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Surface structure and the instability of the formate overlayer at a Pb(110) surface

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A combination of photoelectron and vibrational spectroscopies has established that a high energy formate species generated at a Pb(110)-surface is tilted with respect to the surface normal and decomposes spontaneously through H-bonding interactions with HCOOH(g) at 295 K.

Keywords: Photoelectron spectroscopy; electron energy loss spectroscopy; formic acid; activation by oxygen; lead

We have reported elsewhere [1] that although an atomically clean Pb(100) surface is unreactive to formic acid at 295 K–the surface remaining unchanged judged by both X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED)–the preadsorption of oxygen leads to the facile formation of a formate overlayer. The essential feature of the reaction is proton extraction from HCOOH(a) with oxygen acting as a strong base. However, on more extensive exposure to formic acid the formate overlayer spontaneously decomposed and the Pb(4f), O(1s) and C(1s) spectra together with the LEED pattern indicated that the surface has reverted to close to the clean surface. In this Communication we investigate (a) whether the instability is structurally specific by studying the Pb(110) surface and (b) whether the availability of vibrational spectroscopy provides structural information not previously available which can throw light on the reasons for the formate overlayer's instability. We have used a specially designed spectrometer that enables both X-ray photoelectron and electron energy loss spectra to be obtained.

In fig. 1 are shown O(1s) and C(1s) spectra for the oxygen-induced formation of the formate overlayer at a Pb(110) surface at 295 K. Also shown are the total concentrations of surface oxygen and carbon present at each stage. The O(1s) peak at 529 eV binding energy corresponds to chemisorbed oxygen, the intensity of which decreases with exposure to HCOOH(g) simultaneously with the emergence of a second O(1s) peak at 531.7 eV. The latter is accompanied by a

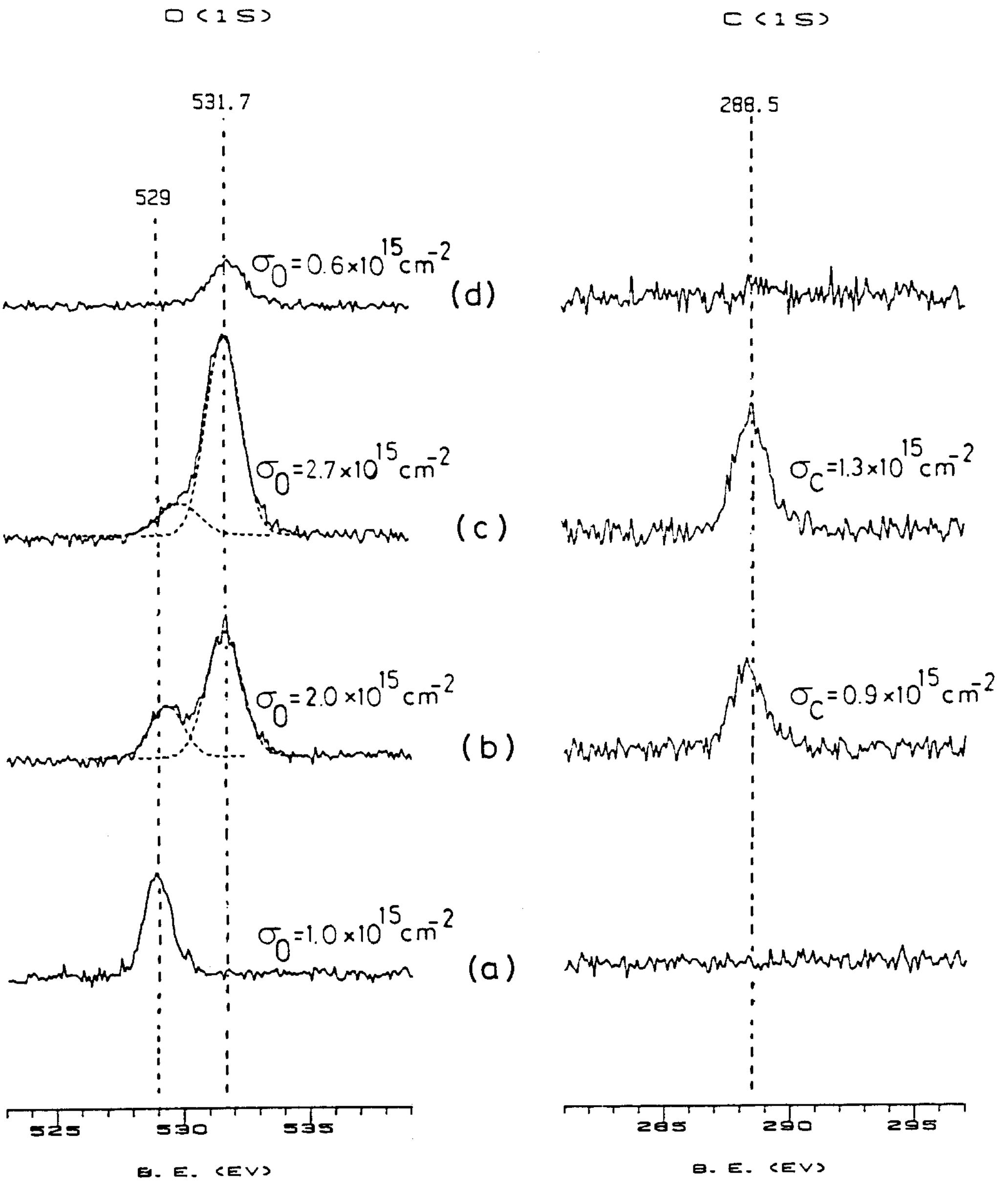

Fig. 1. O(1s) and C(1s) curve-fitted spectra of the interaction of formic acid with a pre-oxidised Pb(110) surface at 295 K: (a) 1.5×10^4 L $O_{2(g)}$; (b) 5 L $HCOOH_{(g)}$; (c) 20 L $HCOOH_{(g)}$; (d) 400 L $HCOOH_{(g)}$. The total surface oxygen and carbon concentrations at each stage are also shown.

corresponding C(1s) peak at 288.5 eV and from a detailed analysis of the spectra (see below) both peaks are attributed to the formation of the formate overlayer COOH(a). The ratio of the oxygen adatoms corresponding to the emerging 531.7 eV peak to the surface carbon atom concentration (C(1s) peak at 288.5

eV) is close to 2:1 throughout the surface reaction (spectra a–c, fig. 1). The original preadsorbed oxygen concentration (1.0×10^{15} cm^{-2} spectrum a) decreased to 0.4×10^{15} cm^{-2} with the simultaneous development of the new O(1s) peak at 531.7 eV corresponding to 2.3×10^{15} cm^{-2} oxygen atoms (spectrum c). In other words every surface oxygen removed is replaced by four 'oxygens' of two surface formate species. The Pb($4f_{7/2,5/2}$) peaks of the clean metal which are initially at binding energies of 137 eV and 141.8 eV undergo shifts of about 2 eV to higher binding energy reflecting the ionic-nature of the formate overlayer. This is similar to what we previously reported [1] for the Pb(100) surface.

The corresponding electron energy loss spectrum for chemisorbed oxygen (fig. 2 spectrum a) exhibits a single loss at 490 cm^{-1} assigned to $\nu_{Pb\text{-}O}$ but on exposure to HCOOH(g) at 295 K new loss features develop at 1350 cm^{-1}, 1600 cm^{-1} and a very broad feature at 2900 cm^{-1}. With the development of these the loss at 490 cm^{-1} ($\nu_{Pb\text{-}O}$) decreases slowly in intensity and shifts to lower frequency (420 cm^{-1}); a new loss feature also develops at 220 cm^{-1}. A much weaker loss-peak is also observed at 750 cm^{-1} during the formation of the formate overlayer. When taken in conjunction with the relevant core-level spectra the loss peaks are assigned as follows: $\nu_{C\text{-}H}$ 2900 cm^{-1}; ν_s(COO) 1350 cm^{-1}; ν_a(COO) 1600 cm^{-1}; δ(OCO) 750 cm^{-1}; and $\nu_{(Pb\text{-}O)}$ 490 cm^{-1}.

Of particular note is that during the oxygen induced formation of the formate overlayer both the symmetric ν_s(COO) and antisymmetric vibrational modes ν_a(COO) develop simultaneously at 295 K (fig. 2, spectra b&c). This is unusual in that for formate overlayers generated at room temperature by the chemisorption of HCOOH(g) at both Cu(100) and Ni(110) surfaces [2,3] the ν_a(COO) mode is absent, the formate being of C_{2v} symmetry in both cases. We therefore conclude that at the Pb(110) surface a formate structure develops at 295 K which is tilted with respect to the surface normal.

Although the interatomic metal-metal distances in the clean Pb(110) surface (5 Å and 3.5 Å) obviously do not allow the formation of a bidendate formate of C_{2v} symmetry where the O–O distance is 2.5 Å we have no precise information on the metal-metal distances in the oxide overlayer. Earlier [4] LEED studies however suggested that oxygen chemisorption reconstructs the surface to generate four domains of surface oxide with dimensions close to that of bulk PbO-orthorhombic. Since the formate is generated by oxygen induced hydrogen abstraction and desorption of water it is not therefore surprising that the formate overlayer is both disordered and involves tilted species. It is in essence a high energy metastable formate.

Although the stable chemisorbed formate at the Cu(100) surface at 295 K is of C_{2v} symmetry it has been shown that tilted formate species with a characteristic ν_a(OCO) stretch at 1650 cm^{-1} can be generated by warming the overlayer formed initially at 120 K to 295 K and then recooling to 120 K. The mechanism of the formation of the tilted species at a Cu(100) surface has been discussed by Dubois et al. [2] and also by Hayden et al. [5] for the Cu(110) surface, and the

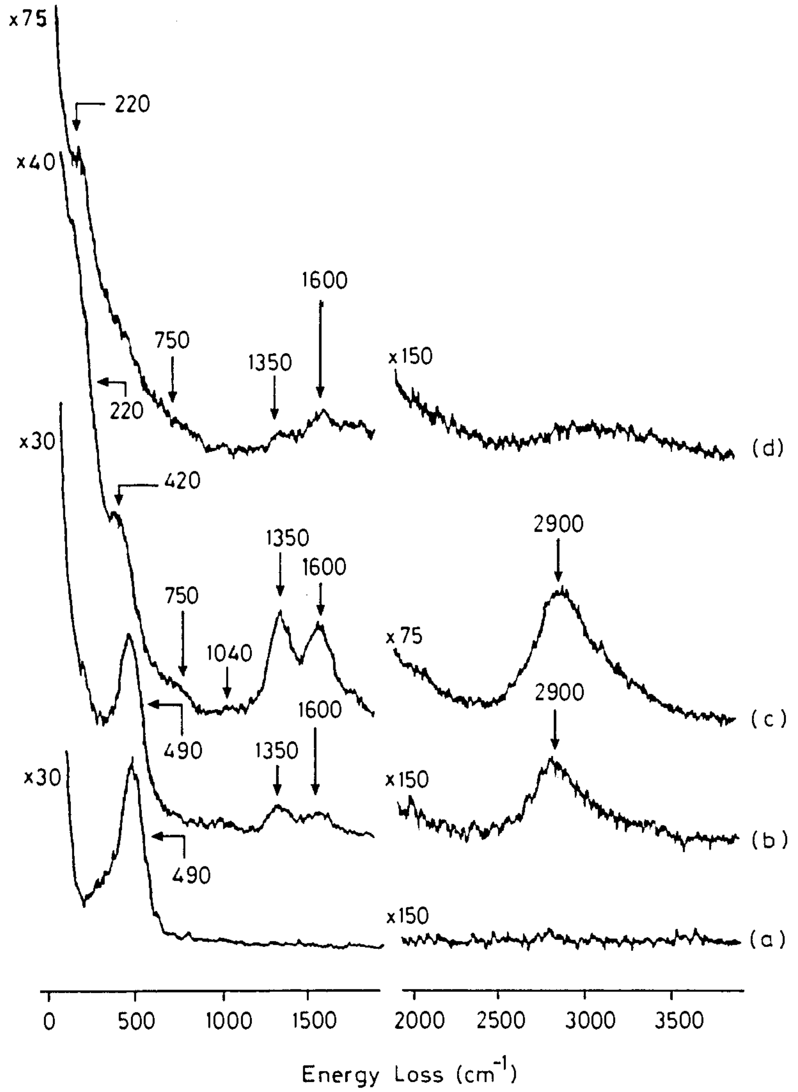

Fig. 2. HREEL spectra of the interaction of formic acid with a pre-oxidised Pb(110) surface at 295 K: (a)–(d) as in fig. 1.

concensus view is that is forms only at high coverage and likely to involve H-bonded formic acid molecules. Davis and Barteau [6] have reported very recently on the interaction of formic acid with a Pb(111)–(2×2)O surface and as with Ni(110) the formate is of C_{2v} symmetry. There is no evidence for a tilted formate species, the ν_a(OCO) loss being absent.

An unusual feature of the electron energy loss spectrum (fig. 2) is the exceptionally large FWHM value (~ 500 cm^{-1}) of the C-H loss at 2900 cm^{-1}. This occurs even at low formate coverages and may be due to H-bonding interactions with either (or both) the oxygen and surface metal atoms i.e.

C-H--O and C-H---Pb. The role of C-H---O electrostatic-type interactions in stabilising carboxylic acid conformation disorder and structure has been confirmed [7] by both neutron diffraction and X-ray crystallography, nevertheless predicting structures stabilised by these weak forces is apparently not yet possible. Although softened CH stretching modes due to weak C-H-metal i.e. H-bond type interactions have been reported for the chemisorption of hydrocarbons at transition metal surfaces [8] no information on such interactions at sp-metals has been reported. In the Cu(100)-formic acid system no spectra were reported by Dubois et al. [2] in the C-H stretch region for the tilted species so that no comparison is possible with our data. For the Cu(100)-formate of C_{2v} symmetry the C-H stretch region was characterised by two distinct but relatively narrow loss peaks centered at 2840 cm^{-1} and 2910 cm^{-1} while at Ni(110) the chemisorbed formate exhibits [3] a rather wide (FWHM ~ 300 cm^{-1}) envelope centered at about 2850 cm^{-1}. This Jones et al. [3] attributed to overtone and combination bands $2\nu_s$(OCO), ν_a(OCO) + ν_s(OCO) and $2\nu_a$(OCO). Why these appear to be absent in other cases, for example the Al(111)-oxygen-formate [9] and Cu(100)-formate systems, is unclear. These combination bands cannot however be excluded as contributing to the prominence of the 2900 cm^{-1} loss feature in the present study (fig. 2).

Although the formate overlayer formed initially at the Pb(110)-O surface (spectra b, figs. 1 & 2) are thermally stable in vacuo up to 400 K on more extensive exposure to HCOOH(g) at 295 K the spectra (O(1s), C(1s), Pb(4f) and the vibrational spectra figs. 1 & 2, spectra d) revert, sometimes quite suddenly, to those more typical of the atomically clean Pb(110) surface. It would appear that weak H-bonding interactions between the high energy formate overlayer and HCOOH(g) are sufficient to destabilise it and lead to spontaneous decomposition. The O(1s), C(1s() and Pb(4f) difference spectra do however indicate that small concentrations of surface formate species are still retained–no chemisorbed oxygen is present–while the vibrational spectra have obvious but relatively weak losses at 220 cm^{-1}, 1350 cm^{-1} and 1600 cm^{-1} with ν_a(OCO) being distinctly more intense than the ν_s(OCO) feature (fig. 2 spectrum d). This provides some support for correlating the 220 cm^{-1} and 1600 cm^{-1} losses with the tilted or bidendate Pb_2COOH surface formate. The loss at 420 cm^{-1} we then assign to the $\nu_{Pb\text{-}O}$ stretch of a monodentate Pb-COOH species.

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