



University of Warwick institutional repository: <http://go.warwick.ac.uk/wrap>

This paper is made available online in accordance with publisher policies. Please scroll down to view the document itself. Please refer to the repository record for this item and our policy information available from the repository home page for further information.

To see the final version of this paper please visit the publisher's website. Access to the published version may require a subscription.

Author(s): M.K. Bradley, J. Robinson, D.P. Woodruff

Article Title: The structure and bonding of furan on Pd(111)

Year of publication: 2010

Link to published article:

<http://dx.doi.org/10.1016/j.susc.2010.02.021>

Publisher statement: "NOTICE: this is the author's version of a work that was accepted for publication in Surface Science. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Surface Science, [VOL: 604, ISSUE: 11-12, June 2010, DOI: 10.1016/j.susc.2010.02.021]"

The structure and bonding of furan on Pd(111)

M. K. Bradley, J. Robinson and D. P. Woodruff[♦],
Physics Dept, University of Warwick, Coventry CV4 7AL, UK

Abstract

The structure and bonding of molecular furan, C₄H₄O, on Pd(111) has been investigated using density functional theory (DFT) calculations and the results compared with those of a recent experimental investigation using scanned-energy mode photoelectron diffraction (PhD). The DFT results confirm the orientation of the molecular plane to be essentially parallel to the surface and show a clear energetic preference for one of the two possible structures identified in the PhD study, namely that with the molecule centred over the hollow sites of the surface. Two slightly different geometries at the hollow sites are found to be essentially energetically equivalent; in both cases, one Pd surface atom bonds to two C atoms, while two other Pd atoms each bond to one C atom. These structures differ in that in one case the pair of C atoms bonding to a single Pd atom are both β -C (C atoms not bonded to O in the furan molecule), whereas in the second case this pair of C atoms comprises one β -C and one α -C (adjacent to the O atom in furan). In both structures the C-Pd bonding is accompanied by displacements of the H and O atoms away from the surface and out of the molecular plane and local C-Pd coordination consistent with a rehybridisation of the C bonding to sp³ character.

Keywords: surface structure; chemisorption; Pd; furan

[♦] corresponding author: email d.p.woodruff@warwick.ac.uk

1. Introduction

Furan, C_4H_4O , is the simplest oxygen-containing aromatic hydrocarbon, and is often used as a model in hydrodeoxygenation studies of such compounds that need to be removed from crude petroleum and liquids derived from coal and biomass [1]. Despite this, there have been rather few surface science investigations of this molecule on well-characterised single crystal surfaces. On the clean noble metal surfaces, Cu(110) [2] and Ag(110) [3], the molecule adsorbs and desorbs intact. On Pd(111) furan adsorbs intact at low temperatures, but around room temperature deoxygenation occurs with the production of CO [4, 5, 6]. Indeed, there is some evidence of partial formation of surface benzene through coupling of a C_3H_3 surface intermediate, although no benzene is produced in the gas phase as this molecule dissociates on Pd(111) on heating. For the Pd(111)/furan system, there is also some experimental structural information. By the application of dipole selection rules in high-resolution electron energy loss spectroscopy (HREELS), Ormerod *et al.* [4] have proposed that, at least at high coverage, the intact furan molecule neither lies flat on the surface nor with its molecular plane perpendicular to the surface, but a quantitative value of the molecular tilt angle cannot be obtained from this technique. Scanning tunnelling microscopy (STM) studies of this adsorption system have been shown to yield images consistent with an essentially flat-lying geometry [7, 8], at least at low coverages. Most recently, a combined near-edge X-ray absorption spectroscopy (NEXAFS) and scanned-energy mode photoelectron diffraction (PhD) investigation [9] has concluded that the molecule does lie flat on the surface to relatively high coverages, and has also identified some preferred adsorption sites. In order to distinguish these alternative bonding structures and remove their associated ambiguity, and to understand the nature of the molecule-substrate bonding, we report here the results of a density functional theory (DFT) study of this adsorption system. In fact one previous DFT investigation of this system has been undertaken [10], but unfortunately this earlier work is only reported in a doctoral thesis. While many aspects of the results of this earlier study are closely similar to our own, there are some important differences. In particular, we find a lowest-energy structure, of reduced symmetry, that was not investigated in the

earlier work. Moreover, our calculations provide additional structural parameter values, not presented previously, that can provide a more complete basis for comparison with the experimental results.

2. Computational details

The DFT calculations reported here were conducted using the Cambridge Serial Total Energy Package (CASTEP4.3) code [11] which utilises a plane wave pseudopotential formalism. The Revised Perdew-Burke-Ernzerhof edition of the Generalized Gradient Approximation (GGA-RPBE) exchange-correlation functional was used throughout the investigation along with ultrasoft pseudopotentials. Additional calculations using GGA-PW91 (Perdew-Wang91) were also performed for comparison. Ensemble DFT (EDFT) electronic minimisation was implemented using a conjugate gradient minimiser with a Gaussian density smearing width of 0.05eV. Geometric convergence tolerances were set for force at 0.05eV/Å, energy at 0.00002eV/atom, and displacement at 0.001 Å, although close inspection of the optimisation in all cases was used to ensure reliable convergence had been achieved. The calculated bulk Pd fcc lattice constant for the GGA-RPBE calculations was 3.922 Å, approximately 1% greater than the experimental value [12, 13]. In GGA-PW91 this lattice constant was found to be 3.909 Å.

The slab calculations used to investigate the furan adsorption included one adsorbed molecule per (3x3) surface mesh (corresponding to a coverage of 0.11ML) with three Pd layers, corresponding to a total of 36 atoms per unit supercell (27 Pd, 4 C, 4 H, and 1O). A supercell height of 20 Å gave a vacuum region of at least 11 Å in all models tested. Test calculations with an additional (fourth) substrate layer caused only small changes (< 0.01 Å) to bond lengths at the surface and no appreciable change to adsorption energy. In all cases the Pd atoms in the top two substrate layers were allowed to relax independently while the bottom substrate layer was constrained to bulk positions. These calculations used a plane wave cutoff of 360 eV and a (7,7,1) k-point sampling mesh (25 inequivalent k-points). Extensive tests on the convergence criteria with respect to the energy cut-off, vacuum gap, and size of the unit mesh to avoid unintended intermolecular interactions,

were performed to determine these parameters. The rather dense k-point sampling of the small reciprocal net is almost certainly more than necessary, but allows a more direct comparison with the previous LDA results of Loui [10].

Reference calculations for the clean surface slab yielded an outwards relaxation of the outermost layer of 0.010 Å. This very small value is consistent with the general trend of almost bulk-like terminations of fcc (111) surfaces and such a small value challenges the precision of any of the available experimental methods; a detailed LEED investigation yielded a value for this parameter of 0.03 ± 0.03 Å [14].

In order to determine the adsorption energies associated with the optimised (minimum energy) structural models calculations were also performed on an isolated furan molecule within an orthorhombic unit cell having sufficiently large dimensions to ensure negligible intermolecular interactions (20 Å x 20 Å x 20 Å). As shown in Table 1, the resulting molecular conformation is in excellent agreement with experimental determinations [15, 16] and with the results of two earlier DFT studies [10, 17]. The labelling convention for the atoms in the furan ring, used for defining the bondlengths and bond angles in this table, is shown in Fig. 1, and follows the labelling used in the experimental structure determination for the molecule adsorbed on Pd(111) [9]. All bondlengths from our calculations agree with one or both of the experimental values within better than 0.02 Å, while the largest discrepancy in bond angles is 0.8°. The scatter of these values in the three calculations is never larger, and in most cases smaller, than these differences. Moreover, the results of our PW91 (not shown) and RPBE calculations agree in the molecular geometrical parameters to within 0.002 Å and 0.1°.

Optimisation of the adsorption geometry for furan on Pd(111) was then undertaken without the imposition of symmetry constraints, starting from a range of geometries shown in Fig. 2, essentially equivalent to the structures explored in the experimental PhD investigation [9]. Note that these models all assume the molecular plane is approximately parallel to the Pd(111) surface, consistent with the experimental NEXAFS and PhD

results, but the DFT optimisation procedure clearly allows the molecules to tilt if this proves to be energetically advantageous.

3. Results and data analysis

Table 2 summarises the adsorption energies, E_a , where

$$E_a = E(\text{clean surface}) + E(\text{furan}) - E(\text{surface} + \text{adsorbed furan})$$

(i.e. the adsorption energy is defined as positive when adsorption is favoured), for the different optimised structural models, including a comparison with comparable values for the models tested in the earlier LDA calculations of Loui [10]. The numerical labels (2a, 2b etc.) assigned to the starting models in the experimental PhD study are also included in Table 2 to simplify comparison, but here we prefer to use the more descriptive names for these structures shown in Fig. 2. Note that no stable adsorption structure was obtained for either the atop or the cross-bridge model using the RPBE functional; in both cases successive iterations in the DFT calculations displaced the molecule further and further from the surface, and led to it adopting the free-molecule conformation. There are four lowest-energy structures with almost identical adsorption energies, all of which correspond to adsorption at, or close to, the two ‘hollow’ sites with the molecule approximately centred over either the hcp hollow (directly above a second-layer Pd atom) or the fcc hollow (directly above a third-layer Pd atom). The adsorption energies are essentially identical when located equivalently relative to either the fcc or hcp hollow. Notice that the two ‘bridging’ geometries form a similar pair, having essentially the same adsorption energy and the same geometry with respect to the outermost Pd atoms layer, the difference only being related to their juxtaposition to the second and third Pd layers. This insensitivity to the distinction between hcp and fcc hollow sites is not surprising. Even for atomic adsorbates, that can typically bond closer to the surface in hollow sites, the energetic distinction between fcc and hcp hollow sites on fcc(111) surfaces is small, although in most (but not all) such cases the fcc sites prove to be energetically preferred (as judged by experimental structure determinations). However, even for simple molecules that bond to the surface through a single atom in hollow sites this is no longer the case. For example, CO adsorption (bonding through the C atoms with the molecular

axis perpendicular to the surface) on Ni(111) leads to equal occupation of the two inequivalent hollow sites. For molecules that bond to such a surface through two or more atoms, typically in a ‘lying-down’ orientation, the energetic difference between hcp-related and fcc-related sites appears to be even smaller, as interaction with second-layer atoms is now negligible. Table 2 shows that the relative adsorption energies of the different optimised structures are almost identical using the RPBE and PW91 functionals, although the absolute energies differ considerably.

The energetic preference for the hollow, rather than bridge, geometries is ~ 0.24 eV and is also reproduced by the earlier calculations of Loui (who did not consider the off-hollow geometries), although the absolute magnitudes of the adsorption energies in the two sets of calculations is very large, differing by more than 1.7 eV. Qualitatively, at least, this difference may be assigned to the established tendency for LDA calculations to over-bind, and GGA calculations to under-bind, although the size of the difference is surprising. An experimental estimate of the furan desorption energy at a coverage of 0.17 ML obtained using laser-induced thermal desorption is 1.03 ± 0.26 eV, approximately a factor of two greater than our calculated value and a factor of two less than that given by Loui’s LDA calculations. As a further check, we have also run LDA calculations for all of the structures of Table 2 and find even larger adsorption energies (by ~ 0.25 eV) than those reported by Loui. The difference between our calculations and those of Loui may, perhaps, be due to the use of different ultrasoft pseudopotentials as he reports a slightly different value (3.859 \AA) for the bulk lattice parameter to the one we calculate (3.842 \AA). The key conclusion, however, is that LDA is strongly overbinding, while the GGA-RPBE calculations lead to strong underbinding. This result, and the fact that GGA-PW91 gets the adsorption energy approximately correct, is consistent with the results of a recent detailed study of thiophene bonding on Cu(110), in which the choice of appropriate functionals and associated approximations is discussed in detail [18]. This paper also considers the role of dispersion forces that are not accounted for in standard DFT calculations and concludes that, in effect, pure GGA-PW91 calculations get about the right adsorption energy for the wrong reasons; a more correct description comes from GGA-RPBE plus the non-local dispersion forces. Recent calculations exploring ways of

accounting for these effects have been undertaken not only for the adsorption of thiophene, but also for other cyclic aromatic molecules, namely benzene, pyridine and pyrazine [19] on Cu(110). In all of these cases adding the effects of van der Waals interactions increases the adsorption energy (by up to ~ 0.5 eV) although the consequences for the minimum energy structures differs. For pyridine and pyrazine large (~ 0.4 Å) changes in adsorbate-substrate bondlengths accompany the inclusion of the dispersion forces, but for benzene and thiophene (the species most similar to furan) this is not the case. As we will show below, the results of our calculations yield adsorbate-substrate bondlengths in excellent agreement with experiment, reinforcing the view that furan appears to behave more like thiophene. Specifically, while our pure GGA-RPBE may seriously underestimate the adsorption energy, the resulting structure, the property of interest here, is correct.

A primary objective in conducting these calculations was to supplement or test the information obtained from the experimental PhD structure determination of this system. This study identified four possible adsorption geometries, but two of these were distinguished from the other two only by their location relative to fcc and hcp hollows. Evidently, this failure to distinguish the structures that differed only in their location relative to the subsurface layers (fcc or hcp) is also a feature of the DFT calculations; our results show the energies to be so similar that one must expect co-occupation of such sites to occur with equal probability. In fact the four structures identified in the PhD investigation correspond to the fcc and hcp versions of the hollow and bridge geometries of Table 2. Our calculations are therefore qualitatively consistent with the experiments in that both identify the hollow sites as possible solutions, the DFT results indicate that, in reality, it is only the hollow sites, and not the bridge sites, that are occupied. The fact that the DFT calculations also indicate that co-occupation of the off-hollow site must occur does not, as we show below, conflict with the information obtained from the PhD experiments.

Figures 3 and 4 show the exact geometry of the adsorbed furan in the hollow and off-hollow sites, respectively. For each structure a top view shows the lateral position of the

molecule while a side view shows the tilt and out-of-plane distortion of the molecule induced by the adsorption. In each case a perspective view is also shown that identifies the Pd-C local bonds. It is these perspective views that show most clearly the distinction between the hollow and off-hollow geometries. In both structures, one of the three nearest-neighbour Pd atoms lies at a bonding distance from two adjacent C atoms in the furan, while the remaining two Pd neighbours are located at bonding distances from the other two C atoms. In the more-symmetric hollow sites it is the two β -C atoms that appear to bond to a single Pd atom, but in the off-hollow structures it is, instead, one β -C atom and the adjacent α -C atom that are at a bonding distance from a single Pd neighbour. The implication is that in all of these structures each carbon is bonded to four other atoms, namely one Pd atom, one H atom and either two C atoms or one C atom and one O atom. Moreover, a consequence of the adsorption is that both the H and O atoms buckle out of the molecular plane. The result is that the C atoms all achieve near-tetrahedral bonding angles, consistent with essentially sp^3 bonding character. On the basis of the optimal geometries, therefore, it appears that this is driven by the change in C bonding character.

A more quantitative comparison of our new theoretical results and those of the PhD experiments is also possible, and this is shown in Table 3. Structural parameters for the optimised geometries are given only for the GGA-RPBE calculations, but the results for the GGA-PW91 calculations differ, at most, by 0.02 Å and 0.2°. In making this comparison it is important to take account of exactly what was determined, and what was inferred, in the experimental results. In particular, in the experiments it proved possible to analyse only PhD data from the α -C component of the C 1s photoemission. The PhD modulations from the β -C component proved too weak to be reliably distinguished from noise, while no O 1s PhD could be used due to the overlap of the O 1s and Pd 3p_{3/2} photoemission signals. In effect, therefore, the experiments were only able to determine the location of the α -C atoms relative to the Pd(111) substrate. The influence of intramolecular scattering in the α -C PhD also provided information of limited precision on the molecular tilt relative to the surface plane, though inferred locations of the β -C and O atom locations (shown in parentheses in Table 3) were based on the assumption that

the C and O atoms all remained coplanar. As the DFT results clearly indicate that the O atom is significantly displaced out of the plane defined by the four C atoms, even for the symmetric hollow sites, it is clear that one may expect a large systematic error in the O atomic position determined by the PhD study, and for this reason these values are placed in double parentheses in Table 3. We should finally remark that in an attempt to narrow the range of possible adsorption structures, the experimental data analysis was conducted on the assumption that the adsorbed molecule and the outermost Pd layer retained a common mirror plane. As such, the off-hollow geometry of Table 2 was not considered in the final optimisation of the experimentally-determined structure. In view of the sparse experimental data set, and doubled number of local structural parameters associated with the inequivalent locations of the two α -C atoms in the off-hollow geometry, it is clear that relaxing the constraints of the experimental data analysis would be most unlikely to lead to a unique and reliable distinction of the hollow and off-hollow geometries, or of any significant refinement of the best-fit structure.

Bearing in mind these constraints, the most meaningful comparison of experiment and theory in Table 3 are those relating to the location of the α -C atoms relative to the Pd(111) substrate, namely the nearest-neighbour α -C-to-Pd distance, $d_{\text{Pd-}\alpha\text{-C}}$, and the offset (parallel to the surface) of the α -C atoms relative to this nearest-neighbour Pd atoms, shown in Table 3 as ‘ α -C off-atop’. For these parameters the agreement between the theoretical result for the hollow site and experiment is generally good; particularly good is the agreement in the Pd-C bondlength, the parameter to which the experiment is most sensitive. For the off-hollow geometry, however, the DFT results lead to two different values of $d_{\text{Pd-}\alpha\text{-C}}$: the shorter one (2.10 Å) corresponds to the α -C that bonds to a Pd atom that bonds only to this C atom, whereas the longer bondlength of 2.21 Å corresponds to the α -C that bonds to a Pd neighbour that also bonds to the adjacent β -C atom. Notice, though, that the shorter of these bonds in the DFT calculation is slightly shorter than the experimental value, and the average of these two bondlengths (2.15 Å) is within the estimated precision of the experimental value. Moreover, if we assume, as indicated by the calculated adsorption energies, that the hollow and off-hollow geometries are co-occupied with equal probability, there are, in total, three short α -C-Pd

bonds and just one longer one. The weighted mean of the DFT bondlengths (the quantity measured in the PhD technique in such a situation) is then 2.13 Å, exactly the value obtained in the experiments. The agreement is somewhat less good between experiment and theory for the off-atop displacement, but for this parameter, too, the co-occupation of the off-hollow site is consistent with the experimental results, the off-atop displacement for this geometry being closer to that measured in the experiment.

4. General Discussion and Conclusions

It is interesting to compare the situation for adsorbed furan with the bonding of the closely-related thiophene molecule, C₄H₄S, on transition metal surfaces. Although there appear to be no published DFT (or experimental structure determination) studies of thiophene adsorption on Pd(111), an investigation has been published on Pd(100), also covering Ni(100) and Cu(100) [20]. On Pd(100), at least, a stable molecular chemisorbed state of thiophene exists with the molecular plane essentially parallel to the surface, and the calculations indicate a similar out-of plane displacement of the H atoms. However, the upward shift of the S atom is small and the S-Pd nearest-neighbour distance is small enough (2.32 Å) that one may infer local bond formation. Consistent with this formation of a S-Pd bond is a lengthening of the S-C bonds from 1.71 Å in the gas phase to 1.80 Å on the Pd(100) surface. By comparison, thiophene adsorbs only weakly on Cu(100) and desorbs intact at 150-240 K [21], and the calculations show the S-C bondlength to be only marginally longer than in the gas phase. On Ni(100) the bonding is even stronger than on Pd(100), and dissociation occurs around 90-100 K [22], but below this temperature range a stable chemisorbed species is found with an even shorter metal-S bond and a longer S-C bond than is found on Pd(100) [20, 23]. These theoretically-computed bondlengths are generally in good agreement with experimental measurements [23, 24, 25]. Of course, S is a significantly larger atom than O, so the difference in terms of the interaction of S and O with the underlying substrate may be, at least partially, steric in origin. The rehybridisation of the C bonding in furan pushes the O atom sufficiently far from the surface that the O-Pd interaction must be very small. A similar distortion in thiophene fails to achieve the same large separation of the S atom and the underlying

substrate, and the resultant S-metal interaction therefore has an impact on the molecular conformation. The rather modest increase in the O-C nearest-neighbour distance in furan on adsorption of $\sim 0.04 \text{ \AA}$ (Table 3) is also consistent with the absence of O-metal interaction; this small increase is probably attributable mainly to the influence of the formation of the α -C-Pd bond. As may be expected the increase in the bondlength between the α -C and β -C atoms ($\sim 0.09 \text{ \AA}$) is significantly larger.

In summary, the results of our DFT calculations present a rather clear picture of the local bonding and geometry of furan on Pd(111). The clear preference for hollow-site occupation is consistent with the results of the earlier theoretical calculations of Loui, but the identification of two slightly different hollow and off-hollow geometries that differ in terms of which pair of adjacent C atoms bond to a single Pd surface atom is new. The almost identical adsorption energy of these two structures is slightly surprising, but the nature of the bonding is so similar that one would certainly expect their energetic difference to be small. These minimum energy structures resolve the ambiguity of the experimental PhD investigation regarding the structure, and are clearly consistent with the key findings of these experiments.

Table 1

Comparison of the interatomic bond lengths, d , and bond angles, θ , of gas-phase furan obtained from experimental results by Bak *et al.* [15] and by Liecheski and Rankin [16] with the results of the GGA-RPBE calculations performed here, and of two earlier DFT calculations. The naming convention for the atoms in the furan ring used here are shown in Fig. 1.

Parameter	Bak <i>et al.</i> [15]	Liecheski & Rankin [16]	This work GGA-RPBE	LDA [10]	B3LYP [17]
$d(\text{O}:\alpha\text{-C})$ (Å)	1.362	1.364	1.361	1.354	1.364
$d(\alpha\text{-C}^1:\beta\text{-C}^1)$ (Å)	1.361	1.364	1.350	1.353	1.360
$d(\beta\text{-C}^1:\beta\text{-C}^2)$ (Å)	1.431	1.430	1.419	1.418	1.436
$d(\text{H}:\alpha\text{-C})$ (Å)	1.075	1.086	1.076	1.079	1.079
$d(\text{H}:\beta\text{-C})$ (Å)	1.077	1.086	1.076	1.081	1.080
$\theta(\alpha\text{-C}^1:\text{O}:\alpha\text{-C}^2)$ (°)	106.6	106.7	106.6	107.1	106.8
$\theta(\text{O}:\alpha\text{-C}^1:\beta\text{-C}^1)$ (°)	110.7	110.5	110.3	110.2	110.5
$\theta(\alpha\text{-C}^1:\beta\text{-C}^1:\beta\text{-C}^2)$ (°)	106.1	106.1	106.4	106.3	105.6
$\theta(\beta\text{-C}^1:\beta\text{-C}^2:\text{H})$ (°)	127.9	127.9	127.1	127.2	127.9
$\theta(\text{O}:\alpha\text{-C}^1:\text{H})$ (°)	115.9	117.3	116.0	116.0	115.8

Table 2

Comparison of the adsorption energies for furan in the optimised versions of the structural models illustrated in Fig. 2. The bracketed labels of the structural models (1a, 2b etc.) are the nomenclature used in the earlier PhD experimental study [9].

Model	Adsorption energy (this work GGA-RPBE) (eV)	Adsorption energy (this work GGA-PW91) (eV)	Adsorption energy (Loui [10], LDA)
atop (1a)	Not bonding	Moves to cross-bridge site	-
cross-bridge (1b)	Not bonding	0.775	-
bridge-h (2a)	0.204	0.855	1.969
bridge-f (3a)	0.203	0.857	1.976
hollow-h (3b)	0.446	1.103	2.184
hollow-f (2b)	0.448	1.104	2.144
off-hollow-h (4a)	0.446	1.101	-
off-hollow-f (4b)	0.443	1.108	-

Table 3: Optimised adsorbate-substrate structural parameter values for the hollow-h and off-hollow-h structural models of furan on Pd(111) obtained in this study from the GGA-RPBE calculations compared with results of the experimental PhD investigation [9] and of the LDA calculations of Loui [10] for the hollow-h structure. The hollow-f and off-hollow-f geometries have essentially identical parameter values to these of the -h structures. Note that the PhD study only determined directly the location of the α -C atoms on the surface; the values for $d_{\text{Pd-}\beta\text{-C}}$ (bracketed) and $d_{\text{Pd-O}}$ were obtained from the combination of the site of the α -C atoms and the optimised value of the molecular tilt, assuming that the complete furan ring is planar. For the O atom, in particular, the DFT calculations clearly indicate that this assumption is not valid, leading to a large systematic error in the experimental value of $d_{\text{Pd-O}}$ which is therefore shown in double-brackets. The ‘oop’ (out-of-plane) angles are relative to the plane defined by the four C atoms for the symmetric hollow sites, and defined relative to the nearest C atoms for the distorted off-hollow geometry. α is the tilt angle of the molecular plane defined by the C atom plane away from the surface; for the off-hollow site this plane is distorted so a representative range of values is given. Also included in the table are a few intramolecular structural parameter values taken from Table 1 to allow comparison with the values following adsorption.

parameter	Free molecule (this study)	Experiment [9] model 3b (hollow-h)	This study hollow-h	This study off-hollow-h	Loui [10] hollow-h
$d_{\text{Pd-}\alpha\text{-C}}$ (Å)	-	2.13±0.03	2.11	2.10, 2.21	2.07
$d_{\text{Pd-}\beta\text{-C}}$ (Å)	-	(2.34±0.14)	2.23	2.13, 2.25	2.21
$d_{\text{Pd-O}}$ (Å)	-	((2.42±0.08))	2.81	2.80, 2.96	2.77
$\alpha\text{-C off-atop}$ (Å)	-	0.59±0.06	0.44	0.50, 0.57	-
$\beta\text{-C off-atop}$ (Å)	-	0.91±0.06	0.97	1.03, 0.83	-
O off-atop (Å)	-	1.41±0.02	1.52	1.45	-
O oop angle (°)	0	0 assumed	21.1	14.7, 16.0	-
H($\alpha\text{-C}$) oop angle (°)	0	-	54.4	28.5, 58.1	-
H($\beta\text{-C}$) oop angle (°)	0	-	21.6	18.7, 37.4	-
$d(\text{O}:\alpha\text{-C})$ (Å)	1.36	-	1.40	1.37, 1.41	1.39
$d(\alpha\text{-C}^n:\beta\text{-C}^n)$ (Å)	1.35	-	1.44	1.40, 1.46	1.45
$d(\beta\text{-C}^1:\beta\text{-C}^2)$ (Å)	1.42	-	1.41	1.44	1.43
α (°)	-	4±7	0.3	5.4-7.3	-

Figure Captions

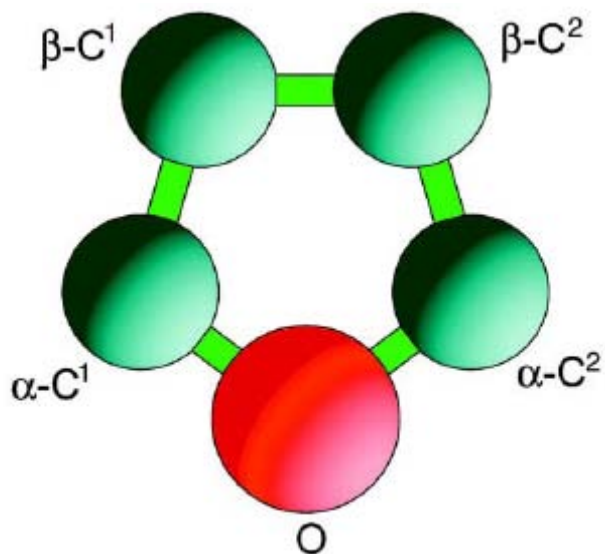


Fig. 1 Schematic diagram of the furan molecule (with H atoms omitted) showing the labelling convention for the constituent atoms used in the text.

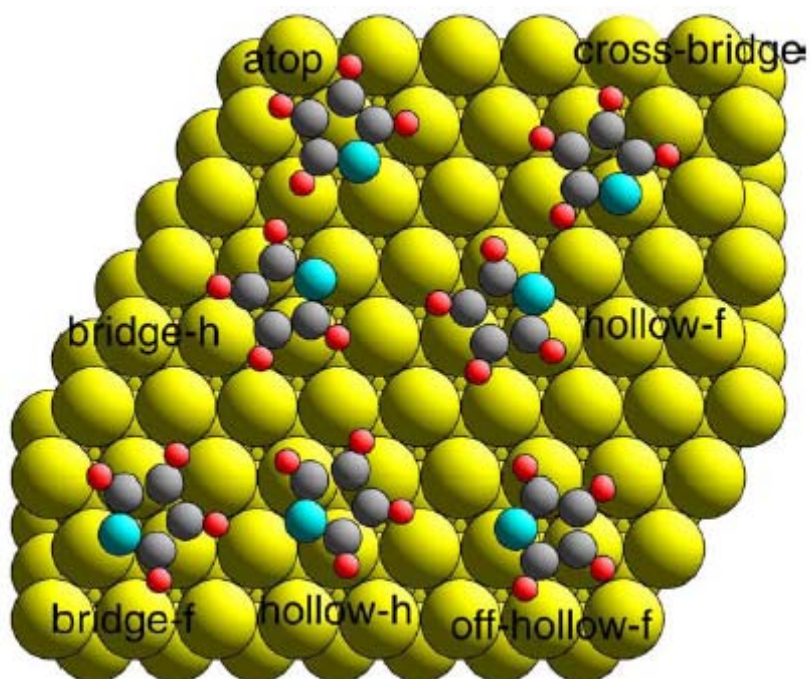


Fig. 2 Basic starting models used in exploring the optimal structure of furan on Pd(111).

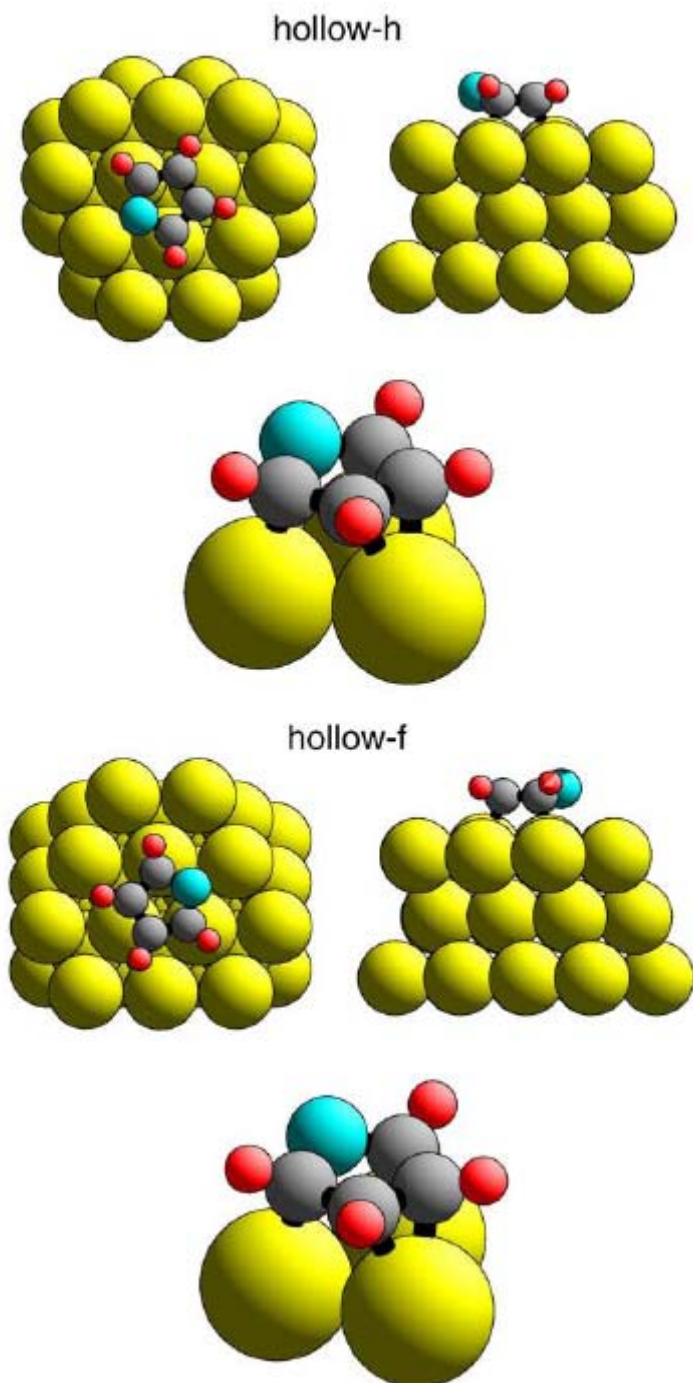


Fig. 3 Schematic diagrams of the two optimised hollow-site models. For each structure a top and side view is shown, together with a perspective view showing the local C-Pd bonds to three nearest-neighbour Pd atoms. Note that one Pd atom is bonded to both β -C atoms.

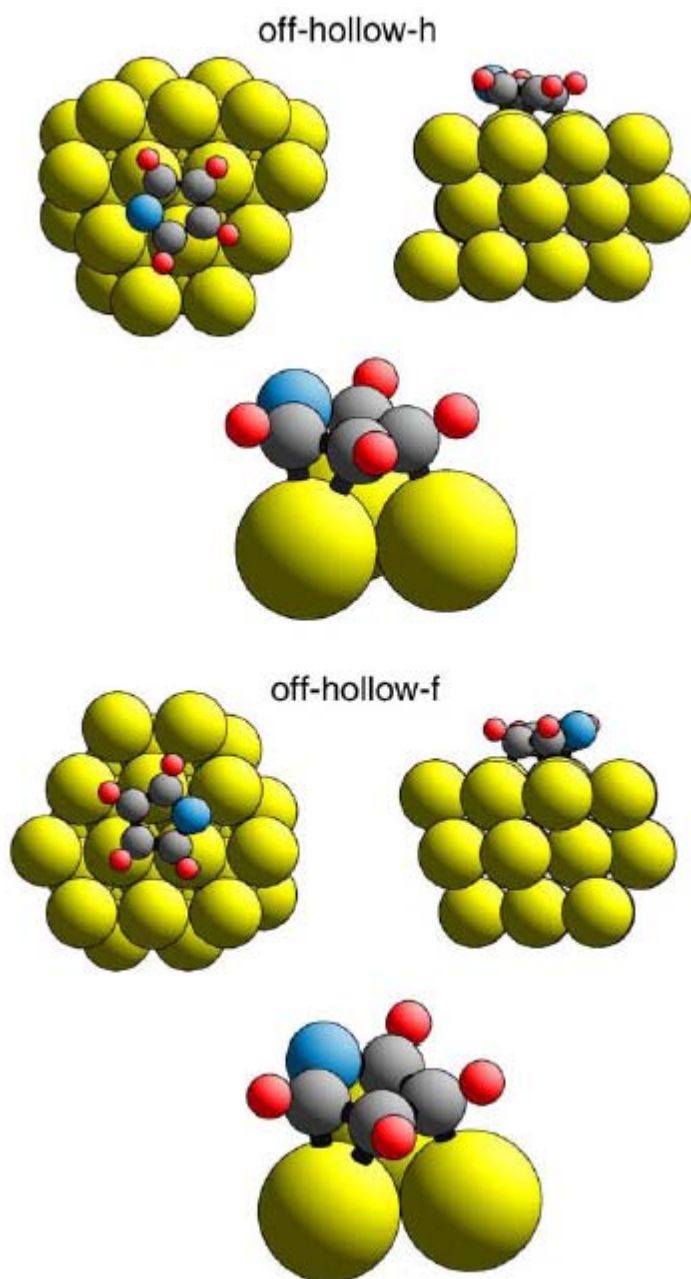


Fig. 4 Schematic diagrams of the two optimised off-hollow-site models. For each structure a top and side view is shown, together with a perspective view showing the local C-Pd bonds to three nearest-neighbour Pd atoms. Note that one Pd atom is bonded to one β -C atom and one α -C atom.

References

- 1 E. Furimsky, *Catal. Rev. Sci. Eng.* 25 (1983) 421
- 2 B. A. Sexton, *Surf. Sci.* 163 (1985) 99
- 3 J. L. Solomon, R. J. Madix, J. Stöhr, *J. Chem. Phys.* 94 (1991) 4012
- 4 R. M. Ormerod, C. J. Baddeley, C. Hardacre, R. M. Lambert, *Surf. Sci.* 360 (1996) 1
- 5 T. E. Caldwell, I. M. Abdelrehim, D. P. Land, *J. Am. Chem. Soc.* 118 (1996) 907
- 6 T. E. Caldwell, D. P. Land, *J. Phys. Chem. B* 103 (1999) 7869
- 7 D. N. Futaba, S. Chiang, *J. Vac. Sci. Technol. A* 15 (1997) 1295
- 8 A. Loui, S. Chiang, *Appl. Surf. Sci.* 237 (2004) 559
- 9 M. J. Knight, F. Allegretti, E. A. Kröger, M. Polcik, C. L. A. Lamont, D. P. Woodruff, *Surf. Sci.* 602 (2008) 2524
- 10 A. Loui, PhD. Thesis, University of California at Davis, 2005
- 11 S.J. Clarke, M.D. Segall, C.J. Pikard, P.J. Hasnip, M.I.J. Probert, K. Refson, M.J. Payne, *Z. Kryst.* 220 (2005) 567
- 12 I.S. Balbaa, P.A. Hardy, A. Sanmartin, P.G. Coulter, F.D. Manchester. *J. Phys. F: Metal Physics*, 17 (1987) 2041.
- 13 W.H. King and F.D. Manchester. *J. Phys. F: Metal Physics*, 8 (1978) 15.
- 14 H. Ohtani, M.A. Van Hove, G.A. Somorjai, *Surf. Sci.* 187 (1987) 372.
- 15 B. Bak, D. Christensen, W.B. Dixon, L. Hansen-Nygaard, J.R. Andersen, M. Schottlander, *J. Mol. Spect.* 9 (1962) 124.
- 16 P.B. Liescheski, D.W.H. Rankin, *J. Mol. Structure*, 196 (1989) 1.
- 17 J.S. Kwiatkowski, J. Leszczynski, I. Teca, *J. Mol. Structure*, 436-437 (1997) 451.
- 18 P. Sony, P. Puschnig, D. Nabok, C. Ambrosch-Draxl, *Phys. Rev. Lett.* 99 (2007) 176401
- 19 N. Atodiresei, V. Caciuc, P. Lazić, S. Blügel, *Phys. Rev. Lett.* 102 (2009) 136809
- 20 H. Orita, N. Itoh, *Surf. Sci.*, 550 (2004) 177
- 21 B.A. Sexton, *Surf. Sci.* 163 (1985) 99
- 22 F. Zaera, E.B. Kollin, J.L. Gland, *Langmuir*, 3 (1987) 555
- 23 A. Imanishi, S. Yagi, T. Yokoyama, Y. Kitajima, T. Ohta, *J. Elect. Spectrosc.* 80 (1996) 151

-
- 24 S. Terada, T. Yokoyama, M. Sakano, A. Imanishi, Y. Kitajima, M. Kiguchi, Y. Okamoto, T. Ohta, *Surf. Sci.* 414 (1998) 107
- 25 A. Imanishi, T. Yokoyama, Y. Kitajima, T. Ohta, *Bull. Chem. Soc. Japan*, 71 (1998) 831