From a detailed analysis of these data in combination with additional experiments it was

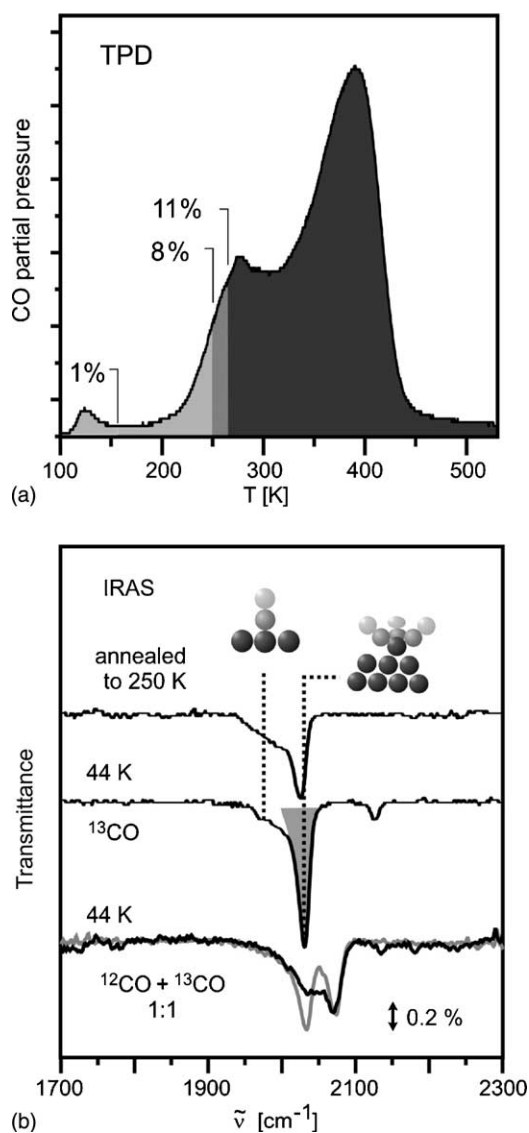


Fig. 2. (a) TPD spectrum of CO adsorbed to 2 Å Co deposited at 300 K. (b) IR spectra taken at 44 K for a saturation coverage of ^{13}CO and after annealing to 300 K. Bottom: saturation coverage of an equimolar mixture of ^{12}CO and ^{13}CO (black trace) and calculated spectrum by superposition of the spectra taken for saturation coverage of ^{12}CO and ^{13}CO scaled by a factor of 0.5 (gray trace).

concluded that cobalt carbonyls $\text{Co}(\text{CO})_n$ with $n = 3$ or 4 have been formed on the surface [11].

From a chemical point of view the formation of a multinuclear carbonyl species requires

coordinatively unsaturated Co atoms as far as the metal–metal bonds are concerned. From STM investigations it is known that Co particles grow in irregular shapes rendering low coordinative sites likely [16].

A striking feature of this carbonyl species is its high IR intensity, even though coordinatively unsaturated metal sites are usually not majority species on surfaces for simple energetic reasons. A quantification of the oscillator strength for different species must address the relative amounts of each species as well as intensity transfer due to dipolar coupling of the oscillators which cannot be done purely on the basis of IR spectroscopy. We have used a combination of TPD and temperature dependent IR spectroscopy to address this question. Fig. 2 shows the TPD spectrum as well as IR spectra of ^{13}CO taken at 44 K after saturation (middle trace) and after annealing to 250 K (upper trace). Upon annealing to 250 K the intensity of the carbonyl band at 2022 cm^{-1} is reduced significantly, whereas the tail associated with the on-top bound molecules is almost unchanged. The total intensity of the IR spectrum drops by 24% upon annealing to 250 K. However, the percentage of CO molecules desorbing up to 250 K, as evaluated by integration of the TPD spectra to 250 K, is just 8%. From the ratio of the two quantities the oscillator strength of the carbonyl species is enhanced by a factor of three as compared to the regular sites. This enhancement factor can only serve as an upper limit, because an integration of the TPD spectrum to the annealing temperature neglects all molecules desorbing during the cooling period of the annealing experiment. Simulations of TPD spectra using experimental temperature profiles of the annealing experiments show that an integration of the TPD spectra 15 K higher than the annealing temperature can account for the additional desorption. The integration to 265 K corresponds to a desorption of 11% of the CO molecules, which gives an enhancement factor of 2.2.

Is the intensity enhancement of the carbonyl species a peculiar effect of the cobalt system or is it a more general phenomenon related to low coordinated metal atoms? To prove the latter hypothesis we deposited at room temperature 0.1 \AA Pd on

top of 2 \AA Co. The Pd atoms decorate the Co islands [16]. The IR spectrum for saturation coverage of CO taken at 44 K is shown as the gray trace in Fig. 3b. As compared to pure Co particles (black trace) an additional band at 2102 cm^{-1} is observed which can be readily assigned to CO bound on-top to Pd (see e.g. Refs. [17–19]). Furthermore, the Pd reduces exclusively the carbonyl band whereas the on-top region of the Co is virtually unchanged. This indicates that the Pd atoms nucleate preferentially at the low coordinated Co sites. Along the lines described above we have correlated the TPD spectrum shown in Fig. 3a

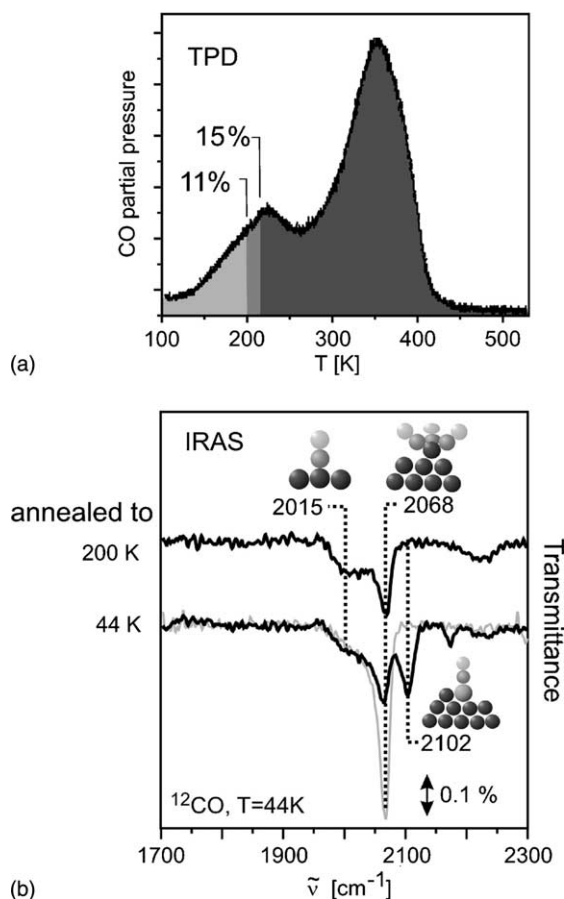


Fig. 3. (a) TPD spectrum of CO adsorbed to 2 \AA Co^{first} + 0.1 \AA $\text{Pd}^{\text{second}}$ deposited at 300 K. (b) IR spectra taken at 44 K for saturation coverage of ^{12}CO (bottom, thick trace; thin gray trace is the pure Co case for comparison) and after annealing to 200 K (upper trace).

with the IR spectra taken after annealing to 200 K (upper trace Fig. 3b). After annealing to 200 K the band at 2102 cm^{-1} disappears whereas the rest of the IR spectrum is almost unchanged. The associated loss of total IR intensity upon annealing is 35%, whereas the TPD spectrum yields 11% of the CO molecules desorbing up to 200 K. An integration of the TPD spectra to 215 K, which accounts for the additional desorption during the cooling period, gives 15% of desorbed CO molecules. Therefore, it is concluded that the oscillator strength of CO bound to the Pd atoms is at least 2.3 times larger than the average CO molecule bound to a Co atom.

What is the microscopic reason for the enhanced IR intensity of CO at low coordinated metal sites? A similar enhancement effect have been observed by Hayden et al. for adsorption at step edges of Pt(1 1 1) surfaces [20]. Greenler et al. have interpreted this effect as a result of a local field enhancement, based on a classical electro-dynamical picture which was corrected empirically for quantum mechanical effects [21]. Beside the simplified consideration of the quantum mechanical effects this treatment ignores all effects due to changes of the CO binding often called chemical effects. We have performed DFT calculations, which include field as well as chemical effects, on small model clusters to gain more insight into the microscopic origin of the effect. The following two situations were considered:

1. CO bound on-top to a regular (1 1 1) facet.
2. CO bound on-top of a metal atom which is itself adsorbed to a close packed facet.

Both situations are sketched in Fig. 4a and b. Table 1 summarizes the results for the pure Co as well as the Co/Pd bimetallic system. Additional

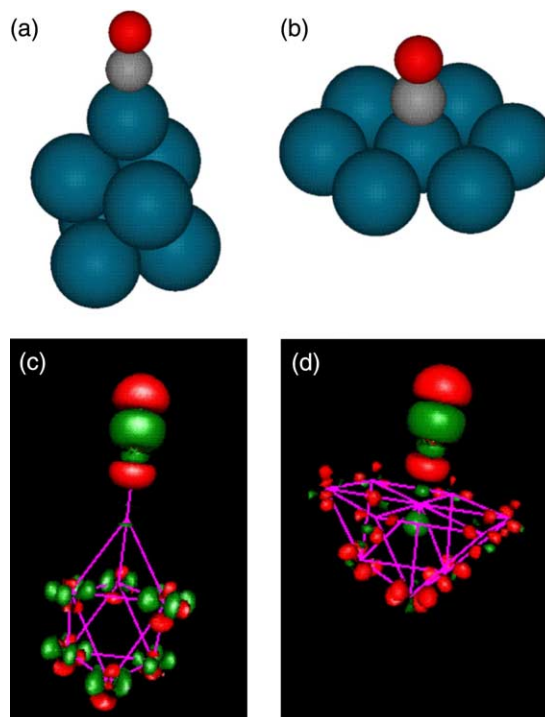


Fig. 4. (a) Schematic representation of the cluster geometry abbreviated $\text{Co}_3\text{Co}_3\text{Co}$ or $\text{Co}_3\text{Co}_3\text{Pd}$. (b) Schematic representation of the cluster geometry abbreviated Co_7 or Co_6Pd . (c) Electron density difference obtained from two calculations of $\text{Pd}_3\text{Pd}_3\text{Pd}$ with different C–O bond length. Positive and negative contours are chosen equal. (d) Electron density difference obtained from two calculations of Pd_7Pd_3 with different C–O bond length. Positive and negative contours are chosen equal.

calculations for pure Pd particles corroborate the results presented here. The dependence of the stretching frequencies on the coordination state of the metal differs significantly for Co and Pd. While Pd shows only a moderate red shift, Co exhibits a more pronounced blue shift for a reduction of metal coordination state, which is in line with the

Table 1

Distances, harmonic stretching frequencies and IR intensities calculated for model cluster calculations. For geometries of the clusters refer to Fig. 4a and b

Cluster	$d_{\text{Me-C}}$ [Å]	$d_{\text{C-O}}$ [Å]	ν^{H} [cm^{-1}]	I [kM mol^{-1}]
$\text{Co}_3\text{Co}_3\text{Co}$	1.9401	1.1505	2073	2769
Co_6Co	1.9308	1.1702	1936	804
$\text{Co}_3\text{Co}_3\text{Pd}$	2.0855	1.1434	2128	2064
Co_6Pd	2.284	1.1406	2156	226

experimental findings. The IR intensities for adsorption on regular facet sites are relatively low as compared to those for CO bound to a low coordinated metal atom showing an enhancement by a factor of 2.5–3.4. For the bimetallic situation an enhancement of the low coordinated Pd sites with respect to CO binding on-top to regular Co sites (the majority species on the Co particles) by a factor of 2.5 was calculated, which is in good agreement with the factor of 2.3 determined experimentally. The reason for the enhanced IR intensity is not connected to the changes in the electronic structure of the CO itself rather than a different response of the metal cluster. To visualize the response of the systems on the CO vibration we have calculated the electron density of the valence electrons for CO adsorbed to a regular surface site as well as a low coordinated metal atom on top of a metal surface with two different C–O bond distances. The electron density difference, derived from the densities calculated at the two CO distances, provides a measure for the electronic response of the system. The corresponding contour plots are shown in Fig. 4c and d. The electron density difference which is directly connected to the change of dipole moment reveals a close similarity in the region of the CO molecule for both situations. However, the response of the metal cluster is quite different. For CO bound to a regular facet the neighboring metal atoms are directly involved in the screening of the electron deficiency induced at the binding metal atom. However, in the carbonyl case the CO binding metal atom shows virtually no change of electron density indicating a complete decoupling of the CO bond from the rest of the metal cluster. On the other hand the metal atoms of the cluster do react on the different charge distribution at the CO molecule. The electron density difference exhibits a four fold symmetric pattern which enhances the dynamic dipole moment. The effect on the dipole moment is relatively pronounced because of the larger distance between the charges. On the contrary, the electron density difference observed on regular facet screens the dipole moment to some extent. This shows that the local field effect mentioned above is indeed to a large extent responsible for the intensity enhancement while chemical effects play only a minor role.

In summary we have shown that IR intensity can serve as a sensitive measure to identify molecules adsorbed to low coordinated metal atoms. In the case of the Pd/Co bimetallic system the difference in the IR frequencies between the regular facet site and the binding to a low coordinated metal site is virtually absent rendering the intensities a powerful tool to discriminate between these sites which may exhibit different chemical properties. From a fundamental point of view the IR enhancement is due to a decoupling of the CO bond to a low coordinated metal atom from those atoms embedded in the metal surface. This shows on an experimental basis that the response of the metal electrons in a carbonyl like species is considerably different from the one of CO bound to a metal surface.

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