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The adsorption of CO on the stepped Pt{211} surface: a comparison of theory and experiment

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Experimental measurements and DFT calculations reveal that, as expected, CO adsorbs most strongly at the step edge of Pt{211}, with similar adsorption energies for bridged and atop CO on the step. Terrace sites are significantly less stable. In the light of our results, we attempt to provide explanations for previous disagreement between experiment and theory.

KEY WORDS: Pt{211}; CO adsorption; density function theory.

1. Introduction

Most experimental and theoretical studies of CO adsorption have been performed on flat surfaces such as the {100}, {110} and {111} planes of various metals. However, real catalysts are far from being flat, or even homogeneous, with many surfaces being expressed which contain large numbers of defects such as steps and kinks. Studies of adsorption on well defined stepped and kinked surfaces are a first step toward understanding the role of these defects in adsorption. With this in mind, we are currently performing an extensive survey of the adsorption of a number of gas molecules on the Pt{211} surface. CO adsorption on Pt{211} was chosen first as there is already a considerable body of work available for comparison [1–8]. Pt{211} exhibits three atom wide terraces with {111} character separated by one atom high steps of {100} character (see figure 1).

Our aim in this paper is to demonstrate the additional detail that our experimental work provides over previous work, whilst also evaluating periodic density functional theory (DFT) methods. The aim of the calculations presented is not to provide a definitive theoretical description, but rather to be an aid in interpreting the experimental data. Hence, we wish to establish whether the relatively cheap computational methods employed here can successfully model known systems and provide accurate geometries and semi-quantitative energetics for adsorption processes at stepped sites.

Compared to the situation on the flat Pt{111} surface, there is very little literature concerning the adsorption of CO on stepped surfaces. Temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) studies of CO adsorption on Pt{211} and Pt{533} [1] show that at low coverage, CO preferentially adsorbs at step sites. Furthermore, on Pt{533} CO adsorbs in atop sites at the step edge at low coverage, followed by step edge bridge sites as coverage increases, with atop and bridge sites on the terrace only being occupied at the highest coverages. On Pt{211}, CO is found to be bound to atop sites on the step edge at low coverage, with a suggestion of bonding to bridge sites on the step edge at higher coverage. In contrast to Pt{533}, these workers [1] found that they could not differentiate between CO in atop sites on the step edge and on the terrace on Pt{211}. They further suggested that the smaller terrace size of Pt{211}, compared with Pt{533}, affected the ability of CO to bind to the bridge sites on the terrace. TPD studies of CO adsorption on Pt{211} [1,3] give an activation energy for CO desorption from Pt{211} of $164\,\mathrm{kJ\,mol^{-1}}$, compared with only $139\,\mathrm{kJ\,mol^{-1}}$ from Pt{111}. Electron stimulated desorption ion angular distribution (ESDIAD) and low-energy electron diffraction (LEED) measurements [2,7] showed that the structure of CO on Pt{211} is complex and strongly coverage dependent. For example, at low coverage (0.19 ML) CO adsorbed on every other atop step site and was tilted by 20° [2]. CO adsorption has also been studied on Pt{321} [9,10], Pt{533} [11–18] and Pt6(111) × (111) [19]. In each case CO adsorbed initially at the steps or kinks and then on the terraces.

The only theoretical study of CO adsorption on Pt{211} to date is that of Hammer and co-workers [20]. They found the bridge site on the step edge to be more stable than the atop site with adsorption energies of 210 and $199\,\mathrm{kJ\,mol^{-1}}$ respectively: contrary to all of the experimental evidence [1–7]. It has been suggested that the disagreement is due to either an artifact of the generalized gradient approximation (GGA) or to CO–CO interactions that were not accounted for. However, the

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vibrational frequencies of 1860 and 2080 cm^{-1}, calculated for CO adsorbed in step edge bridge and atop sites respectively on Pt{211}, were in good agreement with experiment [1]. Similar discrepancies have also been noted in calculations on Pt{111}, leading to much discussion of the so-called "CO/Pt(111) puzzle" [21].

2. Methodology

Non-local DFT calculations were performed with DMOL^3 [22] using the GGA approximation of Perdew *et al.* [23]. Localized DNP (double numeric with polarization) basis sets were used, with the Pt atoms treated with effective core potentials whilst the CO electrons were treated explicitly. Whilst it is more common to use plane wave basis sets to represent the wave function of metal surfaces, several recent papers have suggested that localized basis sets can also provide reliable descriptions of metallic systems, whilst having the advantage of being more computationally efficient [24–28]. Periodic slabs were used, with a vacuum gap of 10 Å. The Pt atoms were fixed using the equilibrium bond length determined for the bulk (2.775 Å), to reduce computational cost. Whilst this is clearly an approximation, Hammer *et al.* [20] have shown that the atomic positions for the Pt{211} surface with CO adsorbed are almost unchanged from those of the bulk. There is some relaxation of the clean surface, but reconstruction is noted [29].

The experiments were performed in a UHV apparatus, with a base pressure of $\leq 2 \times 10^{-10}$ mbar, described in detail elsewhere [30]. The Pt{211} sample was cleaned by repeated cycles of Ar ion sputtering at 300 K, oxygen treatment at 900 K in 5×10^{-8} mbar O_2 and annealing at 1050 K. CO (99.97% purity, BOC Ltd.) was dosed into the chamber by means of a high-precision leak valve. RAIRS experiments were performed with the sample held at ~100 K and were recorded using a Mattson Instruments RS1 series FTIR spectrometer coupled to a narrow band MCT detector. All spectra were taken at a resolution of 4 cm^{-1} and are the result of the co-addition of 256 scans. TPD spectra were taken with a Hiden HAL201 quadrupole mass spectrometer at a heating rate of 4 ± 0.05 K s^{-1}.

3. Results and discussion

3.1. *CO/Pt{111}*

Prior to undertaking a study of the {211} surface, we tested our DFT methods on the simpler {111} surface. A slab with a (3 × 3) unit cell, four layers deep with a vacuum gap of 10 Å, was used. Both the atop and bridge site were considered at coverages of 0.25, 0.5 and 1 ML (table 1). The adsorption energy calculated for the atop site at 0.25 ML coverage is 150 kJ mol^{-1}, in good agreement with previous calculated values of 140 kJ mol^{-1} [31] and 152 kJ mol^{-1} [32]. The difference (4 kJ mol^{-1}) between the bridge and atop sites is also in good agreement with the literature [33]. An initial heat of adsorption of 172 kJ mol^{-1} is obtained by extrapolation back to zero coverage, in good agreement with the experimentally determined value of 180 kJ mol^{-1} [34]. Whilst Feibelman *et al.* [21] have identified possible problems with DFT calculations for CO on Pt{111}, our calculations are in reasonable agreement with other calculations [32,33] and with experiment [34]. We note that even calculations at the highest level of theory consistently find the atop site on Pt{111} to be slightly more stable. Hence, whilst the calculated absolute heats of adsorption may vary with the precise method used, we consider that the calculations performed here will provide (at least) qualitative agreement with higher levels of theory and also experiment. We are therefore confident that we are able to compare the relative stabilities of different adsorption sites on Pt.

Table 1
Results of DFT calculations for CO adsorbed on Pt{111}. At a coverage of 1 ML the bridge site energy is approximate as we were not able to find an energy minimum structure

Adsorption site	Coverage (ML)	Heat of adsorption (kJ mol^{-1})	Pt–C bond length (Å)	C–O bond length (Å)
Atop	0.25	150	1.874	1.152
	0.5	124	1.874	1.154
	1.0	79	1.874	1.156
Bridge	0.25	146	1.504	1.175
	0.5	125	1.514	1.172
	1.0	~57	–	–

3.2. CO/Pt{211}

3.2.1. *Calculations*

There are a greater number of possible adsorption sites on the {211} surface compared with a flat surface. Sites investigated here (figure 1, table 2) were the atop and bridge sites on the step edge, two atop sites on the terrace (labeled terrace sites 1 and 2) and two bridge sites on the terrace (a bridge site between two site 2 atoms and a bridge site between a site 1 atom and a step atom). All attempts to find a stable structure with the CO at the bridge site between two site 1 atoms were unsuccessful.

Step edge sites. The atop site on the step edge was initially considered at a coverage of 0.16 ML. The adsorption energy at this site was calculated to be 245 kJ mol^{-1}, much higher than that obtained for Pt{111}, as expected. As in other theoretical calculations [20], the CO molecule is found to adsorb in an upright position. However, the

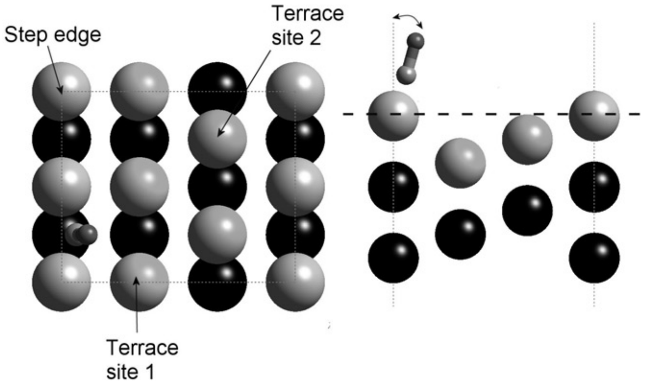

Figure 1. (Left) The (2 × 1) Pt{211} slab used to investigate the adsorption of CO on Pt{211}. The pale circles are the top-layer atoms and the dark circles represent atoms in lower layers. Also marked are the sites for which CO adsorption was calculated. (Right) A side view of the stepped Pt{211} surface showing the optimized geometry for a bridge site. The tilt angle is defined with respect to the normal to the macroscopic surface (indicated as the thick dashed line).

ESDIAD measurements of Yates *et al.* [2] indicate that the atop species is tilted at an angle of 20°.

The bridge site at the step edge was initially considered at a coverage of 0.33 ML. At this site we find the CO tilted by 20° from the surface normal (see figure 1), with a calculated heat of adsorption of 259 kJ mol^{-1}. As indicated above, Yates *et al.* [2] also found CO molecules tilted at the step edge but interpreted their data so to suggest that it was atop molecules that were tilted and not those at bridge sites. We also find that the bridge site is more stable than the atop site, in agreement with Hammer *et al.* [20]. Whilst the absolute values of the heat of adsorption determined here are probably a little high—a likely consequence of fixing the surface geometry, particularly for the clean surface—all the calculations show that adsorption is more favorable on the step sites of Pt{211} than on the flat Pt{111} surface. However, the calculation of a higher heat of adsorption for CO on the step bridge site compared with the step atop site is in direct contrast to our own (see below) and previous experimental measurements [1–7]. We consider, later, possible reasons for such a consistent discrepancy.

Terrace sites. The terrace sites proved much more difficult to optimize successfully than the step edge sites, reflecting the lower stability of the terrace-bound CO species on Pt{211}. Two of the sites considered could not be made to converge to energy minima, and the values given in table 2 are our best estimates from a series of single point calculations. It is clear, however, that all of the terrace sites are much less stable than the step edge sites. For example, the most stable terrace site (atop site 2, farthest away from the step edge) has an adsorption energy some 40–50 kJ mol^{-1} lower than for adsorption at the step sites—further evidence that the step edge is more favorable for adsorption than the terrace. Again, the CO molecule on this terrace site is found to be oriented at ~20° to the surface normal, i.e. perpendicular to the terrace.

3.2.2. *Experimental results*

A series of experiments were also performed in order to ascertain the reliability of the calculations for CO on Pt{211} and to confirm previous observations [1–7]. Details of this work are given elsewhere [30]: only the pertinent results are reported here. RAIRS and TPD experiments were performed with the sample held at ~100 K during CO dosing. By operating at such a low temperature we are able to probe more accurately the potential energy surface and identify the most stable adsorption sites. Such experimental data are also more relevant for comparison to the calculations, which are effectively at 0 K.

RAIR spectra were collected for a series of CO exposures at 106 K (figure 2). The peak at 2071 cm^{-1}, observed at low coverage, corresponds to CO bonded to an atop site, most likely on the step edge, according to both Hammer *et al.* [20] and our calculations. Such step adsorption is also noted in other experimental studies [1–8]. However, all of the theoretical calculations to date suggest that the most stable step site is the bridge site and not the atop site. The difference in adsorption

Table 2

Results of DFT calculations for CO adsorbed on Pt{211}. The results of Hammer and co-workers [20] for the step sites are also included for comparison. For the terrace atop site 1 and terrace bridge site the adsorption energy is approximate, as the structure did not fully optimize. The calculated tilt of the adsorbed CO molecule is defined in figure 1

Site	Coverage (ML)	Heat of adsorption (kJ mol^{-1})	Pt–C bond length (Å)	C–O bond length (Å)	Tilt angle (°)
Step atop [this work]	0.16	245	1.86	1.16	0
Step atop [20]	0.16	200	1.85	1.16	0
Step bridge [this work]	0.33	259	1.47	1.18	20
Step bridge [20]	0.33	211	2.01	1.18	0
Terrace atop site (1)	0.33	~92	–	–	–
Terrace atop site (2)	0.33	211	1.87	1.15	20
Terrace bridge site (2)	0.33	~150	–	–	–
Terrace-step bridge	0.33	206	1.50	1.18	0

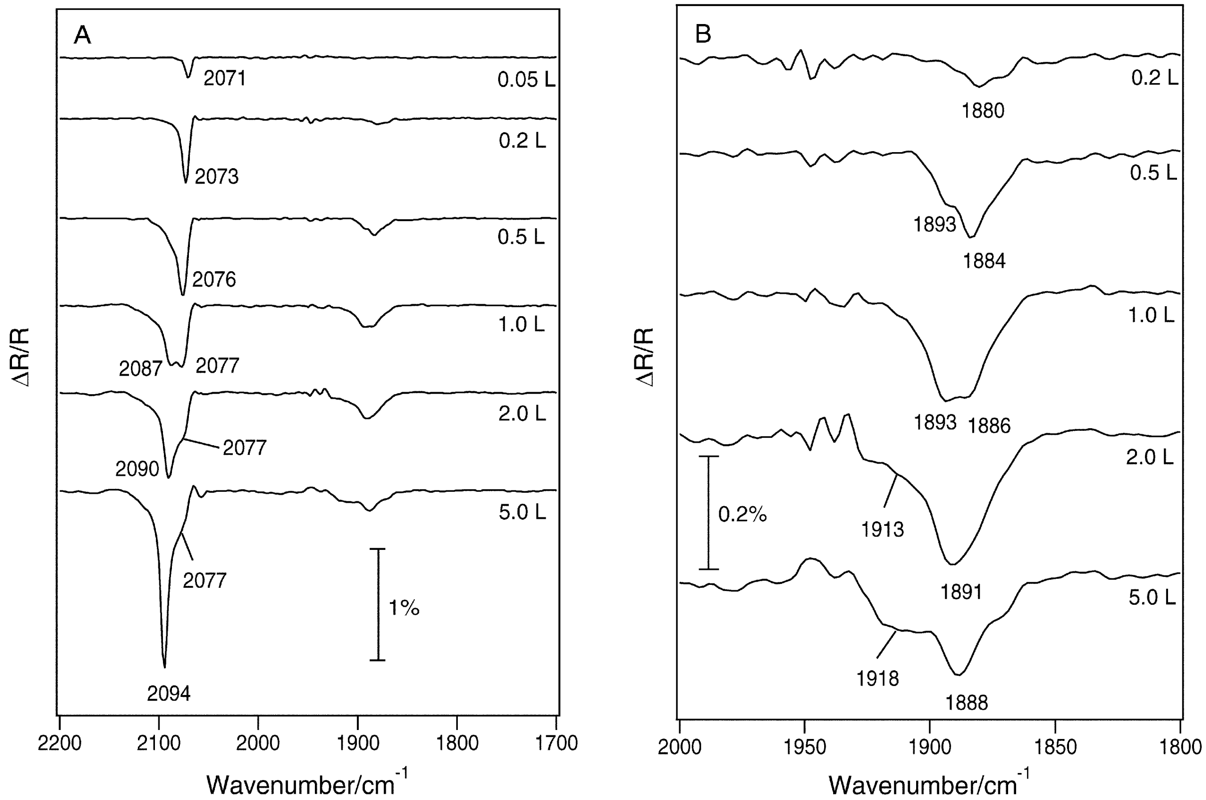

Figure 2. (A) RAIR spectra following exposure of Pt{211} to various doses of CO at 106 K. (B) Close-up of the 1800–2000 cm^{-1} region of the RAIR spectra shown in (A).

energy at these two step sites is calculated by us to be only 14 kJ mol^{-1}. This difference may not be experimentally distinguishable, a suggestion supported by the results of our TPD experiments (see later). Furthermore, the calculations show that the bridged CO on the step edge is tilted by 20°, which would reduce the intensity of the band observed in RAIRS, making it more difficult to detect.

With increasing exposure of the surface to CO (figure 2(A)) the peak increases in intensity and shifts up in frequency, due to dipole coupling, to a maximum wavenumber of 2080 cm^{-1}. At the same time, a second band appears in the spectrum, initially as a shoulder on the 2076 cm^{-1} band (0.5 L exposure), which then shifts in frequency and grows to dominate the spectrum at saturation. The second band can be assigned to the adsorption of CO molecules into atop sites on the terrace, an assignment in agreement with the work of Yates and co-workers [1–7]. This assignment also agrees with our calculations, which show that such a site is the most stable adsorption site (with an adsorption energy of 211 kJ mol^{-1}) on the terrace. Previous studies have shown that there are positive outward dipoles at step sites that decrease the work function [35]. The electric field at the step sites can split the CO orbitals and lower the CO π^* orbital energy, resulting in an increase in back donation from Pt to the CO in the vicinity of the step site [36,37]. Indeed, we find that the charge on CO is consistently higher at the step edge than on the terrace sites in our calculations. Thus, increased back donation causes CO adsorbed at step sites to have a lower vibrational frequency than CO adsorbed at terrace sites, which is consistent with our assignments.

A band is also observed in the RAIR spectra (figure 2) at ~1900 cm^{-1} which increases in intensity with increasing exposure above 0.2 L. The frequency of this band is that expected for CO adsorbed in a bridge site. The intensity of the band is extremely small compared with that seen for the atop bands at ~2100 cm^{-1}: an enlarged view is given in figure 2(B). It is clear that the intensity of this band grows with increasing exposure and two different bridged CO species are present in the spectrum, which, at saturation, give rise to bands at 1918 and 1888 cm^{-1}. It is likely that these species can be assigned to bridged CO at the step edge and bridged CO adsorbed on the terrace. Our calculations show that bridged CO on the step is the most stable species on the surface and that the bridge site between a step and a terrace site is also fairly stable (see table 2). With this in mind, the higher frequency band is assigned to a bridge species between the step and the terrace and the lower frequency band is assigned to a bridged CO species on the step edge. It is not clear why the intensity of the bands is so small, although this observation is in agreement with previous measurements on Pt{211} [1] and Pt{533} [3,17]. It could be that the bridge-bonded CO species are highly

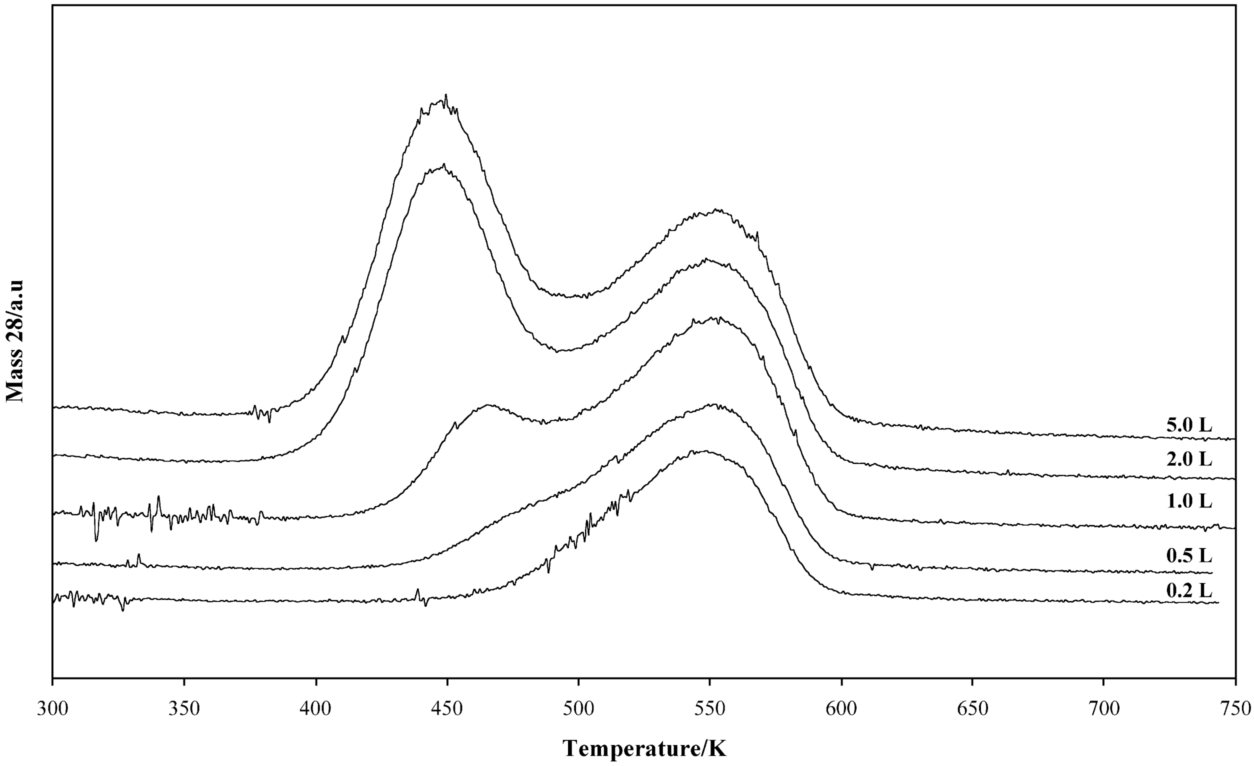

Figure 3. TPD spectra following exposure of Pt{211} to various doses of CO at 110 K. The heating rate was 4 K s^{-1}. No peaks were observed below 300 K and hence this region is not shown.

tilted. Indeed, our calculations do show the bridged CO on the step edge is tilted at an angle of 20°. Alternatively it may be that there are very few bridge-bonded CO molecules present on the surface, implying that the adsorption of CO on Pt{211} is dominated by the formation of atop-bonded CO species.

A series of TPD experiments for increasing CO exposure at 110 K are shown in figure 3. It is clear that a single peak is observed at low exposures with a peak temperature of ~550 K. With increasing exposure a second, low-temperature peak grows in with a peak temperature of ~450 K. These TPD data are in good agreement with previous measurements on Pt{211} [1–3,6] and imply that there are two CO species with different desorption energies present on the surface. At first glance this would seem to be in disagreement with the RAIRS data, which show at least four CO species on the surface. However, our calculations (table 2) show that step atop and bridge species have very similar adsorption energies (245 and 259 kJ mol^{-1}) and so do the two most stable terrace species (the bridge between the step and the terrace has an adsorption energy of 206 kJ mol^{-1} and the terrace atop site 2 has an energy of 211 kJ mol^{-1}). Hence, we assign these two TPD peaks to the desorption of terrace bonded CO at ~450 K and step bonded CO at ~550 K. Further evidence for this assignment comes from a comparison of the TPD data with RAIRS data in figure 2. The band assigned to the terrace-bonded atop CO species (at ~2090 cm^{-1}) is first seen to grow into the spectrum after an exposure of 0.5 L of CO, exactly the same exposure at which the lower temperature peak appears in the TPD, indicating that they are likely to be the same species.

Using the analysis of Redhead for first-order desorption, with an estimated pre-exponential factor of $1 \times 10^{14}\,s^{-1}$ [38], the observed difference of ~100 K between the desorption temperature of the step and terrace CO gives a difference of approximately 27 kJ mol^{-1} in the desorption energy of the two species. This is in good agreement with our calculated difference of ~40 kJ mol^{-1} for adsorption of CO on the step and terrace when extrapolated to zero coverage. We note that this value for the pre-exponential factor should be treated with caution. However, changes in this value of two orders of magnitude change the calculated difference in heat of adsorption by only 4 kJ mol^{-1}.

3.2.3. Comparison of experimental and theoretical results

The experimental evidence in the literature [1–7] and our own data suggest that the atop site on the step edge is more stable than the bridge site. However, all the theoretical studies suggest the converse. Hammer *et al.* [20] have attributed this disagreement to either an artifact of the GGA approximation or to CO–CO interactions that were not accounted for. It is possible that this may also be the case here, particularly given the further approximations made—such as the rigid surface and the use of localized basis sets. However, in addition to these possible sources of disagreement, we make the following comments. First, we note that tilting of the adsorbed molecule is found for a number of sites, experimentally and in the calculations. If the bridged CO species are tilted then they will be more difficult to observe with vibrational spectroscopy. In addition, we note that the calculated difference in adsorption energy for the step atop and bridge species is only 14 kJ mol^{-1} which, as mentioned above, may be difficult to distinguish experimentally. It is common practice to align the crystal surface in RAIRS so as to obtain maximum reflectance of the infrared beam. Here, such an alignment would result in a crystal orientation that would maximize the signal from the atop site, whilst at the same time reducing the response to the tilted bridge site. Hence, although both sites (according to the TPD data) may have similar adsorption energies, their relative contribution to the RAIR spectrum would be considerably different.

We also note the work of Kose [8], who measured the heat of adsorption and sticking probability of CO on Pt{211} at 300 K using single-crystal adsorption calorimetry. A heat of adsorption and sticking probability at zero coverage of 185 kJ mol^{-1} and 0.76 respectively were measured. More significantly a large change in the average heat of adsorption was observed at 0.17 ML, corresponding to a situation where adsorption was occurring at both step and terrace sites. If we now consider the calculations performed here and by Hammer *et al.* [20], they have considered coverages well in excess of 0.17 ML. Such higher coverages are selected to minimize computational expense, by allowing smaller unit cells to be used. However, in addition to reducing the number of atoms considered, such unit cells also impose constraints on the system due to the periodic boundary conditions. Furthermore, the Blyholder model of bonding requires electron transfer between the molecule and the surface. Thus, the larger the unit cell used, the more accurately such electron transfer can be described. For example, by doubling the unit cell size, each molecule at the step edge becomes independent of its neighbor, reducing the constraint of the periodic boundary conditions.

In order to establish the implications of the higher coverage and also any boundary effects, we repeated our calculations using a unit cell doubled in size along the step edge length. In doing so we were able to halve the coverage and reduce the boundary effects by increasing the separation between the adsorbed species. We now find (table 3) that the step atop and bridge sites have adsorption energies of 273 and 284 kJ mol^{-1} respectively; changes of the order of 30 kJ mol^{-1}. Furthermore, when the same coverages as before are now considered in this enlarged unit cell, the charge on the CO is increased showing an enhanced electron transfer, confirming the effect of the periodic boundary conditions. However, there is virtually no change in the optimized geometries. Whilst these results do not resolve the disparity between experiment and theory, they reveal that the small difference due to the choice of functional or basis set may not be the most significant effect. Clearly, in order to determine if coverage, or the presence of simultaneous occupation of different sites (since the adsorption energies are so similar), will resolve the disagreement between experiment and theory requires significant further work.

Table 3
Results of DFT calculations for CO adsorbed on Pt{211} using a unit cell doubled in size along the direction of the step edge

Site	Coverage (ML)	Heat of adsorption (kJ mol^{-1})
Step atop	0.08	273
Step bridge	0.16	284

4. Conclusions

We report here an attempt to combine theoretical and experimental studies to identify the key adsorption sites for CO on the stepped Pt{211} surface. Our calculations suggest adsorption will occur preferentially at the step bridge site, which has a heat of adsorption of 259 kJ mol^{-1}. The atop step site is only marginally less favored with an adsorption energy of 245 kJ mol^{-1}. Adsorption on the terrace is much less favored; an atop terrace site was calculated to have an adsorption energy of 211 kJ mol^{-1}, whilst the bridge site between a step and a terrace atom has a heat of adsorption of 206 kJ mol^{-1}.

Our TPD data are in good agreement with these calculations, with two peaks that can be assigned to desorption of step- and terrace-bound CO. The difference in peak temperatures between these species gives an estimated difference in the desorption energy of the two species of ~30 kJ mol^{-1}: again in good agreement with the calculations. RAIRS experiments are also broadly in agreement with the calculations, as at least four different species are observed in the spectrum. However, in disagreement with the calculations (from this work and others [20]), the RAIRS suggests that it is the atop CO species bonded to the step edge that is the most stable species, not the bridged species.

In an attempt to resolve this contradictory evidence we have shown how coverage and periodic boundary conditions make significant contributions to the calculated structures and energies—certainly of the same order of magnitude as the experimental differences in adsorption energies between the most likely adsorption sites. Furthermore, we suggest that these coverage and simulation size effects are as, if not more, important than methodological differences (such as choice of functional, basis sets, etc.). It is clear that much more intensive computations are necessary to resolve fully this particular "CO/Pt puzzle" [21].

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