

CO₂ ADSORPTION AND REACTION ON Fe(111): AN ANGLE RESOLVED PHOTOEMISSION (ARUPS) STUDY

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Molecular CO₂ adsorption is observed on an Fe(111) surface at 85 K. For the main fraction of molecules the relative binding energies of the valence ion states as determined by ARUPS are consistent with those in the gas as well as in the condensed phase, and indicate that the electronic structure of that fraction of adsorbed molecules is only slightly distorted upon adsorption. There is a fraction of adsorbed molecules at 85 K that can be identified as bent, anionic CO₂⁻ species. While the weakly adsorbed, linear CO₂ molecules desorb at low temperature, the CO₂⁻ species is stable up to 160–180 K. The latter is proposed to be a precursor to dissociation. Above this temperature adsorbed carbon monoxide and oxygen are observed on the surface, and at room temperature the CO₂⁻ signals have disappeared. Heating above room temperature dissociates the CO molecules into carbon and oxygen.

1. Introduction

Recently, the interaction of CO₂ with metal surfaces has received increasing attention [1–7]. CO₂ adsorption on iron surfaces [6] is of particular interest since CO₂ possibly plays an important role in complex reaction systems such as the Fischer–Tropsch synthesis



via the reaction [8]



Also, CO₂ can be formed via the Boudouard equilibrium [9]:



leading to carbon deposition on the iron surface, which then acts autocatalytically [9].

CO oxidation is another interesting reaction in which CO₂ plays a key role [1].

Wedler and coworkers [6] have studied recently CO₂ adsorption on well defined iron surfaces, i.e. Fe(110) and Fe(111), and have found the Fe(111) surface to be particularly reactive. Its reactivity is comparable to polycrystalline iron films [6]. At 80 K, already, two adsorbed CO₂ species are observed one of which is an undistorted physisorbed CO₂ species [6]. Work function measurements [6,10] as well as angle integrated UP spectroscopy suggested that the other species is an anionic, possibly bent CO₂ species. Such species have been postulated recently on the basis of theoretical calculations [4], and were subsequently verified spectroscopically by several experimental techniques for the system Ni(110)/CO₂ [7]. Wedler and coworkers [6] found this species to be stable up to 180 K on Fe(111). They assigned it to be a precursor for dissociation into adsorbed carbon monoxide and oxygen, which occurred above 180 K. At higher temperatures, i.e. above room temperature, the adsorbed CO was found to dissociate into adsorbed carbon and oxygen [6].

In the study mentioned above [6], angle integrated lower resolution UP spectroscopy ($\hbar\omega$: 21.21 eV) has been employed in order to study the electronic structure of the adsorbate. Therefore, some of the conclusions reached are in need of further experimental verification. We use in the present study angle resolved photoelectron spectroscopy with excitation by synchrotron radiation. This allows us to vary the photon energy and therefore to vary the cross section for ionization, which helps to more definitively assign the spectra. The angular resolution is used to apply symmetry selection rules and therefore determine the symmetry of a given ionization band. The present study, in this respect, is very much in the same spirit as the previous similar investigation of CO₂ on Ni(110) [7]. The results of the present investigation corroborate the results of Wedler and coworkers [6] and put their conclusions on a more solid basis. The paper is organized as follows: In section 2 we present the experimental details. Section 3 presents the results and a discussion of the CO₂ adsorbates. Section 4 contains a synopsis.

2. Experimental details

The experiments were performed in a magnetically shielded ultrahigh vacuum system (VG, ADES 400) containing facilities for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), residual gas analysis with a quadrupole mass spectrometer, and angle resolved photoelectron spectroscopy (ARUPS). The electron analyser is rotatable in two orthogonal planes and electrons are collected within an acceptance angle of $\pm 1.5^\circ$. The resolution was typically 100 meV. Excitation of photoelectrons was achieved by synchrotron radiation from the exit slit of a toroidal grating monochroma-

tor (TGM) attached to the storage ring BESSY in Berlin. The base pressure in the system was below 10^{-8} Pa.

The Fe(111) crystal was spot-welded between two tungsten wires which were spot-welded to two tungsten rods mounted on a sample manipulator. With liquid nitrogen the crystal could be cooled to 80 K. Heating was possible either by direct resistive heating or by electron impact onto the reverse side of the crystal. Resistive heating was used to check the influence of CO₂ fragment dissociation products produced by electron bombardment.

The surface was cleaned by argon ion bombardment. After annealing the cleanliness was checked with AES, and surface order and geometry were established by LEED.

Upon adsorption of CO₂ (Linde AG, purity 99.999%) at all the temperatures used, no sharp LEED patterns were observed. Only the background of the sharp substrate LEED pattern appeared blurred upon adsorption. It turned out that interaction between CO₂ and the ion pump as well as the filaments of the ionization vacuummeter within a CO₂ pressure range of 10^{-6} to 10^{-4} Pa led to formation of CO. Therefore this pressure range was avoided, the ion pump and all filaments were switched off during admission of CO₂.

3. Results and discussion

3.1. CO₂ adsorption

In a previous study, Behner et al. [6] reported UP spectroscopic results with 21.21 eV photons indicating that CO₂ adsorbs molecularly at 80 K. Fig. 1 shows photoelectron spectra taken at 85 K of the clean Fe(111) surface (a) and of the same surface after exposure to 5 L of CO₂ (b). The spectra are taken at normal emission and a photon energy of 36 eV with p-polarized light. The most intense bands in the region of the adsorbate peaks are marked with arrows, and the ion state labels from the free, gas phase CO₂ molecule are used. In the previously reported spectra [6] the $4\sigma_g$ ion state has not been observed due to the small ionization cross section of this state at He I excitation [11].

The electron binding energies in table 1 are given with respect to the Fermi energy. In order to compare the values in table 1 with those reported in ref. [6] about 700 meV on the average have to be subtracted off the latter values due to the procedure to determine the Fermi energy in spectra taken at lower resolution. The relative binding energies, as well as the shape of the spectrum of adsorbed CO₂ is fully compatible with condensed CO₂ [12]. Table 1 also gives the electron binding energies of CO₂ adsorbed on Ni(110) [7] at 80 K for comparison. The obvious similarities confirm the assignment of the bands at 7.3, 11.2, and 12.8 eV to molecular CO₂ as given in fig. 1.

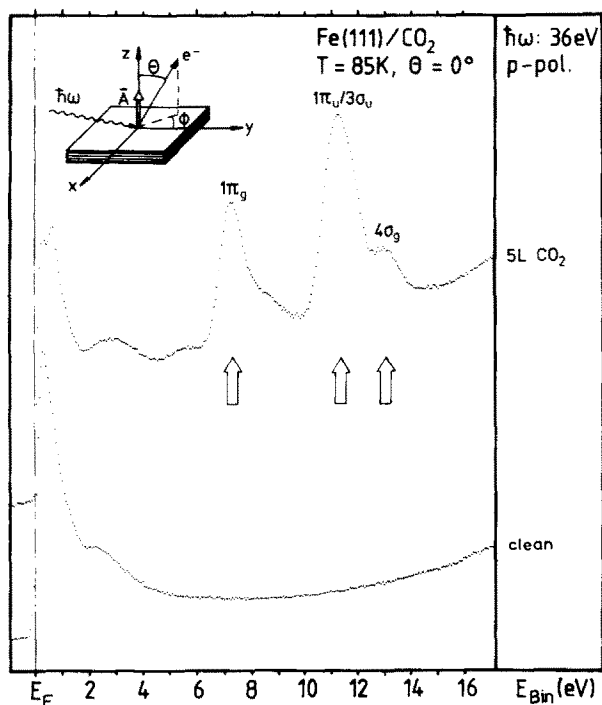


Fig. 1. Photoelectron spectra in normal emission of a clean and CO₂ (5 L) covered Fe(111) surface at 85 K; p-polarized photons with an energy $\hbar\omega$: 36 eV have been used.

Table 1
Ion state energies

Species	Orbital	CO ₂ 5L; <i>T</i> = 85 K	CO ₂ 5L; <i>T</i> = 140 K	CO ₂ 5L; <i>T</i> = 293 K	Ni(110)/CO ₂ 2L; <i>T</i> = 80 K
CO ₂	1π _g	7.3			6.98
	1π _u	11.2			10.89
	3σ _u				11.40
	4σ _g	12.8			12.81
CO	5σ/1π			8.3	
	4σ			11.0	
O	2p	5.5		5.6	
CO ₂ ⁻	6a ₁	3.0	3.2		3.46 ^{b)}
	1a ₂ , 4b ₂		5.6 ^{a)}		5.49 ^{a,b)}
	5a ₁ , 1b ₁	8.7	8.7		8.74
	3b ₂				
	4a ₁		11.0		10.81 ^{b)}

^{a)} Off normal.

^{b)} Values taken at 140 K.

In addition to the bands caused by molecular, undistorted CO_2 there are some extra adsorbate induced features visible in the spectrum, namely at 3.0, 5.5, and 8.7 eV. The set of angle resolved spectra shown in fig. 2 (only adsorbate induced features are presented) reveal the presence of the above mentioned features in a more obvious fashion. Fig. 2a shows angle resolved spectra excited with p-polarized light taken as a function of the polar angle θ , and along two perpendicular azimuthal angles ϕ , i.e. within the incidence plane, and perpendicular to it. The incidence plane is defined by the surface normal and the light propagation direction. The spectra in fig. 2b have been taken under the same conditions, except that s-polarized light has been used. All peaks vary in relative intensities, and via this variation the three peaks at

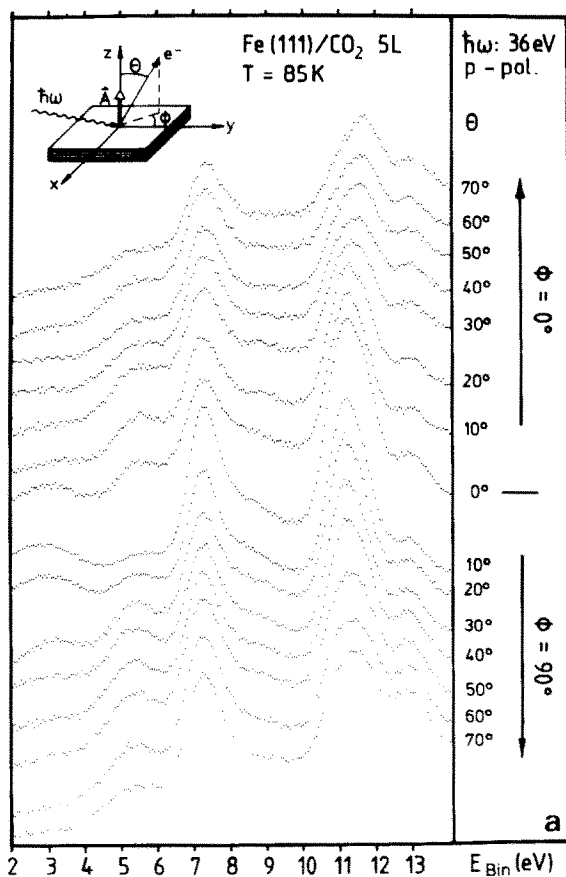


Fig. 2a. Photoelectron spectra of an $\text{Fe}(111)/\text{CO}_2$ adsorbate at 85 K within the range of CO_2 induced peaks as a function of polar angle θ as defined in the insert (upper left side). p-polarized light is used, and the electron current is collected within two azimuths ϕ .

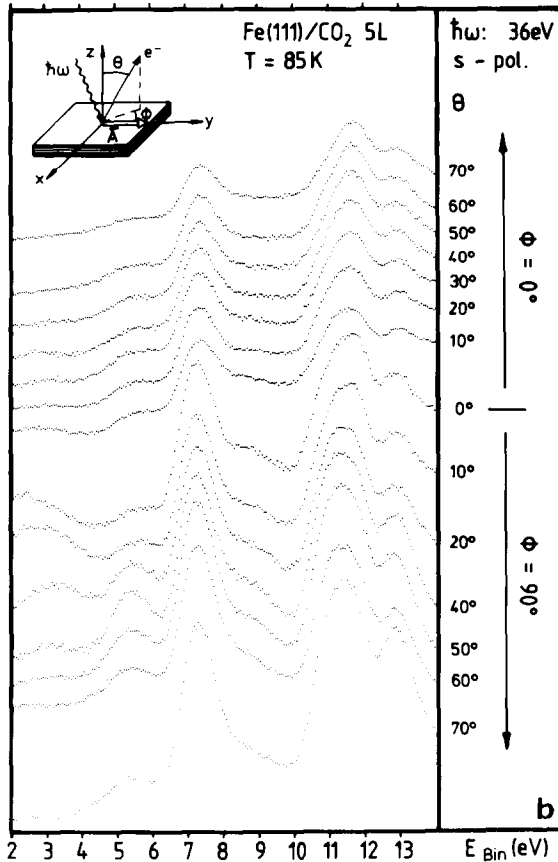


Fig. 2b. Photoelectron spectra of an Fe(111)/CO₂ adsorbate at 85 K within the range of CO₂ induced peaks as a function of polar angle θ as defined in the insert (upper left side). s-polarized (within the incidence plane) light is used, and the electron current is collected within two azimuths ϕ .

3.0, 5.5, and 8.7 eV are clearly visible. We shall come back to a detailed assignment of the features later.

At this point we concentrate on the angular dependence of the CO₂ induced peaks at 12.8, 11.2, and 7.3 eV, and compare it with a similar data set recently published for the system Ni(110)/CO₂ [7]. In contrast to the Ni data [7], the Fe data reveal no dispersion (E versus $k_{||}$) for the CO₂ induced features, probably due to insufficient order in the CO₂ layer. The shift of the peak maximum at 11.2 eV (normal emission) is probably not due to dispersion but rather to the change in relative intensities of the $3\sigma_g$ and $1\pi_u$ ion states as a function of angle. Two ion states contribute to the intensity of this peak. Their

separation in free CO₂ is 0.5 and 0.9 eV in the thick solid film. As far as the change in relative intensities for the CO₂ induced peaks in Fe(111)/CO₂ as a function of polar angle is concerned the situation is less pronounced as in Ni(110)/CO₂. In particular the strong increase of the relative intensity of the 4σ_g ion state for s-polarized light for Fe(111)/CO₂ at grazing incidence is not as strong as in Ni(110)/CO₂. In addition, it appears, that the difference in angular intensity variations between s-polarized and p-polarized excitation is less pronounced for the CO₂ induced levels. However, upon excitation with p-polarized light the ion states with π symmetry dominate over the ion states with σ symmetry in normal emission, which is not consistent with CO₂ oriented mainly perpendicular to the surface. Considering all possibilities (i.e. light polarization, finite angular acceptance of the analyzer, and ordering within the adsorbate [7]) and comparison with Ni(110)/CO₂ [7] we conclude, that the CO₂ molecules are not oriented perpendicular to the surface, but the inclination angle of the CO₂ molecular axis is likely to be larger than ±20° with respect to the surface plane, a value which was deduced for the Ni(110)/CO₂ system [7]. Considering the open structure of the Fe(111) surface with threefold symmetry this appears to be quite reasonable. More definitive conclusions about the relative orientation of CO₂ molecules cannot be drawn at present.

We now return to the assignment of the additional peaks at 3.0, 5.5, and 8.7 eV in figs. 1 and 2. Fig. 3 shows a set of spectra in normal emission with p-polarized excitation ($\hbar\omega = 32$ eV) taken at different surface temperatures. Only the adsorbate induced features are shown. Clearly, upon raising the temperature to 100 K the CO₂ induced peaks (discussed above) at 12.8, 11.2, and 7.3 eV loose intensity, while those at 3 and 8.7 eV show an intensity increase. The peak at 5.5 eV remains weak in normal emission. At 140 K the CO₂ induced peaks have disappeared, and we find a spectrum with bands at 11.0, 8.7, and 3.2 eV in normal emission (see table 1).

Work function measurements by Behner et al. [6] at this temperature revealed an increase by 1.3 eV with respect to the clean surface, a value in excellent agreement with the value found in the present study via the shift of the secondary electron cut off. For CO₂/Ni(110) Bartos et al. [7] observed a somewhat smaller work function increase (1.0 eV), and the maximum value occurred at about 200 K. This difference is probably caused by varying stabilities, expected for the two systems, i.e. Ni(110)/CO₂ and Fe(111)/CO₂.

It appears that the Fe system is more reactive than the Ni system. However, the involved species seem to be basically of the same chemical nature. Even though in the present case high resolution electron energy loss spectra have not yet been taken, the angle dependent photoelectron spectra strongly support the idea of similar species on both the Ni and the Fe surfaces. We shall show in the following that spectrum (d) in fig. 3 (140 K) exhibits the same angular behaviour as the corresponding spectrum at 200 K for the system

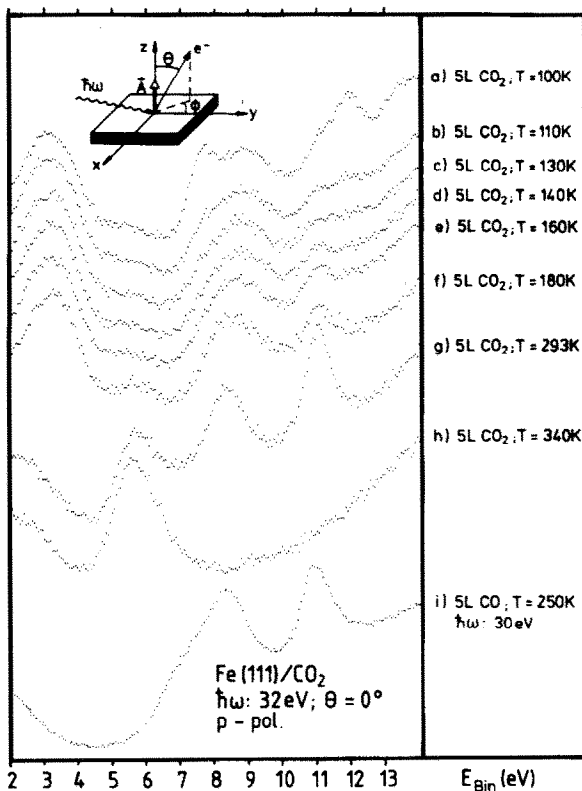


Fig. 3. Photoelectron spectra of an Fe(111)/CO₂ adsorbate at various temperatures (a)–(h) in comparison with a CO covered surface (i). The measurement parameters are listed in the figure.

Ni(110)/CO₂ [7] thus pointing towards the same chemical nature of the adsorbed species on Fe(111).

Fig. 4 shows angle resolved spectra ($\hbar\omega$: 36 eV) at normal and off normal emission angles for p-polarized excitation. The spectrum at $\theta = 0^\circ$ is equivalent to spectrum d in fig. 3. The most obvious result from fig. 4 is the decrease of the peak intensity at 3.0 eV, and the simultaneous increase of the peak intensity at 5.6 eV. The bands centered at 11.0 and 8.7 eV do not exhibit as dramatic an effect.

An interpretation of these findings is given in fig. 5. At the bottom a normal emission spectrum at 85 K is shown. The peaks are assigned on the basis of one-electron orbital energies for gas phase CO₂ calculated in ref. [4]. The energy of the $4\sigma_g$ orbital has been shifted so as to align with the peak at 12.8 eV. Knowing that the peak at 11.2 eV consists of two components there is a one-to-one correspondence between calculation and experiment which allows

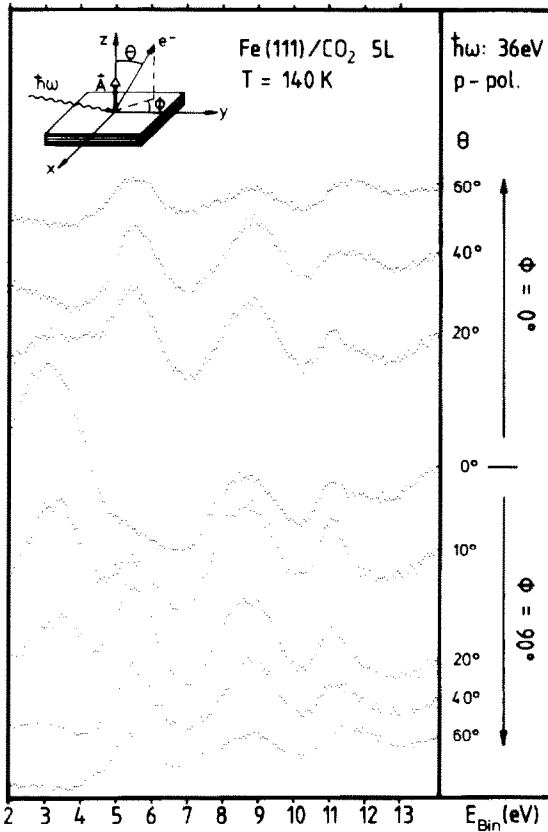


Fig. 4. Photoelectron spectra (p-polarized) of the Fe(111)/ CO_2 adsorbate at 140 K as a function of polar angle θ for two azimuths ϕ .

an unambiguous assignment. At the top of fig. 5 a normal emission spectrum of the adsorbate at 140 K, together with a trace of a 20° off normal spectrum at the same temperature are shown. Previously, we have proposed [4,6,7] a bent anionic CO_2^- species to be adsorbed on the surface. As was done in the case of Ni(110)/ CO_2 we qualitatively compare calculated one-electron orbital energies for CO_2^- with experiment. The energy scale for the anion has been shifted so as to align the orbitals of CO_2 and CO_2^- at highest binding energies ($4a_1$, $4\sigma_g$). The shift necessary to achieve this is approximately equal to a Coulomb stabilization resulting from a positive charge situated about 0.21 nm opposite the center of gravity of the negative charge on CO_2^- . Clearly, the first observation is the wider spread of the CO_2^- orbitals as compared to CO_2 . This can be rationalized in a straight forward manner on the basis of Walsh rules [14]: The closed shell CO_2 molecules can only accommodate an extra electron

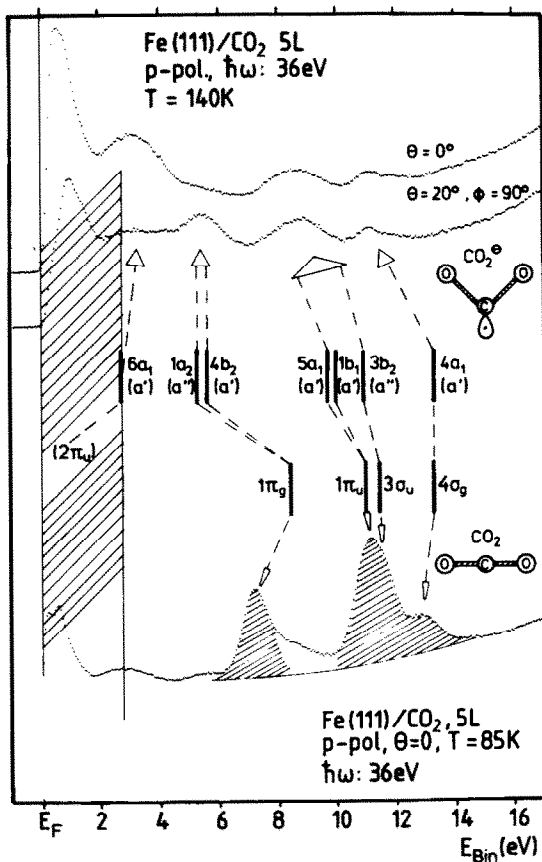


Fig. 5. Assignment of the photoelectron spectra at 85 K (lower curve) and 140 K (normal emission $\theta = 0^\circ$, and off normal emission $\theta = 20^\circ$, $\phi = 90^\circ$) to undisturbed molecular CO₂ and adsorbed CO₂⁻ on the basis of ab initio calculations.

by putting it into a rather high lying unoccupied orbital. This situation is energetically unfavourable as long as the molecule is linear. However, as was shown by Walsh the system gains energy by bending the molecule. This bending leads to breaking of one of the two double bonds and formation of an additional oxygen lone pair. As a consequence, the one-electron orbitals of CO₂⁻ change in a characteristic fashion as compared to linear CO₂. Due to the reduced symmetry of the bent molecule (C_{2v}) the orbitals that are degenerate in CO₂ (D_{∞h}) split and are shifted. For example, the 4b₂ and 1a₂ orbitals of CO₂⁻ originate from the 1π_g level of CO₂, and the energy separation from the 4a₁ (4σ_g in CO₂) increases by a considerable amount. In addition, the extra electron occupies the 6a₁ orbital of CO₂ which originates from the 2π_u orbital

of CO₂ ($D_{\infty h}$) and is stabilized by bending the molecule. The energy difference between $6a_1$ and $4a_1$ orbital of CO₂⁻ is now more than 10 eV as compared to ~ 5 eV in linear CO₂ between $1\pi_g$ and $4\sigma_g$. The experimental spectrum reflects this to a large extent. The spectrum is very similar to the one of Ni(110)/CO₂ at 200 K. Even the angular dependence of the peaks at 3.0 and 5.5 eV for Fe(111)/CO₂ is comparable with Ni(110)/CO₂ and reflects the symmetry of the corresponding ion states [7].

If we now compare the spectra at 85 and 140 K we can directly identify the weak extra features at 8.7, 5.5, and 3.0 eV in the 85 K spectrum as being due to CO₂⁻ which is obviously coadsorbed with linear CO₂ at this temperature. At this point we do not know whether the coadsorbed different CO₂ and CO₂⁻ species interact on the surface, i.e. by solvation of the CO₂⁻ anions with neutral CO₂ [4]. However, the experimental result by Behner et al. [6] that CO₂ does not stick to a flat Fe(110) surface where the formation of CO₂⁻ may be partly inhibited by the larger work function as compared to Fe(111) possibly points towards CO₂/CO₂⁻ interactions. CO₂ adsorption could be dependent on the presence of CO₂⁻, whereas this seems not to be the case for CO₂ condensation.

3.2. CO₂ reaction

We now return to the discussion of fig. 3. As we stated above, upon heating to 140 K the peaks caused by linear, molecular CO₂ disappear, and the CO₂⁻ species dominates the spectrum. Further heating of the substrate leads at room temperature to spectrum g. The spectrum is characterized by three dominant peaks at 5.6, 8.3, and 11.0 eV (table 1) in normal emission. By comparison of spectrum g with spectrum h which is identical to a pure Fe(111)/O spectrum [6] and Fe(111)/CO (spectrum i) we can unambiguously assign the peaks to be due to coadsorbed CO and O.

Figs. 6a and 6b compare the intensity variations as a function of polar angle (p-polarization, $\hbar\omega$: 36 eV) in two perpendicular azimuths for the Fe(111)/CO,O coadsorbate and the pure Fe(111)/CO adsorbate. The intensity variation in the CO 4σ ion state at 11.0 eV is most characteristic. It is most intense in normal emission and drops towards grazing incidence. Both, figs. 6a and 6b, show comparable behaviour, supporting the above assignment [13].

The comparison of the double peak structure in the coadsorbate (CO $5\sigma/1\pi + O2p$) with the resolved $5\sigma/1\pi$ peaks in the pure adsorbate is more difficult. This is due to the fact that one has to take into account, that under the conditions used to prepare the Fe(111)/CO system the CO molecules are in three different binding states [15]. A preliminary study of the shape resonances of the CO σ -states has revealed a rather complex behaviour which may be

connected to the existence of different states on the surface. A more comprehensive account of these effects will be published separately [16].

Upon raising the temperature further to 340 K the molecularly adsorbed CO dissociates, leading to an increase of the O 2p signal around 6 eV (spectrum h, fig. 3). The characteristic molecular CO peaks disappear. The increase of the O 2p signal is self-explanatory. However, one expects at the same time the appearance of a carbon signal. The cross section of the carbon ion states is small and energetically situated close to the d-band [17] and thus not visible. It may be buried under the shoulder at 2.5 eV in fig. 3 (spectrum h).

Thus our conclusion from fig. 3 can be summarized as follows: At low temperature (85 K) CO₂ adsorbs molecularly on Fe(111). Two different CO₂ species are present on the surface. One is a linear, undistorted CO₂ molecule, the second one is a bent, anionic CO₂⁻ species. Upon heating the surface the

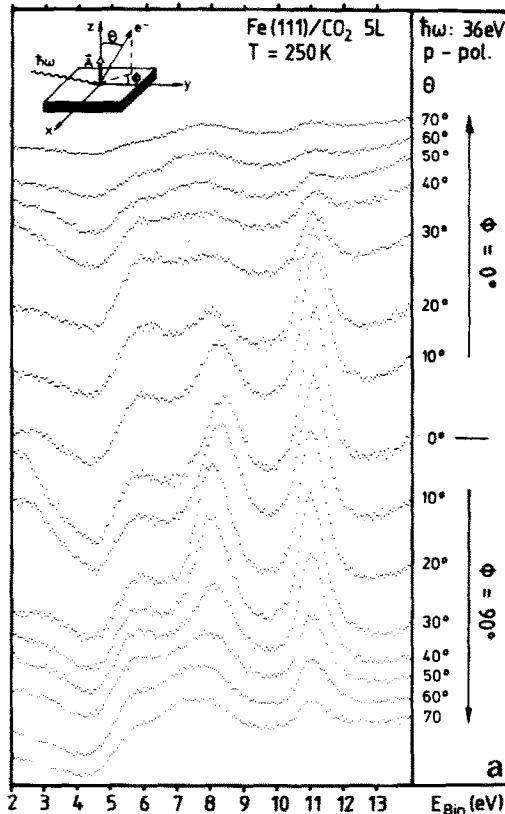


Fig. 6a. Photoelectron spectra of an Fe(111)/CO₂ adsorbate at 250 K within the range of CO₂ induced peaks as a function of polar angle θ and within two azimuths ϕ (p-polarized light).

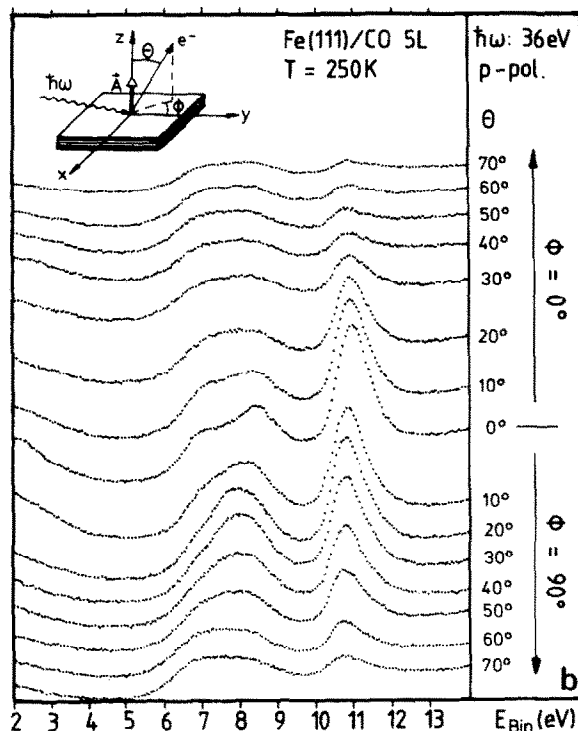


Fig. 6b. Photoelectron spectra of an Fe(111)/CO adsorbate at 250 K within the range of CO induced peaks as a function of polar angle θ and within two azimuths ϕ (p-polarized light).

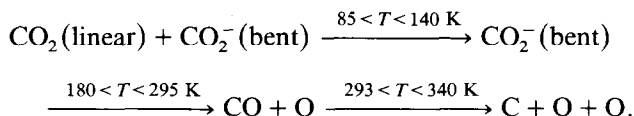
linear species desorbs, while the bent CO_2^- species stays on the surface. At 140 K the latter species is the only one present on the surface. The bent CO_2^- species appears to be a precursor for dissociation of CO_2 into adsorbed CO and oxygen because raising the temperature up to 180 K leads to a decrease of the CO_2^- signal, and the typical carbon monoxide and atomic oxygen bands are observed. At room temperature only CO and oxygen are observed on the surface. Above room temperature the molecular CO signals disappear, consistent with the well-known fact that CO dissociates on Fe(111) under these conditions.

4. Synopsis

In the present work we have studied the adsorption and reaction of CO_2 on an Fe(111) surface by means of angle resolved photoelectron spectroscopy.

At 85 K the admitted CO_2 adsorbs molecularly on a clean Fe(111) surface.

The electronic structure of the main fraction of molecules is not distorted in comparison with the gas phase and a thick solid film. The spectra, however, indicate that part of the adsorbed molecules are already at 85 K in a state that can be identified as a precursor to dissociative adsorption. While for the undistorted CO₂ molecules the spectra exclude a vertical CO₂ adsorption geometry (about $\pm 80^\circ$ with respect to the surface normal), the precursor to dissociation is suggested to be a bent "anionic" CO₂⁻ species according to:



We reach this conclusion by comparison with a similar study for Ni(110)/CO₂ where we find almost identical situations as far as the spectroscopy is concerned [7]. Of course, the Fe(111) and Ni(110) adsorbates differ in the stability of the adsorbed species. It appears, that the Fe(111) surface is considerably more reactive as compared to the Ni(110) surface. In addition the dissociation of CO into carbon and oxygen above room temperature does not occur within the investigated temperature range on Ni(110). The present study corroborates a previous study of Wedler and coworkers [6], who basically were led to the same conclusions.

Acknowledgements

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References

- [1] G. Ertl, Ber. Bunsenges. Phys. Chem. 86 (1982) 425; 90 (1986) 284.
- [2] D.W. Goodman, D.E. Peebles and J.M. White, Surface Sci. 140 (1984) L239.
- [3] F. Solymosi and J. Kiss, Surface Sci. 149 (1985) 17.
- [4] H.-J. Freund and R.P. Messmer, Surface Sci. 172 (1986) 1.
- [5] M.P. D'Evelyn, A.V. Hamza, G.E. Gidowski and R.-J. Madix, Surface Sci. 167 (1986) 451.
- [6] H. Behner, W. Spiess, D. Borgmann and G. Wedler, Surface Sci. 175 (1986) 276.
- [7] B. Bartos, H.-J. Freund, H. Kuhlbeck, M. Neumann, H. Lindner and K. Müller, Surface Sci. 179 (1987) 59.
- [8] H. Kölbl, F. Engelhardt, H. Hammer and J. Gaube: Actes du Deuxième Congrès International de Catalyse, Paris 1960, (Technip, Paris, 1961) p. 953;
H. Kölbl and H. Hammer, Brennstoff-Chemie 7 (1964) 212.
- [9] H. Körner, H. Landes, G. Wedler and H.J. Kreuzer, Appl. Surface Sci. 18 (1984) 361.

- [10] H. Behner, Dissertation, University of Erlangen-Nürnberg, FRG (1986).
- [11] D.W. Turner, A.D. Baker, C. Baker and C.R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, New York, 1970).
- [12] J.-H. Fock, H.-J. Lau and E.E. Koch, *Chem. Phys.* 83 (1984) 377;
J.-H. Fock, Dissertation, University of Hamburg, FRG (1983).
- [13] For a general discussion of angular dependences for adsorbed molecules see:
E.W. Plummer and W. Eberhardt, *Advan. Chem. Phys.* 49 (1982) 533.
- [14] A.D. Walsh, *J. Chem. Soc.* 2266 (1982) 533.
- [15] U. Seip, M.-C. Tsai, K. Christmann, J. Küppers and G. Ertl, *Surface Sci.* 139 (1984) 29.
- [16] H.-J. Freund, B. Bartos, H. Behner, G. Wedler, M. Neumann and H. Kühlenbeck, unpublished.
- [17] K.C. Prince, M. Surmann, Th. Lindner and A.M. Bradshaw, *Solid State Commun.* 59 (1986) 71;
G. Paolucci, R. Rosei, K.C. Prince and A.M. Bradshaw, *Appl. Surface Sci.* 22/23 (1983) 582.