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Adsorption of the formyl species on transition metal surfaces[☆]

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Abstract

The density functional theory (DFT) and the cluster approach were used to get information concerning the adsorption of the formyl species on transition metal surfaces. At first, the adsorption of HCO on four different sites of the Cu (111) surface was studied. An initial η^1-HCO–C conformation was considered in all cases. After optimisation, results obtained pointed towards a preferred η^1-HCO–C adsorption conformation with the carbon atom located between a bridge and a hcp hollow site. The calculated adsorption energy is approximately 140 kJ mol^{-1}. The internal geometrical parameters of the adsorbed species lie in between the calculated bond lengths and angles of the gas phase HCO and HCO$^-$ species. Adsorption of the formyl species on the Au (111) and Pt (111) surfaces was also studied. Starting from the optimised internal geometry of the adsorbed HCO species, a small adsorption energy on the gold surface, ≈ 52 kJ mol^{-1}, and a large adsorption energy on the platinum surface, ≈ 252 kJ mol^{-1} were calculated. The distance from the carbon atom to the metallic surface is 1.9 Å on copper, 2.2 Å on gold and 1.5 Å on platinum. Small C–surface distances led to large C–O bond lengths. The short carbon to surface distance in HCO adsorption on platinum when compared with copper and gold may be responsible for the distinct methanol oxidation on this surface. Calculated vibrational frequencies are in good agreement with previous theoretical and experimental data. The bonding to the surface has a mainly ionic character on copper and a more covalent one on platinum. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: DFT; Chemisorption; Methanol oxidation; Metal surfaces; Formyl intermediate; Heterogeneous catalysis

1. Introduction

The electrocatalytic oxidation of small organic species, especially methanol and its reaction intermediates, at transition metal and related surfaces has long been a subject of widespread practical, as well as fundamental, interest given its importance in fuel-cell research [1]. The central issue for such systems is the nature of the adsorbed species present under reaction conditions and, particularly, their role as reaction intermediates or poisoning species.

One of these intermediates is the formyl species, HCO, which was proposed for the methanol oxidation reaction on various transition metal surfaces [2–17]. Experimental studies concerning the gas phase [2–6] as well as the electrochemical [7–17] oxidation of methanol have reported the adsorption of this species.

The formyl radical has been studied in the gas phase oxidation of methanol on Ni (100) by means of temperature programmed desorption [2] and by infra-red (IR) spectroscopy [3]. A strong band at 1800–1880 cm^{-1} was attributed to adsorbed formyl. At low temperature, it has been studied on the Ru (001) surface by means of high-resolution electron energy loss spectroscopy (HREELS) [4,5]. Vibrational frequencies have been reported for two different adsorption configurations. For a C-bonded η^1-formyl conformation, the C–O and C–H stretching frequencies are 1750 and 2970 cm^{-1}, respectively. The C–O and C–H stretching frequencies for the η^2-formyl, simultaneously bonded to the surface through the carbon and oxygen atoms, are 1190 and 2970 cm^{-1}, respectively. For the same metal surface, HREELS [6] also revealed a band at 590 cm^{-1} assigned to the ν(Ru–HCO) stretching frequency.

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In the electrochemical oxidation of methanol, HCO was proposed as a reactive intermediate on Pt [7–14], Ag [15] and Au [7,10,15–17] surfaces. This species is formed from adsorbed formaldehyde and, in alkaline media, it is thought to be the reactant for formate production written as follows [14,15]:

$$\mathrm{HCO_{ads} + OH_{ads} \rightarrow HCOOH} \tag{1}$$

$$\mathrm{HCOOH + OH^- \rightarrow HCOO^- + H_2O} \tag{2}$$

It has been also proposed [14] that this reactive intermediate is involved in the formation of poisoning species, which have not been exactly identified so far. The poisoning species are oxidised to CO_2 at potentials higher than 0.72 eV as follows:

$$\mathrm{HCO \rightarrow poisoning\ \ species} + n\mathrm{OH_{ads} \rightarrow CO_2} \tag{3}$$

Surface enhanced Raman spectroscopy (SERS) studies [7] of methanol and formic acid decomposition on gold and platinum electrodes revealed a band at 1640 cm^{-1}, which was assigned to the C–O stretching in the adsorbed HCO intermediate. Using IR spectroscopy, Beden et al. [8] observed a band at ca. 1700 cm^{-1}. They postulated that it could be assigned to an adsorbed species containing a C=O bond as adsorbed HCO. Differences found between formaldehyde oxidations on the (100), (110) and (111) Pt and Au surfaces are not significant [10]. This is probably due to the weak adsorption of formaldehyde and its reaction intermediates.

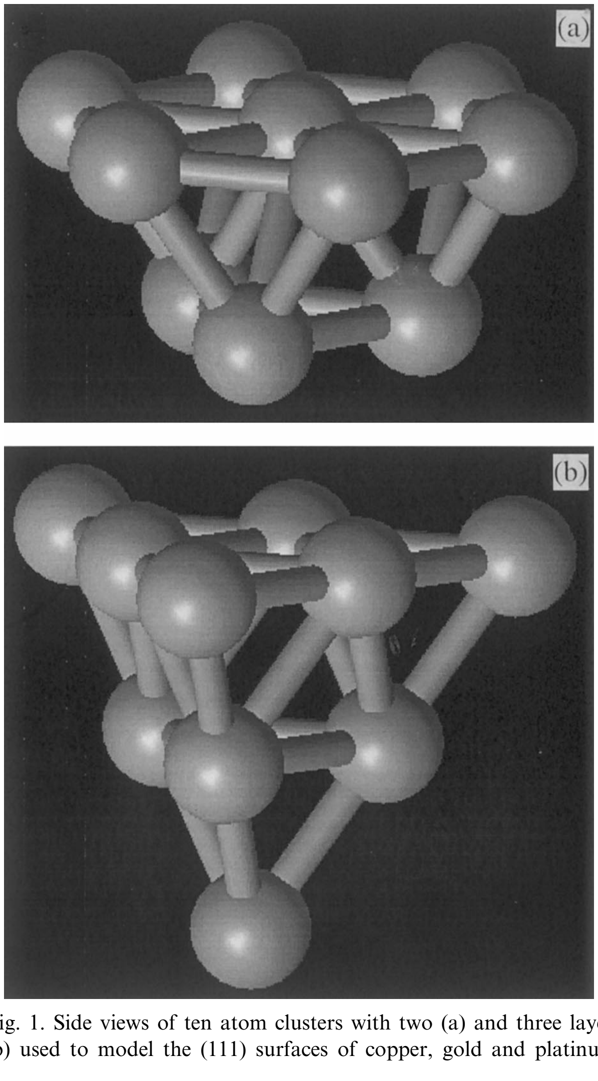

Fig. 1. Side views of ten atom clusters with two (a) and three layers (b) used to model the (111) surfaces of copper, gold and platinum.

Yang et al. studied formyl adsorption on nickel (100) [18] and (111) [19] surfaces. The results show that formyl is preferentially adsorbed on nickel surfaces through its carbon atom. The sites that most efficiently stabilise the HCO radical are the four-fold hollow site on the (100) surface and the top site on the (111) surface. However, on the (100) surface, the difference in the adsorption energy for top, bridge and four-fold hollow sites is only 0.8 kJ mol^{-1}. On the (111) surface, the difference between the energies for the adsorption on the most favourable site and on the other sites is never larger than 10 kJ mol^{-1}. The C–H stretching frequencies lie in the range 2963–2984 cm^{-1} for adsorption on the (111) nickel surface, while on the (100) surface the range is 2933–2950 cm^{-1}. The C–O vibrational frequencies lie in the ranges 1740–1762 and 1758–1761 cm^{-1} for adsorption on the nickel (111) and (100) surfaces, respectively.

Copper has been reported to enhance formic acid oxidation slightly at low coverage [20,21]. In electrochemical studies, the formation of poisoning species on platinum surfaces with copper adatoms [20,22] and also on single gold surfaces [17,23] was not detected. The HCO species is proposed to be the reactive intermediate [14] in the main reaction where formate species are produced (Reactions 1 and 2) as well as in the parallel reaction where poisoning species are produced (Reaction 3). Since both reaction paths take place on platinum while the formation of poisoning species is not observed on copper and golf surfaces, the adsorption properties on platinum as opposed to on copper and gold might be different.

In this work, the adsorption of HCO on copper, gold and platinum surfaces is investigated by means of the density functional theory (DFT). Theoretical details are given in Section 2. The data obtained are collected and compared in Section 3. The main conclusions are reported in Section 4.

2. Theoretical details

In the present work, the interaction of the formyl species with copper, gold and platinum surfaces is studied. For this purpose, the DFT hybrid method B3LYP was used. The B3LYP method is composed of the three-parameter functional of Becke [24] (which mixes DFT and HF terms) using the correlation functional of Lee et al. [25]. The metal surfaces are mod-

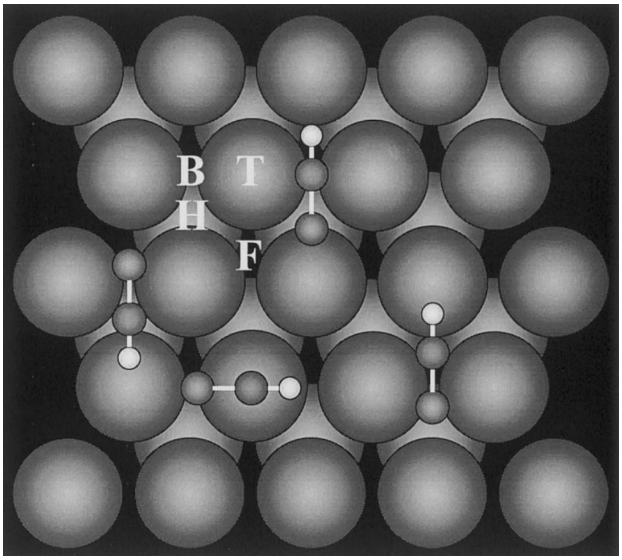

Fig. 2. Starting positions for the η^1-HCO–C species adsorbed on the Cu (111) surface (T)op, (B)ridge, (H)cp hollow and (F)cc hollow sites.

Table 1
Geometry and energy (without zero point energy corrections) for the optimised free HCO^+, HCO and HCO^- species

Free species	HCO^+	HCO	HCO^-
Energy/a.u.	−113.544	−113.857	−113.868
Distance (CH)/Å	1.099	1.125	1.224
Distance (CO)/Å	1.113	1.183	1.242
Angle (OCH)/°	180.0	123.8	109.3

Table 2
Vibrational frequencies/cm^{-1} of free HCO^+, HCO and HCO^- species [a]

Free species	HCO^+	HCO	HCO^-
w(CH)	856	1174	1315
v(CO)	2263	1834	1435
v(CH)	3254	2703	1823

[a] w, in-plane wagging; v, stretch.

elled by two M_{10} metal clusters as shown in Fig. 1. These metal clusters are a section of the ideal (111) metallic surface. The Cu–Cu, Au–Au and Pt–Pt nearest-neighbour distances are taken from the bulk and these values are 2.551, 2.883 and 2.775 Å, respectively.

The adsorption of HCO on the copper surface has been studied intensively. The adsorption sites taken into consideration were the ones where the carbon atom sits on the top, bridge and hollow sites (hcp and fcc), see Fig. 2, since it was found previously [18,19] that the C-bonded η^1-formyl conformation is more favourable. The geometry of the adsorbed species was fully optimised and the copper–copper distance was frozen in order to keep the cluster with the bulk metal characteristics.

After finding the adsorption site and conformation that stabilise the HCO species most efficiently on the copper (111) surface, formyl adsorption on the gold and platinum (111) surfaces was then studied. For the copper surface, the most favourable site and conformation for the adsorption of the HCO^+ and of the HCO^- species was also studied.

All calculations were made for the lowest spin multiplicity systems using the Gaussian 98 package [26]. The metal atoms were described by the large LANL2DZ basis set which treats the outer s, p and d electrons (18 for Pt and 19 for Cu and Au) with a double zeta basis set and the inner electrons with the effective core potential of Hay and Wadt [27]. The non-metallic atoms (H, C and O) are described by the 6-31 + G* basis set of double zeta quality with diffuse and d polarisation functions in carbon and oxygen atoms. The vibrational frequencies were calculated using the analytic second derivatives of the energy of the molecular systems using an infinite mass for the metal atoms.

3. Results

Table 1 lists the computed geometry and energy for the HCO^+, HCO and HCO^- species optimised at the B3LYP/6-31 + G* level. A marked difference is readily observed for bond lengths and HCO bond angles between these three species. The increase in the number of electrons from the cation to the anion has a marked effect on the bond lengths. The bond lengths are longer for the anion and smaller for the cation. The HCO^+ species is linear and the HCO angle decreases to $\approx 124°$ in the radical and to $\approx 109°$ in the anion. This effect is due to the lone pair in the HCO^- carbon atom. The C–O bond distance in the cation is consistent with a bond order of three [28]. The C–H bond distance found in the cation and in the radical species is in agreement with C–H bond lengths calculated for similar compounds [28,29]. In the free formyloxy species, HCO_2, [29] the C–H was found to be 1.100 Å and a similar value was calculated for the gas phase H_2CO and CH_3O [30] species. Calculations for the C–H bond length in HCO_2^- [29] led to a value of 1.1536 Å. The most stable species is the anion.

Vibrational frequencies were computed for the free species and the results are shown in Table 2. Due to the longer C–H bond length, the C–H stretch frequency is much smaller for the anion than for the other two species studied. The same effect is observed for the C–O stretching frequency. This means that the bonds are weaker in the anion. In fact, the strong C–H and C–O bonds in the cation are again confirmed by the large C–H and C–O stretching frequencies. When compared

Table 3
Adsorption energies/kJ mol^{-1}, optimised geometry and charges for η^1-formyl–C [a] adsorbed on the top, bridge, hcp and fcc sites of the Cu (111) surface

HCO/Cu (111)	Top [a]	Bridge [a]	Hcp [a]	Fcc [a]
Adsorption energy/kJ mol^{-1}	−67.2	−139.8	−119.9	−107.6
Distance (CH)/Å	1.120	1.118	1.124	1.121
Distance (CO)/Å	1.249	1.252	1.244	1.257
Distance (SurfO)/Å [b]	2.110	2.060	2.203	2.158
Distance (SurfC)/Å [b]	1.931	1.912	1.943	1.979
Distance (CuO)/Å [c]	2.184	2.131	2.237	2.260
Distance (CuC)/Å [c]	2.075	2.337	2.402	2.020
Angle (HCO)/°	114.0	113.1	113.9	114.1
Angle (SurfCO)/° [d]	7.9	6.8	9.9	11.5
$q_{\text{adsorbate}}$ (NPA)/a.u.	−0.72	−0.74	−0.72	−0.79

[a] Reported adsorption sites refer to the starting position of the formyl carbon atom; adsorption sites after optimisation are shown in Fig. 3.

[b] Distances to the surface plane.

[c] Distances to the nearest-neighbour copper atom.

[d] CO bond deviation from the plane parallel to the surface.

with the cation, the addition of one electron in the radical and two in the anion lead to a shorter OCH angle. Due to the steric effects between the H and O atoms, an increase in the C–H and C–O bond lengths is obtained. This results in a larger in-plane wagging for the anionic species. Another vibration frequency with the same value as the one found for the wagging in the cation was also calculated.

The adsorption energy, geometrical parameters and charges for the HCO species adsorbed on the copper (111) surface are summarised in Table 3. Small differences are detected for the adsorption on the different sites considered due to the similarity between the final optimised structures, see Fig. 3. The reason for this result arises from considering the full geometry optimisation. When compared with the free HCO species, the effect of the adsorption on the C–H bond length is minimal with calculated values around 1.12 Å. The same effect is not observed with the C–O bond length. The distance between the carbon and oxygen atoms in the adsorbed species increases to ≈ 1.25 Å. The calculated HCO angle is close to 114°. Larger variations, between geometric parameters for the adsorption on the different sites under study, are obtained for oxygen and carbon to surface distances. However, these differences are all smaller than 0.15 Å. The C–O bond is almost parallel to the surface with the carbon atom closer to the surface than the oxygen atom. The deviation from the planar C–O bond lies between 6.8° for the adsorption on the bridge site and 11.5° for the adsorption on the fcc site. Despite the fact that geometry of the adsorbed HCO species on the different sites is almost unchanged, the differences in adsorption energies are large. The most stable adsorption site is the one with the oxygen atom placed almost above one copper atom and with the carbon atom located between an hcp hollow and a bridge site, see Fig. 3. The starting geometry was the one with the carbon atom adsorbed on the site labelled ‘B’ in Figs. 2 and 3. The most unstable adsorption conformation is the one labelled ‘top’ in Table 3. In this situation, the final adsorption geometry resembles η^2-formyl–C,O with the carbon and oxygen atoms located almost above two short-bridge copper atoms. The distances from the carbon and oxygen atoms to the nearest-neighbour copper atoms is almost the same. This result shows that the η^1 conformation of the surface formyl is preferred to the η^2 conformation. From Table 3 it is observed that the final geometries that stabilise the adsorbed HCO species more efficiently are the ones where the carbon–copper

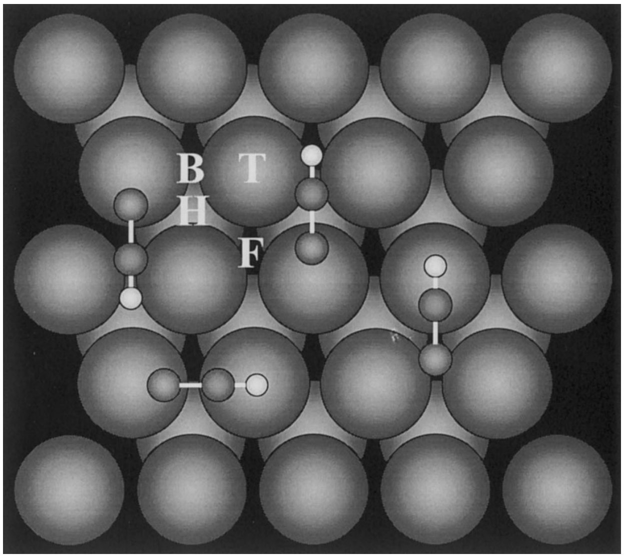

Fig. 3. Optimised geometry for the η^1-HCO–C species adsorbed on the Cu (111) surface.

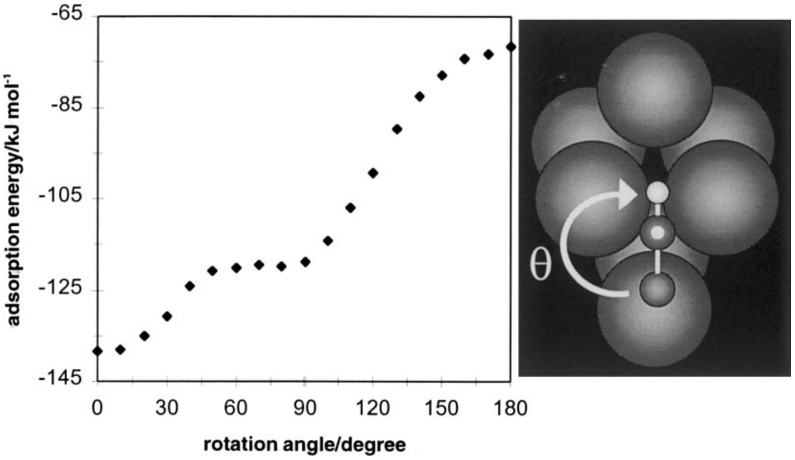

Fig. 4. Adsorption energy variation with rotation of the HCO species adsorbed on the bridge site. The internal geometric parameters and the formyl to surface distance are kept fixed at their optimised values.

Table 4
Adsorption energies/kJ mol^{-1}, optimised geometry and charges for η^1-HCO$^+$–C, HCO and HCO$^-$ adsorbed on Cu (111) surface bridge site and for η^1-HCO–C adsorbed on the Au and Pt (111) surfaces

(111) Surfaces	HCO$^+$/Cu	HCO/Cu	HCO$^-$/Cu	HCO/Au	HCO/Pt
Adsorption energy/kJ mol^{-1}	−469.4	−139.8	−267.4	−52.3	−252.1
Distance (CH)/Å	1.114	1.118	1.122	1.114	1.095
Distance (CO)/Å	1.249	1.252	1.254	1.211	1.318
Distance (SurfO)/Å	2.021	2.060	2.115	2.560	1.820
Distance (SurfC)/Å	1.918	1.912	1.927	2.156	1.497
Distance (CuO)/Å	2.104	2.131	2.178	2.798	1.987
Distance (CuC)/Å	2.334	2.337	2.355	2.603	2.067
Angle (HCO)/°	113.6	113.1	112.8	118.8	114.7
Angle (SurfCO)/°	4.7	6.8	8.6	19.5	14.2
$q_{\text{adsorbate}}$ (NPA)/a.u.	−0.67	−0.74	−0.76	−0.34	−0.39

distance is larger than the oxygen–copper length. This happens for the sites labelled ‘bridge’ and ‘hcp’ in Table 3. The charge transferred from the metal surface to the adsorbate was calculated by performing a natural population analysis (NPA). The charge was found to be − 0.72 *e* for HCO adsorbed on the top and hcp hollow site, − 0.74 *e* for adsorption on the bridge site and − 0.79 *e* for adsorption on the fcc hollow site.

Adsorption energy changes upon HCO rotation around the axis normal to the surface which crosses the C atom are shown in Fig. 4. The initial geometry is the one obtained for the full optimisation of the HCO species adsorbed on the bridge site. The internal parameters and the HCO to surface distance are kept fixed. For a 180° rotation, the HCO geometry is similar to the one obtained in the optimisation of the formyl species adsorbed on the fcc hollow site. The energy change for the 0–90° rotation is approximately 20 kJ mol^{-1} and for the 90–180° it is approximately 50 kJ mol^{-1}. For comparison, a rotation barrier of ≈1 kJ mol^{-1} for HCO adsorbed on the Ni (100) surface [18] was calculated. However, in the work of Yang et al., the carbon atom of the HCO species was kept fixed on the adsorption sites under study. On the copper surface, the 70 kJ mol^{-1} barrier makes the rotation of the HCO species very unlikely.

Starting with the optimised geometrical parameters for HCO adsorbed on the most favourable site of the copper (111) surface, the adsorption of the HCO$^+$ and HCO$^-$ species on the Cu (111) surface and of HCO on the Au (111) and Pt (111) surfaces was studied. The optimised results are summarised in Table 4 and compared with the geometrical parameters of the radical adsorbed on the copper surface. The adsorption energies of the cation and the anion are larger than the one calculated for the radical. As expected, the differences in geometrical parameters are not significant. This is due to the metallic character of the substrate which can accept charge from, or donate charge to, the adsorbate. The final charge on the adsorbate is ≈0.7 *e*. The formyl adsorption on the gold surface is weak. The low adsorption energy, ca. 52 kJ mol^{-1}, and the large HCO to surface distance is likely to mean that the HCO species is physisorbed on the gold surface. Due to the weak interaction with the metal surface, the C–O bond length is shorter in the case of adsorption on gold when compared with copper. The C–O bond is tilted away from the parallel to the surface by ≈20°, well above that observed on the copper surface. On Au (111), the charge on the adsorbate is half of the calculated charge for the copper surface due to the larger HCO to surface distance in the former case. The present authors have reported earlier [31] that the interaction of the methoxy species adsorbed on the gold (111) surface is weaker than that for the adsorption on the copper (111) surface.

The computed values for formyl adsorption on the platinum surface are also reported in Table 4. A strong interaction with the Pt (111) surface is obtained. The calculated adsorption energy is ca. 250 kJ mol^{-1}. This strong interaction is followed by the approach of the HCO species to the metal surface. The HCO carbon atom sits 0.3 Å closer to the Pt surface than to the Cu surface. As observed for the adsorption on the copper and gold surfaces, the C–H bond length is close to the calculated value for the free species. However, the C–O bond length is much longer than in the case of HCO adsorption on the two other surfaces studied and for the gas phase structures. The longer C–O and the shorter C–H bond lengths suggest a possible preference for C–O bond cleavage. This is in disagreement with experimental data because the HCO species has been proposed as an intermediate in the reaction where carbon monoxide is produced (poisoning species). On the other hand, the C–O bond length is still much lower than the experimental C–O distance in methanol, 1.428 ± 0.005 Å [28]. The large C–O bond length is only a sign of the strong interaction of HCO on Pt (111). The C–O bond is tilted 14.2° away from the plane parallel to the surface. The charge transferred from the metal surface to the adsorbate is 0.39 *e*. In Fig. 5, the adsorption energy variation with the adsorbate to surface distance is presented. The curves show that the energy variation is small for HCO adsorbed on Au due to the weak interaction with the surface and the variation is larger on copper and on platinum.

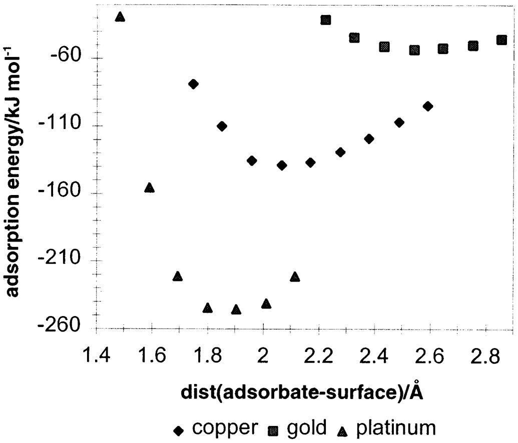

Fig. 5. Adsorption energy variation as a function of the distance of the HCO species to the copper, gold and platinum surfaces.

Table 5
Vibrational frequencies/cm^{-1} for η^1-HCO adsorbed on Cu, Au and Pt (111) surfaces bridge site [a]

(111) surfaces	HCO/Cu	HCO/Au	HCO/Pt
ν(CH)	2812	2844	3103
ν(CO)	1507	1693	1184
$w_{\text{in-plane}}$ (CH)	1335	1232	1205
$w_{\text{out-of-plane}}$ (CH)	557	540	824
ν(C–Surf.)	375	351	600
ν(HCO–Surf.)	255	164	461

[a] *w*, wagging; *ν*, stretch.

Vibrational wavenumbers calculated for the HCO species adsorbed on the copper, gold and platinum (111) surfaces are shown in Table 5. The computed results show that the bonding of the HCO intermediate to the metal surfaces considered is stronger for platinum and weaker for gold. The stretching HCO–surface wavenumbers are 461 cm^{-1} for Pt, 255 cm^{-1} for Cu and 164 cm^{-1} for Au. The ν(CO) results presented in Table 5 show that the formyl C–O bond is weakened for adsorption on the platinum surface. The calculated value for the C–O stretching is 1184 cm^{-1}. This finding is close to the band at 1190 cm^{-1} reported for η^2-formyl bonded to the Ru (001) surface [4,5]. Beden et al. [8], have found experimentally a band at ca. 1700 cm^{-1} for HCO on platinum, characteristic of a η^1-formyl conformation. This probably means that both conformations are possible for the adsorbed HCO species as reported for adsorption on the Ru (001) surface [4,5]. The shorter C–O bond length for HCO on Cu (111) and Au (111) yields higher ν(CO) stretching wavenumbers when compared with adsorption on Pt (111). The calculated ν(CO) values are 1507 and 1693 cm^{-1} for HCO adsorbed on copper and on gold, respectively. The latter value is in good agreement with the SERS result [7] where a strong band was reported at 1640 cm^{-1} assigned to the C–O stretching of the adsorbed HCO species. The C–H stretching wavenumbers show that the C–H bond is similar for HCO adsorbed on Cu or Au and higher for adsorption on Pt.

The curves concerning the variation of the dipole moment with the distance of the adsorbate to the metal surfaces are plotted in Fig. 6. Results shown in Fig. 6 give information about the type of bonding to the surface and this method was proposed by Bagus and co-workers [32–34]. The straight line observed for HCO adsorption on the copper surface means that the bonding of the adsorbate to the surface has a mainly ionic character. The slope of this curve is −0.64 a.u. A small curvature is found for adsorption on gold, which

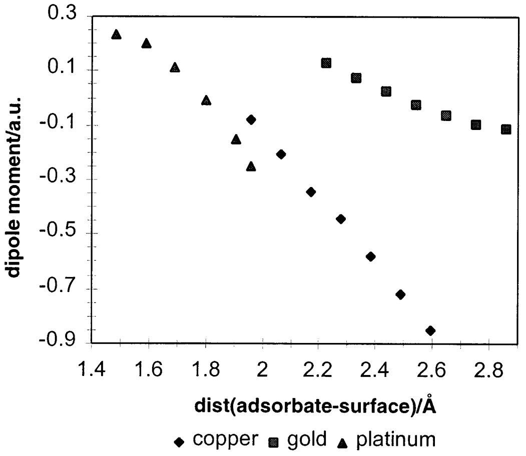

Fig. 6. Change in dipole moment variation with distance from the HCO species to the copper, gold and platinum (111) surfaces. The curves were obtained for distances close to the optimised geometry.

means that the bonding to the surface is less ionic than on copper. The small value calculated for the slope, -0.21 a.u., is in agreement with the smaller charge transfer to the adsorbate observed for HCO on gold. The variation of the dipole moment with the distance of the adsorbate to the platinum surface has a large curvature. This means that the bonding to the surface has a rather covalent character.

4. Conclusions

The DFT results reported above for formyl adsorption on copper, gold and platinum (111) surfaces show that the adsorbate is stable on all surfaces. On the copper surface, four possible adsorption sites were studied. A η^1-conformation where the carbon atom is closer to the surface than the oxygen atom appears to be preferred. The C–O axis of the HCO species is approximately parallel to the surface. The largest deviation from the normal to the surface is $\approx 11°$. The largest adsorption energy is found for the adsorption conformation where the carbon atom is placed between a bridge site and an hcp hollow site with the oxygen pointing towards a copper atom. The calculated rotation barrier is rather high, about 70 kJ mol^{-1}. The charge transferred from the metal surface to the adsorbate is ca. 0.7 *e*.

The adsorption energy of HCO on the gold surface is very small and characteristic of a physisorbed species. On the platinum surface, the interaction of the formyl species is very strong. The calculated results are in disagreement with the work of Adzic et al. [10] who proposed that reaction intermediates are weakly adsorbed on both gold and platinum surfaces. Different behaviour on the platinum surfaces was expected since poisoning species were reported on this surface while unseen on copper or on gold surfaces. In fact, the geometrical parameters of HCO adsorbed on platinum are very different when compared with the computed parameters for adsorption on the copper and gold surfaces. The C–O bond distance is much higher on platinum than on the other two surfaces. The major difference is observed in the carbon to surface distance. For adsorption on the copper surface this distance is 1.91 Å, 2.16 Å on gold and 1.50 Å on platinum. This difference may be responsible for the much larger adsorption energy calculated for the platinum surface and also for the different electrochemical behaviour of methanol and its reaction products on this surface when compared with the oxidation on copper and gold.

The charge transferred from the metal surface to the formyl species is much smaller on gold and platinum than on copper.

The adsorption properties of the HCO^+ and HCO^- species on Cu (111) are very similar to the calculated ones for the radical. The C–O bond in HCO adsorbed on gold and platinum is tilted away from the plane parallel to the surface by 14.2 and 19.5°, respectively.

Vibrational frequencies calculated for HCO adsorbed on copper, gold and platinum surfaces are in good agreement with experimental values found for the η^1 and η^2-formyl bonded conformations. The stretching wavenumbers show that the bonding to the surface is stronger on platinum and weaker on gold, which is in agreement with the calculated adsorption energies. The formyl C–O bond is weak for adsorption on Pt due to the strong interaction with the surface. A reverse effect was found for the C–H bond.

The bonding scheme to the metal surface has a mainly ionic character on copper and a less ionic character on platinum.

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