

# CO adsorption on the surface of MgO(0 0 1) thin films

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## Abstract

We report infrared reflection–absorption and thermal desorption spectra of CO adsorbed at low temperature (30 K) on the surface of MgO(0 0 1) thin films. The high similarity of the observed IR bands as compared to data reported for MgO(1 0 0) single crystals and sintered MgO particles gives evidence for the identical surface morphology of the different substrates. CO adsorption series taken at constant temperature/variable pressure, variable temperature/constant pressure, as well as isotope mixing experiments reveal almost no diffusion of CO on MgO(0 0 1) at low temperature, but high adsorbate mobility at slightly elevated temperature.

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## 1. Introduction

The interaction of CO with the surface of MgO is considered as one of the prototype systems for studying adsorption properties of ionic surfaces. Pioneering experimental work in this regard has been performed by Adriano Zecchina and coworkers. They followed the approach of controlling the morphology of MgO particles using different preparation conditions, and combining CO probe spectroscopy with high-resolution transmission electron microscopy (TEM) imaging to assign the spectral features. In a series of papers these authors were able to identify several CO infrared absorption bands due to CO bound to differently coordinated Mg sites on the surface of MgO powder [1–5]. In the limit of highly regular MgO particles, perfect agreement with IR studies on vacuum-cleaved MgO single crystals was achieved, bridging the gap between pure surface science and real catalyst studies [4].

The experimental results provided also a reference to test theoretical methods for the calculation of vibrational frequencies and binding energies of CO interacting with different sites on the MgO surface [6]. From the theoretical results, it was concluded that CO binds weakly with its carbon end down to regular terrace Mg sites in an almost purely electrostatic manner [7]. Adsorption at low-coordinated sites, e.g. at steps or corners, leads to an increase of the polarization of the molecule,

resulting in a blue shift of the CO stretching frequency and increasing binding energies as compared to CO adsorbed to regular terrace sites [8–11]. The magnitude of the CO binding energy was controversially discussed since early TDS experiments carried out on thin MgO films suggested an unusually high adsorption energy [12], which could not be reproduced theoretically. However, CO-TDS data from vacuum-cleaved MgO single crystals resolved this discrepancy in favor of the theoretical predictions [13]. These results were recently confirmed for appropriately prepared MgO thin films [14].

Although MgO thin films have been characterized in detail by a variety of methods, infrared data of CO adsorbed on MgO, which are especially useful to compare this system to MgO powders, have not been exploited in detail yet. Previous studies were limited to an adsorption temperature of 80 K [15], where CO binds only to the strongest binding sites, i.e. corner Mg or vacancy sites. In order to allow for a more complete comparison with IR data available for vacuum-cleaved single crystals as well as powder samples, an infrared study of CO adsorption on MgO thin films at low temperature (30 K) was carried out. These experiments were complemented with TDS experiments to support the conclusion drawn from infrared spectroscopy.

## 2. Experimental

MgO(0 0 1) thin films were prepared under ultra-high vacuum (UHV) conditions on a Mo(0 0 1) substrate. The Mo(0 0 1)

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crystal was cleaned by oxidation at 1500 K in  $1 \times 10^{-6}$  mbar  $O_2$  and subsequent annealing to 2300 K. MgO(0 0 1) thin films of typically 20 monolayer (ML) thickness were grown by depositing Mg in an oxygen background of  $1 \times 10^{-6}$  mbar  $O_2$  and a substrate temperature of 600 K. The deposition rate was 1 ML/min. For cooling of the sample the crystal was mounted on a He-cryostat, which allowed to achieve sample temperatures down to 30 K. IR experiments were performed in reflection–absorption geometry. The spectral resolution was  $4 \text{ cm}^{-1}$  and 1000 scans were accumulated to obtain a reasonable signal-to-noise ratio. The heating rate in TDS experiments was 0.5 K/s.

### 3. Results and discussion

Fig. 1 shows a comparison of infrared spectra taken at monolayer saturation coverage from three different MgO substrates. In the case of a vacuum-cleaved single crystal (Fig. 1a), three bands at 2151, 2137 and  $2132 \text{ cm}^{-1}$  are observed with p-polarized light after adsorption of CO below 40 K [16]. The main band at  $2151 \text{ cm}^{-1}$  was assigned to the dynamic dipole of perpendicular oriented CO molecules adsorbed on regular terrace sites, while the latter two bands were attributed to the in-phase and out-of-phase vibrational excitation of tilted CO, respectively. This assignment is supported by the fact that only the band at  $2132 \text{ cm}^{-1}$  is

detected with s-polarized light [16] and is in line with previous interpretations of helium atom scattering (HAS) and LEED experiments, where a  $c(4 \times 2)$  overlayer was observed [17,18]. The characteristic superstructure as well as the two bands for the in-phase and out-of-phase vibrational excitation disappear at temperatures above 40 K giving evidence for dynamical reordering of the CO layer as well as partial desorption of CO molecules.

The presence of similar structures may be obtained at higher temperatures by applying a sufficiently high CO partial pressure. This was demonstrated by Zecchina and coworkers for CO adsorption on MgO powders at 60 K as seen in Fig. 1c [4]. Again, all three characteristic infrared bands due to perpendicular and tilted CO molecules are observed.

However, the infrared spectrum taken for the same CO coverage on a 20 ML MgO(0 0 1) thin film supported on Mo(0 0 1) at 30 K lacks the band at  $2132 \text{ cm}^{-1}$  (Fig. 1b). This is due to the metal surface selection rule which limits the observable transitions to those with dynamic dipole moments oriented perpendicular to the surface. Thus, the observation of two bands at 2152 and  $2137 \text{ cm}^{-1}$  is in perfect agreement with the results obtained on MgO single crystals and powders. In addition to the spectra of the latter two systems, the IR spectrum of CO adsorbed on MgO thin films (Fig. 1b) shows a pronounced shoulder on the high-frequency side of the band at  $2152 \text{ cm}^{-1}$ . As shown experimentally by Zecchina and coworkers and corroborated by theoretical calculations, this band can be assigned to CO molecules adsorbed at lower coordinated sites, e.g. at steps or corners [5,11]. Thus, the thin MgO films exhibit the highest concentration of low-coordinated sites among the samples compared here.

The number of low-coordinated sites can be reduced by heating the pristine film to 1200 K. This can be deduced from the decrease of the infrared intensity of the high energy shoulder of the peak at  $2152 \text{ cm}^{-1}$  as shown in Fig. 2a. However, a direct interpretation of infrared intensities in terms of number of molecules is not straightforward. Therefore, we compare the infrared data to corresponding thermal desorption spectra shown in Fig. 2b. Both thermal desorption spectra exhibit two desorption peaks at 52 and 68 K, respectively. The peak at 52 K corresponds to desorption of CO molecules adsorbed on regular terrace sites, in agreement with similar studies on MgO single crystals and thin films [13,14]. From these TDS data, a desorption energy of 15 kJ/mol was extracted. This is in perfect agreement with the binding energy derived from CO pressure-dependent IR intensity of the band at  $2152 \text{ cm}^{-1}$  measured for MgO smoke [4]. A similar analysis of the thermal desorption peak at 68 K gives a desorption energy of 25 kJ/mol [19], which is in perfect agreement with the desorption energy ( $E_{\text{des}}$ ) derived for low-coordinated sites on MgO powders from the infrared intensities of the corresponding blue-shifted IR bands [5]. Upon annealing the intensity ratio of the thermal desorption peaks at 52 and 68 K changes significantly in favor of the signal corresponding to terrace sites, corroborating a reduction of defect sites. A comparable change of the intensity ratio is observed for the infrared signal at  $2152 \text{ cm}^{-1}$  as compared to the shoulder at  $2158 \text{ cm}^{-1}$

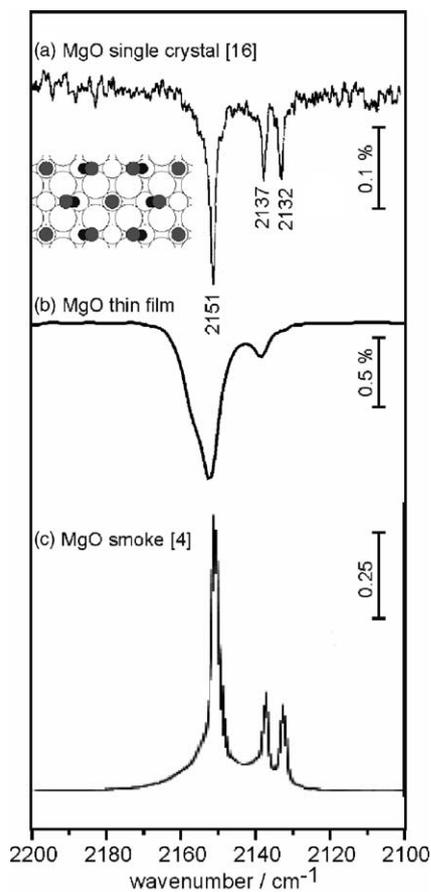


Fig. 1. Infrared spectra of monolayer coverage CO on different MgO substrates: (a) single crystal [16], (b) thin film and (c) MgO smoke [4]. The low-temperature CO- $c(4 \times 2)$  superstructure is shown in the inset.

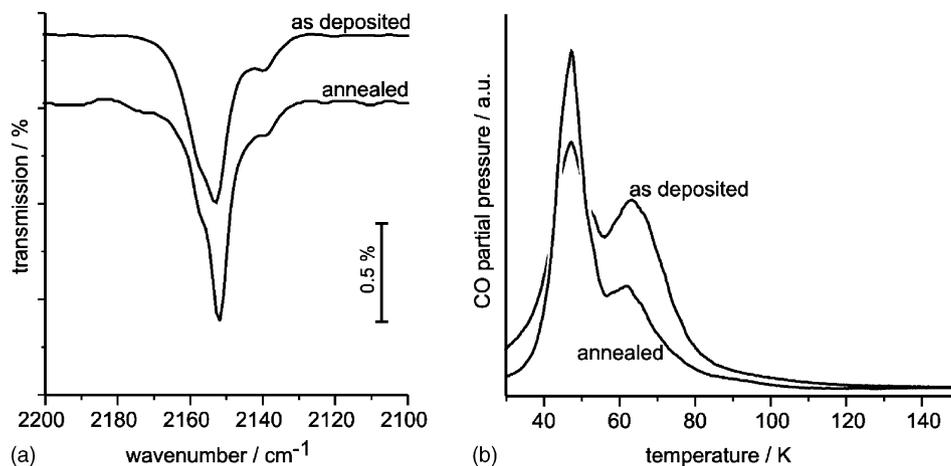


Fig. 2. (a) IR and (b) TDS spectra of a 20 ML MgO(0 0 1) thin film after deposition and after annealing to 1200 K, respectively.

(Fig. 2a). Therefore, both methods can be used as a good estimate for the surface roughness of the films, i.e. the relative abundance of low-coordinated step or corner sites.

It is interesting to have a closer look at the dynamics of the adsorption and desorption process. For this purpose, we compare CO infrared spectra taken after dosing a constant amount of 1 L CO (1 L =  $10^{-6}$  torr s) at variable temperature with a series of IR spectra recorded after dosing increasing amounts at 30 K. The former series is shown as grey traces in Fig. 3. Starting with an adsorption temperature of 83 K, we observe the evolution of an almost symmetric absorption band, which shifts from 2175 to 2160  $\text{cm}^{-1}$  when the adsorption temperature is lowered down to 52 K. On the other hand, for a constant adsorption temperature of 30 K and CO dosed step-wise up to 0.35 L (Fig. 3, black traces), the bands are shifted to lower wavenumbers and are clearly asymmetric.

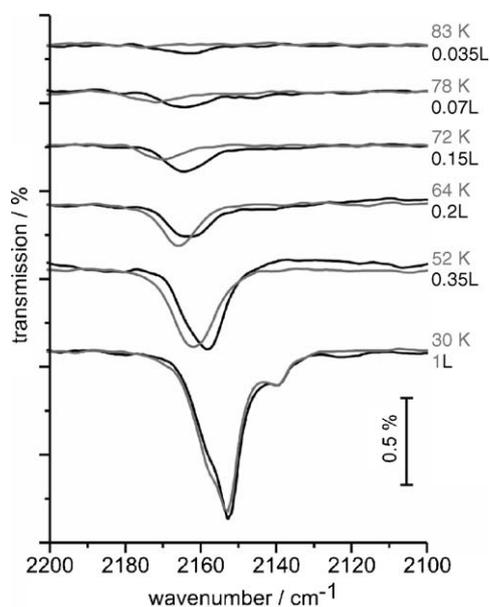


Fig. 3. Grey traces: infrared spectra taken after dosage of 1 L CO at the indicated temperatures; black traces: infrared spectra taken after different amount of CO dosed at 30 K.

As inferred from the TD spectra, the symmetric infrared band found for adsorption at  $T \geq 52$  K corresponds to molecules exclusively adsorbed to low-coordinated sites. The shift of the IR band with increasing coverage results from dipolar coupling effects between neighboring CO molecules.

However, the isothermal experiment shows an asymmetric line-shape indicating CO adsorption to both step and terrace sites simultaneously. Therefore, the diffusion length of CO molecules adsorbing on the surface at 30 K is sufficiently small to prevent a preferred population of the energetically more favorable low-coordinated sites.

The dynamics of the adsorbate systems can be elucidated in more detail by isotope experiments using the fact that low-coordinated sites can be populated exclusively by an appropriate choice of the temperature. In this study, we dosed  $^{13}\text{CO}$  at 52 K. The IR band at 2117  $\text{cm}^{-1}$  (Fig. 4a, upper trace) is shifted, according to the isotopic ratio of  $^{13}\text{CO}/^{12}\text{CO}$ , to lower wavenumbers as compared to the one observed in the similar experiments described in Fig. 3. Subsequently, the sample was cooled to 30 K and saturation coverage of  $^{12}\text{CO}$  was added to populate terrace sites (Fig. 4a, lower trace). The position of the new  $^{12}\text{CO}$  band at 2152  $\text{cm}^{-1}$  is perfectly in line with the expectations due to adsorption at terrace sites. However, the position and shape of the  $^{13}\text{CO}$  band have dramatically changed. The additional red shift of 8  $\text{cm}^{-1}$ , from 2117 to 2109  $\text{cm}^{-1}$ , arises from the influence of dynamic coupling of CO adsorbed on terrace sites next to the step sites in the high-coverage state. Furthermore, the intensity of the  $^{13}\text{CO}$  band at saturation coverage is dramatically reduced. The most simple explanation, namely an exchange of terrace bound CO with the preoccupied low-coordinated sites can be excluded by the lack of infrared intensity at the high energy side of the peak at 2152  $\text{cm}^{-1}$ . Dynamic intensity transfer, which may give rise to redistribution of infrared intensity from the low to the high energy band, can be excluded by reversing the adsorption order (population of low-coordinated sites with  $^{12}\text{CO}$  and terrace sites with  $^{13}\text{CO}$ ), which gives exactly the same intensity ratio. Thus, it is concluded that the reduction of the infrared intensity is due to a decrease of the dynamic dipole moment of the molecules, which may arise from a change of the adsorbate structure, e.g. a tilt of CO molecules.

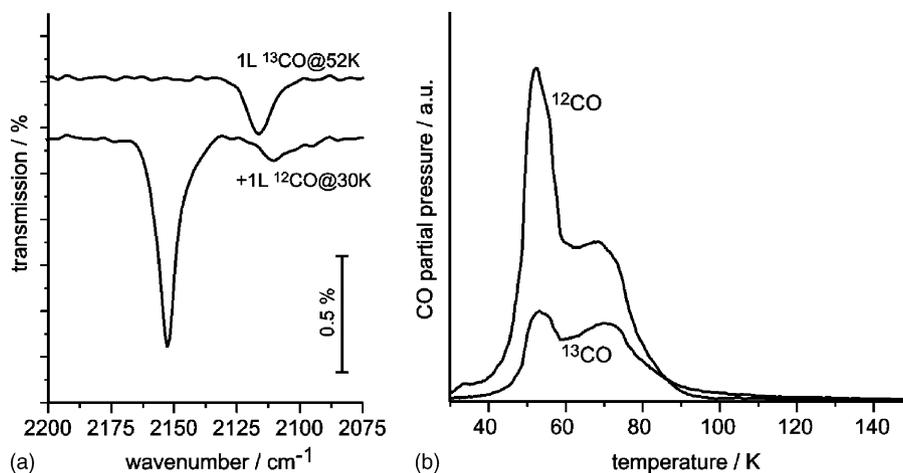


Fig. 4. (a) Upper trace: infrared spectrum after saturation coverage of  $^{13}\text{CO}$  at 52 K; lower trace: infrared spectrum taken for the preparation of the upper trace and subsequent saturation with  $^{12}\text{CO}$  at 30 K. (b) TD spectrum taken from the preparation corresponding to the lower infrared spectrum in (a).

Fig. 4b shows the two mass channels corresponding to  $^{12}\text{CO}$  and  $^{13}\text{CO}$  of a thermal desorption spectrum obtained from the mixed isotope adsorption experiment described above. The desorption spectrum clearly shows that the separation of  $^{12}\text{CO}$  and  $^{13}\text{CO}$  to terrace and low-coordinated sites, respectively, is no longer reflected in the TD spectrum. Instead, both isotopes are present in either of the desorption peaks at 52 and 68 K assigned to terrace and low-coordinated sites, respectively. It is interesting to note that about 2/3 of the intensity of the peak at 68 K is found in the  $^{12}\text{CO}$  channel. The very same intensity ratio was also observed previously by temperature dependent infrared experiments [19]. The infrared experiment shows further that the redistribution of CO molecules starts already at temperatures as low as 43 K. This scrambling of molecules between different sites indicates a strong coupling between CO molecules bound to the vicinity of the low-coordinated sites. One may think of it as a multinuclear carbonyl like species that decomposes above 40 K statistically into a single CO molecule adsorbed on a low-coordinated site, thus, giving rise to the mixing of the isotopes.

#### 4. Conclusion

In this study, we have presented a combined infrared and thermal desorption study of CO molecules adsorbed at low temperature on the surface of MgO thin films. The infrared data obtained on thin films are in perfect agreement with similar data obtained on MgO single crystals and MgO powders, except for the higher surface roughness of MgO thin films. By thermal annealing, both IR and TDS experiments indicate a flattening of the surface with a substantial decrease of the defect related

spectroscopic features. The isotope experiments reveal a strong interaction of terrace and defect bound CO at high-coverage which lead to scrambling of CO between these sites upon desorption.

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