CO_2 Activation on Transition Metal Surfaces

J. Wambach[2] and H.-J. Freund[1]*

[1]DEPARTMENT OF PHYSICAL CHEMISTRY, RUHR UNIVERSITÄT BOCHUM, D-44780 BOCHUM, GERMANY

[2]LABORATORY OF APPLIED PHYSICS, THE TECHNICAL UNIVERSITY OF DENMAR DK-2800 LYNGBY, DENMARK

1. INTRODUCTION

The adsorption behavior of CO_2 on metal surfaces has been studied during the last decade in quite some detail[1-36] and Table 1 summarizes some of the systems that have been investigated.

Table 1 Systems studied in the literature

System	CO_2 physisorbed	CO_2 chemisorbed	reference
Ni(100)	yes	no	32
Ni(110)	yes	yes	1,2
Ni(111)	yes	no	33
Fe(110)	yes	no	6
Fe(100)	yes	yes	34
Fe(111)	yes	yes	5
Re(0001)	yes	yes	3,4
Rh(111)	yes	no	12
Pt(111)	yes	no	36
Pd(100)	yes	no	10
Pd(111)	yes	no	9
Cu(100)	yes	no	31
Cu(110)	yes	no	15
Ag(110)	yes	no	35

We have restricted this collection to those studies carried out on non modified single crystal surfaces. After the initial controversy whether CO_2 chemisorbs at all on clean metal surfaces[37-39], it has been realized that in some cases two states of molecular associative adsorption may be observed for CO_2 on the clean metal surfaces: a physisorbed linear CO_2 state and a bent chemisorbed CO_2^- state. The chemisorbed, partially negatively charged species turns out to be the precursor for CO_2 dissociation [1-2]. It is generally accepted now that electron transfer drives the formation of the chemisorbed bent species but it is not clear where this process happens at the surface. There are indications that low work function of the metal[40] in conjunction with appropriate surface sites, such as steps or atomic roughness[41] are important in this respect. However there are surfaces without high step density where CO_2 chemisorption takes place[1-5,34].

We shall review in this paper our view of CO_2 chemisorption on transition metals and then go on to study chemical reactivity of the chemisorbed CO_2 towards coadsorbed species.

We begin by considering some basic properties of gaseous CO_2.

2. BASIC PROPERTIES OF CO_2

Figure 1 shows a schematical potential energy diagram of CO_2 and CO_2^- where the energy in kcal/mol is plotted as a function of the C-O distance and the O-C-O bond angle[42,43].

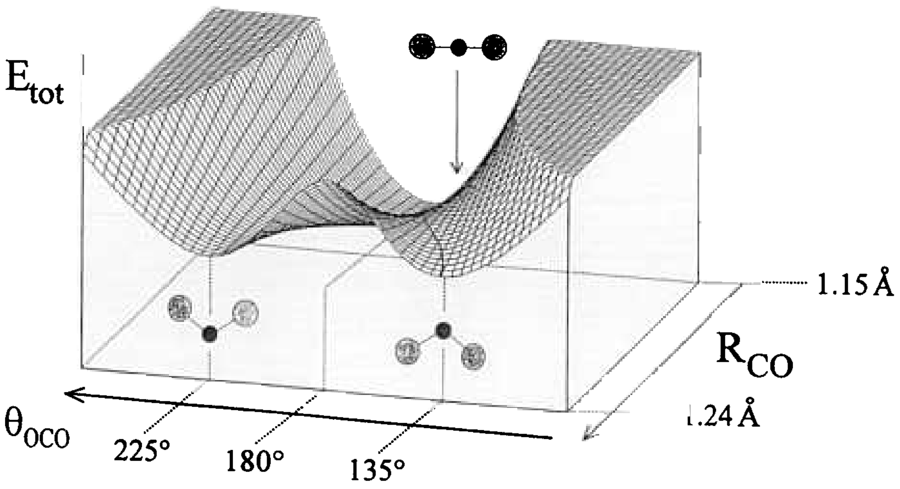


Figure 1 Schematic potential energy diagram of the system CO_2 and CO_2

The ground state of the CO_2 system is shown at the back representing the linear system with an enthalpy of formation of 393 kcal/mol[44]. The double-well ground state of the CO_2^- is shown in front representing a bent geometry with elongated C-O bonds and an enthalpy of formation of 382 kcal/mol[45], *i.e.* about 0.5 eV higher than for linear CO_2. This value corresponds to the adiabatic electron affinity of CO_2 in contrast of the vertical electron affinity which is considerably higher. The CO_2^- molecule in its equilibrium geometry is metastable with a life time of 60-90 msec[45,46] kinetically stabilized by a barrier of 10 kcal/mol (0.4 eV)[47]. CO_2^- can be experimentally observed in the gas phase after thermal decomposition of solid oxalates[48]. Therefore the vibrational spectrum is known[48] and can be used in comparison to linear CO_2 as a fingerprint to identify the CO_2^- species. Similarly, the photoelectron spectra of gaseous CO_2, which has been measured[49] in comparison with the calculated spectrum of CO_2^-[50] may be employed to identify the adsorbed species[50].

The CO_2^- moiety becomes unstable because the electron wants to autodetach[47]. If the electron density of the extra electron is kept high, e.g. through the presence of a metal surface, the linear geometry of the CO_2 molecule becomes unstable with respect to a bent geometry[50]. Qualitatively, the so called Walsh diagrams[51] or "17-electron-rules"[52] reveal this as has been discussed previously[50].

In addition, the stability of the CO_2^- may be considerably enlarged by forming $(CO_2)_2^-$ dimers. The anionic dimer is stabler by 0.9 eV[53] and its structure has been suggested via *ab initio* calculations as shown in Figure 2 [54]. The main point is that the dimer basically may be looked at as a CO_2^- "solvated" by a largely undisturbed neutral CO_2 molecule[50,54]. The structure of the dimer anion in relation of the structure of solid neutral CO_2 has been discussed in detail before[50] and will not be repeated. We only note that solvation of the anion may be important in stabilizing it on a metal surface[50] in particular at high CO_2 coverages.

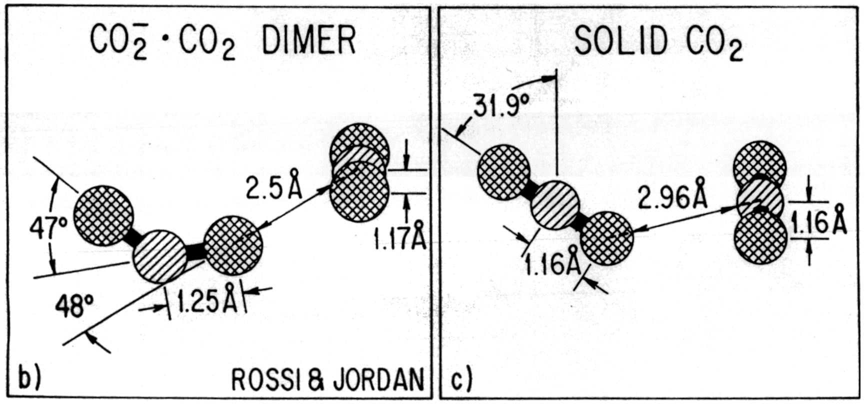


Figure 2 Schematic diagram of the intermolecular arrangement of the CO_2 moieties in the $(CO_2)_2^-$ dimer anion as compared with solid CO_2.

3. CHEMISORBED BENT CO_2^-

The signature of the chemisorbed CO_2^- species has been primarily its vibrational spectrum[48]. Table 2 collects the vibrational frequencies for some of those single crystal systems where the species has been clearly identified[1-4,9,34,55,56]. The absence of the asymmetric CO_2^- stretching frequency on Ni(110) has been taken as an indication that the molecular plane is oriented perpendicular to the surface and the symmetry of the species in C_{2v}. This was verified through NEXAFS and DLEED[2] measurements (see below). In all other cases studied so far the asymmetric vibration was identified and C_s symmetry has been assigned to the CO_2^- species.

Figure 3 shows a series of HEELS spectra as a function of temperature taken from the work of Bartos et al.[1]. The lowest trace represents the situation at T=140 K. The peaks are assigned to the two states of CO_2 and CO_2^- as indicated. The small peak at 1350 cm^{-1} will be discussed in detail below. The lowest frequency vibration can be assigned to the motion of the molecule with respect to the surface. In the case of Ni(110) this frequency is at 403 cm^{-1}. This has been used to argue that the CO_2^- in C_{2v} symmetry is bound as was proposed by cluster calculations through its oxygen atoms and not its carbon atom to the Ni(110) surface[50]. The clear proof for the oxygen coordination can be given through a comparison with formate bound to Ni(110)[56] where it is obvious that bonding is established via the oxygen atoms because the carbon carries a hydrogen atom. Table 2 contains the vibrational frequencies for $HCOO^-$/Ni(110) and it is clear that the value for the low frequency vibration is in close correspondence to the system CO_2^-/Ni(110).

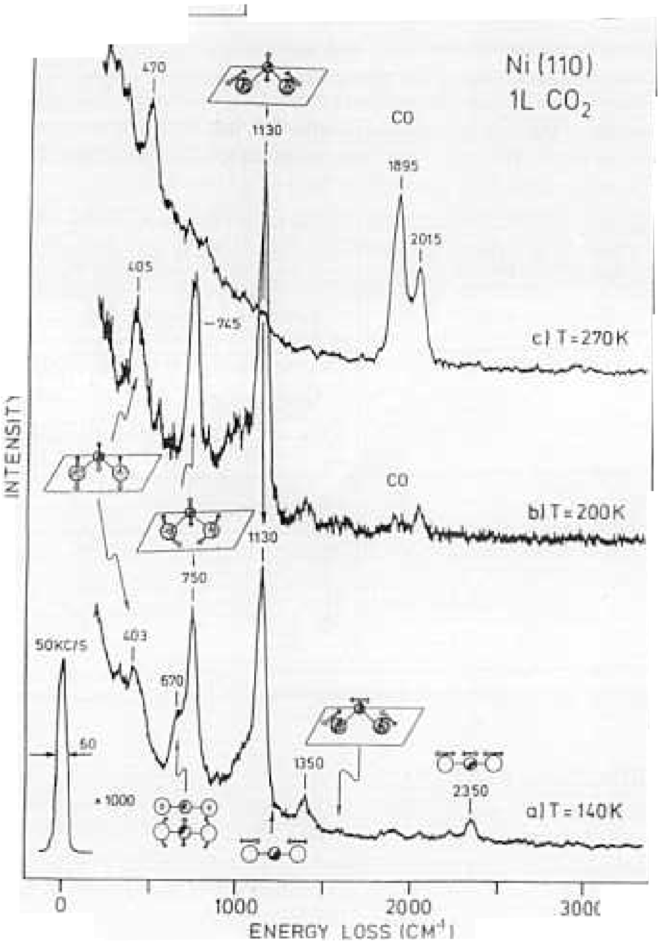


Figure 3 Electron energy loss spectra of CO_2 on Ni(110) as a function of temperature

Table 2 Vibrational frequencies of chemisorbed CO_2 in cm

System	ν_{M-mol}	δ_{bend}	ν_{sym}		ν_{C-H}	Reference
CO_2/Ni(110)	403	727	130			
CO_2/Re(0001)		650	1230	1625		3,4
CO_2/Fe(100)		1232	1634		34	
CO_2/Na/Pt(111)		820	1340	1600		55
CO_2/Na/Pd(111)	282	744	1210	1530	9	
$HCOO^-$/Ni(110)	403	727	1353		2904	56

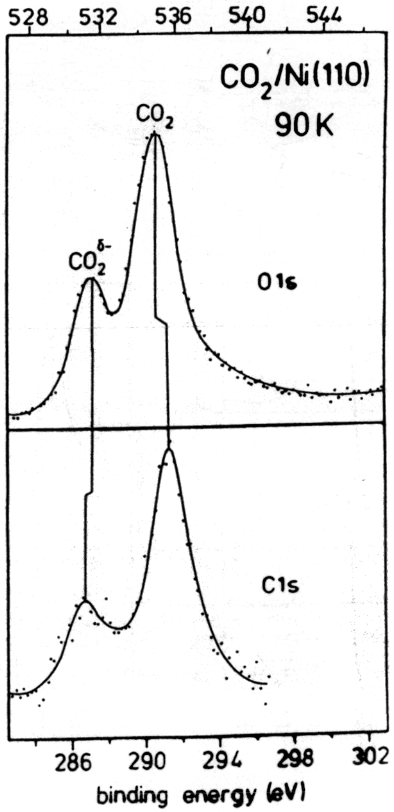
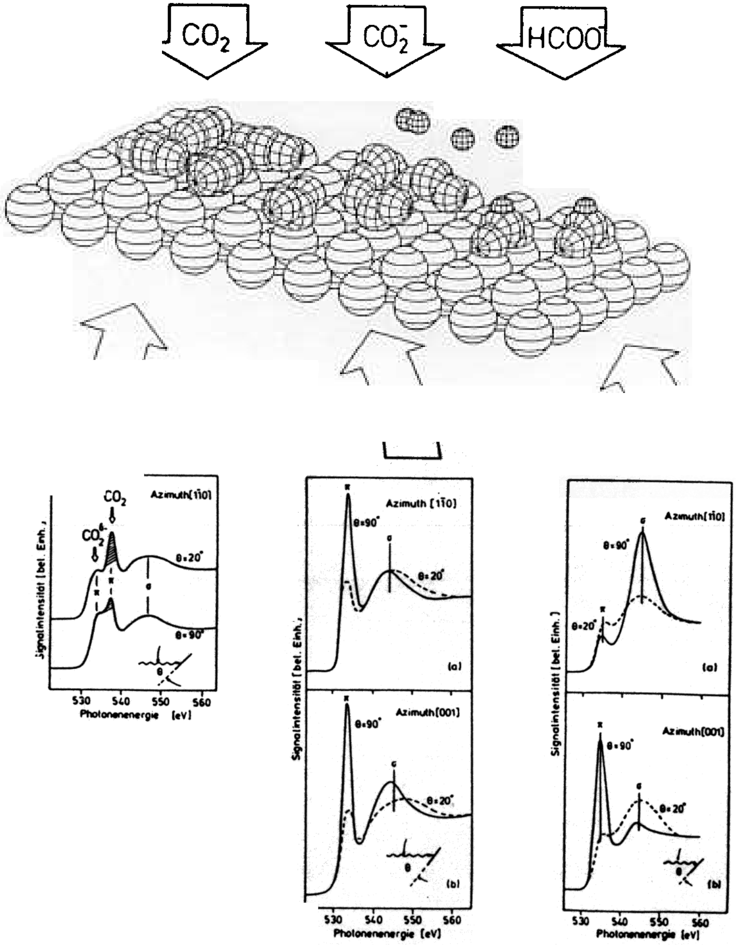


Figure 4 X-ray photoelectron spectra of CO_2 adsorbed on Ni(110) in the range of the C1s and O1s ionizations.

At T=200K the physisorbed CO_2 has disappeared and there are already small CO signals present on the surface. At T=270K CO_2^- has completely dissociated and only molecular CO can be found. Therefore CO_2^- may be regarded as the precursor for CO_2 dissociation on metal surfaces[40]. HREEL spectra do not always reflect the relative coverages of physisorbed CO_2 and chemisorbed CO_2^-. The coverages can be judged better via X-ray photoelectron spectra as shown in Figure 4 [2].

At T=90K the C1s and O1s features due to physisorbed CO_2 dominate the spectra. The CO_2^- features are shifted to lower binding energies as expected. A detailed evaluation of relative intensities can be used to prove that the stoichiometry of the anionic species indeed is C:O=1:2.



igure 5 Schematic reaction scheme for CO_2 on Ni(110): From physisorbed CO_2 on the left to chemisorbed CO_2^- in the middle to the reaction product $HCOO^-$ of the reaction between CO_2 and hydrogen on the right. At the bottom the corresponding NEXAFS spectra are shown. The light incidence is marked in the figure.

4. REACTIVITY OF CHEMISOBED CO_2

CO_2^- on Ni(110) is stable in a temperature range up to T=150K. The molecule represents a species with unsaturated valencies at the carbon atom. We may therefore envisage reactions of the CO_2^- molecule with other atomic or molecular species from the gas phase or within the adsorbate. A combination of two CO_2^- molecules is rather unlikely because the negative charge should lead to strong intermolecular coulombic repulsion (see however reference 14). Figure 5 schematically shows at the top the reaction of CO_2 with hydrogen on Ni(110) to form formate[57].

This scheme is not meant to indicate that CO_2^- reacts with hydrogen from the gas phase in the sense of a Eley-Rideal mechanism. In fact, we know that the reaction takes place via a Langmuir-Hinshelwood mechanism[57]. We have followed the reaction via HREELS and XPS as shown in Figure 6.

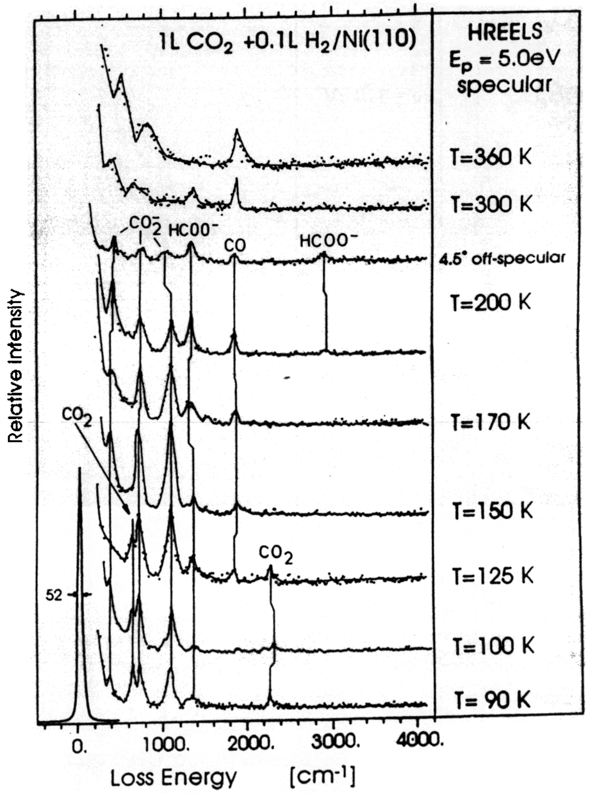


Figure 6 Electron energy loss spectra of a CO_2/H_2 co-adsorbate as a function of temperature. The assignment of the features is indicated by lines.

In Figure 6 we have plotted a series of HREEL spectra starting at T=90K. The surface has been exposed first to 1L CO_2 and subsequently to 0.1L H_2. The reverse exposure does not lead to reaction. At T=90K the spectrum is very similar to the spectrum at the bottom of Figure 3. If we increase the temperature the physisorbed CO_2 disappears and the CO_2^- bands increase. Note, that even at low temperature there is a small peak around 1350cm^{-1}. At T=200K, when CO_2^- on the clean surface has already dissociated, it is still on the surface in the presence of hydrogen. However, the peak at 1350cm^{-1} has increased in intensity. Also, at off specular scattering conditions a C-H vibration can be detected close to 2900cm^{-1}. A comparison with the vibrational frequencies given in Table 2 indicate that the new bands are due to adsorbed formate. It is mainly the symmetric stretching frequency that shifts by approximately 200cm^{-1}, while the asymmetric stretch and the bending mode as well as the molecule-surface vibration are basically at the same frequency as in the case of CO_2^-.

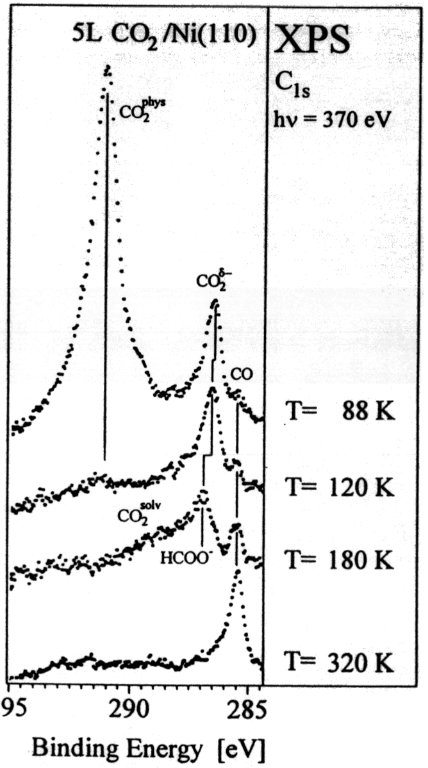


Figure 7 High resolution x-ray photoelectron spectra in the C1s regime of a CO_2/H_2 coadsorbate as a function of temperature[57].

There is, however, a considerable difference in the structure of the formate adsorbate as compared with the CO_2^- adsorbate: NEXAFS data at the oxygen edge, shown in Figure 5, reveal the sharp π-resonances and the broad σ-resonances of both the CO_2^- and $HCOO^-$ moieties[2,58]. While for the case of CO_2^- there is no dependence on the azimuthal direction of the incoming light with respect to the relative changes of intensities upon variation of the polar angle Θ, the $HCOO^-$ species does exhibit a pronounced azimuthal dependence. The observed behavior of the polar angle variations are on one hand in line with the orientation of the molecular plane perpendicular to the surface plane for both species, and on the other hand in line with a preferential azimuthal orientation along the (110) of the formate species as opposed to a random orientation of the CO_2^- species. It would be interesting to understand this difference, but sofar its origin is not yet clear. The formation of the formate species on the surface may also be followed by XPS measurements[57]. The spectra taken at high resolution are shown in Figure 7.

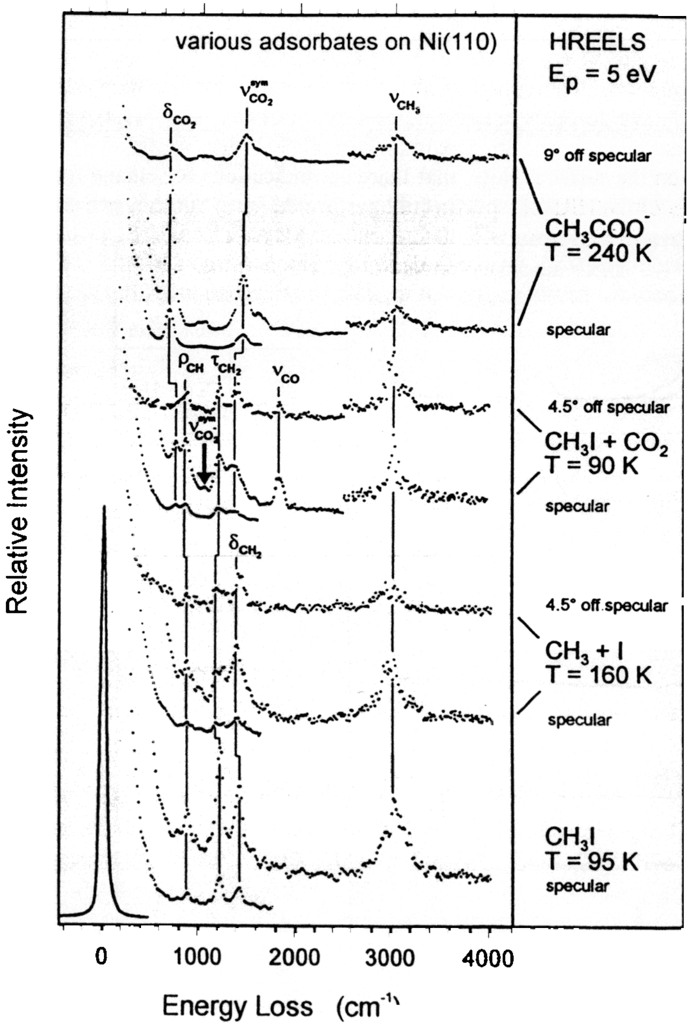


Figure 8 Electron energy loss spectra of various adsorbates on Ni(110)

At the top we find coadsorbed CO_2 and CO_2^- at low temperature. Then, upon temperature increase the physisorbed species desorbs, and there are already indications for the formation of CO. At around T=180K the changing chemical shift indicates the formation of formate which at higher temperature eventually dissociates and CO remains on the surface. It is thus quite obvious from a series of measurements with a variety of different methods that CO_2 reacts with hydrogen to form formate on the surface of a Ni single crystal.

Consequently, it is near at hand to try to react CO_2^- with other coadsorbed species[59]. A particular interesting reaction would be between CO_2^- and coadsorbed methyl groups to form acetate with a carbon-carbon bond. We have created these CH_3 species by dissociative adsorption of CH_3I according to the literature[60,61]. Figure 8 shows the HEELS spectrum of an exposure of 2L CH_3I on a Ni(110) surface at T=95K[59]. The assignments of the bands is given via comparison with literature data[60]. When the adsorbate is heated, CH_3I dissociates, and adsorbed I atoms and methyl groups are formed (see Figure 8) as indicated by the shift of the C-H stretching frequencies. These methyl groups are reactive as indicated by the TD spectra shown in Figure 9[59]. We do observe not only desorption of CH_3 and CH_4 but also of ethane leading to a sharp desorption signal with maximum around T=135K. We believe that the ethane is actually formed on the surface. Note, that there are indications for ethane formation via a very detailed analysis of the HREEL spectra (not performed here) but they are not conclusive.

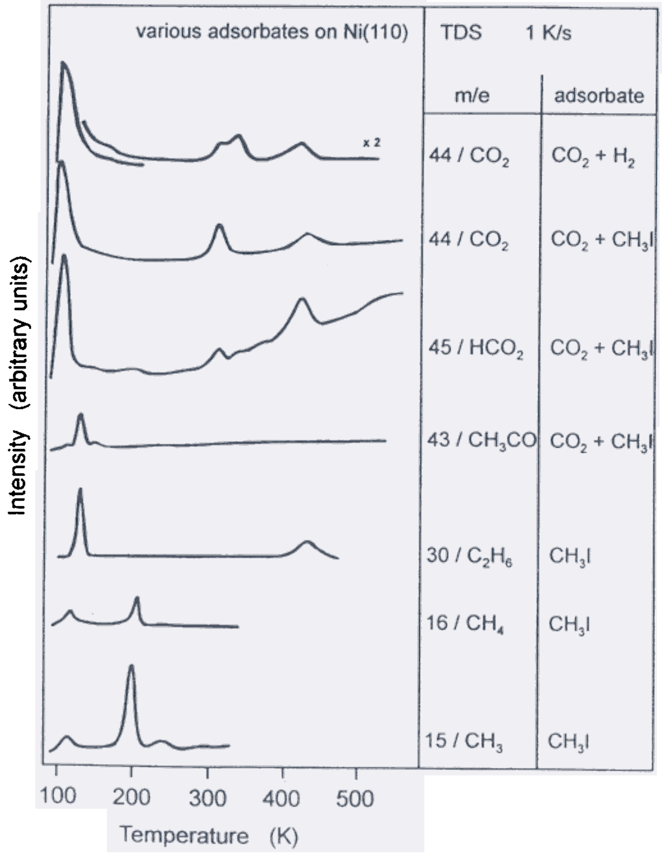


Figure Thermal ion spectra for ferent m/e adsorbates c Ni(110).

If we now preadsorb CO_2 and then coadsorb CH_3I (see Figure 7) we do see the CO_2^- signals in the HEEL spectra (Figure 8) attenuated without simultaneous desorption of CO_2. Concomitantly, we observe the formation of a carboxylic species, indicated by the observed frequencies, but it is very difficult at present to differentiate between formate and acetate formation. In order to identify uniquely the presence of acetate versus formate we would have to identify the C-C stretching vibration. However, even for pure acetate adsorbates[62-65] its intensity is weak (see Figure 8), which renders the problem hardly solvable at present. Isotopic labelling experiments and FTIR investigations on the same system are under way to shed more light onto this question. There is one hint towards the formation of acetate in the recorded TD spectra[59]. At rather low temperature, in the range where CO_2^- becomes unstable with respect to dissociation we find a peak characteristic of CH_3CO (m/q=43), the major fragment in the fragmentation pattern of CH_3COOH. This points at least to the formation of a carbon-carbon bond in the system; whether this bond is established between CO_2^- and CH_3 or CH_3 and CO is not clear at present. The TD spectra for CO_2 (m/q=44) and HCOO (m/q=45) are similar those seen in connection with formate adsorption[59].

Summarizing the reactivity of CO_2^-, we find that at low temperatures CO_2^- reacts with coadsorbed hydrogen to form formate on the surface. The formation of acetate from CO_2^- and CH_3 is likely but not fully convincingly proven. In the latter direction more studies have to be done in the near future, in particular in view of the possibility to synthesize acetic acid from carbon dioxide and methane.

ACKNOWLEDGEMENTS

Our research has been supported by Deutsche Forschungsgemeinschaft, Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, Fonds der Chemischen Industrie and the Brite-Euram program of the European Communities. We would like to thank G. Illing for the XP-measurements, and B. Dillmann, and Th. Risse for technical help.

REFERENCES

B. Bartos, H.-J. Freund, H. Kuhlenbeck, M. Neumann, H. Lindner and K. Müller, Surf. Sci., 1987, 179, 59.
H. Lindner, D. Rupprecht, L. Hammer and K. Müller, J. Electron Spectrosc. Rel. Phen., 1987, 44,141.
G. Illing, D. Heskett, E.W. Plummer, H.-J. Freund, J. Somers, Th. Lindner, A.M. Bradshaw, U. Buskotte, M.Neumann, U. Starke, K. Heinz, P.L. De Andres, D. Saldin and J.B. Pendry, Surf. Sci., 1988, 206, 1.
M. Asscher, C.-T. Kao and G.A. Somorjai, J. Phys. Chem.,1988, 92, 2711.
H. Peled and M. Asscher, Surf. Sci., 1987, 183 , 201.
H.-J. Freund, H. Behner, B. Bartos, G. Wedler, H. Kuhlenbeck and M. Neumann, Surf. Sci., 1987, 180, 550.
H. Behner, W. Spiess, G. Wedler and D. Borgmann, Surf. Sci.,1986, 175, 27.
R.G. Copperthwaite, P.R. Davies, M.A. Morris, M.W. Roberts and R.A. Ryder, Catalysis Letters, 1988, 1, 11.
R. Brosseau, T.H. Ellis and H. Wang, Chem. Phys. Lett., 1991, 177 , 118.
D. Ehrlich, S. Wohlrab, J. Wambach, H. Kuhlenbeck and H.-J. Freund, Vacuum, 1990,

41 157;
S. Wohlrab, D. Ehrlich, J. Wambach, H. Kuhlenbeck and H.-J. Freund, Surf. Sci., 1989, 220, 243;
J. Wambach, G. Odörfer, H.-J. Freund, H. Kuhlenbeck and M. Neumann, Surf. Sci., 1989, 209, 159.
10. F. Solymosi and A. Berkó, J. Catal., 1986, 101, 458.
11. A Berkó and F. Solymosi, Surf. Sci., 1986, 171, L498.
12. J. Kiss, K. Revesz and F. Solymosi, Surf. Sci., 1988, 207, 36.
13. F. Solymosi and L. Bugyi, J. Chem Soc., Faraday Trans. 1, 1987, 83, 2015.
14. J. Paul, Surf. Sci., 1989, 224 , 348;
J. Paul, F.M. Hoffmann, J.L. Robbins, J. Phys. Chem., 1988, 92, 6967;
J. Paul, R.A. dePaola, F.M. Hoffmann in "Physics and Chemistry of Alkali Metal Adsorption" (Eds.H.P. Bonzel, A.M. Bradshaw, G. Ertl) Material Science Monographs, 1989, 57, 213, Elsevier, Amsterdam .
15 J.A. Rodriguez, W.D. Clendening and C.T. Campell, J. Phys. Chem., 1989, 93 5238.
16 R.J. Behm and C.R. Brundle, J. Vac. Sci. Technol., 1983, A1, 1223.
17. S. Schubert, U. Imke and W. Heiland, Surf. Sci., 1989, 219 , L567.
18. M.A. Barteau and R.J. Madix, J. El. Spec. Rel Phen., 1983, 31, 101.
19. E.M. Stuve, R.J. Madix and B.A. Sexton, Chem .Phys. Lett., 1982, 89 , 48.
20. C.T. Au, W. Hirsch and W.Hirschwald, Surf. Sci., 1988, 199, 507.
21. A.F. Carley, D.E. Gallagher and M.W. Roberts, Spectrochimica Acta, 1987, 43A, 1447; Surf. Sci., 1986, 183, L263.
22 J. Mundenar, K.-D. Tsuei and B. Bartos, private communication.
23 K.J. Maynard and M. Moskovits, Surf. Sci., 1990, 225, 40.
24 K.J. Maynard and M. Moskovits, J. Chem. Phys., 1989, 90, 6668.
25 M. Pirner, H. Bauer, D. Borgmann and G. Wedler, Surf. Sci., 1987, 189/190, 147.
26 A. Erdöhelyi, E. Anneser, Th. Bauer, K. Stephan, D. Borgmann and G. Wedler, Surf. Sci., 1990, 227, 57.
27 R. Dziembay and G. Wedler, Surf. Sci., 1983, 134, 283.
28 F. Solymosi and H. Knözinger, J. Catal., 1990, 122, 166.
29 R.P. Eischens and W.A. Pliskin, Advan. Catalysis, 1957, 9, 662.
30 J. Onsgaard, E.V. Thomsen, Europhysics Conference Abstracts (ECOSS-13), 1993, 17E, FrM-P24.
31 P.B.Rasmussen, P.A. Taylor, I. Chorkendorff, Surf. Sci., 1992, 269/270, 352 .
32 H. Lindner, K. Müller, private communications.
33 W. Heiland, Surf. Sci., 1991, 251/252, 942.
34 M. H. Nassir, D.J. Dwyer, J. Vac. Sci. Technol., 1993, A11, 2104 .
35 M. Bowker, M.A. Barteau, R.J. Madix, Surf. Sci., 1980, 92, 528.
36. J. Segner, C.T. Campbell, G. Doyen, G. Ertl, Surf. Sci., 1983, 138, 505.
C. T. Campbell, G. Ertl, H. Kuipers, J. Segner, J. Chem. Phys., 1980, 73, 5862.
37 W. H. Weinberg, Surf. Sci., 1983, 128, L224 .
38 L.H. Dubois, G.A. Somorjai, Surf. Sci., 1983, 128, L23.
39 D. W. Goodman, D.E. Peebles, J.M. White, Surf. Sci., 1984, 140, L239.
40 B. Bartos, H.-J. Freund, H. Kuhlenbeck, M. Neumann, Springer Series in Surface Science, Vol. 8, "Kinetics of Interface Reactions" (Eds. M. Grunze, H.J. Kreuzer), Springer Verlag, 1987, 164.
41 W. Akemann, A. Otto, Surf. Sci., 1992, 272, 211; ibid., 1993, 278, 104.
J. Pacanski, U. Wahlgren, P.S. Bagus, J. Chem. Phys., 1975, 62, 2740.
W.B. England, Chem. Phys. Letters, 1981, 78, 607.

44. P.W. Atkins, "Physical Chemistry", 4th Edition, Oxford University Press (1990).
45. R.N. Compton, P.W. Reinhardt, C.D. Cooper, J. Chem. Phys., 1975, 63, 3821.
46. C. D. Cooper, R.N. Compton, Chem. Phys. Letters, 1972, 14, 28.
47. D.W. Ovenall, D.H. Wiffen, Mol. Phys., 1961, 4, 135.
48. K. O. Hartman, I.C. Hisatsume, J. Chem. Phys., 1966, 44, 1913.
49. D.W. Turner, A.D. Baker, C. Baker, C.R. Brundle, "Molecular Photoelectron Spectroscopy" Wiley, New York (1970).
50 H.-J. Freund and R.P. Messmer, Surf. Sci., 1986, 172, 1.
51 A.D. Walsh, J. Chem. Soc., 1953, 2266.
52 J.M. Hollas, "High Resolution Spectroscopy", Butterworths, London (1982).
53 K.H.Bowen, G.W.Liesegang, R.A.Sanders, D.R.Hershbach, J. Phys. Chem., 1983, 87 557.
54. A.R. Rossi, K.D. Jordan, J. Chem. Phys., 1979, 70, 4422.
55. Z.M. Liu, Y. Zhou, F. Solymosi, J.M. White, J. Phys. Chem., 1989, 93, 4383.
56. T. Jones, M.R. Ashton, N.V. Richardson, J. Chem. Phys., 1989, 90, 7564;
T. Jones, N. V. Richardson, Surf. Sci., 1989, 211, 377.
57. J. Wambach, G. Illing, H.-J. Freund, Chem. Phys. Letters, 1991, 184, 239.
58. M.D. Crapper, G.E. Riley, D.P. Woodruff, A. Puschmann, J. Haase, Surf. Sci., 1986, 171, 1.
59. J. Wambach, Thesis, Ruhruniversität Bochum (1991), unpublished.
60. M.A. Henderson, G.E. Mitchell, J.M. White, Surf. Sci., 1987, 184, L235.
61. X.-L. Zhou, J.M. White, Surf. Sci., 1988, 194, 438.
62. J.L. Davis, M.A. Barteau, Langmuir, 1989, 5, 1289.
63. Q. Gao, J.C. Hemminger, J. Electr. Spectr. Rel. Phen., 1990, 54/55, 667.
64. Q. Gao, J.C. Hemminger, Surf. Sci., 1990, 228, 45.
65. N.R. Avery, J. Vac. Sci. Technol., 1982, 20, 592.