

## INFLUENCE OF ALKALI CO-ADSORPTION ON THE ADSORPTION AND REACTION OF CO<sub>2</sub> ON Pd(111)

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The Pd(111) surface has been extensively used as a model substrate to study CO oxidation. The reverse reaction, CO<sub>2</sub> dissociation, however, has not been investigated to a comparable extent on this surface. We report angle-resolved photoemission studies on the system CO<sub>2</sub> (+ Na)/Pd(111). On a clean Pd(111) surface at 85 K no CO<sub>2</sub> adsorption takes place. Upon small precoverages of Na, adsorption of CO<sub>2</sub> occurs at  $T=85$  K. Via an analysis of the angular dependence of the photoelectron spectra we obtain information about the orientation of the adsorbed molecules. Upon annealing the surface to 125 K, CO<sub>2</sub> reacts to form co-adsorbed CO and O. For a thick Na film on Pd(111) we also find CO<sub>2</sub> adsorption but the reaction of the adsorbed species occurs along different reaction channels, ending at adsorbed carbonate species.

### 1. Introduction

Recently, CO<sub>2</sub> adsorption and reaction has been studied by several groups on various single crystal substrates, such as Rh(111) [1], Pd(100) [2], Pd(111) [3], Ni(110) [4–6], Ni(100) [7], Fe(110) [8], and Fe(111) [9]. For CO<sub>2</sub> adsorbates on clean Ni(110) and Fe(111), angle-resolved photoelectron spectroscopic (ARUPS) measurements [4,5,9], HREELS (high resolution electron energy loss spectroscopy) [4], NEXAFS [6] (near edge X-ray absorption fine structure), XPS [6] (high energy photoelectron spectroscopy), and DLEED [6] (diffuse low energy electron diffraction) have been applied to deduce electronic and geometric structure models of physisorbed linear CO<sub>2</sub>, and chemisorbed, bent CO<sub>2</sub><sup>-</sup>. The chemisorbed species turns out to represent an intrinsic precursor for CO<sub>2</sub> dissociation into CO and oxygen, which occurs

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between 140 K [9] and 200 K [4,5] depending on the surface. On clean Pd(100) [2] and Pd(111) [3] surfaces, however, CO<sub>2</sub> does not chemisorb, while it physisorbs at lower temperature.

Alkali co-adsorption, on the other hand, is known to promote adsorption and reaction in certain cases where adsorption is accompanied by electron transfer from the metal to the adsorbed species [10]. It is, therefore, near at hand to try to pre-dose the Pd surface with alkali before exposing it to CO<sub>2</sub>. Solymosi and coworkers [1,2] studied co-adsorption of K and CO<sub>2</sub> on Pd(100) and Rh(111) using TDS, ELS, and, recently, UPS/XPS [16] and concluded that after pre-exposure of potassium CO<sub>2</sub> chemisorbs on the Pd(100) and Rh(111) surfaces. They speculated that the species formed on the alkali-covered surface are anionic CO<sub>2</sub> species and surface carbonates. Matsushima [17] reports TDS for the system CO<sub>2</sub> + K/Pd(111). In the present study we report photoelectron spectroscopic results on the system CO<sub>2</sub> + Na/Pd(111) with varying Na precoverage using synchrotron radiation. We show that at a Na coverage where there are still Pd sites available on the Na precovered surface CO<sub>2</sub> adsorbs and dissociates above 130 K into adsorbed CO and oxygen. On a thick Na layer CO<sub>2</sub> adsorbs as well, but the reaction pattern is completely different: while CO<sub>2</sub> dissociation into adsorbed CO and oxygen cannot be observed we find a carbonate species as the main reaction product.

## 2. Experimental details

The experiments were performed in a magnetically shielded ultrahigh vacuum system (VG, ADES400) 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  $\pm 1.5^\circ$ . Excitation of photoelectrons was achieved by synchrotron radiation from the exit slit of a toroidal grating monochromator (TGM) attached to the storage ring BESSY in Berlin. The resolution was typically 100 meV. The base pressure in the system was below  $10^{-8}$  Pa.

The Pd(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 85 K. Heating was possible either by electron impact onto the reverse side of the crystal or by passing a current through the sample. 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. For work function measurements using the high energy cut-off of the photoemission spectrum the crystal was biased by  $-10$  V. Na was provided by a commercial SAES getter [11].

The LEED pattern of an adsorbate with  $\theta_{\text{Na}} = 0.4$  coverage (defined relative to the number of Pd surface atoms) shows a  $(\sqrt{7}/3 \times \sqrt{7}/3)\text{R}10.9^\circ$  structure. The Na getter was heated by always the same current. Assuming that the characteristic of the getter does not change with time, the coverage was determined by measuring the time for Na admission relative to the admission time to achieve a  $(\sqrt{7}/3 \times \sqrt{7}/3)\text{R}10.9^\circ$  structure. After CO<sub>2</sub> exposure no LEED pattern in addition to the substrate spots was observed. In order not to influence the adsorption behaviour all filaments in the UHV chamber were turned down or off upon admission of CO<sub>2</sub>.

### 3. Results and discussion

Fig. 1 shows the work function of the Pd(111) surface as a function of Na coverage. It exhibits the well known behaviour found for many other alkali transition-metal systems [10]: the work function decreases by about 3 eV from close to 6 eV to less than 3 eV where it reaches a minimum close to a coverage of  $\theta_{\text{Na}} = 0.4$ . Further increase of the Na coverage leads to an increase of the work function to a shallow maximum. A thick Na layer, finally, exhibits the work function of metallic Na with a value of approximately 2.5 eV. In the vicinity of the minimum the Na/Pd(111) system exhibits a  $(\sqrt{7}/3 \times \sqrt{7}/3)\text{R}10.9^\circ$  LEED pattern which is consistent with a coverage of  $\theta_{\text{Na}} = 0.4$ . No other LEED pattern has been observed under the conditions used in the present study. The adsorption studies reported in the following have been

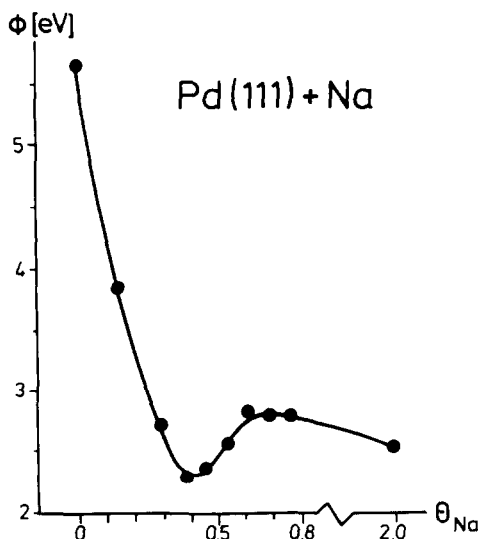


Fig. 1. Work function of the Pd(111) surface as a function of Na coverage  $\theta_{\text{Na}}$ .

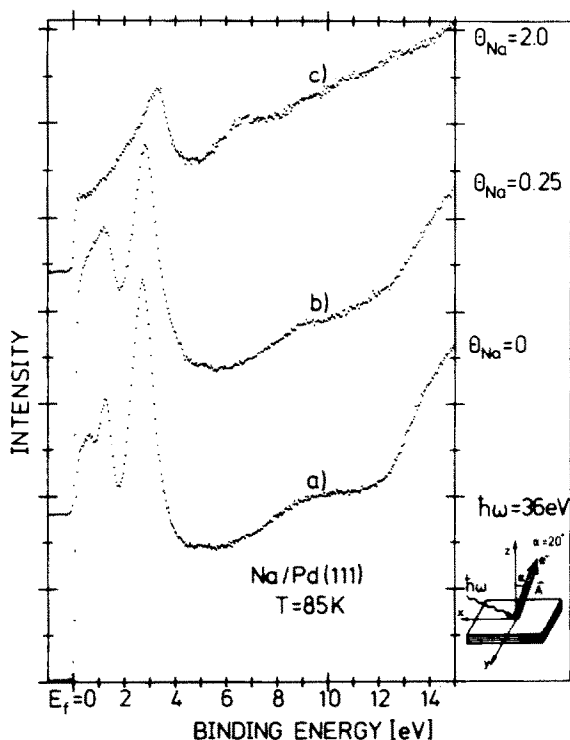


Fig. 2. Photoelectron spectra in normal emission and taken with  $z$ -polarized light of the clean Pd(111) surface (a) and the Na covered surface with  $\theta_{\text{Na}} = 0.25$  (b), and  $\theta_{\text{Na}} = 2.0$  (c).

undertaken at two characteristic Na coverages, namely at lower coverages ( $\theta_{\text{Na}} = 0.25$ ) than the one corresponding to the work function minimum leaving unoccupied Pd sites exposed to the gas phase (discussed in section 3.1), and at high Na coverages corresponding to a thick Na film ( $\theta_{\text{Na}} = 2.0$ ) with no transition metal surface sites exposed to the gas phase (section 3.2). Section 3.3 presents a comparative discussion of the adsorption and reaction behaviour in the two regimes and a consistent assignment of the spectral features.

Fig. 2 shows ARUP spectra of a clean Pd(111) surface in comparison with Na covered surfaces in normal emission and at a photon energy of 36 eV. The spectrum of the clean surface (spectrum a) is consistent with literature data, and its detailed interpretation and assignment is not important in the context of the present study. Upon adsorption of Na ( $\theta_{\text{Na}} = 0.25$ ) the spectrum of the system changes gradually. All Pd-based features are still clearly distinguishable. Indications for some changes between  $E_{\text{F}}$  and 1.5 eV binding energy are found. Upon adsorption of a thick Na layer ( $\theta_{\text{Na}} = 2.0$ ) the spectrum shows

further changes. The Pd induced features near  $E_F$  are attenuated, and the spectrum is dominated by a feature around 3.3 eV. This is still due to the strong Pd signal in this energy range, shifted by 0.45 eV. The emission signal of the Na layer covers the region down to 2.5 eV below  $E_F$  as known from the work of Plummer et al. [12]. There is a slight indication of adsorbed oxygen as documented by the weak feature at 6 eV binding energy. It was not possible under the chosen conditions to completely avoid oxygen contamination on the thick Na layer.

### 3.1. CO<sub>2</sub> adsorption and reaction at lower Na precoverage ( $\theta_{Na} = 0.25$ )

Fig. 3 shows a series of spectra where a Na precovered Pd(111) surface has been exposed to CO<sub>2</sub> at  $T = 85$  K. Upon exposing the Na precovered surface to 2 L of CO<sub>2</sub>, the CO<sub>2</sub> induced features known from previous CO<sub>2</sub> adsorption studies [1,4,5,8,9] are found (spectrum b). A comparison with spectra of adsorbed CO<sub>2</sub> [4,5,8,9] and condensed CO<sub>2</sub> [13] from the literature allows us

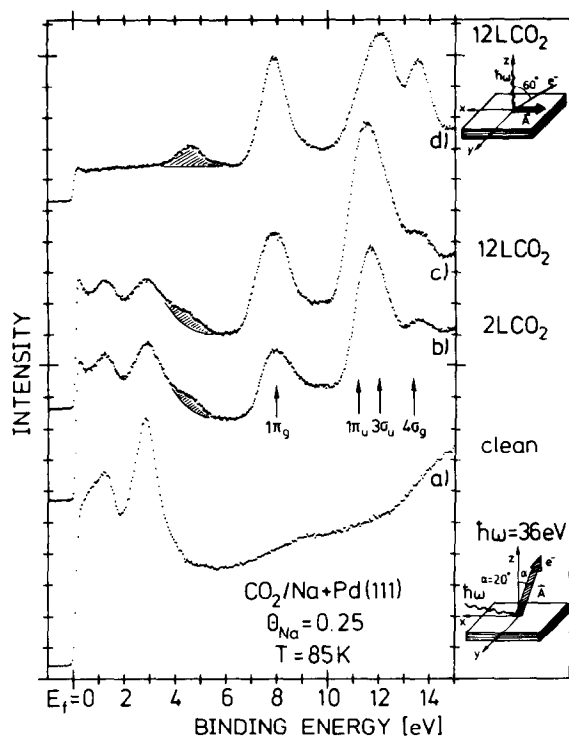


Fig. 3. Photoelectron spectra in normal emission and taken with z-polarized light of the Pd(111) surface with  $\theta_{Na} = 0.25$  (a), CO<sub>2</sub> exposure 2 L (b), and 12 L (c). In (d) is shown a spectrum after 12 L CO<sub>2</sub> exposure taken with s-polarization and off-normal ( $60^\circ$ ) electron emission.

to clearly identify the bands to be due to the four lowest energy ion states of electronically undistorted CO<sub>2</sub>. At the exposure of 12 L CO<sub>2</sub> the adsorbate layer appears to be saturated as judged by the intensities of the spectral features. We see an increase of only 30% in the CO<sub>2</sub> induced features at 12 L exposures (spectrum c). In addition to the observation of the adsorbate bands we find changes in the region of the metal states (shaded areas). If we consider the CO<sub>2</sub> molecules as electronically undistorted these intensities can be caused by scattering of the metal photoelectrons by the adsorbed molecules. Another possibility, however, is the existence of an additional species on the surface which is chemisorbed and causes the additional bands. The position of the additional peaks in the region of the metal states is clearly seen in the spectrum taken in off-normal emission (spectrum d). Spectrum d in fig. 3 shows an electron distribution curve within the plane of light incidence at 60° off-normal emission. The peak at 4.5 eV binding energy is rather pronounced. However, on the basis of the present data alone, a final assignment of these features to a definite chemical species cannot be carried out, and consequently, the first explanation can not be ruled out. Another interesting point can be made if we compare the relative intensities of the adsorbate induced features in normal and off-normal emission.

Clearly, the 4σ<sub>g</sub> ionization appears considerably more intense in the off-normal as compared to the normal emission spectra. This behaviour has been found before, i.e. in the case of adsorbates where CO<sub>2</sub> is physisorbed [4,5,9], and it is consistent with an orientation of the CO<sub>2</sub> molecular axis more or less parallel to the metal surface. For a detailed discussion of the intensity behaviour of the 4σ<sub>g</sub> state and its use for geometry determination we refer to ref. [4].

We now turn to the reaction behaviour of the CO<sub>2</sub> adsorbate at  $\theta_{\text{Na}} = 0.25$  which is displayed in fig. 4. The adsorbate has been prepared at  $T = 85$  K by exposing the Na precovered surface to 12 L CO<sub>2</sub>. After preparation the surface has been heated in steps of 5–10 K to room temperature. After increasing the temperature above 130 K the adsorbate spectrum did not change upon further temperature increase. Therefore in fig. 4 we only show the series up to this temperature. The identification of the species contributing to the spectra is straightforward: at 130 K the spectrum is typical for a CO adsorbate on Pd(111), i.e. the peaks at 8.6 eV and 11.2 eV are due to the combined 5σ/1π and the 4σ ionizations of CO bound to a transition metal surface [14,15], respectively. We have carried out reference measurements where CO has been adsorbed on a Na precovered surface [16], and we find basically the same results. Since we must conclude, and the following discussion shall verify this, that the adsorbed CO has been formed via dissociation of CO<sub>2</sub> we expect to find oxygen-induced features in the spectrum. However, it is well known [18], that especially on Pd(111) oxygen is very hard to detect in valence photoemission. Therefore, the absence of oxygen features has to be expected, and does

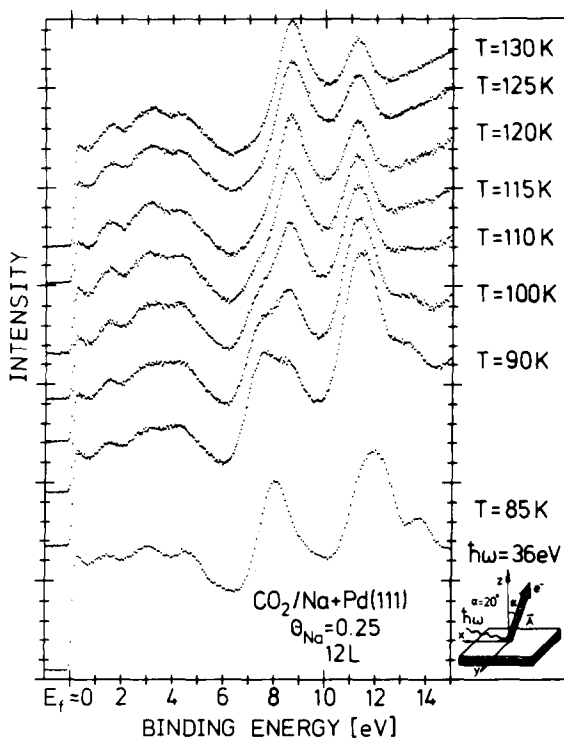


Fig. 4. Photoelectron spectra in normal emission and taken with z-polarization of a CO<sub>2</sub> exposed (12 L) Na ( $\theta_{\text{Na}} = 0.25$ )/Pd(111) surface at various temperatures after preparation at  $T = 85$  K.

not represent a contradiction. The series of spectra shown in fig. 4 can now be understood as a superposition of CO<sub>2</sub> and CO bands with varying amounts of the two species on the surface. At the lowest temperature there is exclusively CO<sub>2</sub> present on the surface. Upon increasing the temperature by 5 K we already find considerable amounts of CO. Parallel to the appearance of CO, the CO<sub>2</sub> features shift to lower binding energy. This is caused by the work function increase induced via CO chemisorption [16]. The ionization energies of physisorbed CO<sub>2</sub> are pinned to the vacuum level, and consequently shift to lower binding energies relative to  $E_F$  (see also section 3.3). Note that as soon as all CO<sub>2</sub> has disappeared from the surface, the structure in the region of the metal states has changed, i.e. the peak at 4.5 eV has disappeared. Interestingly, the conversion of adsorbed CO<sub>2</sub> to CO is almost complete at temperatures as low as  $T = 115$  K, which shows that the Na precovered Pd(111) surface ( $\theta_{\text{Na}} = 0.25$ ) is the most reactive single crystal system with respect to CO<sub>2</sub> dissociation studied so far. On the basis of the present photoelectron spectroscopic results alone it cannot be decided whether the conversion from CO<sub>2</sub> to

Table 1  
Binding energies in eV

		Pd(111) <sup>a)</sup>			CO <sub>2</sub> film	Li <sub>2</sub> CO <sub>3</sub>	Ni(110)	Fe(111)
		$\theta_{Na} = 0.03$	$\theta_{Na} = 0.25$	$\theta_{Na} = 2.0$				
CO <sub>2</sub>	1 $\pi_g$	7.0	7.8	10.1	13.0		6.98	7.3
	1 $\pi_u$ + 3 $\sigma_u$	11.2	11.6	14.1	16.7/17.6		10.89/11.4	11.2
	4 $\sigma_g$	12.3	13.5	15.8	18.8		12.81	12.8
CO <sub>3</sub>	1a <sub>2</sub> '			5.1		7.7 <sup>b)</sup>		
	1e'' + 4e'			6.4		9.3 <sup>b)</sup>		
	3e' + 1e <sub>2</sub> '			11.0		13.7 <sup>b)</sup>		
	4a <sub>1</sub> '			12.9		15.3 <sup>b)</sup>		
CO <sub>2</sub> <sup>-</sup>	6a <sub>1</sub>						3.5	3.2
	1a <sub>2</sub> /4b <sub>2</sub>						5.5	5.6
	5a <sub>1</sub> /1b <sub>1</sub> /						8.7	8.7
	3b <sub>2</sub>							
	4a <sub>1</sub>						10.8	11.0
$\Delta\phi$	+ Na	-0.5	-1.7	-3.2				
	+ CO <sub>2</sub>			+0.6		+0.5		
$\phi$		5.2	4.0	3.1		5.0		

<sup>a)</sup> Exposed to 12 L CO<sub>2</sub>.

<sup>b)</sup> Ref. [23].

CO and oxygen proceeds via a precursor, i.e. the bent CO<sub>2</sub><sup>-</sup> as was shown for other CO<sub>2</sub> adsorbate systems [4,6,9] (table 1). HREELS experiments are presently carried out to get further insight into the reaction mechanism on Pd(111) [19].

### 3.2. CO<sub>2</sub> adsorption and reaction at high Na coverage ( $\theta_{Na} = 2.0$ )

Fig. 5 shows a series of spectra recorded after exposing the Na preadsorbed Pd(111) surface ( $\theta_{Na} = 2.0$ ) to varying amounts of CO<sub>2</sub>. At 2 L CO<sub>2</sub> we find intense adsorbate-induced features between 5 and 18 eV binding energy relative to  $E_F$  (table 1). Upon increasing the CO<sub>2</sub> dose the peaks at 10.1, 14.1, and 15.8 eV (table 1) increase in intensity, until they saturate at an exposure of 12 L CO<sub>2</sub>.

These peaks can be identified to be due to electronically undistorted CO<sub>2</sub> as will be discussed in section 3.3 in comparison with the adsorbate with lower Na precoverage. One clue to this assignment is offered via the series of spectra taken as a function of temperature which is shown in fig. 6. The spectra taken at various temperatures can be simulated by superimposing the spectrum of electronically undistorted CO<sub>2</sub> with the spectrum of the surface at  $T = 130$  K taking the work function of the system into account to fix the position of the CO<sub>2</sub> levels. It appears therefore that as a function of temperature CO<sub>2</sub> desorbs



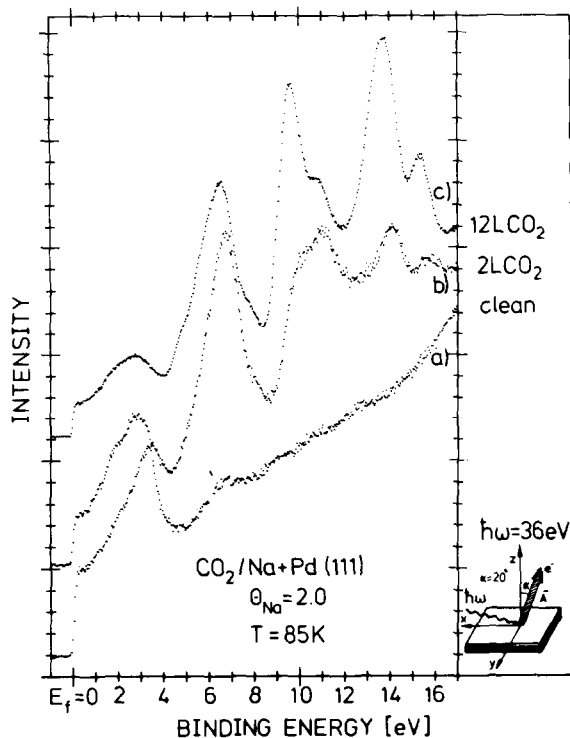


Fig. 5. Photoelectron spectra in normal emission and taken with  $z$ -polarized light of the Pd(111) surface with  $\theta_{\text{Na}} = 2.0$  (a), CO<sub>2</sub> exposure 2 L (b), and 12 L (c).

from the surface leaving a species on the surface that has already partly been formed at the lowest temperature. If we assume that the broad peak at  $E_{\text{B}} \approx 6$  eV is due to this species, an intensity analysis reveals that the amount of this species increases by 150% at elevated temperatures. This shows that probably CO<sub>2</sub> not only desorbs but also reacts. We have predicted earlier [20] that a possible reaction channel for adsorbed CO<sub>2</sub> is the disproportionation of two CO<sub>2</sub> molecules into CO<sub>3</sub> and CO. Reactions of CO<sub>2</sub> with alkali and alkali oxides have been extensively studied [21]. While the produced CO does not stick to the alkali surface [22] CO<sub>3</sub> remains on the surface bound to the alkali metal.

It is therefore possible that the species present on the surface is a carbonate species. A comparison of the adsorbate spectrum with a spectrum of Li<sub>2</sub>CO<sub>3</sub> [23] as shown in fig. 7 confirms this assumption and allows us to assign the spectral features as given in the figure. We have shifted the Li<sub>2</sub>CO<sub>3</sub> spectrum such as to align the sharp peak at 6 eV and the agreement is very satisfactory.

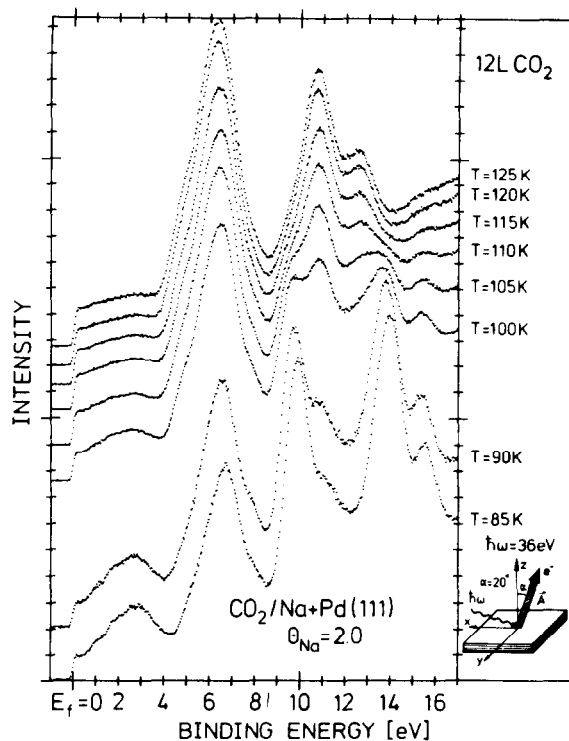


Fig. 6. Photoelectron spectra in normal emission and taken with z-polarization of a CO<sub>2</sub> exposed (12 L) Na ( $\theta_{\text{Na}} = 2.0$ )/Pd(111) surface at various temperatures after preparation at  $T = 85$  K.

It is therefore legitimate to conclude that a carbonate species is formed on the surface. Whether this carbonate is formed via disproportionation of CO<sub>2</sub> or, possibly via reaction of CO<sub>2</sub> with oxygen contamination [17] cannot be claimed with final safety yet, but the fact that more CO<sub>3</sub> forms upon increasing the temperature is an indication of a reaction. We have made an attempt to determine the geometry of adsorbed CO<sub>3</sub> via ARUPS but failed due to noncharacteristic intensity changes as a function of electron emission angle. The only effect that points towards a preferential orientation of part of the adsorbed molecules is the relative intensity increase of the CO<sub>3</sub>-1a<sub>2</sub>' orbital at off-normal emission angles in the forbidden geometry. Such a behaviour must be expected for flat lying CO<sub>3</sub> moieties.

### 3.3. Comparative assignment of CO<sub>2</sub> adsorbate spectra

In the last section we have left the question of the assignment of some of the adsorbate induced bands open. In particular, we realize by inspection of

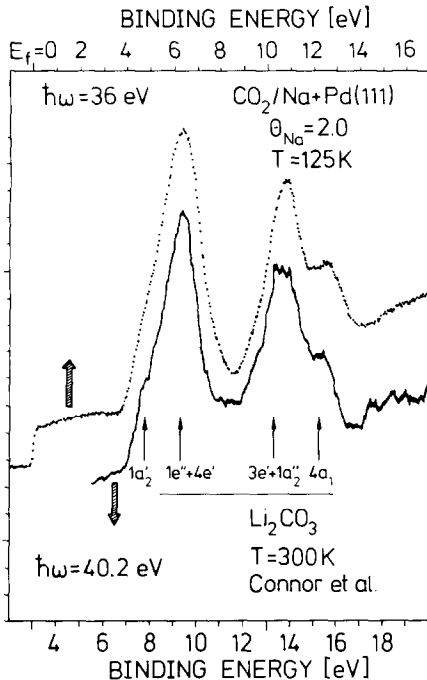


Fig. 7. Comparison of the photoelectron spectrum of the surface carbonate with the spectrum of Li<sub>2</sub>CO<sub>3</sub> [23].

fig. 8, where a series of spectra with varying Na coverages and constant CO<sub>2</sub> exposure at  $T = 85$  K is shown, that there is one common set of bands (marked with arrows) which has a similar appearance in all adsorbates. This set has been assigned to CO<sub>2</sub> induced bands in our above discussion. The remarkable observation in fig. 8 is the common shift of the CO<sub>2</sub> bands to higher binding energies with increasing Na coverage. Table 1 collects the binding energies relative to  $E_F$  for the adsorbates compared in fig. 8. In addition, the changes in work function are listed for comparison. The shift of the CO<sub>2</sub> peaks parallels the shift in work function which indicates that the proper reference level for this species is the vacuum level. For the thick Na layer this statement can be quantitatively verified: if we add the work function  $\phi = 3.1$  to the measured binding energies relative to  $E_F$  we find the binding energies relative to the vacuum level, and these are within 0.1 eV the same as those as for a condensed CO<sub>2</sub> film [16]. For the lower Na coverage the work function changes upon CO<sub>2</sub> admission have not been recorded, so that a quantitative correlation cannot be carried out. It is clear from the comparison

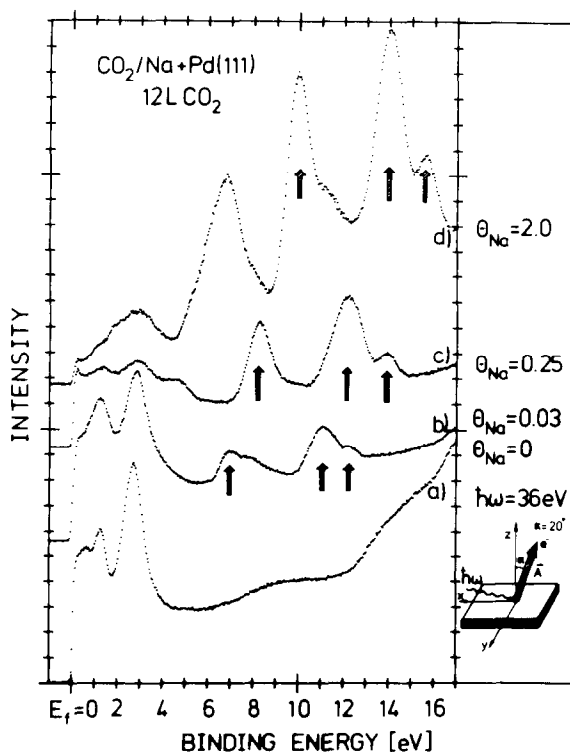


Fig. 8. Photoelectron spectra of a Pd(111) surface with varying Na coverages and constant CO<sub>2</sub> (12 L) exposure.

of the adsorbate spectra at low and high Na precoverage that the surface reactions must be very different for the two Na coverages.

#### 4. Conclusions

We have shown that while CO<sub>2</sub> does not chemisorb on clean Pd(111), adsorption and reaction can be promoted by the presence of alkali on the surface. This finding is in line with the results of Solymosi and coworkers for CO<sub>2</sub> adsorption on K/Pd(100) and K/Rh(111) [1]. At low Na precoverages we find that CO<sub>2</sub> adsorbs as linear, electronically little or undistorted molecules with the orientation of the molecular axis parallel to the surface plane. The CO<sub>2</sub> molecules in this layer dissociate by heating the surface from  $T = 85$  K to  $T = 120$  K into CO and oxygen. The CO molecules appear to be bound to the Pd surface. In contrast to Ni(110) [4–6] and Fe(111) [9] there is no

indication so far from ARUPS for an intrinsic dissociation precursor like CO<sub>2</sub><sup>-</sup> on Pd(111).

A completely different adsorption and reaction behaviour is found for high Na precoverage. Even at the lowest temperatures accessible, i.e.  $T = 85$  K, CO<sub>2</sub> reacts with the surface to form a species, which by comparison with Li<sub>2</sub>CO<sub>3</sub> spectra [23] can be identified as carbonate. Together with the carbonate, electronically undisturbed CO<sub>2</sub> physisorbs at low enough temperature. Upon heating the surface the amount of adsorbed carbonate increases and CO<sub>2</sub> desorbs. It is not clear how the CO<sub>2</sub> reacts to form carbonate. A possible reaction mechanism is the disproportionation of two CO<sub>2</sub> molecules to form carbonate and CO, which itself does not stick to the alkali layer and desorbs from the surface, or the reaction of CO<sub>2</sub> with adsorbed oxygen.

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