We review first-principles calculations relevant to the adsorption of aromatic molecules on metal surfaces. Benzene has been intensively studied on a variety of substrates, providing an opportunity to comment upon trends from one metal to another. Meanwhile, calculations elucidating the adsorption of polycyclic aromatic molecules are more sparse, but nevertheless yield important insights into the role of non-covalent interactions. Heterocyclic and substituted aromatic compounds introduce the complicating possibility of electronic and steric effects, whose relative importance can thus far only be gauged on a case-by-case basis. Finally, the coadsorption and/or reaction of aromatic molecules is discussed, highlighting an area where the predictive power of theory is likely to prove decisive in the future.

Keywords: density functional theory; adsorption; aromatic molecules; metal surfaces

1. Introduction

Aromatic molecules constitute a large and important class of organic compounds, whose unique properties and ubiquitous nature render them central to much of modern chemistry. Unsurprisingly, therefore, the surface science of such molecules has long been of interest, both on semiconductor surfaces (where the emphasis is upon adsorbate-induced modification of substrate electro-optical properties) and on metal surfaces (where substrate-induced modification of adsorbate chemical properties is more to the point). Substantial experimental literature exists in both fields, and the interested reader is referred to appropriate reviews for more information (Zaera 1995; Wolkow 1999; Filler & Bent 2003; Held 2003; Barlow & Raval 2003; Witte & Wöll 2004).

Since around the turn of the millennium, however, experimental investigations of aromatic adsorption have been supplemented by state-of-the-art calculations, carried out within the framework of first-principles density functional theory (DFT). As regards surface DFT calculations, the phrase ‘state-of-the-art’ is here taken to imply use of at least the following: (i) a slab-based geometry, with a sufficiently thick slab for convergence, (ii) full relaxation of both the adsorbate
and enough layers of the slab to ensure convergence, (iii) a generalized gradient approximation (GGA) for the exchange-correlation functional, and (iv) either a projector-augmented wave or an ultrasoft pseudopotential description of the electron–ion interaction. These calculations have shed light upon the nature of the adsorbate–substrate bond, aided in the interpretation of experimental studies, and pointed the way towards a systematic understanding of aromatic reactivity. Equally, it must also be recognized that while DFT seemingly succeeds in providing reliable structural, electronic and reaction parameters for these species, it singularly fails accurately to reproduce other key features, such as the adsorption energy, in anything approaching a consistent manner. The purpose of this review is to examine what has thus far been learnt and to identify those areas where theory is currently lacking; it is concerned solely with adsorption on metals, for reasons of brevity.

The scope of the review includes the relatively extensive literature on the theory of benzene adsorption on simple, ferromagnetic, platinum group and coinage metals. Several polycyclic and heterocyclic aromatic adsorbates have also been studied theoretically, and these are included together with a range of substituted aromatic adsorbates. A small number of calculations concerning the coadsorption of benzene with non-aromatic surface species are also discussed, as are theoretical studies of hydrogenation/dehydrogenation reactions and their products.

2. Theoretical overview

In developing a theoretical model for the adsorption of aromatic molecules on metal surfaces, two crucial issues must be addressed. The first is the extent to which one’s model can be trusted to represent the aromaticity of the adsorbate; the second relates to the adequacy of one’s description of electronic correlation. Clearly, the first issue arises only when considering aromatic adsorbates, while the other is a general matter to be borne in mind whenever dealing with such relatively large molecules. Before embarking upon the review proper, therefore, it will be advisable to critically assess the performance of first-principles DFT on these two criteria.

(a) Description of adsorbate aromaticity

Aromatic molecules (or aromatic groups within a larger molecule) are characterized by a fully conjugated cyclic structure having notable stability with respect to ring opening, notable lack of reactivity with respect to substitution or addition and notable diamagnetic ring current effects in nuclear magnetic resonance. In the simplest terms, a monocyclic molecule (or part of a molecule) may be identified as aromatic according to whether or not it satisfies the so-called Hückel rule, which requires that it have $4n + 2$ electrons within its conjugated $\pi$ system. This rule reflects the energy distribution of the ring’s molecular orbitals, ensuring that occupation of bonding $\pi$ orbitals is maximized while minimizing the occupation of antibonding $\pi$ orbitals. A fully conjugated five-membered ring possesses three bonding and two antibonding $\pi$ orbitals, a six-membered ring possesses three bonding and three antibonding $\pi$ orbitals and a seven-membered ring possesses three bonding and four antibonding $\pi$ orbitals; in each case,
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precisely six electrons would be required to completely fill all the bonding $\pi$ orbitals without occupying any of the antibonding $\pi$ orbitals. In the familiar case of benzene ($C_6H_6$), each carbon atom in the six-membered ring provides a single $\pi$ electron, so the Hückel rule is satisfied and the molecule is aromatic. For the neutral cyclopentadienyl ($\bullet C_5H_5$) and cycloheptatrienyl ($\bullet C_7H_7$) radicals, in contrast, the Hückel rule is not satisfied and the ring is not aromatic; the neutral cyclopentadienyl radical has one electron too few to fully occupy all of its bonding $\pi$ orbitals, while the neutral cycloheptatrienyl radical has one electron too many to avoid partially occupying one of its antibonding $\pi$ orbitals. On this basis, however, it should be no surprise that the cyclopentadienyl anion ($C_5H_5^-$) is well known to be aromatic (Korolev & Nefedov 1993).

This simple picture of aromaticity is highly instructive, but falls short of providing a complete description of all relevant contributions to the chemical properties of actual molecules. The organic literature is replete with discussions of phenomena requiring a more subtle approach, often associated with heterocyclic or polycyclic systems, electron-donating or electron-withdrawing substituents, etc. To fully capture such effects within a theoretical model, it is necessary at least to invoke a molecular orbital scheme, of which DFT is a highly successful example (Parr & Yang 1989; Koch & Holthausen 2000).

Put simply, the DFT approach invokes the observation that all ground state properties of a system are fully determined by the total ground state electron density, and thereby recasts the difficult problem of determining the $N$-electron wave function in terms of the simpler problem of determining $N$ one-electron wave functions. Each one-electron wave function is evaluated iteratively within a mean-field approach, where the electrostatic and exchange-correlation energies are obtained as functionals of the total electron density. Traditional quantum chemical approaches based upon the Hartree–Fock model achieve a similar separation into one-electron wave functions, but tend not to describe metals with sufficient accuracy to allow reliable adsorption calculations on such substrates.1

One major drawback of the DFT approach is that, while its ability to describe ground state properties is theoretically well founded, its ability to describe electronically excited states is not. It is, in fact, well known that DFT tends to severely underestimate the gap between occupied and unoccupied states in non-metallic systems (whether insulating solids or isolated molecules). Thus, considerable care must be taken with the interpretation of DFT-derived electronic energy levels. Fortunately, however, sufficient collective experience now exists to allow one to say, with some confidence, that the relative energetics among all the occupied levels will typically be reproduced fairly well, as will the relative energetics among all the unoccupied levels; to a first approximation, one can consider the unoccupied states to have been erroneously shifted relative to the occupied states by a more-or-less uniform offset. Furthermore, experience also shows that the eigenfunctions associated with these energy levels will usually be highly reliable in comparison with those obtained using other quantum chemical techniques. Of maximum importance in the binding of benzene to metal surfaces, 1The problem with applying Hartree–Fock methods to metals is that electron correlation becomes very important, beyond the ability of a perturbative scheme (such as the Møller–Plesset approach) to correct. Configuration interaction calculations would, presumably, provide the most accurate solution, but remain prohibitively expensive for systems of the size considered in this review.

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for instance, is the description of its two degenerate highest occupied molecular orbitals (HOMOs) and its two degenerate lowest unoccupied molecular orbitals (LUMOs), and these the DFT approach supplies in good order.

In short, DFT ought to be considered capable of providing a high-quality description of aromatic systems, so long as the relative energetic positions of the occupied and unoccupied electronic states are treated with due caution. As a general point, however, it should also be recognized that the use of a local density approximation (LDA) for the exchange-correlation functional will likely produce poor results for molecules, and a GGA should be considered much more appropriate.

(b) Description of correlation interactions

Contributions to the binding of molecules on metal surfaces can be either chemical or physical in nature. Chemical binding typically implies either an ionic interaction, through wholesale transfer of charge between substrate and adsorbate, or a covalent interaction, where orbitals deriving from the adsorbate and the substrate form new bonding and antibonding linear combinations. Physical binding, on the other hand, can arise through interaction of the permanent surface dipole with any intrinsic molecular dipole that may exist, through the interaction of the permanent surface dipole with a statically induced molecular dipole or through interaction between instantaneous dipoles mutually induced in the adsorbate and the substrate. The latter contribution is, in effect, the surface manifestation of the van der Waals (VdW) interaction.2

In general, VdW interactions are typically considered to be inaccessible within the framework of standard DFT. The problem is that they arise via dipolar excitations of the electronic system away from its ground state, and since DFT guarantees us only a window onto ground state properties, we should not expect reliable answers from this direction. In fact, however, the VdW interaction can fruitfully be regarded as the correlation interaction existing between two regions of high electron density, separated by an intervening region of low electron density. Because the correlation contribution to the energy of the electron gas is included within DFT at the mean-field level, the extent to which DFT does or does not describe the VdW interaction is therefore more accurately a question of whether the mean-field approximation is capable of describing the electronic correlation in a highly inhomogeneous situation. It is not inconceivable, therefore, that a sufficiently complex exchange-correlation functional might succeed in better representing the VdW interaction. Equally, it may be that no such functional can be derived within a mean-field approach. For the present, the best summary of the situation is that standard DFT is known to produce a too-rapid fall-off in the interaction energy between two distinct entities as their separation is increased. In the limit of very small separation, the correlation energy captured within DFT might well include a significant fraction of the VdW interaction, but as the separation increases one enters a regime where the VdW interaction is genuinely absent from standard DFT.

2It is worth noting that important differences in usage exist. For some authors, the VdW force includes all non-covalent forces, while for others it is synonymous with the London dispersion force (i.e. the interaction between mutually induced instantaneous dipoles). We follow the latter convention.
What all of this means for the adsorption of aromatic molecules is that the accuracy of DFT adsorption energies is very much in question. These are typically quite large molecules (by the standards of surface DFT calculations) that often bind in geometries apt to maximize their VdW interaction with the surface. For the reasons just discussed, some portion of this VdW interaction should be captured by the exchange-correlation functional, but quite a bit may not be. We should therefore expect a fairly significant underestimate of adsorption energy owing to the missing fraction of the VdW interaction. On the other hand, experience with small non-aromatic molecules generally suggests that DFT calculations provide a rather sound picture of the covalent chemisorption bond, albeit one that should ideally be supplemented by an estimate of the physisorptive contribution of the VdW interaction; LDA calculations, in contrast, provide adsorption energies that may sometimes lie coincidentally closer to experiment, but almost certainly do so fortuitously by misrepresenting the strength of the covalent chemisorptive component, rather than by more accurately representing the physisorption effect. We shall comment further on this issue in specific cases reviewed below.

3. Adsorbed benzene

The starting point for any review of aromatic adsorption on metal surfaces must, inevitably, be the literature on benzene itself. The simplest and most symmetrical of the aromatic molecules, benzene, was also the first to be tackled in first-principles adsorption studies within the slab-based approach. The earliest such study emerged from the group of Hafner, and dealt with adsorption on the Al{111} surface (Duschek et al. 2000). The lack of d electrons in the substrate material will have allowed considerable computational savings compared with the more interesting transition metal elements, and the avoidance of ferromagnetic materials for this first study was doubtless also economic. Nevertheless, significantly more challenging calculations on the Ni{100}, Ni{110} and Ni{111} surfaces followed from the same group during the course of the very next year (Mittendorfer & Hafner 2001a), together with a contribution on Ni{111} from the present author and co-workers at around the same time (Yamagishi et al. 2001). Ongoing investigations from several groups have, by now, extended the set of surfaces studied to include not only simple metals (Al) and ferromagnetic metals (Fe, Co and Ni), but also platinum-group metals (Ru, Rh, Pd, Ir and Pt) and the coinage metals (Cu, Ag and Au).

(a) On simple metals

Adsorption of benzene on Al{111} was studied theoretically by the group of Hafner, at a coverage of 0.14 ML in a ($\sqrt{7} \times \sqrt{7}$)R19.1° surface unit cell (Duschek et al. 2000). Several different adsorption sites were considered, but the energetic differences between them were found to be within about 0.01 eV (beyond the reliability of DFT to distinguish). The adsorption energy was calculated as
0.35 eV per molecule, and the vertical distance between the C atoms and the uppermost Al atoms ranged between 3.73 and 3.84 Å, dependent upon adsorption site and azimuthal orientation. In all cases, the molecule was flat-lying, with minimal distortion from its gas-phase geometry. The theoretical results were fully consistent with angle-resolved ultraviolet photoemission spectroscopy (ARUPS), high-resolution electron energy loss spectrosocpy and temperature-programmed desorption (TPD) measurements reported in the same work (Duschek et al. 2000). The rather weak bonding of benzene to this simple sp metal was accounted for by mutual polarization of the adsorbate and substrate, with no substantial charge transfer from one to the other; a calculated reduction in work function of 0.39 eV was attributed to the same effect (Duschek et al. 2000). With such weak bonding, however, it must be questionable to what degree DFT fully captures the important physical properties of the system, especially the VdW interaction between the substrate and the adsorbate.

(b) On ferromagnetic metals

In contrast to the case of simple metals, adsorption of benzene on transition metals invariably involves a significantly stronger interaction and greater perturbation of both adsorbate and substrate. The first relevant slab-based DFT studies were those of Mittendorfer & Hafner (2001a), who considered adsorption on Ni{111}, Ni{100} and Ni{110}, and of Yamagishi et al. (2001), whose work concentrated on Ni{111}. On the Ni{111} surface, benzene is known to form an ordered (√7 × √7)R19.1° overlayer at saturation coverage, believed, based on photoelectron diffraction (PhD) (Schaff et al. 1996), low-energy electron diffraction (LEED) (Held et al. 1996) and ARUPS (Huber et al. 1989), to involve 0.14 ML flat-lying molecules centred over the hcp hollow site, with its C–C bonds oriented along the in-plane ⟨110⟩ directions. At lower coverages, PhD experiments (Schaff et al. 1996) suggest a clear preference for the molecules to centre instead on the bridge site, with two C–C bonds oriented along the in-plane ⟨211⟩ directions. Both theoretical studies, however, indicated a definite preference for the ⟨211⟩-oriented bridge site in the high coverage regime, and neither group reported calculations at lower coverage (Mittendorfer & Hafner 2001a; Yamagishi et al. 2001). It remains unclear whether the DFT calculations fail to obtain the correct adsorption site, due to their inadequate inclusion of intermolecular VdW interactions, or whether the experimental site assignments are themselves weak; certainly the interpretations placed on the PhD and LEED data in the high coverage regime are not straightforward (Held et al. 1996; Schaff et al. 1996), and the site sensitivity of the ARUPS experiment (Huber et al. 1989) may be insufficient to regard it as a conclusive indicator in isolation.

Reported bridge-site adsorption energies of 1.01 eV per molecule (Mittendorfer & Hafner 2001a) or 0.91 eV per molecule (Yamagishi et al. 2001) are significantly greater than previously calculated for benzene on Al{111}, suggesting a much stronger adsorbate–substrate interaction than on the simple metal. The best hcp-site models yield adsorption energies only around 0.1 eV smaller (as do the best fcc-site models) suggesting that they too involve substantial binding interaction. Indeed, the calculations reveal that the C–H bonds bend away from the surface, making angles with the plane of 19°/28°
1.09 (0.04) [0.00] 0.00
1.90 (1.89) [1.91]
0.21 (0.08) (0.06)
1.90 (1.94)
0.04
1.83
0.08
1.99
0.02
2.01
2.04
18.6°
1.08
0.16
0.34
0.02
1.90
0.21
1.86
1.93
0.07
0.02
2.01
2.04
1.44
1.44 (1.44)
1.42 (1.43)
1.40 (1.40)
1.98
[0.13]
[1.79]
[0.09]
Furthermore, the aromatic ring expands somewhat, with C—C bonds increasing in length by around 2–4% on average, in a pattern consistent with the symmetry of the adsorption site (Mittendorfer & Hafner 2001a; Yamagishi et al. 2001). Topological analysis of the electron density, within the formalism developed by Bader (1990), confirms that this expansion is correlated with a partial decrease in the effective C—C bond order (Yamagishi et al. 2001). The slab-based calculations concur that C atoms of the aromatic ring lie on average around 1.92 Å higher than the uppermost Ni atoms (Mittendorfer & Hafner 2001a; Yamagishi et al. 2001) in much better agreement with PhD and LEED analyses (Held et al. 1996; Schaff et al. 1996) than earlier cluster-based studies (Myers et al. 1987; Jing & Whitten 1991) that had yielded estimates significantly in excess of 2 Å.

Bonding of the benzene molecule to the Ni{111} surface was described in depth, both by Mittendorfer & Hafner (2001a) and by Yamagishi et al. (2001). Both groups essentially concluded that bonding is primarily due to covalent combination of π orbitals from the molecule (predominantly the two degenerate HOMOs and the two degenerate LUMOs) with d orbitals from the metal. The resulting mixed orbitals are clearly visible in the calculated density of states (Mittendorfer & Hafner 2001a), in the electron density change upon adsorption (Mittendorfer & Hafner 2001a; Yamagishi et al. 2001) and in the net spin density (Yamagishi et al. 2001) (see figure 2). Overall, the dominance of back-donation of electrons into the LUMO, as opposed to donation from the HOMO, is reflected in the net gain of electrons by benzene, amounting to approximately 0.5 e⁻. Notably, the magnetic moments of Ni atoms immediately involved in bonding to the molecule are substantially reduced (more than halved, relative to the clean surface value) while those not directly involved are hardly affected (Mittendorfer & Hafner 2001a; Yamagishi et al. 2001); the molecule itself gains a slight magnetic moment opposed to the majority spin of the substrate, indicative of weak interaction between the LUMO and the minority-spin sp electrons (Ge et al. 2000; Jenkins et al. 2001; Yamagishi et al. 2001).
Figure 2. Electronic signatures of adsorption in the case of \((\bar{2}11)\)-oriented bridge-bound benzene on Ni\{111\} in the \(\sqrt{7} \times \sqrt{7}\)R19.1\(^\circ\) phase: (a) electron density change upon adsorption, with red showing accretion and green showing depletion, and (b) spin density of adsorbed species, with gold showing majority spin and silver showing minority spin. Adapted from Yamagishi et al. (2001). Copyright © (2001) American Institute of Physics.

Figure 3. Calculated geometries for benzene adsorbed on (a) Ni\{100\} in a c\((4 \times 4)\) arrangement and (b) Ni\{110\} in a c\((4 \times 2)\) arrangement. Bond lengths and interplanar separations are given in ångstrom units. Adapted from Mittendorfer & Hafner (2001\textit{a,b}). Copyright © (2001), with permission from Elsevier.

On the Ni\{100\} surface, benzene is known from experiment to form a c\((4 \times 4)\) overlayer (Bertolini \textit{et al.} 1977; Weinelt \textit{et al.} 1998), studied theoretically by Mittendorfer & Hafner (2001\textit{a}). In this case, their DFT calculations showed a very clear energetic preference for flat-lying adsorption centred over the hollow site, although the azimuthal orientation of the molecule was less certain: an arrangement in which two C–C bonds lie along one of the \(\langle 011 \rangle\) directions (with an adsorption energy of 2.13 eV per molecule; see figure 3\textit{a}) was found to be just 0.04 eV per molecule more stable than one in which two such bonds lie along one of the \(\langle 001 \rangle\) directions. Clearly, benzene is adsorbed much more strongly to Ni\{100\} than to Ni\{111\}, but surprisingly its geometry is no more distorted, nor does it lie any closer to the surface (Mittendorfer & Hafner 2001\textit{a}). Indeed, apart from the binding energy and the obvious difference in substrate symmetry, the adsorption of benzene on the two flat surfaces of Ni appears to be remarkably similar.
Moving away from flat surfaces, however, the story becomes more complex, as exemplified by the calculations of Mittendorfer & Hafner (2001a) for c(4 × 2) benzene adsorption on Ni{110} (i.e. the highest-symmetry stepped facet for an fcc metal (Pratt et al. 2005; Jenkins & Pratt 2007)). Here, the preferred adsorption site was found to bridge across the trough, from one ridge to the next, with a substantial geometric asymmetry (figure 3b): the aromatic ring remains almost planar, but is canted by 5° with respect to the surface plane about an axis lying along the ⟨110⟩ trough direction (Mittendorfer & Hafner 2001a). Similarly, canted adsorption has been noted in calculations by Delle Site & Sebastiani (2004) for the adsorption of benzene on Ni{221}, although that stepped surface is of lower symmetry in the first place and features much wider {111} terraces against which the adsorbate lies almost parallel. On Ni{110}, the benzene molecule is itself wider than the {111}-like microfacets, and no such simplifying observation is possible. Nevertheless, Mittendorfer & Hafner (2001a) argue that bonding on the {110} facet occurs through combination of metal d states with the molecular π states, just as was the case for the {111} and {100} surfaces; that the calculated adsorption energy of 1.78 eV per molecule is intermediate in magnitude also argues for an interaction of similar origin.

Supplementary to the relatively comprehensive studies on Ni described above, a few calculations have also been reported for benzene adsorption on the other ferromagnetic metals, namely Co and Fe. We first note the work of Pussi et al. (2004) on the Co{0001} surface. The {0001} facet of an hcp crystal is its only flat face, and is structurally very similar to the {111} facet of an fcc crystal (Jenkins & Pratt 2007). We should not, therefore, be surprised that the adsorption of benzene on Co{0001} shows certain similarities to its adsorption on Ni{111}, most notably that it forms a (√7 × √7)R19.1° overlayer at saturation coverage and that quantitative LEED analysis (Pussi et al. 2004) indicates a preference for adsorption in the ⟨12̅0⟩-oriented hcp site3 (the ⟨12̅0⟩ directions being close-packed in-plane directions analogous to the ⟨111⟩ directions in the fcc-{111} plane (Jenkins & Pratt 2007)). On the other hand, the LEED analysis also indicates that the C atoms of the aromatic ring lie some 2.20 Å above the uppermost Co atoms, which is considerably higher than on Ni{111} (around 1.92 Å by experiment and theory (Held et al. 1996; Schaff et al. 1996; Mittendorfer & Hafner 2001a; Yamagishi et al. 2001)) so the analogy should clearly not be over-stressed.

In their DFT calculations, Pussi et al. (2004) expressly neglected to consider the possibility of adsorption in a truly ⟨1̅100⟩-oriented bridge model, which is unfortunate, as this is the closest possible analogue to the ⟨211⟩-oriented bridge model favoured by DFT on Ni{111} (Mittendorfer & Hafner 2001a; Yamagishi et al. 2001). They do report calculations for seven other plausible site/orientation combinations, however, finding that the ⟨12̅0⟩-oriented fcc and hcp models are jointly the most favourable of those considered. On the basis of their LEED analysis, they then discard the fcc site and concentrate only on the ⟨12̅0⟩-oriented hcp model. Interestingly, the calculated height of the benzene molecule above

3Unfortunately, the published work of Pussi et al. (2004) erroneously interchanges the labels [11̅20] and [1̅100] throughout. Assuming that their figure depicting the preferred geometry from LEED is correct in the location of the atoms, the C–C bonds in that structure are aligned along ⟨11̅20⟩ directions and not the ⟨1̅100⟩ directions stated in the caption and text.
the surface in this model is just 1.96 Å, which is much closer to that found on Ni\{111\}, and in quite poor agreement with the LEED analysis reported in the same work; otherwise, the structural results are in quite good accord, including the now familiar upward bend of the C–H bonds (Pussi et al. 2004).

On Fe\{100\}, which is a kinked bcc surface (Pratt et al. 2005; Jenkins & Pratt 2007), Sun et al. (2007a,b) report a preference for adsorption of benzene in the hollow site, oriented with two of its C–C bonds aligned along one of the \(\langle 001 \rangle\) directions (i.e. exhibiting the same symmetry as on the flat fcc Ni\{100\} surface (Mittendorfer & Hafner 2001a)), although alternative azimuthal orientations were not considered in this instance. It is interesting that the calculated adsorption energy of 1.07 eV per molecule on Fe\{100\} is much lower than the value of 2.13 eV obtained by Mittendorfer & Hafner (2001a) in the case of Ni\{100\}. Induced spin-polarization of the adsorbate molecule was found to be highly sensitive to the adsorption site, and included distinct majority- and minority-spin components (Sun et al. 2007a,b). Higher coverage 0.25 ML tilted geometries have also been explored by Sun et al. (2008b) within a \((2 \times 2)\) unit cell, aiming to explain changes in spin-polarization at the onset of multilayer growth.

(c) On platinum-group metals

Considerable attention has also been devoted to the adsorption of benzene on the platinum-group metals, not least because of their role in catalytic hydrogenation or dehydrogenation of aromatic compounds. Among the earliest first-principles calculations for such an adsorption system were those reported as part of a combined LEED/DFT study of deuterated benzene on Ru\{0001\} by Held et al. (2001). In that work, a \((\sqrt{7} \times \sqrt{7})R19.1^\circ\) overlayer was observed experimentally, and an equivalent perodicity adopted in the theoretical investigation. Analysis of the LEED data indicated adsorption at the hcp site, with the molecule oriented to have its C–C bonds aligned along \((\bar{1}100)\) directions (i.e. differing from the orientation preferred in hcp sites on Ni\{111\} and Co\{0001\}). DFT calculations were performed for only this single adsorption model, producing results in excellent agreement with the LEED structural analysis. For instance, the height of the C atoms above the uppermost Ru atoms was calculated by DFT to be 2.10 Å, to be compared with 2.04 Å from LEED. Most significantly, this work was the first to provide experimental evidence for the strong outward deflection of the C–D bonds; in LEED, three C–D bonds formed angles of 9° with the surface plane, and three others made an angle of 22°, whereas DFT predicted corresponding angles of 14° and 24°; lateral positions of the D atoms were, however, difficult to determine with accuracy from the LEED data (Held et al. 2001). Notwithstanding zero-point energy effects, it is reasonable to assume that similar results would hold for non-deuterated benzene; the deuterated form was used in these experiments to exploit the stronger scattering of electrons by deuterium relative to hydrogen. The calculated adsorption energy of 1.31 eV per molecule is rather higher than the values calculated for adsorption on Ni\{111\} (variously 0.91 eV per molecule (Yamagishi et al. 2001) or 1.01 eV per molecule (Mittendorfer & Hafner 2001a)), though still considerably less than that for adsorption on Ni\{100\} or Ni\{110\} (2.13 and 1.78 eV per molecule, respectively (Mittendorfer & Hafner 2001a)).
Adsorption of benzene on the \{111\} surfaces of Pt, Pd and Rh has been comprehensively addressed in a series of studies by Saeys et al. (2002, 2003), by Morin et al. (2003b, 2004a,b, 2006) and by Orita & Itoh (2004b). All of these studies assumed a (3 × 3) overlayer, corresponding to a lower coverage than the (\(\sqrt{7} \times \sqrt{7}\))R19.1\(^\circ\) calculations described above and reveal a consistent preference for adsorption in the (211)-oriented bridge geometry relative to the ‘next best’ (110)-oriented hcp model. The actual adsorption energies suffer from a fair degree of variation between different studies, however, so the work by Morin et al. (2004b), in which the three different substrates are studied together, is the best place to look for trends: these authors report adsorption energies of 0.90 and 0.67 eV per molecule for the competitive bridge and hcp structures on Pt\{111\} (cf. 1.21 and 0.78 eV per molecule in the work of Saeys et al. (2002), energies of 1.19 and 1.03 eV per molecule for the same structures on Pd\{111\} (cf. 1.43 and 1.17 eV per molecule in the work of Orita & Itoh (2004b)) and energies of 1.53 and 1.51 eV per molecule on Rh\{111\}. Thus, the absolute adsorption heat increases on changing substrate from Pt to Pd to Rh, while the relative difference between the two most-favoured models decreases to the point of negligibility.

By far, the highest adsorption energy reported for benzene on any transition metal substrate, however, is the value of 2.88 eV calculated recently by Yamagishi et al. (2008) for adsorption on Ir\{100\}. Here, the molecule adopts a flat-lying geometry, centred over the hollow site in an assumed c(4 × 4) arrangement, with two of its C–C bonds oriented along one of the \langle001\rangle directions. The orientational preference is thus opposite to that found by Mittendorfer & Hafner (2001b) on the Ni\{100\} surface, where two of the C–C bonds lay along one of the \langle0\overline{1}1\rangle directions, although in both cases the calculated energy differential is less than 0.05 eV per molecule. The adsorption energy, it should be noted, has been adjusted to include the energy needed to lift the (1 × 5) reconstruction of the clean Ir\{100\} surface and would otherwise be somewhat greater. Although much higher than for the corresponding \{111\} surface the adsorption energy of 2.03 eV per molecule calculated by Orita & Itoh (2004b) for benzene on Pd\{100\} is hardly comparable with that on Ir\{100\}.

In comparison to the flat \{111\} and \{100\} surfaces of platinum-group metals, the stepped \{110\} surface facet has gained much less attention from theorists. We are aware of only one investigation in this area, reported by Favot et al. (2000) and relating to the adsorption of benzene on Pd\{110\}. Their paper does not mention the value obtained for the adsorption energy, and it is worth noting that gradient corrections are not included in the exchange-correlation functional, but nevertheless the calculated geometry is entirely reasonable in comparison with results for adsorption on Ni\{110\} (Mittendorfer & Hafner 2001b).

\((d)\) On coinage metals

Adsorption on the coinage metals typically involves a major contribution from the substrate sp electrons, the d-band being relatively inert due to its position well below the Fermi level. We might therefore expect benzene adsorption on these substrates to be somewhat intermediate between the cases of simple and transition metals discussed at length above.
On the Au\{100\} surface, however, Chen et al. (2006) report a surprisingly high adsorption energy of 1.92 eV per molecule in a hollow site, very nearly independent of orientation; other sites are found to be considerably less stable. The calculated height of the C atoms above the uppermost Au atoms is reported as 2.38 Å for the marginally most stable hollow site model (with two C–C bonds aligned along one of the \langle 011 \rangle directions) and 2.22 Å for the other (with two C–C bonds aligned along one of the \langle 001 \rangle directions); angles of deflection for the C–H bonds are 13° and 16° from the surface plane for these two models, respectively (Chen et al. 2006). Significant electron transfer, from adsorbate to substrate, of around 0.7 e\textsuperscript{−} per molecule is also indicative of a rather strong bonding interaction (Chen et al. 2006).

On Cu\{100\}, the same group reports similarly large adsorption energies in the range 1.95–2.28 eV per molecule for flat-lying benzene in the hollow site at various coverages; the calculated height of the C atoms above the Cu atoms is in the range 2.00–2.06 Å, while the C–H bonds are deflected outwards to make an angle of around 15° with the surface plane (Chen et al. 2005). Furthermore, an extremely large electron transfer from substrate to adsorbate, of around 3.5 e\textsuperscript{−} per molecule, is reported, which must surely be unphysical. Indeed, earlier DFT calculations by Lorente et al. (2003) had produced a much more reasonable adsorption energy for benzene on Cu\{100\}, of just 0.68 eV per molecule, with the adsorbate located in the hollow site and oriented to have two C–C bonds parallel to one of the \langle 011 \rangle directions. The geometry calculated by Lorente et al. (2003) also differs considerably from that provided by Chen et al. (2005), in that the C atoms lie rather further from the uppermost Cu atoms, at a height of 2.23 Å, and the outward deflection of the C–H bonds amounts to only 8° from the surface plane. Finally, it is noteworthy that the calculated magnitude and direction of electron transfer in the work of Lorente et al. (2003) is entirely in line with expectations. It therefore seems that the calculations of Chen et al. (2005, 2006) for benzene adsorption on the Au\{100\} and Cu\{100\} surfaces may suffer from some significant systematic error, possibly related to the use of the LDA functional rather than one of the more reliable GGA functionals (i.e. they overestimate the covalent contribution to adsorbate–substrate binding).

Even weaker binding has been calculated for benzene on Cu\{111\}, Ag\{111\} and Au\{111\}, where Bilic et al. (2006) report maximum adsorption energies of 0.03, 0.05 and 0.08 eV per molecule, respectively, assuming a (3 × 3) overlayer. As those authors point out, adsorption in these systems is likely to be dominated by physisorptive VdW effects not captured within the DFT formalism, so the details of calculated atomic and electronic structure are of limited relevance except in demonstrating a lack of chemisorptive bonding and a relatively featureless lateral potential energy surface. Similarly weak adsorption (0.05 eV per molecule) has also been reported by Schravendijk et al. (2005) for benzene on Au\{111\}, while slightly higher adsorption energies of 0.24 and 0.40 eV per molecule have been calculated for benzene on Cu\{110\} by Bilic et al. (2006) and Atodiresei et al. (2008a,c), respectively. A much higher benzene adsorption energy of 1.13 eV per molecule has also been claimed by Rogers et al. (2004) for the Cu\{110\} case, but it is notable that this unexpectedly high value is again associated with the use of an LDA functional; while it lies close to the experimental value, it seems likely that it does so because the lacking VdW interaction is fortuitously compensated by exaggerated covalent bonding.

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4. Polycyclic aromatic adsorbates

When two benzene rings are fused along an edge, with the elimination of four hydrogen atoms, each ring in the resulting molecule continues to satisfy the Hückel rule and is thus aromatic. Indeed, fusing any number of benzene rings in similar fashion will result in an aromatic compound, and so a whole class of polycyclic aromatic molecules may be envisaged. The lower orders of this sequence include linear arrangements of the fused rings (e.g. naphthalene, anthracene, tetracene and pentacene) as well as nonlinear arrangements (e.g. phenanthrene, pyrene and chrysene). A limited number of first-principles studies have addressed the adsorption of these larger molecules on metal surfaces, which we now summarize.

(a) Naphthalene

The adsorption of naphthalene (two fused benzene rings, C\textsubscript{10}H\textsubscript{8}) was first studied via DFT on Pt\{111\} by Morin et al. (2004\textit{b}) and on Pt\{111\}, Pd\{111\} and Rh\{111\} by Santarossa et al. (2008).

Utilizing a (4 \times 3) unit cell, Morin et al. (2004\textit{b}) calculate an adsorption energy of 1.37 eV per molecule for naphthalene on Pt\{111\} in the preferred geometry (where each ring is positioned similarly to the \(\langle 211 \rangle\)-oriented bridge model favoured by benzene). Santarossa et al. (2008) determined a very similar adsorption energy of 1.31 eV per molecule for naphthalene on Pt\{111\} within their slab calculations of (6 \times 6) overlayers. Additional calculations for adsorption on Pt\{111\}, Pd\{111\} and Rh\{111\} were performed within a cluster-based approach, and although exhibiting some finite size effects nevertheless give an interesting insight into chemical trends; adsorption energies of 1.51, 1.29 and 2.86 eV per molecule were calculated for the three substrates, respectively (Santarossa et al. 2008). In line with the findings of Morin et al. (2004\textit{a}) for benzene, the work of Santarossa et al. (2008) reveals a substantially higher adsorption energy for naphthalene on Rh\{111\} when compared with either Pt\{111\} or Pd\{111\}.

(b) Anthracene

In addition to benzene and naphthalene, Morin et al. (2004\textit{b}) also studied the adsorption of anthracene (three linearly fused benzene rings, C\textsubscript{14}H\textsubscript{10}) on Pt\{111\}, finding an adsorption heat of 1.79 eV per molecule within a (5 \times 3) unit cell; in this instance, a geometry with each ring positioned by analogy with benzene and naphthalene (i.e. in a \(\langle 211 \rangle\)-oriented bridge arrangement) was assumed, rather than determined.

It is evident that the DFT adsorption energies of benzene, naphthalene and anthracene calculated by Morin et al. (2004\textit{b}) (i.e. 0.90, 1.37 and 1.79 eV) vary fairly linearly with the number of C atoms present. Deviations from precise linearity, however, arise owing to a misfit between the ring spacing of the polycycle

4It is important to point out that while some polycyclic aromatic compounds contain a total of \(4n + 2\) \(\pi\) electrons across the entire molecule (e.g. naphthalene, C\textsubscript{10}H\textsubscript{8}) this is not the absolute requirement that it would be for monocycles; in general, polycyclic aromatic compounds are those for which each of the constituent monocycles is aromatic in at least one resonance structure of the polycyclic molecule, and consequently some such aromatic compounds will have a total number of \(\pi\) electrons differing from \(4n + 2\) (e.g. pyrene, C\textsubscript{16}H\textsubscript{10}).
and the lattice spacing of the substrate and should be expected to become increasingly apparent as the size of the molecule increases. Indeed, using a simple model for the degree of misfit, and incorporating terms representing the distortion of both molecule and surface, Morin et al. (2004b) estimate covalent chemisorption energies of 1.3 and 0.7 eV per molecule for tetracene and pentacene (consisting, respectively, of four and five linearly fused benzene rings). Full DFT calculations to confirm these predictions are still awaited.

Interestingly, calorimetric experiments by Campbell and co-workers (Ihm et al. 2004; Gottfried et al. 2006) indicate that the DFT calculations of Morin et al. (2004b) underestimate the adsorption energies of benzene and naphthalene on Pt{111} by approximately 0.14 eV per C atom (figure 4). Assuming that this degree of error holds true for larger molecules (which seems reasonable, given that it most likely arises owing to missing VdW interactions within the DFT formalism), one can suggest supplementing the energies calculated and predicted by Morin et al. (2004b) with 0.84, 1.40, 1.96, 2.52 and 3.08 eV for molecules containing 6, 10, 14, 18 and 22 C atoms. Thus, the ‘empirically corrected’ adsorption energies would become: 1.74 eV for benzene, 2.77 eV for naphthalene, 3.75 eV for anthracene, 3.82 eV for tetracene and 3.78 eV for pentacene. Intriguingly, such a sequence suggests that adsorption heats become more or less constant for the C14, C18 and C22 compounds, as the increasing contribution of the VdW interaction is offset by the greater misfit and distortion associated with the chemisorption bond.

(c) Tetracene

The adsorption of tetracene (four linearly fused benzene rings, C18H12) has been investigated via DFT on Cu{100} by Dou et al. (2008) and on Ru{1010} by Lu et al. (2006).

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(a) possible adsorption geometries considered by Lu et al. (2006), who report very similar adsorption energies for Model 3 (4.19 eV per molecule) and Model 11 (4.23 eV per molecule) and (b) an STM image illustrating the coexistence of two orthogonal orientations for the adsorbate. Adapted from Lu et al. (2006). Copyright © (2006), with permission from Elsevier.

The work of Dou et al. (2008) reveals a preference for a flat-lying adsorption geometry on Cu{100} in which the fused benzene rings are located above hollow sites, oriented such that two C−C bonds from each lie along one of the ⟨011⟩ directions, similar to the geometry determined for benzene itself by Lorente et al. (2003) on the same substrate. The calculated adsorption energy in this model is 2.44 eV per molecule (Dou et al. 2008), again broadly consistent with the value of 0.68 eV calculated previously for a single benzene ring (Lorente et al. 2003). A very slight outward bend is apparent in the two terminal rings, amounting to a maximum vertical separation of 0.20 Å between the lowest and highest lying C atoms; the height of the molecule above the surface is in the region of 2.20 Å (Dou et al. 2008).

On Ru{1010}, Lu et al. (2006) report two competitive adsorption geometries for flat-lying tetracene, aligned with its long axis either parallel or perpendicular to an in-plane ⟨1120⟩ direction (adsorption energies of 4.23 and 4.19 eV per molecule respectively; see figure 5). In the ⟨1120⟩-oriented case, the molecule lies along and slightly to one side of a surface ridge, with its centre of mass located above a three-fold hollow site and exhibiting a slightly concave internal geometry (i.e. the ends of the molecule bow a little away from the surface); in the ⟨0001⟩-oriented case, the centre of mass is located above a ridge bridge site, with the molecule spanning across three ridges in all and exhibiting a slightly convex internal geometry (i.e. the ends of the molecule bow a little towards the surface). Scanning tunnelling microscopy (STM) images presented in the same paper provide good evidence for substantial (approximately equal) occupancy of both conformations on the surface (Lu et al. 2006).

(d) Pentacene

Finally, for this section, we turn to the adsorption of pentacene (five linearly fused benzene rings, C_{22}H_{14}), which has been studied by means of DFT on Al{100} by Simeoni et al. (2004), on Au{100} by Lee & Yu (2005), Lee et al.
(2007), on Cu{100} by Ferretti et al. (2007) and on Fe{100} by Sun et al. (2008a). On the simple and coinage metals, binding is expected to be relatively weak, as indeed borne out by calculated chemisorption energies of 0.32 eV per molecule for Al{100} (Simeoni et al. 2004) and 0.28 eV per molecule for Au{100} (Lee & Yu 2005; Lee et al. 2007) when employing a GGA functional. Unsurprisingly, the use of LDA functionals yields very much higher chemisorption energies of 2.42 eV per molecule for Al{100} (Simeoni et al. 2004) and 3.21 eV per molecule for Au{100} (Lee & Yu 2005; Lee et al. 2007), which both groups involved recognize as unphysically high. Doubtless the GGA values are themselves too low, owing to missing VdW interactions (for a point of comparison, experiment indicates an adsorption energy of 1.14 eV per molecule for pentacene on Au{111} (France et al. 2003)) but at least they are likely to reproduce geometries and the electronic features of chemisorption with reasonable accuracy. Ferretti et al. (2007), for example, present a detailed and convincing comparison between their calculated GGA electronic structure and that obtained via ARUPS experiments. The various LDA calculations, on the other hand, almost certainly represent spuriously strong covalent chemisorption, featuring highly distorted adsorbate molecules and/or anomalously short adsorbate–substrate distances (Simeoni et al. 2004; Lee & Yu 2005; Ferretti et al. 2007; Lee et al. 2007). Unsurprisingly, the calculated adsorption energy for pentacene on Fe{100} is genuinely high, reported by Sun et al. (2008a) as 3.99 eV per molecule within the GGA (cf. 1.07 eV and 2.46 eV per molecule for benzene and anthracene, calculated by the same group).

5. Heterocyclic aromatic adsorbates

Thus far, we have considered the adsorption of benzene and of molecules consisting of fused benzene rings. In all these cases, covalent binding to the metal surface involves the whole molecule and is, to that extent, an essentially delocalized affair. In general, all of these species seem to adopt a flat-lying or nearly flat-lying geometry, in order to maximize not only the delocalized adsorbate–substrate covalent interaction, but also the VdW interaction with the surface.

In contrast, the class of heterocyclic aromatic compounds involves rings containing at least one non-carbon atom. Here, the symmetry of the ring is broken, and the possibility exists that one or more of the ring atoms may interact significantly more or less strongly with the substrate than do the others. Consequently, the geometry of the molecule is likely to be tilted to some degree, even on a perfectly flat surface.

Among the simplest of the heterocyclic aromatic molecules are six-membered rings containing one or more non-hydrogenated nitrogen atoms (e.g. pyridine and pyrimidine), five-membered rings containing a hydrogenated nitrogen atom (e.g. pyrrole) and five-membered rings containing a non-hydrogenated oxygen or sulphur atom (e.g. furan and thiophene). Polycyclic heteroaromatics include examples where only a single ring is heterocyclic (e.g. quinoline, indole) and others where several are (e.g. purine). As regards the adsorption of these species on metal surfaces, only thiophene has attracted sustained attention from theorists, supplemented by isolated studies on pyridine and pyrrole. The adsorption of furan and pyrimidin on metals appears to have been ignored in the DFT literature to date.
(a) Pyridine and pyrrole

The pyridine (C₅H₅N) and pyrrole (C₄H₄NH) molecules together highlight an important aspect of heterocyclic aromatic chemistry, namely the issue of basicity. In the case of the six-membered pyridine ring, the non-hydrogenated N atom employs two electrons in forming $\sigma$ bonds with neighbouring C atoms, contributes one electron to the $\pi$ system and retains its two remaining electrons as a lone pair; the localization of non-$\sigma$-bonding electrons on the N atom renders the molecule basic. Conversely, in the case of the five-membered pyrrole ring, the hydrogenated N atom employs three electrons in forming $\sigma$ bonds with neighbouring C and H atoms and contributes its two remaining electrons to the $\pi$ system; the complete delocalization of these last two electrons renders the molecule non-basic.

The adsorption of pyridine on Cu{110} and Ag{110} has been studied by Atodiresei et al. (2008b), who report that flat-lying geometries are strongly disfavoured in comparison with upright geometries bonding via the N lone pair (i.e. the HOMO). On both substrates, they find a preference for the molecular plane to lie parallel to the ⟨001⟩ surface direction with DFT adsorption energies of 0.76 eV for Cu{110} and 0.45 eV for Ag{110}. In these two instances, therefore, the basicity of pyridine dominates its binding to the surface, preventing any significant interaction through the aromatic ring itself. We note, in passing, that these authors make plausible estimates of the missing VdW contributions to the adsorption energies of 0.21 and 0.15 eV per molecule in the most stable geometries on Cu{110} and Ag{110}, respectively, based upon a semi-empirical correction scheme proposed by Grimme (2006).

Abdallah et al. (2004) report calculations for pyridine adsorption on Mo{110}, a flat bcc surface (Pratt et al. 2005; Jenkins & Pratt 2007), in which the strongest binding is found for a flat-lying adsorbate geometry with the N atom and the two ‘meta’ C atoms located in near-atop sites (adsorption energy 1.54 eV per molecule). Upright models were found to bind far less strongly (with a maximum reported adsorption energy of just 0.66 eV per molecule), although the authors suggest that such a state may become populated at high coverage (Abdallah et al. 2004).

For the non-basic pyrrole molecule, Abdallah & Nelson (2005) report a clear preference for flat-lying geometries on Mo{110}, centred approximately over the hollow site, with binding energies in the vicinity of 1.30 eV (varying with azimuthal orientation). The molecule displays a marked outward deflection of the C–H and N–H bonds, reminiscent of benzene on transition metal surfaces.

(b) Thiophene

In contrast to the, respectively, basic and non-basic natures of pyridine and pyrrole, thiophene (C₄H₄S) may be considered to exhibit both basic and non-basic characteristics simultaneously. Within the five-membered thiophene ring, the non-hydrogenated S atom employs two electrons in forming $\sigma$ bonds with neighbouring C atoms, contributes two electrons to the $\pi$ system and retains two more electrons as a lone pair; the donation of two electrons from the S atom into the delocalized $\pi$ system is indicative of a non-basic molecule, but the retention of a localized lone pair on the S atom implies a residual basic character.
Early calculations by Blyth et al. (2001) for the adsorption of thiophene on Al\{111\} indicated very weak binding in a flat-lying geometry; the calculated adsorption energy of 0.54 eV per molecule is only slightly higher than that obtained for benzene on the same substrate (Duschek et al. 2000), and the authors found little evidence of substantial electron transfer between substrate and adsorbate. On the Ni\{100\} surface, by way of contrast, Mittendorfer & Hafner (2001b) calculated a very high adsorption energy of 2.57 eV per molecule, associated with a structure in which the aromatic ring is heavily disrupted. Indeed, their optimum geometry sees one of the two C–S bonds broken, enabling each of these atoms to more comfortably occupy neighbouring bridge sites; the molecule has become, in effect, a highly curved but non-closed C₄–S chain, with no remaining evidence of aromaticity (Mittendorfer & Hafner 2001b). A second, somewhat less stable but fully intact adsorption geometry is also reported, in which the molecule is flat-lying and centred over the hollow site with its S atom in a near-atop location; the calculated adsorption energy in this case is 2.23 eV, and the molecule retains its aromaticity, albeit with quite strong geometric distortion (Mittendorfer & Hafner 2001b). The split-ring state has been suggested by the same authors as a possible intermediate in the desulphurization of thiophene, and moderate reaction barriers for such a route have indeed been calculated (Mittendorfer & Hafner 2003). It appears that all of these calculations were performed without spin polarization, but qualitatively similar results were subsequently obtained in spin-polarized calculations for thiophene adsorption structures on Ni\{100\} by Orita & Itoh (2004b) (adsorption energy 2.88 eV in the split-ring structure, 2.46 eV in the intact molecular structure, both at lower coverage than the earlier work). On the Pd\{100\} surface, only the flat-lying intact molecular adsorption mode was found to be stable, with a calculated adsorption energy of 2.20 eV per molecule (Orita & Itoh 2004b), while on the Cu\{100\} surface the same authors report very low adsorption energies for thiophene, with several flat-lying geometries yielding values in the range 0.30–0.50 eV per molecule (Orita & Itoh 2004b).

The adsorption and dissociation of thiophene on Ni\{110\} has been studied theoretically by Morin et al. (2003a), who determine the most stable adsorption geometry to be one in which the molecule is flat-lying and bridges from one surface ridge to the next (adsorption energy 2.02 eV per molecule, from spin-polarized calculations). Two alternative geometries, in which the molecule exhibits different azimuthal orientations, are also reported to have relatively high adsorption energies (1.49 and 1.68 eV per molecule), and furthermore would dissociate trivially (activation barriers below 0.20 eV) into an acyclic thiolate, and thence ultimately to a S adatom and a hydrocarbon. The authors argue, therefore, that adsorbing molecules landing on the surface in one of these reactive geometries will dissociate more readily than diffusing into the stable molecular state (Morin et al. 2003a).

Recently, Sony et al. (2007) have investigated the adsorption of thiophene on Cu\{110\}, making use of an exchange-correlation functional specially formulated with the aim of accounting for VdW interactions (Dion et al. 2004). Indeed, the calculated adsorption energy of 0.50 eV per molecule is claimed to arise solely from the VdW interaction (Sony et al. 2007), consistent with an equilibrium adsorbate–substrate distance of nearly 3 Å. Further examination of the merits of this interesting development lie beyond the scope of the present review.

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6. Substituted aromatic adsorbates

The effect of substituent groups on the adsorption of aromatic molecules might be expected to be twofold, arising owing to either electronic or steric considerations. Hydroxy (–OH) or methoxy (–OCH₃) groups, for example, are generally regarded as electron-donating, while carboxylic (–COOH) groups are electron-withdrawing, and it is interesting to consider whether these attributes are recognizable in the influence they exert on aromatic adsorption. On the other hand, the sheer spatial extent of these different groups will inevitably itself have some bearing on the degree to which an aromatic ring can lie flat on the surface without placing significant internal strain on the molecule. Whether the electronic or the steric effects dominate is, of course, a key question for theory to address.

(a) Phenol and anisole

The hydroxy group is among the simplest of electron-donating moieties that might be considered as substituents to an aromatic ring. Consequently, phenol (C₆H₅OH) has been the most frequent example of substituted aromatic adsorption tackled within the first-principles DFT approach. The first to do so were Delle Site et al. (2003), who examined several different adsorption sites and orientations for flat-lying phenol on Ni{111}. The most remarkable aspect of their results is the lack of any strong substituent effect; the molecule favours adsorption at a bridge site with two C–C bonds oriented along ⟨211⟩ directions and only a relatively small sensitivity to which C atom binds the –OH group. From a structural perspective, the aromatic ring distorts in fashion very similar to benzene, with a slight increase in the average C–C bond lengths and an outward bend of the C–H bonds. The C–O bond is also deflected away from the surface, indicating a repulsive interaction that accounts for an adsorption energy (0.91 eV) a little more than 0.1 eV less than that calculated by the same authors for benzene (Delle Site et al. 2003). Various geometries for phenol adsorbed with a vertical ring plane, binding to the surface via its O atom, have been calculated on Ni{111}, Ni{110} and Ni{221}, but all have adsorption energies much smaller than those for the flat-lying geometry (Ghiringhelli et al. 2007).

Orita and Itoh (2004a), meanwhile, studied theoretically the adsorption of phenol on Pd{111} and Pd{100}. On the Pd{111} surface, they report an adsorption energy of 1.39 eV per molecule for phenol, compared with 1.43 eV per molecule for benzene, while on the Pd{100} surface the adsorption energy of phenol is reported as 1.94 eV per molecule, compared with 2.04 eV per molecule for benzene (Orita & Itoh 2004a). As on Ni{111}, it seems likely that the steric effect of the –OH group is primarily responsible for reducing the overall strength of adsorbate–substrate binding.

The methoxy group represents another relatively simple electron-donating moiety, whose substitution for a hydrogen atom might be expected to influence the reactivity of an aromatic ring. The adsorption of anisole (C₆H₅OCH₃) has therefore been studied theoretically on Pt{111} by Tan et al. (2005), with a view to investigating electronic versus steric effects. When adsorbed with the aromatic ring in a flat-lying geometry, the phenyl–O bond was deflected away from the surface by around 12°, while the O–methyl bond remained nearly parallel to
Figure 6. Electron density change upon adsorption of anisole on Pt{111}, showing accumulation with dark isosurfaces and depletion with light ones. Note the similarity to the equivalent charge redistribution upon benzene adsorption (figure 2a) despite the presence of the methoxy substituent. Adapted from Tan et al. (2005). Copyright © (2005), with permission from Elsevier.

the surface. A very similar geometry has since also been reported from cluster studies of anisole on Pt{111} (Bonalumi et al. 2006). The adsorption energy was calculated by Tan et al. (2005) to be 0.76 eV per molecule, somewhat less than the values in the range 0.9–1.2 eV per molecule calculated for benzene on the same substrate by other groups (Saey et al. 2002; Morin et al. 2004a). Crucially, the electron density redistribution upon adsorption was found to resemble closely that expected for a regular benzene ring and to bear very little resemblance to the HOMO and LUMO of gas-phase anisole (figure 6). This was interpreted as evidence that molecular distortion, driven by steric effects, interferes with the inductive electronic influence of the –OCH₃ group (Tan et al. 2005).

In both the phenol and anisole cases, effects due to the electron-donating character of the –OH or –OCH₃ groups are essentially negligible, in part because distortion of the molecule essentially decouples the orbitals of the substituent from those of the aromatic ring, and in part because electron donation and withdrawal owing to interaction with the surface is dominant over any intramolecular phenomena. Steric considerations, on the other hand, not only account for much of the molecular distortion, but also explain the generally weaker binding of the molecule to the surface compared with benzene.

(b) Miscellaneous molecules

Ghiringhelli & Delle Site (2008) have performed calculations for the adsorption of phenylalanine (C₆H₅CH₂CHNH₂COOH) on various metallic substrates. On coinage metal surfaces {Cu{111}, Ag{111} and Au{111}}, they find a preference for adsorption geometries in which the molecule binds via its N atom, with the aromatic ring elevated well away from the surface; it is possible that DFT underestimation of VdW interaction may be an important consideration here. On transition metal surfaces {Ni{111}, Pd{111} and Pt{111}}, they report strong
bonding of the molecule to the surface via both the N atom and the aromatic ring. Indeed, the molecule exhibits considerable internal strain in order to achieve this favourable configuration.

The adsorption of two even more complex aromatic molecules has been studied on Rh\{111\} by Barbosa & Sautet (2003), the first containing a benzyne (C\(_6\)H\(_4\)) ring and the second a pyridyne (C\(_5\)H\(_3\)N) ring, each with methyl and pyroglutamic substituents attached in place of the two missing H atoms. In both cases, the preference is for binding via the aromatic ring, stabilized further by bonding through the pyroglutamic side group; the authors argue this latter effect ensures that only one side of the ring can attach to the surface, with profound consequences for enantioselective catalysis (Barbosa & Sautet 2003).

7. Coadsorption and reaction

A small number of theoretical studies have considered coadsorption systems involving benzene. Unsurprisingly, the focus of such work has typically been the elucidation of interactions between the coadsorbed species, considered from both the energetic and the electronic points of view. In addition, some efforts have been made towards a theoretical understanding of simple reactions involving aromatic molecules, for the most part focusing upon the transition states, intermediates or reaction products of benzene hydrogenation and dehydrogenation. This final substantive section summarizes these investigations.

(a) Benzene coadsorption with O or CO

Although it is relatively rare for benzene to form ordered overlayers on metal surfaces, it is notable that coadsorption with other species can sometimes induce ordering to occur. A classic example is to be found in the coadsorption of benzene with either O atoms or CO molecules on Ni\{111\}, which in either case leads to a \((2\sqrt{3} \times 2\sqrt{3})\) overlayer. The DFT calculations of Yamagishi et al. (2004) reveal that the preference of the non-aromatic adsorbate to reside in a hollow site forces the benzene molecule to likewise occupy such a site, despite the calculated preference for bridge-site adsorption in the single-component system (the fcc site is marginally preferred when the coadsorbate is O, the hcp is preferred when it is CO). Furthermore, the driving force towards formation of an intimately coadsorbed overlayer (as opposed to phase separation) was found to differ in the two cases. When coadsorbed with O, the dominant effect opposing segregation is strong repulsion between the adatoms at high local coverage, with repulsion between benzene molecules providing a small additional contribution, and attractive interactions between benzene and the adatoms being almost negligible. When coadsorbed with CO, on the other hand, the repulsion between benzene molecules plays an equal role with the attraction between benzene and carbon monoxide, and the repulsion between the non-aromatic molecules is of only minor importance (Yamagishi et al. 2004). Morin et al. (2004a) meanwhile tackled the \((3 \times 3)\) structure formed by coadsorption of benzene with CO on Rh\{111\}, also concluding that the marked preference of the non-aromatic adsorbate to occupy a hollow site rather than a bridge site drives the benzene molecule to occupy such a site itself.
Figure 7. Calculated structural parameters for benzyne on Ir{100} in the c(2 × 4) phase. Bond lengths and interplanar separations are given in ångstrom units, with values derived from LEED experiments provided in parentheses for comparison. Adapted from Yamagishi et al. (2002). Copyright © (2002), American Institute of Physics.

(b) Dehydrogenation of benzene

Removal of a single H atom from benzene results in the phenyl radical (C₆H₅), and removal of a second H atom from an adjacent C atom yields singlet ortho-benzyne (C₆H₄). In general, both species are plausible products of benzene dehydrogenation on metal surfaces, and a particularly interesting instance is to be found on Ir{100}. On that substrate, benzene adsorbs at low temperature in a disordered flat-flying fashion, but upon heating to 465 K a c(2 × 4) LEED pattern develops coincident with evolution of hydrogen (Johnson et al. 2001). Stoichiometric considerations strongly imply that the remaining surface species is benzyne rather than phenyl, and indeed quantitative analysis of the LEED-IV spectra indicates the ortho form of the molecule, bonding through the dehydrogenated C atoms and inclined with its ring plane at approximately 47° to the surface. Subsequent first-principles calculations by Yamagishi et al. (2002, 2003) yielded an adsorption geometry (figure 7) in remarkable agreement with the experimental observation (e.g. tilt angle 48°) and analysis of the electronic structure demonstrated that adsorbate–substrate binding was due in part to σ bonds involving the dehydrogenated C atoms, and in part due to bonding through the π orbitals of the aromatic ring. When coadsorbed in a c(4 × 4) arrangement with C, calculations show that the presence of adatoms in neighbouring hollow sites forces benzyne to adopt a fully upright geometry, in which the π orbitals of the aromatic ring make a negligible contribution to the binding (Yamagishi et al. 2008).

On Cu{100}, by way of contrast, calculations by Bocquet et al. (2006) indicate that both phenyl and benzyne prefer a fully upright geometry in the absence of any coadsorbates. Furthermore, comparison of simulated inelastic
tunnelling spectroscopy (IETS) with the corresponding experimental spectra was presented as evidence favouring the existence of phenyl rather than benzyne after STM-induced dehydrogenation of benzene (Bocquet et al. 2006). The same group has recently reported calculated transition states for C–H scission in benzene on Cu\{111\}, Cu\{100\} and Cu\{110\}, finding that the stepped surface presents the lowest reaction barrier (1.70 eV on Cu\{110\}), while the two flat surfaces yield rather higher barriers (1.85 eV on Cu\{100\}; 2.20 eV on Cu\{111\}) (Lesnard et al. 2007, 2008). Further dehydrogenation of phenyl to yield benzyne is reported to involve a barrier of just 1.58 eV on Cu\{100\}, but is not believed to be readily surmounted in the non-thermal reaction conditions imposed by STM tip voltage pulses (Lesnard et al. 2007, 2008).

(c) Hydrogenation of benzene

The stepwise hydrogenation of benzene to 1,4-cyclohexadiene (C\(_6\)H\(_8\)) has been studied theoretically by Mittendorfer & Hafner (2002) and Hafner (2008), who report an activation barrier of 0.73 eV for addition of the first H atom and 0.40 eV for addition of the second; the first reaction is asserted to be the rate-determining step in the full hydrogenation to cyclohexane (C\(_6\)H\(_{12}\)), but no further barriers are reported to support this claim (Mittendorfer & Hafner 2002; Hafner 2008).

On the Pd\{111\} and Pt\{111\} surfaces, Morin et al. (2006) report energies for a comprehensive set of intermediates en route from benzene to cyclohexane, albeit without calculating any reaction barriers. Nevertheless, invoking the Brønsted–Evans–Polanyi picture, whereby activation barriers are linearly related to reaction enthalpy, these authors argue that the highly endothermic first hydrogenation step is rate limiting on Pd\{111\}, whereas the same step is only moderately endothermic and probably not rate limiting on Pt\{111\} (Morin et al. 2006); earlier cluster calculations had indeed already identified the fifth hydrogenation step as rate limiting on this latter surface (Saeys et al. 2004, 2005).

8. Conclusions

Adsorption of benzene has been quite thoroughly, though not yet exhaustively, studied on a variety of different metal substrates. In general, the molecule adopts a flat-lying, or very nearly flat-lying, geometry, binding to the surface through donation of electrons from one or both of its two degenerate HOMOs and back-donation into one or both of its two degenerate LUMOs. Among transition metal substrates, adsorption energies appear to be substantially stronger on the fcc-{100} facet (typically greater than 2.0 eV) than on the fcc-{111} facet (typically less than 1.5 eV); non-fcc substrates have been considered only sporadically. On the coinage metals, in contrast, binding energy owing to covalent donation/back-donation is much weaker (at least when calculated using GGA functionals) and VdW interactions likely play a dominant role. Efforts to include such non-covalent binding within DFT-based calculations show some promise, but are far from routinely applied.

The adsorption of polycyclic aromatic molecules has also been subject to a certain amount of theoretical attention, in particular focusing upon naphthalene, anthracene, tetracene and pentacene. In general, the covalent contribution to the binding may be expected to increase with the addition of each successive ring.
to the molecule, but lack of registry with the substrate inevitably compromises this effect. Meanwhile, the role of VdW interactions becomes progressively more important for larger and larger molecules, so the suitability of standard DFT becomes ever more questionable as the number of rings increases. Again, appropriate methods for inclusion of VdW effects will be crucial for further progress in this direction.

In the case of heterocyclic aromatic adsorbates, efforts have predominantly been aimed towards pyridine, pyrrole and thiophene. In the former two cases, both flat-lying and vertical geometries have been reported on different substrates, while for thiophene a flat-lying geometry seems to be predominant. Relatively few different substrates have been investigated to date, however, so it would be dangerous to extrapolate trends from such limited data.

The adsorption of substituted aromatic molecules raises the question of whether electronic or steric effects are capable of substantially modifying behaviour away from that of benzene. In the case of phenol and anisole, the electron-donating substituent groups (hydroxy and methoxy, respectively) appear to have remarkably little effect on the nature of adsorption. Indeed, there is some evidence that distortion of the molecule upon adsorption to some degree decouples the substituent group from the ring (that is, from the point of view of the \( \pi \) electronic structure). Only a small steric effect remains, which slightly reduces the adsorption energy. In other cases, with more complex substituents, the molecule can bond simultaneously through the aromatic ring and through some other part of the molecule. Here, the effect is likely to be highly dependent upon the particular molecule considered, so again it becomes difficult to draw general conclusions.

Finally, we note that coadsorption of benzene with other species and surface reactions of benzene have also been subjected to theoretical study over recent years. In the case of coadsorption, the interest lies in understanding how the aromatic and non-aromatic species interact, and the evidence suggests that both attractive and repulsive interactions have a role to play in dictating the coadsorption geometry. As for reactions, the dehydrogenation of benzene to form phenyl or benzyne has been considered on a handful of occasions, as has the hydrogenation towards cyclohexane. Needless to say, both are important topics that warrant much more sustained effort into the future.

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