Adsorption and Reaction of CO₂ on Metal Surfaces. Detection of an Intrinsic Precursor to Dissociation

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1. Introduction

In the late seventies much progress was made in understanding the mechanism of the CO oxidation reaction using the spectroscopic machinery of surface science [1-2]. ERIL and his group [3-5] unambiguously showed by molecular beam and other experiments that CO oxidation on transition metal surfaces proceeds via a Langmuir-Hinshelwood mechanism rather than an Eley-Rideal mechanism. This implies that both reactants, CO and oxygen, are adsorbed on the surface when CO₂ is formed. The latter is readily desorbed at the temperatures used in the above-mentioned studies. Therefore, adsorbed CO₂ has not been observed in those studies but only detected after desorption in the gas-phase [3-5]. In light of the fact that in addition to the importance of CO oxidation, CO₂ dissociation [6-9], the reverse reaction, is of considerable - even technical - interest, several groups have started to investigate the interaction and reactivity of CO₂ with and on metal surfaces [7-9, 12-18]. In particular, from molecular beam experiments on CO₂ reaction dynamics performed on different surfaces a picture arises that can schematically be represented in a simplified manner by the two-dimensional potential energy diagram shown in Fig. 1/17-18/. CO₂ approaches the surface along the entrance channel and may, after passing through some kind of physisorbed (van der Waals) state, be trapped into an intermediate state which then dissociates along the exit channel into adsorbed CO and adsorbed oxygen. In favour of the existence of an intermediate state, which from the standpoint of an intrinsic precursor to dissociation, and whose electronic and geometric structure is not yet known, is the observed cosine-like angular distribution of scattered CO₂ for certain surfaces, e.g. Ni(100) /13/ and Pd(111) /13, 14/.

Most of the studies referenced above proposed some kind of bent CO₂ species as an intermediate, transient species. Many authors consider the bent species to represent the transition state of the reaction rather than the stable intermediate. In a recent theoretical study /15/ we have tried to evaluate possible interaction and reaction channels between CO₂ and a metal via cluster calculations. Upon interaction between CO₂ and metal the CO₂ molecule bends due to partial electron transfer from the metal to the molecule. Bonding to the metal can be established either by pure carbon, bidentate CO₂ oxygen coordination or by the C-O bond, i.e. mixed carbon-oxygen coordination. The total binding energy is rather small, approximately of the order of 10 kcal/mol.

In the present paper we review in some detail experimental results for the system CO₂/Ni(110) and CO₂/Fe(111) and mention results for other metal surfaces, i.e. the face specificity of CO₂ adsorption observed recently by NEDER and coworkers /9/.

2. CO₂ Adsoption

Figure 2 shows angle-resolved photoelectron spectra (normal emission) of the CO₂ covered Fe(111) and Ni(110) surfaces in comparison with the clean

![Diagram](image_url)
surfaces at $T = 85$ K and $T = 80$ K, respectively. CO$_2$ exposure leads to three (four) strong peaks marked with lines and some weaker bands marked with arrows. The assignment of the strong peaks to the 1ng, 1mu, 3mg and 4mg ion states of CO$_2$ is obvious when comparing the measured spectra with those in the gas phase /9,20/ or in the solid phase /21/. Clearly, CO$_2$ adsorbs molecularly on both surfaces without a strong influence on the electronic structure of the adsorbed species. However, the binding energies of adsorbed CO$_2$ are lowered slightly as a function of increasing coverage /9,14,16,22/ indicating some interaction between the adsorbed species. To explain these findings the changes in work function of the metal surfaces for increasing exposure to CO$_2$ at 80-85 K was measured /9,16/. Up to an exposure of about 11 the work function increases, passes through a maximum, drops by a smaller amount and saturates. This is explainable in terms of the competition of two different adsorbed species, one causing a strong work function increase, the other one a smaller work function decrease. On this basis we interpret the peaks marked by arrows in fig. 2 as due to the species that increases the work function, while CO$_2$, which dominates the spectrum, decreases the work function.

Even though for none of the CO$_2$ adsorbrates a sharp LEED pattern has been observed, E vs k dispersions observed in angle resolved photoelectron spectra indicate some long-range order /23/, i.e., on the Ni(110) surface. Some of the ionization bands (independent of the indication of long-range order) show pronounced intensity variations as a function of polar angle. The intensity variations contain information on the local geometry of the adsorbate. The strongest intensity variation was observed for the totally symmetric 4mg ion state within the (110) azimuth for s-polarization. The intensity of the 4mg state varies with respect to the 1ng state, whose intensity is almost independent of polar angle. We have plotted in Fig. 3 the intensity ratio 4mg/1ng along the azimuth (100) and (110). We observe a rather pronounced peaking of the 4mg along the (110) azimuth. The physics is very simple. The 4mg state is mostly localized on the oxygen atoms. It represents one of the oxygen lone pairs with strong O2pz character (z is along the molecular axis). By symmetry the main emission direction from this orbital has to be pointing along the molecular axis. Symmetry also asks for vanishing 4mg intensity in normal emission (see Fig. 3) if the linear CO$_2$ molecules were all oriented with their axis parallel to the (110) azimuth. This is at variance with observations.

The contribution to the cross-section in normal emission is mainly due to the carbon 2s-character in the 4mg-orbital. In other words, a polarization component perpendicular to the molecular axis could explain the observed emission perpendicular to the surface. There are several possibilities how such a situation could be achieved. A structure model /15/ that accounts for many of the observations is shown in Fig. 4. Half of the molecules is oriented along the (110), the other half along the (100) azimuth. Such a structure is closely related to the (001) plane of solid CO$_2$ /24/. In the representation of atomic quadrupoles /26/ this arrangement of linear quadrupoles is concerned. A fit of calculated ionization intensities to the observed values (Fig. 3) as a function of polar angle suggests a tilt of the molecules from perfect parallel orientation within ± 20°. A detailed discussion including band structure will be published elsewhere /26/. For the Fe(111)/CO$_2$ system, which does not show dispersion, a similar intensity analysis indicates a larger tilt angle, which is consistent with the more open structure of the bcc(111)-surface.

![Fig. 3: Experimentally determined relative intensities (referring to the 1ng level intensity) of the 4mg ion state as a function of polar angle θ for CO2/N(110); 21L exposure.](image)

3. Reaction of Adsorbed CO

Figure 5 shows a set of photoelectron spectra of clean and adsorbate covered Ni(110) (Fig. 5a) and Fe(111) (Fig. 5b) surfaces at various temperatures and exposure conditions. Firstly, we discuss the Ni(110)/CO$_2$ system. Spectrum (a) (taken from Fig. 2) represents molecular CO$_2$ that is adsorbed without strong distortion of its molecular electronic structure. Only adsorbate-induced features are shown. Upon heating this layer to 114 K (spectrum (b)) and 140 K (spectrum (c)) the spectrum changes considerably as compared to 80 K: Firstly, the adsorbate-induced features lose intensity relative to the substrate emission close to the Fermi edge indicating partial desorption of the adsorbate layer. Secondly, there are
extra spectral features observed at 3.5 eV and 8.7 eV, and the CO2 band at 10.6 eV binding energy loses intensity upon increasing the temperature. At 140 K it is only visible as a shoulder of less than half the intensity at 80 K. It appears that the lower the intensity of the 10.6 eV band is, the more intense are the bands at 3.5 eV and 8.7 eV binding energy. Up to about 200 K the spectrum remains basically unchanged except that more and more undisturbed CO2 is desorbed. At 140 K the work function increases up to 0.9 eV due to the loss of coadsorbed undisturbed CO2. The observed work function change can be reached either by admitting CO2 at 140 K surface temperature or by heating a saturated CO2 layer produced at 80 K to 140 K. Further heating of the adsorbate decreases the CO2 induced features until they vanish at 200 K (spectrum (d)). This intensity decrease is accompanied by a slight further increase in work function up to 1 eV. Upon heating up to room temperature (spectrum (e)) a distinctly different photoelectron spectrum is observed. Also, the work function decreases considerably to 0.5 eV indicating a change in the magnitude of surface polarization. The photoelectron spectrum at room temperature consists of three bands at 5 eV, 8.1 eV and 10.8 eV binding energy. By using spectrum (g) in Fig. 5a which shows the photoelectron spectrum of a disordered CO/Fe(110) adsorbate at room temperature, the peaks at 10.8 eV and 8.1 eV binding energy can be identified as being due to CO. The band at 5 eV binding energy in spectrum (e) is situated within the typical "oxygen range". Even though a spectrum of an oxygen overlaver, created by exposing the surface to 1L of O2 at room temperature, spectrum (f) shows a binding energy about 1 eV larger than in the CO/O coadsorbate the assignment of the peak at 5 eV in spectrum (f) to adsorbed oxygen is reasonable. The Ni(110) surface is known to undergo rather complex reconstructions upon oxygen adsorption /27/ and the oxygen peak is expected to shift in binding energy depending on the surface structure, i.e. coordination number etc. /3/. The position of the oxygen peak in a spectrum taken for an oxygen CO adsorbate prepared at 80 K is much closer to the position of the oxygen peak in spectrum (e). Summarizing so far, we are led to the conclusion that CO2 undergoes dissociation when adsorbed molecularly at low temperature and subsequently heated to room temperature.

Figure 5b shows a set of spectra for CO2/Fe(111) in normal emission with p-polarized excitation (\(\hbar \omega = 32\) eV) taken at different surface temperatures. Again only the adsorbate-induced features are shown. Clearly, upon raising the temperature to 100 K some CO2 induced peaks (marked with arrows in Fig. 2) lose intensity, while those that must be attributed to a second species, show an intensity increase. Upon heating to 140 K the peaks caused by a linear, molecular CO2 disappear, and the intermediate species dominate the spectrum. Further heating of the substrate leads at room temperature to spectrum (g). By comparison of spectrum (i) with spectrum (j) which is a pure Fe(111)/O spectrum and a pure Fe(111)/CO spectrum (spectrum (i)), we can unambiguously assign the peaks to be due to coadsorbed CO and O. Upon raising the temperature further to 340 K the molecularly adsorbed CO dissociates.

Both sets of spectra (Fig. 5a and b) indicate the existence of an intermediate molecular species that seems to be the precursor for dissociation of CO2.

In a previous theoretical paper /15/ we have proposed a bent anionic CO2 species coordinated to the metal as a possible candidate for such a precursor. Such a bent CO2 species can be formed by transferring electron charge from the metal to the CO2 molecule. The presence of charge transfer onto the adsorbate is corroborated by the strong work function increase observed at 140 K, where much of the coadsorbed linear
CO2 has been desorbed. In the language of molecular orbital theory, the extra charge transferred from the metal occupies a previously unoccupied orbital (2μ) of linear CO2, which consequently becomes a 17-electron system. Such a system tends, according to the Walsh rules /28/, to avoid a linear geometry. On the basis of one-electron orbital energies we show in Fig. 6 a correlation diagram for CO2 and a bent CO2 species as calculated in ref. /15/. On the left, the comparison is made with the experimental Ni(110) data, on the right with the Fe(III) data set. The energy scale for the anion has been shifted so as to align the orbital at highest binding energy (4μ). Clearly, the first observation is that while the CO2 spectrum spreads over about 5-6 eV binding energy, the CO2− spectrum extends over more than 10 eV /29/. Let us try to assign spectrum (d) in Fig. 5a in comparison to theory /15/ in Fig. 6a. It is most obvious to assign the peak at 3.5 eV binding energy to the 6a1 orbital. The 6a1 orbital is mainly localized on the carbon atom /15/. It is therefore appropriate to compare its binding energy with carbon-induced bands in resolved spectra of such systems. On Ni(110) carbon adsorption leads to a peak at 4.1 eV binding energy relative to E_F. Our 6a1 orbital therefore appears to be in the correct energy range. However, formation of atomic carbon in the course of our experiments is very unlikely at the low temperatures used. Note, that for preparation of the carbon adlayers the metal surface was exposed to CO around 200°C /30/. Coming back to our assignment in Fig. 6a the next set of orbitals is expected between 5-6 eV binding energy. The following one should be situated between 9-10 eV and the final one at approximately 12 eV. Based on the observed energies the assignment proposed by the arrows in Fig. 6 is obvious, except that there is no peak observed between 5-6 eV. However, off normal a peak in the energy region in question clearly shows up which is demonstrated for the CO2/Fe(III) system in Fig. 6b. The observation that the peaks at 3.5 eV, 8.7 eV and 11.4 eV show considerable intensity in normal emission, while the peak at 5.6 eV is absent in normal emission is consistent with the symmetry of the states given for CO2− in Fig. 6: Those regions of binding energies that are assigned to groups of orbitals containing totally symmetric (a1) orbitals should contribute to electron emission normal to the sample surface. On the other hand the orbitals of non totally symmetric character should lead to emission that peaks off normal. The orbital assignment given in Fig. 6 for the bent species refers to the C2v point group. Clearly, the local geometry of the precursor state is such that there is still a mirror plane present in the system, since otherwise there would be no selection rule. Possible coordination sites with mirror plane symmetry are shown in Fig. 7, while the sites on the left and right hand side of Fig. 7 have C2v symmetry, the one in the middle has C3v symmetry. The symmetry of the CO2− orbitals in C3v symmetry are given in Fig. 6 in parentheses. Such a symmetry corresponds to coordination of one of the C=O bonds to the surface. Obviously, the orbital with 4b2 character in C2v symmetry becomes totally symmetric in C3v symmetry, while the 4a1 orbital in C2v remains non totally symmetric in C3v. Thus, were the symmetry of the adsorbed molecule Cs we would expect some intensity in the energy range around 6 eV binding energy. However, the absence of appreciable intensity in the corresponding energy region suggests that the adsorbed molecule has C2v symmetry.

![CO2− Possible Coordination Sites](image)

**Fig. 7:** Possible coordination sites of CO2− together with the corresponding point group symmetries.

The results of an electron energy loss study /16/ parallel to a large extent the results of the photoemission studies and it appears that a C2v coordination site with direct oxygen coordination is more likely than a carbon coordinated site. This conclusion is in line with the results of our theoretical study /15/. If the assignment given in Fig. 6 and discussed above is correct the shaded peaks in the upper curve of Fig. 5a are not caused by the bent CO2 species but rather by neutral linear CO2 as can be clearly seen by comparison with the spectrum shown at the bottom of Fig. 6a and b. Here the assignment is unambiguous as discussed in section 3 and indicated by the calculated ionization energies which have been shifted rigidly so as to line up with the experimental 4a2 ionization energy. It appears that some CO2− is formed at low temperature and coexists with neutral CO2 on the surface. We do not know at present whether the CO2 and the bent CO2 species are adsorbed in separate islands or are coadsorbed forming a homogeneous phase. It is known from gas phase
experiments on CO$_2$ clusters that a bent CO$_2$-anion can be stabilized by solvation with neutral CO$_2$ molecules /31,32/.

4. Synopsis

We have reviewed in the present work mainly photoemission results on adsorption and reaction of CO$_2$ on Ni(110) and Fe(111). Exposed at 80-85 K CO$_2$ adsorbs molecularly on the clean surfaces. The electronic structure of the main fraction of molecules is, if at all, only slightly distorted in comparison to the gas phase and a thich solid film. However, even at low temperature part of the molecules adsorb into a state that is identified as a precursor to dissociation (CO$_2$ad → COad + Oad) which occurs at elevated temperatures. The precursor is suggested via the photoemission results /14,16/ the HREELS study /16/ and supported by a theoretical study /15/ to be a bent "anionic" CO$_2$- species. All studies favor a coordination site with C$_2$v symmetry. Whether the species is oxygen or carbon coordinated (see Fig. 7) is not yet clear, although oxygen coordination is more plausible. Recently, the structure of the formate ion (HCOO$^-$) coordinated to a Cu surface has been determined by SEXAFS /33,34/. This species, which differs from our proposed CO$_2$- species only by the hydrogen atom attached to the carbon atom, has been shown to have C$_2$v symmetry with a similar coordination site as proposed in the present work for CO$_2$. Interestingly, the stability of the precursor towards dissociation depends on the particular system as is evident from a comparison of the Ni(110) with the Fe(111) system. Decomposition of CO$_2$ starts to occur above 200 K on Ni(110) while it starts at lower temperature T ≥ 180 K on the Fe(111) surface. Parallel to the lower dissociation temperature for CO$_2$ on Fe(111) the formation of the dissociation precursor seems to be facilitated on Fe(111) indicated by the larger CO$_2$- signals at low adsorption temperature (compare Fig. 2a and Fig. 2b). At present, we can only speculate on the reason for these observations. A key quantity that determines the formation of the dissociation precursor could be the work function. WEDLER and coworkers /9/ e.g. observed a strong function for CO$_2$ adsorption on different Fe surfaces: Table 1 collects work function values in addition to those of other single crystal surfaces for which CO$_2$ adsorption has been studied. It appears that large work functions inhibit the formation of CO$_2$. This is reasonable, since we know from our theoretical work that the bonding of CO$_2$ to transition metals is dominated by Coulomb interactions: The more energy it takes to transfer an electron from the metal to the CO$_2$ molecule the more unstable becomes the CO$_2$ coordination complex. If one therefore changes the work function, i.e. decreases it via alkali coadsorption or increases it via oxygen coadsorption, one can influence the stability of the CO$_2$- moiety (see Table 1). Also, the presence of the CO$_2$- anion may be key for subsequent CO$_2$ adsorption due to possible CO$_2$ - CO$_2$ interactions.

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6. References

Influence of Electronic and Geometric Structure on Desorption Kinetics of Isoelectronic Polar Molecules: NH₃ and H₂O

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Consideration of the thermal desorption kinetics for isoelectronic NH₃ and H₂O from certain metal surfaces reveals an interesting contrast, which relates to geometrical and electronic structural effects in the adsorbed layers. Both NH₃ and H₂O are polar molecules bonded to the surface via lone pair orbitals on N and O, respectively. Hydrogen-bonding attractive interactions between neighboring H₂O molecules lead to formation of 2-d and 3-d clusters; thermal desorption kinetics of H₂O are characterized by sharp desorption peaks over narrow temperature ranges (the full width at half maximum (fwhm) is \( \Delta T \lesssim 10 \text{K} \) in some cases). In distinction, lateral interactions between neighboring NH₃ molecules are largely repulsive (dipole-dipole interactions) and the thermal desorption spectra are considerably broader in temperature than for H₂O (fwhm \( \Delta T \lesssim 70 \text{K} \) to 150K, depending on substrate). In the following paragraphs, we summarize results obtained in our laboratory during the last few years which illustrate these points for desorption of NH₃ and H₂O from metal surfaces, including Ni(111), Ru(0001) and Ag(110). In each of these cases, the adsorption of NH₃ and H₂O is molecular, and desorption proceeds without dissociation.

First, consider the bonding geometry and adsorbate lateral interactions for adsorbed H₂O and NH₃. In the free H₂O molecule, there are two lone pair orbitals associated with the O atom; in liquid and solid H₂O, hydrogen-bonding interactions involving the H-atoms and the lone pair orbitals result in tetrahedral coordination of the O atoms. There is a great deal of evidence from high resolution electron energy loss spectroscopy (EELS), work function measurements, ultraviolet photoemission spectroscopy (UPS), and electron-stimulated desorption ion angular distribution (ESDIAD) [1-3] that bonding of H₂O to metal surfaces occurs via one of the lone pair orbitals, with the other lone pair orbital available for participation in attractive hydrogen-bonding interactions with neighboring molecules. This leads to the formation of two and three-dimensional clusters on the surface even at cryogenic temperatures, where surface...